Research Article

Effect of Ce Addition on Adsorption and Oxidation of NO over MnO$_x$/Al$_2$O$_3$

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1. Introduction

The combustion of massive fossil fuels brings about the harmful emission of nitrogen oxides (NO$_x$). The problem has attracted great attention in recent decades, for the close relationship between NO$_x$ and many serious environmental issues, including acid rain, city photochemical smog, and tropospheric ozone depletion [1–4]. To reduce the poisonous NO$_x$ emissions, many techniques have been researched and applied to thermal power plants and diesel engines. Reductive denitration technology has been extensively researched, including selective catalytic reduction (SCR) and selective noncatalytic reduction (SNCR). Due to its high efficiency, SCR has always been regarded as an effective method to remove fixed emission sources such as power plants [5–8]. In the common SCR process, injected NH$_3$ reduces noxious NO$_x$ to harmless N$_2$ with the aid of efficient catalysts. The typical reactions are as follows [9, 10].

Standard SCR : $4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$ (1)

Fast SCR : $2\text{NH}_3 + \text{NO} + \text{NO}_2 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}$ (2)

NH$_3$-SCR has also exposed many problems in a wide range of industrial applications, such as high investment and operating costs, NH$_3$ escape, N$_2$O generation, and catalyst deactivation [11, 12]. The greenhouse effect of N$_2$O is up to 300 times that of carbon dioxide. The almost inevitable escape of NH$_3$ is particularly worrying. It not only increases the operation cost but also easily results in serious air preheater blocking. Therefore, how to remove NO$_x$ from coal-burning exhaust gas with low cost, pollution-free, and high
efficiency has become a research focus. Recently, NO catalytic oxidation removal is drawing much attention for its getting rid of NH₃ during NO₂ removal [13–15]. Although over 90% of NO₂ formed in fuel combustion is insoluble NO, its oxidation product NO₂ is rather soluble. Therefore, with the participation of catalysts, it is feasible to use the remaining O₂ in the flue gas to oxidize NO to NO₂, which is then captured by alkali liquor in a wet flue gas desulphurization plant [11, 16, 17].

Although many noble metal catalysts have shown good performance in NO catalytic oxidation, the high cost limits their wide application in coal-fired power plants [18–20]. Transition metal oxides have been proven with excellent performance compared to noble metal catalysts, with a wide range of sources, low prices, simple preparation processes, and good thermal stability. Therefore, they have received extensive and in-depth research in recent years [21–23]. Wu et al. prepared a series of MnOₓ/TiO₂ composite nanoxides by deposition-precipitation method, and the sample with the Mn/Ti ratio of 0.3 showed a superior activity for NO oxidation, reaching 89% at 250°C [24]. Mn-based catalysts impregnated on TiO₂ with different crystalline phases were studied by An et al. for the oxidation of NO to NO₂, and 10% MnOₓ/TiO₂ exhibited the highest efficiency 83% at 300°C [22]. The NO oxidation on Cu₂O with molecular oxygen, dissociated oxygen, and lattice oxygen was studied by Sun et al. using periodic density functional theory, and the Eley-Rideal mechanism was favored to explain the catalytic effect of Cu₂O on NO oxidation [25].

Active Al₂O₃ has the characteristics of large adsorption capacity, large specific surface area, good thermal stability, nontoxicity, and noncorrosiveness. Therefore, it is regarded as an excellent catalyst support material and has received extensive attention in the field of catalysis. Wang et al. [26] used a sol-gel method to prepare a series of Ce-based catalysts, selecting Co, Mn, Fe, Cr, and Ni as the doping metal elements. At a reaction temperature of 230°C, the order of NO catalytic activity is Co > Mn > Cr > Ni > Fe.

Although much work has been carried out on NO catalytic oxidation over transition metal oxides, there are some deficiencies along with these studies [21–25]. Firstly, only oxidation efficiency but not removal efficiency was focused on during the experiments. Secondly, the temperature window of the researched catalysts was relatively narrow, not suitable for large-scale practical application. In this investigation, we prepared a series of MnOₓ/Al₂O₃ and Ce-doped MnOₓ–CeOₓ/Al₂O₃ catalysts and investigated the oxidation denitration performance of these catalysts. The effect of Ce doping on the catalyst physicochemical properties was discussed, and microcharacterization analysis was carried out to explore the key points affecting efficiency.

