Synthesis of Both Powdered and Preformed MnOₙ−CeO₂−Al₂O₃ Catalysts by Self-Propagating High-Temperature Synthesis for the Selective Catalytic Reduction of NOₓ with NH₃

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ABSTRACT: MnOₙ−CeO₂−Al₂O₃ powdered and preformed catalysts were prepared through self-propagating high-temperature synthesis (SHS) and impregnation methods. Compared to the traditional impregnation method, the SHS method has a shorter catalyst preparation cycle and simpler preparation process. The characterization results showed that mixed crystals of cerium, aluminum, and manganese oxides were formed through the SHS method, the binding energy of Mn⁴⁺ increased, and the active components were distributed uniformly. The MnOₙ−CeO₂−Al₂O₃ powdered catalyst had an extensive pore structure, with a Brunauer–Emmett–Teller surface area of approximately 136 m²/g, a pore volume of approximately 0.17 cm³/g, and an average pore diameter of approximately 5.1 nm. Furthermore, the MnOₙ−CeO₂−Al₂O₃ powdered catalyst achieved a NOₓ conversion higher than 80% at 100–250 °C. Coating liquids with identical metal-ion concentrations were used to enhance SCR activity owing to its ability to create surface and bulk oxygen vacancies needs to be improved. The surface and bulk oxygen vacancies can improve the catalytic activity in the SCR of NO with NH₃ by generating Ce³⁺/Ce⁴⁺ redox couples. The surface and bulk oxygen vacancies can enhance the catalytic activity in the SCR of NO with NH₃ by generating Ce³⁺/Ce⁴⁺ redox couples.

1. INTRODUCTION

In recent years, haze has appeared frequently, and it seriously affects the quality of people’s lives. Haze is caused by dust, sulfur dioxide, and nitrogen oxide. At present, industrial dust and sulfur dioxide are well under control, but the governance of nitrogen oxides is still a challenge. Nitrogen oxide, the main component of atmospheric pollution, not only causes serious harm to the environment, but also affects people’s health. Toward the control of nitrogen oxide emissions from coal-fired power plants, the NH₃ selective catalytic reduction (SCR) method has been studied for many years. V₂O₅−WO₃(MoO₃)/TiO₂ is the most used commercial catalytic system for the NH₃-SCR method, and its market share has reached 95%. Although V catalysts have been employed in industrial applications for many years, they have some deficiencies, such as a narrow operation temperature window (300–400 °C). At high temperatures, flue gas contains a large amount of industrial dust and sulfur dioxide, which can cause catalyst poisoning. Furthermore, the fusion and volatilization of vanadium cause the catalyst to release poisonous gas, resulting in secondary pollution and other issues. Desulfurization and denitrification are difficult to achieve simultaneously at an intermediate temperature. After dust removal and desulfurization for catalyst protection, the temperature of the flue gas is low. Therefore, vanadium-free NH₃-SCR catalysts that operate at low temperatures are gradually becoming a hot research topic.

Mn-based catalysts have been found to be highly effective in the low-temperature SCR of NO with NH₃, TiO₂, Al₂O₃, SiO₂, and active carbon have been widely used as supporters for low-temperature SCR catalysts. In many studies, CeO₂ has been used to enhance SCR activity owing to its ability to create surface and bulk oxygen vacancies by generating Ce³⁺/Ce⁴⁺ redox couples. The surface and bulk oxygen vacancies can enhance the catalytic activity in the SCR of NO with NH₃ by promoting the oxidation of NO to NO₂. However, the specific surface area of CeO₂ is not large enough, and its ability to create surface and bulk oxygen vacancies needs to be improved. Extensive research by Dong’s group has shown that CeO₂ exhibits good catalytic performance in NO reduction in CO model reactions. Qi et al. prepared manganese–cerium oxide catalysts using a coprecipitation (CP) method for the low-temperature SCR of NO with ammonia in the presence of excess O₂. A mechanistic pathway for this reaction was proposed.

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Lewis acid sites of the catalyst and then reacts with nitrite species to produce \( \text{N}_2 \) and \( \text{H}_2\text{O} \). Liu et al.\textsuperscript{22} prepared a \( \text{MnO}_x\text{CeO}_2/t\text{-ZrO}_2 \) catalyst via impregnation with nano-t-ZrO\(_2\) as the support. It showed good catalytic activity in the low-temperature SCR of NO with \( \text{NH}_3 \). The catalyst had excellent redox ability on the surface, which predominantly featured Lewis acid sites.

