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Article

Influence of preparation methods on the physicochemical properties and catalytic performance of $\text{MnO}_x\text{-CeO}_2$ catalysts for $\text{NH}_3\text{-SCR}$ at low temperature

Xiaojiang Yao ^{a,*}, Kaili Ma ^b, Weixin Zou ^b, Shenggui He ^c, Jibin An ^d, Fumo Yang ^{a,e,#}, Lin Dong ^{b,\$}^a Key Laboratory of Reservoir Aquatic Environment of CAS, Chongqing Institute of Green and Intelligent Technology, Chinese Academy of Sciences, Chongqing 400714, China^b Key Laboratory of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, Jiangsu, China^c Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China^d Chongqing Key Laboratory of Environmental Materials and Remediation Technology, Chongqing University of Arts and Sciences, Chongqing 402160, China^e Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, Fujian, China

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ABSTRACT

This work examines the influence of preparation methods on the physicochemical properties and catalytic performance of $\text{MnO}_x\text{-CeO}_2$ catalysts for selective catalytic reduction of NO by NH_3 ($\text{NH}_3\text{-SCR}$) at low temperature. Five different methods, namely, mechanical mixing, impregnation, hydrothermal treatment, co-precipitation, and a sol-gel technique, were used to synthesize $\text{MnO}_x\text{-CeO}_2$ catalysts. The catalysts were characterized in detail, and an $\text{NH}_3\text{-SCR}$ model reaction was chosen to evaluate the catalytic performance. The results showed that the preparation methods affected the catalytic performance in the order: hydrothermal treatment > sol-gel > co-precipitation > impregnation > mechanical mixing. This order correlated with the surface Ce^{3+} and Mn^{4+} content, oxygen vacancies and surface adsorbed oxygen species concentration, and the amount of acidic sites and acidic strength. This trend is related to redox interactions between MnO_x and CeO_2 . The catalyst formed by a hydrothermal treatment exhibited excellent physicochemical properties, optimal catalytic performance, and good H_2O resistance in $\text{NH}_3\text{-SCR}$ reaction. This was attributed to incorporation of Mn^{n+} into the CeO_2 lattice to form a uniform ceria-based solid solution (containing Mn-O-Ce structures). Strengthening of the electronic interactions between MnO_x and CeO_2 , driven by the high-temperature and high-pressure conditions during the hydrothermal treatment also improved the catalyst characteristics. Thus, the hydrothermal treatment method is an efficient and environment-friendly route to synthesizing low-temperature denitrification (deNO_x) catalysts.

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* Corresponding author. Tel: +86-23-65935909; Fax: +86-23-65935924; E-mail: yaoxj@cigit.ac.cn

Corresponding author. Tel: +86-23-65935909; Fax: +86-23-65935924; E-mail: fmyang@cigit.ac.cn

\$ Corresponding author. Tel: +86-25-83592290; Fax: +86-25-83317761; E-mail: donglin@nju.edu.cn

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1. Introduction

Recently, the harmful nature of nitrogen oxides (NO_x) has become a serious environmental issue that has attracted public attention. It has been recognized that NO_x are major atmospheric pollutants, mainly emitted from stationary sources, such as coal-fired power plants, and mobile sources, such as motor vehicles. These emissions not only cause acid rain and photochemical smog, but also act as a precursor for airborne particulate matter ($\text{PM}_{2.5}$), which can damage human health and plant growth [1–3]. Elimination of NO_x is an urgent environmental concern. Among currently available technology, selective catalytic reduction of NO_x by NH_3 (NH_3 -SCR) has been proved to be an efficient, reliable, and economical way to control NO_x emissions [4].

A $\text{V}_2\text{O}_5/\text{TiO}_2$ sample promoted by WO_3 or MoO_3 is the commercial catalyst for NH_3 -SCR process, which exhibits excellent catalytic performance between 300 and 400 °C [5–7]. However, to reach these operating temperatures, the NH_3 -SCR device has to be located upstream of electric precipitator and desulfurizer units in a power station setting. Under these conditions, the catalyst may become blocked and deactivated by dust and sulfur-containing compounds in flue gas [3,5,8]. Furthermore, there may not be enough space to place an NH_3 -SCR device before the electric precipitator and desulfurizer units in old coal-fired power plants. Therefore, there is demand for low-temperature (below 200 °C) NH_3 -SCR catalysts that would allow the NH_3 -SCR device to be placed downstream of the electrostatic precipitator and desulfurizer units, after dust and SO_2 have been eliminated [3,9,10].