2. Experimental

2.1. Catalyst Preparation. All tested samples in the study were prepared via an ultrasonic impregnation method. Chemicals used here were of analytical grade. Firstly, 0.04 mol (10.04 g) Mn(NO₃)₂·4H₂O was dissolved in 20 mL deionized water. Afterwards, with continuous magnetic stirring, 0.1 mol (10.20 g) Al₂O₃ was added into the solution (particle size = 20 nm; specific surface area ≥ 160 m²/g). Then, the mixture experienced an ultrasonic oscillation lasting for 0.5 h to help to uniformly mix. After standing at room temperature overnight, the suspension was dried in an oven at 105°C for 12 h. The obtained solid product was calcined at 600°C for 5 h and then crushed and sieved to 60–80 mesh. Because the molar ratio of added Mn and Al was 0.4 in the sample, it was denoted as Mnₙ/Alₘ.

For samples with different Ce addition, a specific amount (0.005 mol, 0.01 mol, and 0.02 mol, respectively) of Ce(NO₃)₃·6H₂O was dissolved in deionized water with Mn(NO₃)₂·4H₂O together in the first preparation step. Other preparation procedures were the same as mentioned above. The finally prepared samples were denoted as Mnₙ₋₅Ceₓₜ/Al, Mnₙ₋₅Ce₀.₅/Al, and Mnₙ₋₅Ce₁/Al, respectively.

2.2. Catalytic Activity Test. The catalyst activity test system is shown in Figure 1. The catalytic activity test was carried out in a fixed-bed quartz tube furnace. 0.5 g sample was fixed on the bottom of the quartz glass tube by quartz wool. The total gas flow rate was fixed to 1 L/min (STP), with 600 ppm NO, 8 vol% O₂, and balanced N₂. The exhaust gas after the reaction at a certain temperature was introduced into a 0.5 mol/L sodium hydroxide aqueous solution for absorption, after which the outlet gas composition was examined online by a Fourier transform infrared spectroscopy gas analyzer (Gasmet DX4000, Finland).

The NO removal efficiency was calculated according to the following equation:

\[
\text{NO removal efficiency} (\%) = \left(1 - \frac{[\text{NO} \text{out}] + [\text{NO}_2 \text{out}]}{[\text{NO}_\text{in}]} \right) \times 100.
\]

2.3. Catalyst Characterization. N₂ adsorption-desorption measurement was performed on a full-automatic physical-chemical adsorption instrument (Micromeritics ASAP2020, USA) to determine the textural properties of samples. The specific surface area was acquired by the Brunauer-Emmett-Teller (BET) method, while the total pore volume and mean pore diameter were obtained according to the Barrett-Joyner-Halenda (BJH) method. The micromorphologies of samples were monitored by a field emission scanning electron microscope (FESEM, GeminiSEM 500, Germany). An X-ray diffraction (XRD) meter (Xpert pro, Netherlands) was adopted to identify the crystal phases of samples. The scanning angular velocity was 7°/min, and the scanning angle range was 20°–80°. An X-ray photoelectron spectroscopy (XPS, AXIS ULtrabld, UK) was employed to analyze the catalyst surface atomic concentrations, using C1s at 284.8 eV as the calibration.

3. Results and Discussion

3.1. Catalytic Activity. 600 ppm NO, 8 vol% O₂, and balanced N₂ were introduced into the reactor to explore the performance of catalysts with different contents of active component Ce (Figure 2). As the reaction temperature increased
from 20°C to 500°C, the NO removal efficiency was peaked at 400°C for all samples. The oxidation of NO to NO₂ is exothermic, and the reaction is limited by the thermodynamic equilibrium: the temperature rises, and the equilibrium shifts to the left. Therefore, the temperature increased, the NO oxidation rate decreased, and the denitrification efficiency decreased. It was apparent that the removal efficiency of the Ce-doped Mn₀.₄/Al catalyst was higher than that of the Ce-free Mn₀.₄/Al catalyst, indicating the promotion effect of Ce addition on NO oxidation removal. In addition, the temperature window of Mn₀.₄Ce₀.₀₅/Al catalyst is wider than that of Mn₀.₄/Al. The denitrification efficiency of Mn₀.₄Ce₀.₀₅/Al at 300-450°C can be above 80%.