Catalyst cost is a significant aspect of denitration technology in industrial applications. Therefore, many studies have attempted to simplify the preparation processes of catalyst powders and shorten the catalyst preparation cycle to reduce the cost. Using a citric acid-based method, Baiker et al.\textsuperscript{23} prepared a manganese–cerium mixed oxide catalyst, which showed superior catalytic activity to those of pure manganese oxides and cerium oxides. Yang et al.\textsuperscript{24} loaded \( \text{Mn}_{x}\text{Ce}_{y}\text{O}_x \) catalysts on TiO\(_2\) carbonaceous materials using a sol–gel method. A de-\( \text{NO}_x \) efficiency higher than 90\% was achieved with a \( \text{Mn}_{x}\text{Ce}_{y}\text{O}_x/\text{TiO}_2 \)-carbon nanotube catalyst at 75–225 °C and a gas hourly space velocity (GHSV) of 36 000 h\(^{-1}\). The de-\( \text{NO}_x \) efficiency increased to 99.6\% upon adding 250 ppm \( \text{SO}_2 \) at 100–250 °C. Liu et al.\textsuperscript{25} prepared a series of \( \text{Mn}_{x}\text{Ce} \) mixed oxide catalysts using the surfactant-template (ST) and conventional coprecipitation (CP) methods. The best \( \text{Mn}_{x}\text{Ce} \) mixed oxide catalyst prepared by the ST method achieved nearly 100\% \( \text{NO}_x \) conversion at 100–200 °C. Moreover, it showed stronger resistance to \( \text{H}_2\text{O} \) and \( \text{SO}_2 \). Liu et al.\textsuperscript{26} also prepared a \( \text{Mn}_{x}\text{Ce}_{y}\text{Ti} \) mixed oxide catalyst using the hydrothermal method. This catalyst exhibited excellent \( \text{NH}_3\text{-SCR} \) activity and strong resistance to \( \text{H}_2\text{O} \) and \( \text{SO}_2 \) with a broad operation temperature window for diesel engines. Smirniotis’ group\textsuperscript{27} prepared \( \text{Mn}/\text{TiO}_2 \) and a series of \( \text{Mn}_{x}\text{Ni}/\text{TiO}_2 \) catalysts using the incipient wetness technique. For the nickel-doped \( \text{Mn}/\text{TiO}_2 \) catalysts, the low-temperature reduction peak was shifted to much lower temperatures. This increase in reducibility and the extremely dominant \( \text{MnO}_2 \) phase seem to be the reasons for the high SCR activity of the \( \text{Mn}_{x}\text{Ni}/\text{TiO}_2 \) catalysts.

The self-propagating high-temperature synthesis (SHS) method is highly regarded and respected in the fields of composite materials and synthetic polymers because of its simple procedure, low energy consumption, and high conversion rate.\textsuperscript{28,29} Roy et al.\textsuperscript{30} showed that catalysts prepared by the SHS method have excellent nanostructures and exhibit excellent performances. The SHS method also provides a new direction for SCR catalyst preparation. Peng et al.\textsuperscript{31} prepared a series of bulk \( \text{MnWO}_4 \) and supported \( \text{MnWO}_4/\text{TiO}_2 \) catalysts with \( \text{MnWO}_4 \) structures via the SHS, CP, and impregnation methods. They found that \( \text{Mn}_3\text{WO}_6/\text{TiO}_2 \) prepared by the SHS method showed the best de-\( \text{NO}_x \) performance.

In this study, we prepared a \( \text{MnO}_x\text{CeO}_2\text{Al}_2\text{O}_3 \) powdered catalyst using the SHS method and compared it with a catalyst obtained by the traditional impregnation method. Cerium oxide and manganese oxide were the active components so that the disadvantages associated with vanadium in the catalytic process could be avoided. An analogue flue gas composed of \( \text{NO}_x \), \( \text{O}_2 \), \( \text{NH}_3 \), and \( \text{N}_2 \) was used to study the catalytic performance of the \( \text{MnO}_x\text{CeO}_2\text{Al}_2\text{O}_3 \) powdered catalyst at low temperature. The obtained samples were studied systematically using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Brunauer–Emmett–Teller (BET) analysis, scanning electron microscopy (SEM), and \( \text{H}_2 \) temperature-programmed reduction (TPR). Furthermore, a \( \text{MnO}_x\text{CeO}_2\text{Al}_2\text{O}_3 \) preformed catalyst was prepared using the SHS method. Its catalytic performance at different temperatures was evaluated and compared to that of a preformed catalyst prepared using the impregnation method. The effects of \( \text{H}_2\text{O} \) and \( \text{SO}_2 \) on NO...
conversion over the MnO$_x$-CeO$_2$-Al$_2$O$_3$ preformed catalyst were also studied.