In recent years, considerable efforts have been devoted to developing novel NH_3 -SCR catalysts that show good low-temperature catalytic performance. Some examples include supported noble-metal catalysts [11], metal-ion exchanged molecular sieves [12–14], and manganese-based catalysts [5,8,9,15–18]. Among these, manganese-based catalysts have attracted considerable attention owing to their good redox properties and excellent oxygen migration ability, which are beneficial for oxidation of NO to NO_2 , and lead to relatively high conversion of NO_x at low temperatures through a “fast NH_3 -SCR” route [3,19]. However, the low N_2 selectivity, poor H_2O resistance, and narrow operating temperature window of manganese-based catalysts require further improvements [20–22]. Efficient low-temperature NH_3 -SCR catalysts are required, which not only exhibit high catalytic activity at low temperatures, but also have a wide operation temperature window, good H_2O resistance and high N_2 selectivity at low temperatures.

Ceria (CeO_2) has been widely used to eliminate NO_x owing to its good redox properties and high oxygen storage/release capacity associated with oxygen vacancies in the material and the $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox couple [2,23–29]. It has also been reported that CeO_2 can promote adsorption of NO_x , provide stronger Brønsted acidic sites, enhance oxidation of NO to NO_2 , and improve the water and sulfur resistance of catalysts, which would be particularly beneficial for the NH_3 -SCR model reaction [10,19,26,30]. Therefore, a combination of manganese oxide

(MnO_x) and CeO_2 to form MnO_x - CeO_2 catalysts might improve the materials catalytic performance for the NH_3 -SCR of NO_x . This is because of the synergistic interaction between MnO_x and CeO_2 , and other advantages. Shen *et al.* [31] synthesized a supported $\text{MnO}_x/\text{CeO}_2$ catalyst for the low-temperature NH_3 -SCR model reaction, which showed more than 90% NO conversion between 120 and 220 °C owing to a high dispersion of MnO_x , favorable redox properties, and good adsorption of oxygen species. However, the operating temperature window, H_2O resistance, and N_2 selectivity of this catalyst need further improvement.

It has been widely reported that the physicochemical properties and catalytic performance of redox catalysts are highly dependent on their preparation methods [22,32]. In the present work, we synthesized a series of MnO_x - CeO_2 (MnCe) catalysts for a low-temperature NH_3 -SCR model reaction, using several different preparation methods. The obtained samples were characterized by X-ray diffraction (XRD), Raman spectroscopy, N_2 physisorption, H_2 temperature-programmed reduction (TPR), NH_3 temperature-programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), and *in situ* diffuse reflectance Fourier-transformed infrared spectroscopy (DRIFTS). Moreover, a $\text{NO}+\text{NH}_3+\text{O}_2$ model reaction was chosen to evaluate the catalytic performance of these catalysts. The purpose of this paper is to first examine the influence of different preparation methods on the physicochemical properties and catalytic performance of MnO_x - CeO_2 catalysts and to screen for an optimal preparation method. Second, we investigate the interaction of NH_3 and $\text{NO}+\text{O}_2$ with these catalysts by *in situ* DRIFTS in the temperature range of 25–350 °C to further understand the reaction mechanism of NH_3 -SCR over MnO_x - CeO_2 catalysts.

2. Experimental

2.1. Catalyst preparation by different methods

2.1.1. Mechanical mixing method (MMM)

The MnCe -MMM catalyst was prepared by a mechanical mixing method. MnO_x and CeO_2 were obtained by separate thermal decompositions of $\text{Mn}(\text{NO}_3)_2$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ at 500 °C for 5 h in air, after grinding the precursors in an agate mortar. The desired amounts of MnO_x and CeO_2 were then mixed together in an agate mortar for 1 h to prepare the sample.