3.2. XRD. The XRD patterns of Mn₀.₄/Al and Mn₀.₄Ce₀.₀₅/Al expressing the crystal phases on the catalyst surface are depicted in Figure 3. MnO₂ and CeO₂ are the main research objects, so the Al₂O₃ carrier is not shown in Figure 3. There were only diffraction peaks corresponding to Mn₂O₃ in the XRD patterns of Mn₀.₄/Al, indicating the well-crystallized Mn₂O₃ for Mn₀.₄/Al catalysts. As for Mn₀.₄Ce₀.₀₅/Al, the diffraction peaks at 28.8°, 41.2°, and 67.2° were attributed to MnO₂, while the diffraction peaks at 28.9°, 36.5°, and 57.8° were ascribed to Mn₃O₄.

In the XRD patterns of Mn₀.₄Ce₀.₀₅/Al, the diffraction peaks of MnO₂ and MnO₄ were very weak, and no diffraction peaks of Mn₃O₄ existed. However, the diffraction peaks of MnO₂ and MnO₄ were very weak, and no diffraction peaks of Mn₃O₄ were detected. It is worth noting that we also did not detect the crystalline phase of Ce in the XRD pattern, which indicated that Ce was evenly dispersed on the surface of the catalyst, or Ce enters the lattice of manganese. We speculate
that Ce atoms may enter the lattice of Mn$_2$O$_3$, resulting in the disappearance of a large amount of Mn$_2$O$_3$ crystal structure on the catalyst surface and resulting in the increase of the crystal structure of MnO$_2$ and Mn$_3$O$_4$ on the catalyst surface.

After adding active component Ce to Mn$_{0.4}$/Al catalyst, manganese and cerium interacted in a solid solution manner, and manganese ions entered the cerium oxide lattice to increase the oxygen storage capacity of the cerium oxide and the oxygen migration activity of the surface oxide [29]. This interaction was related to the electron transfer between manganese and cerium and the gain and loss of oxygen, and it also influenced the crystal structure of the catalyst and the valence state of manganese and cerium compounds. Therefore, related characterization analysis was carried out.

3.3. XPS. The XPS spectra for Mn 2p of Mn$_{0.4}$/Al and Mn$_{0.4}$Ce$_{0.05}$/Al are separately drawn in Figure 4(a) and Figure 4(b). Mn2p peaks for Mn oxides have many multiplet-split components, and the binding energy of Mn$^{4+}$ is greater than Mn$^{3+}$ [30]. In Figure 4(a), the binding energy peaks at 641.0 eV and 652.5 eV represent Mn$^{3+}$; the binding energy peaks at 642.8 eV and 653.4 eV represent Mn$^{4+}$. The relative size of the energy spectrum peak area represents the relative content of different manganese oxides on the catalyst surface. The Mn$^{4+}/$(Mn$^{3+}$ + Mn$^{4+}$) ratio and the Mn$^{3+}/$(Mn$^{3+}$ + Mn$^{4+}$) ratio were 46.1% and 53.9%, respectively.

On Mn$_{0.4}$Ce$_{0.05}$/Al, the binding energy peaks of 641.3 eV and 652.8 eV represent Mn$^{3+}$; the binding energy peaks at 642.8 eV and 654.2 eV represent Mn$^{4+}$ in Figure 4(b). Compared with Mn$_{0.4}$Ce$_{0.05}$/Al, the energy level was shifted upward. The Mn$^{4+}/$(Mn$^{3+}$ + Mn$^{4+}$) ratio and the Mn$^{3+}/$(Mn$^{3+}$ + Mn$^{4+}$) ratio were 31.0% and 69.0%, respectively. The results indicated that partial Mn$^{4+}$ converted to Mn$^{3+}$ as a result of the addition of cerium. The increase of Mn$^{3+}$ and the decrease of Mn$^{4+}$ favored the catalyst oxidation activity, which was consistent with the results of Atribak et al. [31]. They also confirmed that the activity of Mn$^{4+}$ for NO oxidation was lower than that of Mn$^{3+}$.