2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation. 2.1.1. Impregnation Method. For the preparation of a CeO$_2$-Al$_2$O$_3$ composite oxide carrier, the requisite quantities of Ce(NO$_3$)$_3$·6H$_2$O as the Ce source and Al(NO$_3$)$_3$·9H$_2$O as the Al source were dissolved in distilled water and stirred for 2 h. "CeO$_2$-Al$_2$O$_3" indicates that the Ce/Al molar ratio is 1:2. Then, excess ammonia (30%) was added slowly with vigorous stirring until the pH was 10. The resulting solution was stirred for another 6 h, aged for 24 h, and then filtered and washed several times with distilled water until there was no pH change (pH = 7). The obtained cake was oven-dried at 110 °C for 12 h and finally calcined at 550 °C in air for 5 h. Mn(CH$_3$COO)$_2$·4H$_2$O was used as the Mn source to load 18 wt % Mn on the CeO$_2$-Al$_2$O$_3$ composite oxide carrier. The MnO$_x$/CeO$_2$-Al$_2$O$_3$ powdered catalyst was prepared using the wetness impregnation method with a Mn(CH$_3$COO)$_2$·4H$_2$O solution. The mixture was stirred for 2 h and then evaporated at 100 °C in an oil bath. The resulting material was dried at 110 °C for 12 h in an oven and then calcined at 450 °C in air for 5 h. The obtained catalyst will be referred to as the powdered catalyst; its Mn/ Ce/Al molar ratio was 1:1:2. Figure 1a shows a diagram of the catalyst preparation.

For the preparation of the MnO$_x$/CeO$_2$-Al$_2$O$_3$ preformed catalyst, the requisite quantities of ethylene glycol and citric acid were added to water \( (n(H_2O)/n(\text{citric acid})/n(\text{ethylene glycol}) = 15:1.5:1) \) and then the solution was heated at 80 °C for 2 h, affording a sticky transparent liquid. Then, a certain amount of MnO$_x$/CeO$_2$-Al$_2$O$_3$ powdered catalyst was added to the sticky transparent liquid and the resulting mixture was stirred for 2 h, affording a 40 wt % catalyst slurry. A cordierite honeycomb (CHC) carrier was immersed in the catalyst slurry and then a compressor was used to generate holes. The resulting material was calcined at 500 °C in air for 4 h. The obtained catalyst will be referred to as the MnO$_x$-CeO$_2$-Al$_2$O$_3$ preformed catalyst. Figure 1d shows a diagram of the catalyst preparation. For the preparation of the MnO$_x$-CeO$_2$-Al$_2$O$_3$ preformed catalyst, a combustion liquid of the catalyst was prepared using the above method; its metal-ion concentration was the same as that used for the catalyst prepared with the impregnation method. A cordierite honeycomb carrier was immersed in the catalyst slurry and then a compressor was used to generate holes. The resulting material was calcined at 500 °C in air for 5 h. The obtained catalyst will be referred to as the MnO$_x$-CeO$_2$-Al$_2$O$_3$ preformed catalyst. Figure 1c shows a diagram of the catalyst preparation. It could take about half a day to prepare MnO$_x$-CeO$_2$-Al$_2$O$_3$ preformed catalyst via the SHS method.

2.2. Catalyst Characterization. To investigate the crystalline structures of the obtained catalysts, powder XRD was conducted using a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation \( (k = 1.5406 \text{ Å}) \) at 40 kV and 40 mA, with a 2θ scanning range of 10–90°. XPS was conducted with a Thermo ESCALAB 250XI spectrometer using a monochromatized Al Kα X-ray source \((225 \text{ W})\) with a minimum energy resolution of 0.45 eV \((\text{Ag 3d}_{5/2})\) and a minimum XPS analysis area diameter of 3 μm. To eliminate the interference associated with surface carbon contamination, the C 1s peak energy was defined as 284.6 eV. The microstructural surface characteristics, including the specific surface areas and pore volumes of the samples, were determined using an ASAP 2020C surface area and porosity analyzer (Micromeritics Instrument Corporation). First, the samples were degassed for 6 h at 200 °C and then analyzed using N$_2$ adsorption–desorption at −196 °C under a liquid nitrogen environment. SEM was conducted using an S-4800 field-emission microscope (Hitachi High-Technologies Corporation).
Corp., Japan) with an accelerating voltage of 0.5−30 kV. TPR experiments were conducted with an AutoChem 2720 catalyst characterization system (Micromeritics Instrument Corporation). The catalysts were pretreated by passing high-purity N2 (40 mL/min) through the system at 100 °C for 20 min and then cooled to room temperature. The samples were subsequently heated from 50 to 900 °C at 10 °C/min and 10% H2−Ar (40 mL/min) was passed through the system.