2.1.2. Impregnation method (IM)

The MnCe -IM catalyst was prepared by an impregnation method. CeO_2 (obtained by thermal decomposition of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ at 500 °C for 5 h in air) was impregnated with an aqueous solution containing the desired amount of $\text{Mn}(\text{NO}_3)_2$ for 2 h. The resulting solid was then heated at 100 °C using an oil bath to evaporate residual water. The sample was dried at 110 °C in an oven for 12 h and finally calcined at 500 °C for 5 h in air.

2.1.3. Hydrothermal treatment method (HTM)

The MnCe-HTM catalyst was prepared by a hydrothermal treatment method. The required amounts of $\text{Mn}(\text{NO}_3)_2$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in deionized water and stirred together for 2 h, followed by introduction of NaOH (6 mol/L) to achieve a solution of pH 10. The resulting solution was stirred for another 3 h to obtain a suspension and then transferred to a Teflon autoclave. The mixture was heated to 120 °C at a rate of 2 °C/min and held at that temperature for 24 h. The obtained precipitate was centrifuged, washed several times with deionized water and one time with anhydrous ethanol until the solution pH did not change. After drying at 60 °C for 12 h in an oven, the sample was finally calcined at 500 °C for 5 h in air.

2.1.4. Co-precipitation method (CPM)

The MnCe-CPM catalyst was prepared by a co-precipitation method. The required amounts of $\text{Mn}(\text{NO}_3)_2$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in deionized water and stirred together for 2 h, and then added dropwise to an excess of ammonia (25%) with magnetic stirring until the solution reached pH 10. The resulting solution was stirred for another 3 h, aged for 24 h, then filtered, and washed with deionized water until the solution pH did not change. The obtained precipitate was dried at 110 °C for 12 h and then calcined at 500 °C for 5 h in air.

2.1.5. Sol-gel method (SGM)

The MnCe-SGM catalyst was prepared by a sol-gel method. Briefly, the desired amounts of $\text{Mn}(\text{NO}_3)_2$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in deionized water and stirred together for 2 h. Citric acid ($\text{C}_6\text{H}_8\text{O}_7$ /(Mn+Ce) = 0.3 molar ratio) was then introduced into the mixed solution, and stirred for another 2 h. Subsequently, the obtained solution was heated to 50 °C to react for 3 h, and then heated at 100 °C with stirring to evaporate residual water. Finally, the sample was dried at 110 °C for 12 h and calcined at 500 °C for 5 h in air.

For all catalysts, the molar ratio of Ce to Mn was fixed at 7:3. The chemical reagents used in the present work were of analytical grade and used without further purification.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns of the synthesized samples were recorded on a Philips X'Pert3 Powder diffractometer using Ni-filtered $\text{Cu } K_\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$). The X-ray tube was operated at 40 kV and 40 mA. The intensity data were collected over a 2θ range of 10°–80°. The scan speed was set at 10°/min with a step size of 0.02°. The mean crystallite size (D_β) and lattice parameters (a) were determined from the strongest peak of these samples by $D_\beta = K\lambda/\beta\cos\theta$ (Debye-Scherrer equation) and $d = 3^{1/2}n\lambda/2\sin\theta$ (Bragg equation), respectively. In these equations K is the particle shape factor, taken as 0.89, λ is the X-ray wavelength, β is the full-width at half maximum height (FWHM) in radians, θ is the diffraction angle, d is the interplanar spacing, and n is the diffraction order number.

Raman spectra of the synthesized samples were collected on a Renishaw inVia Reflex Laser Raman spectrometer using an Ar^+ laser beam. The Raman spectra were recorded with an ex-

citation wavelength of 532 nm and a laser power of 5 mW. The intensity data were collected from 200 to 1000 cm^{-1} .

Surface characteristics of the synthesized samples were obtained by N_2 physisorption at –196 °C on a Belsorp-max analyzer. We used the Brunauer-Emmet-Teller (BET) method to determine the specific surface area and the Barrett-Joyner-Halenda (BJH) method to determine the pore distribution. Prior to each analysis, the catalyst was degassed under vacuum at 300 °C for 4 h.