Figure 5 shows the XPS spectra for O 1s of Mn$_{0.4}$/Al (Figure 5(a)) and Mn$_{0.4}$Ce$_{0.05}$/Al (Figure 5(b)). There were two kinds of oxygen in catalysts, i.e., surface absorbed oxygen (denoted as O$_{\alpha}$) and lattice oxygen (denoted as O$_{\beta}$). In
Figure 5(a), peaks at 532.9 and 531.6 eV were attributed to O$_\alpha$, while the peak at 529.4 eV corresponded to O$_\beta$. And in Figure 5(b), peaks at 533.0 and 531.5 eV were attributed to O$_\alpha$, while the peak at 529.3 eV corresponded to O$_\beta$. Although the binding energy for each peak showed few differences in Figure 5(a) and Figure 5(b), the intensity varied greatly, especially the relative intensity of O$_\alpha$ and O$_\beta$. The proportion of O$_\beta$ to (O$_\alpha$ + O$_\beta$) in Figure 5(a) was as low as 20.4%, whereas the proportion in Figure 5(b) increased to 34.3%.

Figure 6: XPS spectra for Ce 3d of the Mn$_{0.4}$Ce$_{0.05}$/Al catalyst.

Table 2: Physical properties of catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m$^2$/g)</th>
<th>BJH pore volume (cm$^3$/g)</th>
<th>Average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$_{0.4}$/Al</td>
<td>86.61</td>
<td>0.143</td>
<td>23.17</td>
</tr>
<tr>
<td>Mn$<em>{0.4}$Ce$</em>{0.05}$/Al</td>
<td>69.44</td>
<td>0.139</td>
<td>28.69</td>
</tr>
</tbody>
</table>

Figure 5: XPS spectra for O 1s of (a) the Mn$_{0.4}$/Al catalyst and (b) the Mn$_{0.4}$Ce$_{0.05}$/Al catalyst.
Lattice oxygen played an important role in NO oxidation. After adsorption on the catalyst surface, NO was first oxidized by the active lattice oxygen to form nitrite or nitrate on the surface of the catalyst [32]. The higher proportion of O$_\beta$ signified the more lattice oxygen in catalysts, so Mn$_{0.4}$Ce$_{0.05}$/Al exhibited better catalytic oxidation activity than Mn$_{0.4}$/Al. Xiang et al. [33] built a model of manganese oxide loaded on alumina and analyzed the adsorption of NO and O$_2$ on the Mn/Al surface by density functional theory. Calculations have found that O$_2$ is not easy to stably adsorb on the Mn/Al surface, so the surface lattice oxygen O$_\beta$ is more likely to participate in the oxidation of NO by the MvK mechanism. This was consistent with our experimental conclusions that the Mn$_{0.4}$Ce$_{0.05}$/Al catalyst with higher lattice oxygen content had a stronger ability to oxidize NO.

Figure 6 shows the XPS spectra for Ce 3d of Mn$_{0.4}$Ce$_{0.05}$/Al. The Ce 3d spectrum consists of two series of spin-orbit lines Ce3d$_{3/2}$ and Ce3d$_{5/2}$ [34]. There were eight distinct characteristic peaks, of which the peaks at 881.8 eV, 889.2 eV, 897.7 eV, 902.3 eV, 907.0 eV, and 916.0 eV correspond to Ce$^{4+}$ [26, 35], and the peaks at 902.2 eV and 884.0 eV correspond to Ce$^{3+}$ [36, 37]. It indicated that Ce in Mn$_{0.4}$Ce$_{0.05}$/Al had two forms of Ce$^{4+}$ and Ce$^{3+}$ after calcination at high temperature. The Ce$^{4+}$/Ce$^{3+}$
+ Ce⁴⁺) ratio and the Ce³⁺/(Ce³⁺ + Ce⁴⁺) ratio were 20.56% and 79.44%, respectively.