2.3. Catalytic Performance Tests. A microstructured fixed-bed reactor was used to evaluate the catalytic performances of the powdered catalysts in the NH3-SCR reaction in the laboratory. Figure 2 shows a schematic illustrating the catalytic performance evaluation device employed in the experiments. The reaction tube was custom-manufactured with a cross-sectional area of 0.78 cm². The simulated flue gas was composed of 40% NO (1277 ppm), 40% NH3 (1268 ppm), and 5% O2 with N2 as the volume diluent, and the total volume flow was 100 mL/min. The initial NO content of the simulated flue gas was therefore 500 ppm, which will be referred to as C0.

In the tests, a catalyst sample was placed in the reaction tube and its SCR reaction performance was evaluated at different temperatures under flowing simulated flue gas after a 30 min initialization period. The NOx conversion was calculated as follows

\[
\text{NOx conversion} = 1 - \frac{C_1}{C_0} \times 100\%
\]

The N2 selectivities were calculated according to the input concentrations of NOx and NH3 and the output concentrations of N2O, NO2, NO, and NH3 as follows

\[
S(N_2) = \frac{1 - (2[NO_2]_{out} + [NO_3]_{out})}{([NO]_{in} + [NH_3]_{in} - [NO]_{out} - [NH_3]_{out})} \times 100\%
\]

The catalytic performances of the preformed catalysts were evaluated using another microstructured fixed-bed reactor, whose schematic is shown in Figure 3. The reaction tube was custom-manufactured with a cross-sectional area of 19.625 cm². The simulated flue gas was composed of 500 ppm NO and 500 ppm NH3 with air as the volume diluent, and the total volume flow was 10 L/min. In the tests, a catalyst sample was placed in the reaction tube, and its SCR reaction performance was evaluated at different temperatures under flowing simulated flue gas after a 2 h initialization period. The NOx conversion was calculated using the same equation as that used for the powdered catalysts.

The coating of the preformed catalysts was evaluated through the shock removal rates. The preformed catalysts were weighed (m0) and then submerged completely in water in a beaker. Then, they were ultrasonicated at 30 MHz for 30 min. The resulting material was dried at 130 °C for 12 h and then weighed (m1). The shock removal rate was calculated as follows

\[
R(s) = (1 - m_1/m_0) \times 100\%
\]

3. RESULTS AND DISCUSSION

3.1. Crystalline Structure Analysis of the Powdered Catalysts. Figure 4 displays the XRD patterns of the MnOx/...
CeO$_2$−Al$_2$O$_3$ and MnO$_x$−CeO$_2$−Al$_2$O$_3$ powdered catalysts. In the diffraction line profile of the MnO$_x$/CeO$_2$−Al$_2$O$_3$ powdered catalyst, the diffraction peaks at 28.5, 33.0, 47.4, 56.3, 59.1, 69.4, 76.7, 79.0, and 88.4° were attributed to CeO$_2$. The diffraction peaks of MnO$_x$ were complex. The peaks at 28.6, 37.4, and 56.7° were attributed to MnO$_2$, those at 33.1 and 55.3° were attributed to Mn$_2$O$_3$, and those at 18.0 and 59.8° were attributed to Mn$_3$O$_4$.32–33 In addition, no crystal Al$_2$O$_3$ was observed because the diffraction peaks of $\gamma$-Al$_2$O$_3$ probably overlapped with the broadened XRD peaks.34–35 The diffraction peaks of CeO$_2$ and MnO$_x$ of the MnO$_x$/CeO$_2$−Al$_2$O$_3$ powdered catalyst were shifted to lower angles compared to those of the MnO$_x$/CeO$_2$−Al$_2$O$_3$ powdered catalyst or were absent. Two reasons account for this phenomenon. First, MnO$_x$, Al$_2$O$_3$, and CeO$_2$ simultaneously formed composite oxides when the SHS method was used. During this process, Mn and Al were inserted into the CeO$_2$ grid and formed a solid solution, causing the characteristic MnO$_x$ and Al$_2$O$_3$ diffraction peaks to weaken or even disappear.36–37 Furthermore, Mn and Al formed oxides with final crystal types that the instrument could not detect.38 In addition, the MnO$_x$/CeO$_2$−Al$_2$O$_3$ powdered catalyst had highly dispersed active components and smaller particles than the MnO$_x$/CeO$_2$−Al$_2$O$_3$ powdered catalyst.

To investigate their elementary oxidation states and surface compositions, XPS was conducted on the synthesized MnO$_x$/CeO$_2$−Al$_2$O$_3$ and MnO$_x$/CeO$_2$−Al$_2$O$_3$ powdered catalysts, and the results are displayed in Figure 5. Their respective binding energies are listed in Table 1. In addition, the peaks were numerically fitted using Gaussian components to determine the respective valence states of the elemental components. The corresponding atomic concentrations of the different elements on the surfaces of the catalysts based on this fitting are listed in Table 2.

![Figure 5](image_url)

**Table 1. Binding Energies of the Characteristic Peaks for Various Elements in the Catalyst Samples**

| sample                  | Mn$^{4+}$ 2p$_{3/2}$ | Ce$^{4+}$ 3d$_{5/2}$ | Ce$^{3+}$ 3d$_{5/2}$ | O$_{lat}$ | O$_{ads}$ | O$_{surf}$ |
|-------------------------|----------------------|----------------------|----------------------|-----------|-----------|-----------|
| MnO$_x$/CeO$_2$−Al$_2$O$_3$ | 641.2                | 883.0                | 903.9                | 529.8     | 531.8     | 533.4     |
| MnO$_x$/CeO$_2$−Al$_2$O$_3$ | 641.8                | 882.8                | 903.7                | 529.3     | 531.6     | 533.2     |

5696

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The Mn 2p spectra of these representative samples were numerically fitted with two components, as shown in Figure 5a. The binding energies of Mn 2p\(_{3/2}\) and Mn 2p\(_{1/2}\) of MnO were approximately 641 and 653 eV, respectively.\(^{39}\) The binding energies of Mn 2p\(_{3/2}\) were 641.8 and 641.2 eV, suggesting that Mn\(^{4+}\) was the main valence state of Mn in these catalysts. Interestingly, the Mn 2p\(_{3/2}\) peak of the MnO\(_x\)−CeO\(_2\)−Al\(_2\)O\(_3\) powder catalyst appeared at a higher binding energy compared to the MnO\(_x\)/CeO\(_2\)−Al\(_2\)O\(_3\) powder catalyst because MnO and CeO\(_2\) formed composite oxides simultaneously when the SHS method was used, leading to the higher Mn\(^{4+}\) binding energies.\(^{40}\)

Table 2 shows that the two samples have similar Mn contents, but the Mn\(^{4+}/\)Mn ratio of the MnO\(_x\)−CeO\(_2\)−Al\(_2\)O\(_3\) powder catalyst was clearly higher than that of the MnO\(_x\)/CeO\(_2\)−Al\(_2\)O\(_3\) powder catalyst. This indicates that there was synergism between Ce and Mn in the composite metal oxide because Ce can provide oxygen to Mn to increase the valence state and enhance the oxidation ability of Mn and that the activity of the SCR reaction was improved.\(^{41}\)

The complex Ce 3d spectra for these samples were decomposed into eight components, and the assignments are shown in Figure 5b. According to the literature, the bands labeled u’ and v’ represent the 3d\(^{10}\)4f\(^1\) initial electronic state corresponding to Ce\(^{3+}\), whereas the other six bands labeled u” and v”, u’’ and v’’, and u’’’ and v’’’ were related to Ce\(^{4+}\).\(^{42-44}\) The peaks of Ce\(^{3+}\) are weak because electrons are transferred from Ce\(^{3+}\) to O/Mn during the formation of solid oxides.\(^{45}\) From Table 2, the ratio of Ce\(^{3+}\) on MnO\(_x\)/CeO\(_2\)−Al\(_2\)O\(_3\) catalyst was much higher than that on MnO\(_x\)/CeO\(_2\)−Al\(_2\)O\(_3\) catalyst, which was calculated by Ce\(^{4+}/\)Ce. The number of surface oxygen vacancies increased because of the higher relative ratio of Ce\(^{3+}\), which promoted the adsorption of activate reactants or intermediate species in SCR reaction during 100−200 °C.\(^{41}\)

At the same time, the previous reports demonstrated negative charge transfer from either Mn to Ce or Ce to Mn.\(^{9}\) The charge transfer would lead to the strong interaction between Ce and Mn. The Mn\(^{4+}\) and Ce\(^{3+}\) could absorb and activate NO and O\(_2\); thus, the cations of Mn\(^{4+}\) and Ce\(^{3+}\) could serve as active sites to promote the loss of an electron from NO and the capture of an O\(^−\) ion to generate NO\(_2\).\(^{26}\)

Al\(_2\)O\(_3\) played a supporting role in the oxide formation, providing a large number of active sites for the active components, MnO\(_x\) and CeO\(_2\). The Al 2p spectra of these representative samples were numerically fitted with two characteristic peaks, as shown in Figure 5c. The binding energies of Al 2p\(_{3/2}\) and Al 2p\(_{1/2}\) were 70−78 and 78−85 eV, respectively.\(^{35}\) The peak of the MnO\(_x\)/CeO\(_2\)−Al\(_2\)O\(_3\) powder catalyst was wider than that of the MnO\(_x\)/CeO\(_2\)−Al\(_2\)O\(_3\) powder catalyst, but the peak height was slightly lower because MnO\(_x\), Al\(_2\)O\(_3\), and CeO\(_2\) formed composite oxides simultaneously when the SHS method was used, decreasing the binding energies of Al\(^{3+}\).