Ce had strong oxygen storage capacity and stores and releases oxygen through the transformation of Ce⁴⁺ and Ce³⁺, which was consistent with the higher lattice oxygen content on the surface of Mn₀.₄Ce₀.₀₅/Al. It can be seen from Figure 1 that Ce doping improved the low-temperature activity of the catalyst, which was consistent with the study of other scholars [38, 39]. In addition, the doping of Ce element led to a reduction in the amount of O atoms combined with Mn, which in turn converted Mn⁴⁺ to Mn³⁺ with better activity.

The results of the XPS characteristics of Mn₀.₄/Al and Mn₀.₄Ce₀.₀₅/Al are listed in Table 1. According to the analysis above, the increase of Mn³⁺ and lattice oxygen was important for the effective improvement of catalyst activity.

The physical properties of Mn₀.₄/Al and Mn₀.₄Ce₀.₀₅/Al are listed in Table 2, mainly including the BET surface area, the BJH pore volume, and the BJH average pore diameter. From Table 2, it could be found that the surface area and the pore volume of the Mn₀.₄Ce₀.₀₅/Al catalyst were lower than those of the Mn₀.₄/Al catalyst. On the contrary, the pore diameter of the Mn₀.₄Ce₀.₀₅/Al catalyst was higher.

According to the XRD analysis results, cerium ions entered the manganese oxide lattice, resulting in an increase in the weight per unit volume of the pore structure and resulting in the decrease in the specific surface area and pore volume of the catalyst [40]. And it could be found in Table 1 that the Oₓ of Mn₀.₄Ce₀.₀₅/Al catalyst was less than that of Mn₀.₄/Al. The decrease of Oₓ was probably because of the decrease of the catalyst pore volume. Larger pore size will enhance the contact of NO and O₂ with the active sites on the catalyst surface and reduce the resistance of the reactants during internal diffusion, so Mn₀.₄Ce₀.₀₅/Al exhibits stronger NO removal performance.

3.4. FESEM. The FESEM images with magnification times (×10000) of Mn₀.₄/Al and Mn₀.₄Ce₀.₀₅/Al are shown in Figure 7. As shown in Figure 7(a), the Mn₀.₄/Al surface was evenly distributed with fine particles. According to the above XRD analysis results, they were likely to be Mn₂O₃ particles. As shown in Figure 7(b), there were many needle-like substances on the Mn₀.₄Ce₀.₀₅/Al surface. The surface of Mn₀.₄Ce₀.₀₅/Al was rougher, which was conducive to generating more active sites and also conducive to the adsorption of reactants, which strengthens the catalytic oxidation of NO on the surface.

4. Conclusions

The NO oxidation removal activity of Mn₀.₄/Al catalysts with different Ce contents (Mn₀.₄/Al, Mn₀.₄Ce₀.₀₅/Al, Mn₀.₄Ce₀.₀₅/Al, and Mn₀.₄Ce₀.₀₅/Al) was studied experimentally. The results showed that the activity of Mn₀.₄/Al catalysts was effectively promoted with Ce addition, and the Mn₀.₄Ce₀.₀₅/Al performed the best. Simultaneously, the physical-chemical properties and microstructures of Mn₀.₄/Al and Mn₀.₄Ce₀.₀₅/Al were compared and analyzed by various characterization methods, which was helpful to reveal the mechanism of catalytic oxidation of NO by Mn-based catalysts and the effect of Ce addition. The characterization results showed that (1) the entry of cerium ions into the manganese oxide lattice led to the change of crystal structure of the catalyst surface and the decrease of specific surface area and pore volume; (2) the decrease of Mn⁴⁺ and the increase of Mn³⁺ on the catalyst surface were beneficial to the NO oxidation; (3) Ce doping increased the lattice oxygen content on the surface of the Mn₀.₄Ce₀.₀₅/Al, which was favorable for NO oxidation.

Data Availability

All data, models, and code generated or used during the study appear in the submitted article.

Conflicts of Interest

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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References