Table 2. Surface Atomic Concentrations of Various Elements in the Catalyst Samples

| sample               | Ce     | Mn    | Al    | O     | Ce\(^{3+}/\)Ce | Mn\(^{4+}/\)Mn | O\(_{lat}\) | O\(_{ads}\) | O\(_{surf}\) | O\(_{surf}/(O_{lat} + O_{ads} + O_{surf})\) |
|----------------------|--------|-------|-------|-------|----------------|----------------|------------|------------|------------|--------------------------------------------------|
| MnO\(_x\)/CeO\(_2\)-Al\(_2\)O\(_3\) | 9.56   | 12.32 | 21.51 | 56.61 | 14.3           | 6.11           | 22.47      | 17.99      | 16.15      | 28.5                                              |
| MnO\(_x\)-CeO\(_2\)-Al\(_2\)O\(_3\) | 10.64  | 12.60 | 21.48 | 55.27 | 12.6           | 7.29           | 22.03      | 15.84      | 17.41      | 31.5                                              |

Figure 5b. XPS images of (a, b) MnO\(_x\)/CeO\(_2\)-Al\(_2\)O\(_3\) and (c, d) MnO\(_x\)-CeO\(_2\)-Al\(_2\)O\(_3\) powdered catalysts.
attributed to bonding with the metal cations, chemisorbed oxygen, and surface hydroxyl groups and adsorbed water, respectively. From Table 1, we noted that the differences between the binding energies of the three O 1s components of the O’ peak are quite small. In addition, Table 2 shows that the relative concentration ratios Osurf/(Osurf + Olatt + Oads) of the MnOx−CeO2−Al2O3 and MnOx−CeO2−Al2O3 powdered catalysts were approximately 31.5 and 28.5%, respectively. In some studies, Oads was defined as the active oxygen, which captured free electrons easily. Therefore, Oads may promote the oxidation of NO to NO2,48 as does a high Osurf/(Osurf + Olatt + Oads) ratio, and facilitate the reaction over the catalysts.49,50 Moreover, the active oxygen originated from either the free oxygen in the simulated flow gas or the chemisorbed oxygen on the surface. Therefore, increasing the Oads content on the surface may have positive effects on the SCR reaction.51

3.2. Microstructures of the Powdered Catalysts. SEM images of the MnOx−CeO2−Al2O3 and MnOx−CeO2−Al2O3 powdered catalysts are shown in Figure 6. These images show that the MnOx−CeO2−Al2O3 powdered catalyst particles were well distributed, and coarse granular protuberances, ravines, and a large number of widely distributed pores existed on the surface, as shown in Figure 6a. The MnOx−CeO2−Al2O3 powdered catalyst showed a folded shape and a lamellar structure with a smooth surface, as shown in Figure 6c. However, the lamellar structure was thin and small enough to ensure a large specific surface area. The pictures with 5000x magnification (Figure 6b,d) show that a large number of pores were distributed in the cross section of the MnOx−CeO2−Al2O3 powdered catalyst, which ensures that the catalyst has an ideal specific surface area. The following mechanism can be proposed for the reaction in the SHS method. After the combustion liquid of the catalyst is placed in a ceramic crucible and the moisture is evaporated, it gradually becomes a sticky colloidal solution. At the same time, a large number of air bubbles are produced and the gel swells, eventually becoming lighter and spreading out. Just before the water is removed completely, the air temperature is higher than that of the crucible. When the ignition point of urea is reached, the SHS reaction begins from the surface of the liquid. The solid does not deform easily, and the liquid expands outward, spreading the pore structure of the formed layer.

Figure 7 shows the N2 adsorption–desorption isotherm plots and the corresponding Barrett–Joyner–Halenda (BJH) pore size distribution curves of these samples. Figure 7a shows that both samples were classical type IV, as defined by IUPAC,61 and this is the characteristic of mesoporous materials owing to the textural interparticle mesoporosity. A well-defined H2-type hysteresis loop with a sloping adsorption branch and a relatively steep desorption branch was observed at the high relative pressure range (p/p0) for both samples. This H2-type hysteresis loop is typical for wormhole-like mesostructures and intrinsic mesoporous structures formed through nanoparticle assembly.52,53 Furthermore, the pore size distribution curves of the MnOx−CeO2−Al2O3 and MnOx−CeO2−Al2O3 powdered catalysts obtained using the BJH method from the adsorption branches of the corresponding isotherms exhibit a narrow peak centered at 2–8 and 10–30 nm, respectively. The textural data of these samples are listed in Table 3. The CeAl2 composite oxide carrier was doped with Mn54, leading to a reduction in the specific surface area of the MnOx−CeO2−Al2O3 powdered catalyst.6,54 The SEM images showed that coarse granular protuberances, ravines, and a large number of widely distributed pores existed on the surface of the MnOx−CeO2−Al2O3 powdered catalyst, but the two samples had similar average pore diameters and pore volumes. The images also suggest that the interior of the MnOx−CeO2−Al2O3 powdered catalyst have many pores.

3.3. Reduction Performance of the Powdered Catalysts. The reduction properties of these samples were evaluated using H2-TPR, and the results are shown in Figure 8. The reduction peak of MnOx−CeO2−Al2O3 powdered catalysts could be divided into three component peaks by fitting with

![Figure 7](image-url)

**Figure 7.** (a) N2 adsorption–desorption isotherms and (b) BJH pore size distribution curves of the MnOx−CeO2−Al2O3 and MnOx−CeO2−Al2O3 powdered catalysts.
Al₂O₃ and MnO consumed more H₂ than did the MnO
°
60% at 50
CeO₂
Al₂O₃ could activate the reduction ability of MnO
°
x
Temperature the MnO
°
x
Furthermore, the reduction curves of the MnO
°
x
Gaussian curves at around 329, 421, and 545 °C attributed to
MnO₃ → Mn₂O₄, Mn₂O₄ → MnO,
°
and Ce⁴⁺ → Ce³⁺, respectively. Interestingly, the reduction peak of the MnO
°
− CeO₂−Al₂O₃ powdered catalyst was a strong peak at 419 °C. This suggested that the interaction between CeO₂, MnO
°
x
Ce³+,⁵⁶ and Ce⁴⁺
hinshelwood mechanism.²¹,⁶¹

3.4. Catalytic Performances of the Powdered Catalysts. The activities of the powdered catalysts at a GHSV of 15
384 h⁻¹ are shown in Figure 9a. We noted that the MnO₃− CeO₂−Al₂O₃ powdered catalyst achieved a NO₂ conversion of 60% at 50 °C, whereas that achieved by MnO₃/CeO₂−Al₂O₃ was only 34%. When the reaction temperature was increased from 50 to 200 °C, the NO₂ conversions increased gradually for both powdered catalysts. For both samples, the NO₂ conversion reached a maximum at 200–250 °C. This suggested that the Mn−Ce−Al catalysts prepared using the two methods had similar catalytic behaviors at low temperatures. The NO₂ conversion curve showed that the MnO₃−CeO₂−Al₂O₃ powdered catalyst displayed better catalytic performance below 250 °C. As the temperature increased, the NO₂ conversion for both powdered catalysts decreased. However, the NO₂ conversion decreased significantly more slowly for MnO₃/CeO₂−Al₂O₃ which indicated that the Mn−Ce−Al catalyst prepared using the impregnation method showed good catalytic performance at high temperatures. The operation temperature window, in which the NO₂ conversion is greater than 80%, was 100–250 °C for the MnO₃/CeO₂−Al₂O₃ powdered catalyst. This operation temperature window was 225–320 °C for the MnO₃/CeO₂−Al₂O₃ powdered catalyst. From Figure 9b, we noted that the N₂ selectivity of both MnO₃/CeO₂−Al₂O₃ and MnO₃−CeO₂−Al₂O₃ powdered catalyst was stable and higher than 90% at below 150 °C and decreased sharply when the reaction temperature was above 150 °C. However, at reaction temperatures above 300 °C, the decrease rate of the N₂ selectivity decreased as the temperature increased and showed a tendency to increase for some catalysts.

Before the SCR reaction began, the analogue flue gas contained no N₂O or NO₂. However, the postreaction gases included numerous byproducts, and their concentrations increased with increasing temperature. From Figure 10a, we noted that the concentration of N₂O increased rapidly, reached a peak value at 300 °C for the MnO₃−CeO₂−Al₂O₃ powdered catalyst, and then decreased at above 300 °C. For the MnO₃/CeO₂−Al₂O₃ powdered catalyst, the concentration of N₂O became constant at above 200 °C. The NO could be reacted with NH₃ to form N₂O due to the Eley−Rideal mechanism below 200 °C. With increasing temperature, intermediate NH₂NO₃ was easily formed and decomposed to N₂O and H₂O due to the Langmuir−Hinshelwood mechanism.

From Figure 10b, we noted that NO was oxidized directly to NO₂ despite the presence of NH₃ owing to the presence of O₂ in the analogue flue gas. When the reaction temperature was below 250 °C, the concentration of NO₂ was very low and fluctuated slightly for the MnO₃−CeO₂−Al₂O₃ powdered catalysts.
catalyst. However, when the reaction temperature was 250 °C or higher, the NO2 concentration increased sharply and reached a peak value at 350 °C. In contrast, the concentration of NO2 for the MnOx/CeO2−Al2O3 powdered catalyst remained low at below 300 °C and then increased. Along with this trend, we noted from Figure 9b that the N2 selectivity decreased accordingly because of the high concentration of byproducts. This suggests that the concentration of NH3 was suitable for the reduction 2NH3 + NO + NO2 → 2N2 + 3H2O at high temperatures.

3.5. Microstructures of the Preformed Catalysts.

Figure 11 shows the SEM images of the Mn−Ce−Al preformed catalysts. The SEM image in Figure 11a shows that there is an obvious interface between the cordierite honeycomb (CHC) carrier and the catalyst coating and that the catalyst coating and CHC carrier are closely linked with the MnOx/CeO2−Al2O3 preformed catalyst. In addition, the dense coating featured a number of pores, and a large number of granular protuberances existed on the surface of the catalyst coating, which increased the specific surface area of the preformed catalyst. The thickness of the catalyst coating was approximately 30 μm, whereas the thickness of the entire catalyst was 50 μm. For the MnOx−CeO2−Al2O3 preformed catalyst, the SHS reaction occurred in the CHC carrier material; it was difficult to find the interface between the CHC carrier and the catalyst coating because the CHC carrier absorbed liquid. The catalyst coating was dense with well-developed porosity, and the coating surface featured a thin layer with a large amount of flakes. The thickness of the catalyst coating was approximately 25 μm. The shock removal rates of the MnOx/CeO2−Al2O3 and MnOx−CeO2−Al2O3 preformed catalysts were 2.5 and 0.5%, respectively. This suggested that the catalyst coating containing the catalyst prepared using the SHS method had stronger adhesion.

3.6. Catalytic Performances of the Preformed Catalysts.

Catalyst coating liquids with identical metal-ion concentrations of 2.65 mol/L were prepared. After one coating of the catalysts prepared using the SHS and impregnation methods was applied to the CHC carrier, the loading capacities of the resulting preformed catalysts were approximately 18 and 13%, respectively. The activities of the preformed catalysts at a GHSV of 4076 h−1 are shown in Figure 12. For the MnOx−CeO2−Al2O3 preformed catalyst, the NOx conversion increased gradually as the reaction temperature was increased from 50 to 250 °C and reached 82% at 250 °C. When the reaction temperature was increased further, the NOx conversion decreased gradually. The operation temperature window, in which the NOx conversion is higher than 70%, was 200−350 °C. For the MnOx−CeO2−Al2O3 preformed catalyst, the highest NOx conversion, approximately 70%, was achieved at 300 °C. This suggested that NOx conversion is related to the loading capacity and that the MnOx−CeO2−Al2O3 preformed catalyst showed better de-NOx performance. The volume of the MnOx−CeO2−Al2O3 preformed catalyst was adjusted, the NOx conversions under different space velocities were evaluated, and the results are displayed in Figure 13. When the space velocity was increased, the NOx conversion decreased gradually, and the...
4. CONCLUSIONS

The present work was a comparative study on the performances of Mn–Ce–Al catalysts prepared using the SHS method and impregnation methods in NO reduction by NH3. On the basis of the experimental and characterization results, the following several conclusions were obtained:

(1) The MnO2–CeO2–Al2O3 powdered and preformed catalysts showed good performances in the NH3-SCR of NOx. The MnO2–CeO2–Al2O3 powdered catalyst achieved a NOx conversion higher than 80% at 100–250 °C. Coating liquids with identical metal-ion concentrations were prepared with the catalysts, and the preformed catalyst obtained using the SHS method had a higher loading capacity after the first coating. For the MnO2–CeO2–Al2O3 preformed catalyst, the NOx conversion was higher than 70% at 200–350 °C.

(2) The characterization results showed that mixed crystals of cerium, aluminum, and manganese oxides were formed through the SHS method, the binding energy of Mn4+ increased, and the active components were distributed uniformly. The MnO2–CeO2–Al2O3 powdered catalyst had an extensive pore structure, with a BET surface area of approximately 136 m2/g, pore volume of approximately 0.17 cm3/g, and average pore diameter of approximately 5.1 nm. In addition, the catalyst coating obtained using the SHS method had stronger adhesion.

(3) The SHS method involves a simpler catalyst preparation process and shorter preparation cycle; the synthesis period is only 6 h. This suggests that the SHS method is applicable to the industrial manufacture of MnO2–CeO2–Al2O3 preformed catalysts.

Figure 12. Catalytic activity of the MnO2/CeO2–Al2O3 and MnO2–CeO2–Al2O3 preformed catalysts.

Figure 13. NOx conversion of the MnO2–CeO2–Al2O3 preformed catalyst at different GHSVs.

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