The H_2 -TPR experiments were performed in a quartz reactor connected to a thermal conductivity detector with an H_2 -Ar mixture (7.0% H_2 by volume, 30 mL/min) as the reductant. Prior to reduction, the sample (50 mg) was pretreated in a highly purified N_2 stream at 300 °C for 1 h and then cooled to room temperature. The H_2 -TPR was started from 100 °C and increased to the target temperature at a rate of 10 °C/min.

The NH_3 -TPD experiments were performed on a multifunction chemisorption analyzer with a quartz reactor, and measured by a thermal conductivity detector. About 200 mg of catalyst was pretreated by a flow of high purity N_2 (30 mL/min) at 300 °C for 1 h. After the pretreatment, the catalyst was saturated with NH_3 - N_2 mixture (1.0% NH_3 by volume, 30 mL/min) at 50 °C for 1 h and then flushed with a flow of high purity N_2 (30 mL/min) at the same temperature for 1 h to remove gaseous NH_3 , before allowing the catalyst to cool to room temperature. The catalyst was then heated from room temperature to 600 °C at a rate of 10 °C/min in a flow of high purity N_2 (30 mL/min).

X-ray photoelectron spectra (XPS) of the synthesized samples were performed on a PHI 5000 VersaProbe system, with monochromatic $\text{Al } K_\alpha$ radiation (1486.6 eV) operating at an accelerating voltage of 15 kW. Before the measurement, the catalyst was outgassed at room temperature in a UHV chamber ($< 5 \times 10^{-7} \text{ Pa}$). Sample charging effects were compensated by calibrating all binding energies (BE) to the adventitious C 1s peak at 284.6 eV, which gave BE values with an accuracy of $\pm 0.1 \text{ eV}$.

The *in situ* DRIFTS of the representative samples were collected on a Nicolet 5700 FT-IR spectrometer equipped with a high-sensitivity mercury cadmium telluride detector cooled by liquid N_2 . The DRIFTS cell (Harrick) was fitted with a ZnSe window and a heating cartridge that allowed the sample to be heated to 350 °C. A fine catalyst powder placed on the sample holder was carefully flattened to enhance IR reflection. Before the DRIFTS test, the sample was pretreated by a flow of high purity N_2 at 300 °C for 1 h to remove physisorbed water. A sample background at each target temperature was collected during the cooling process. At room temperature, the sample was exposed to a controlled stream of NH_3 - N_2 (1% NH_3 by volume) or/and NO - N_2 + O_2 - N_2 (1% NO and 5% O_2 by volume) at a rate of 50 mL/min for 1 h to achieve saturation. For *in situ* DRIFTS of NH_3 adsorption, residual gaseous NH_3 was purged by a high purity N_2 stream (50 mL/min) for 1 h at room temperature. Desorption/reaction studies were performed by heating the samples and the spectra of adsorbed species were recorded at a rate of 10 °C/min from room temperature to 350 °C, by subtraction of the corresponding background reference.

2.3. Catalytic performance measurements

The catalytic performance of the synthesized samples for the NH_3 -SCR model reaction in the presence of excess oxygen was determined in a steady state, involving a feed stream with a fixed composition: 500 ppm NO, 500 ppm NH_3 , 5% O_2 , 5% H_2O (when used), and N_2 in balance. The catalyst (100 mg) was placed a quartz tube, pretreated in a high purity N_2 stream at 300 °C for 1 h and then cooled to room temperature, before switching on the mixed reaction gases. The reactions were carried out at different temperatures with a space velocity of 60000 $\text{mL g}^{-1} \text{h}^{-1}$. The concentrations of NO, NH_3 , NO_2 , and N_2O were detected at 150 °C by a Thermofisher IS10 FTIR spectrometer equipped with a 2 m path-length gas cell (250 ml volume). The NO conversion (%) and N_2 selectivity (%) were calculated from the following equations:

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

$$\text{N}_2 \text{ selectivity} = ([\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}} + [\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}} - [\text{NO}_2]_{\text{out}} - 2[\text{N}_2\text{O}]_{\text{out}}) / ([\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}} + [\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}}) \times 100\% \quad (2)$$

3. Results and discussion

3.1. Catalytic activity and selectivity ($\text{NO} + \text{NH}_3 + \text{O}_2$ model reaction)

The catalytic activity and N_2 selectivity of these synthesized catalysts for the selective catalytic reduction of NO by NH_3 (NH_3 -SCR model reaction) in the presence of excess oxygen are shown in Fig. 1. The catalytic activity of CeO_2 was negligible (< 30%) over the whole reaction temperature range (50–350 °C), as shown in Fig. 1(a), and increased only slightly at higher temperatures. MnO_x exhibited a considerable catalytic activity in the range 50–350 °C, but this did not exceed 60%. Compared with CeO_2 and MnO_x , the prepared MnO_x - CeO_2 catalysts featured remarkably high catalytic performance (except for MnCe-MMM) owing to the synergistic interaction between MnO_x and CeO_2 . Moreover, the catalytic activity of the MnO_x - CeO_2 catalysts obtained by different preparation methods exhibited similar temperature dependences, first increas-

ing to a maximum value and then declining as temperature was increased. The temperature increases provided energy which enhanced the interactions between MnO_x and CeO_2 and in turn promoted transformation of NO, accelerating the catalytic reduction of NO by NH_3 . The increased movement and collision of reactant molecules at higher temperatures caused a clear enhancement of the catalytic activity in the low temperature range (below 200 °C). However, an NH_3 oxidation side reaction, which consumed the NH_3 reductant to generate N_2O , NO, and NO_2 , dominated the reaction at higher temperature, leading to decreased catalytic activity and selectivity for N_2 . In addition, we found that the catalytic activity of these MnO_x - CeO_2 catalysts depended on the method used to prepare the catalyst, in the order $\text{MnCe-HTM} > \text{MnCe-SGM} > \text{MnCe-CPMM} > \text{MnCe-IM} > \text{MnCe-MMM}$, over the whole reaction temperature range (50–350 °C). The MnCe-HTM catalyst not only showed the highest catalytic activity but also possessed the widest operating temperature window, exhibiting a catalytic activity of nearly 100% in the range 100–325 °C. Fig. 1(b) shows the N_2 selectivity of the synthesized samples and exhibited a similar trend, which declined with increasing temperature due to generation of N_2O and NO_2 from NH_3 oxidation. The MnO_x catalyst showed the worst N_2 selectivity, but was clearly improved when combined with CeO_2 to form MnO_x - CeO_2 catalysts. Notably, the N_2 selectivity of the MnCe-HTM catalyst (having the highest catalytic activity) was greater than 70% when the temperature was no higher than 200 °C.

Water is an inevitable contaminant in the practical denitrification (deNO_x) process, so it is important to investigate the influence of water on the catalytic performance of our deNO_x catalysts. Therefore, the H_2O resistance of the MnCe-HTM catalyst during the NH_3 -SCR model reaction at 200 °C was evaluated through a long-time test, and the corresponding results are displayed in Fig. 2. For the first 3 h, without H_2O , we observed that the MnCe-HTM catalyst showed full NO conversion and greater than 70% N_2 selectivity in the NH_3 -SCR of NO. When H_2O was introduced into the catalytic reaction system, the NO conversion declined slightly from 100% to around 80%–90%, while the N_2 selectivity increased from 70% to 90% in the

Fig. 1. Catalytic performance of the synthesized MnO_x - CeO_2 catalysts for $\text{NO} + \text{NH}_3 + \text{O}_2$ model reaction. (a) NO conversion; (b) N_2 selectivity.

Fig. 2. The H₂O resistance of MnCe-HTM catalyst at 200 °C.

presence of 5% H₂O. This was attributed to the effects of competitive adsorption among NO, NH₃, and H₂O [33]. Furthermore, both the NO conversion and N₂ selectivity were stable during the whole test range of H₂O resistance (3–45 h), which indicated good H₂O resistance of the MnCe-HTM catalyst. When H₂O was removed (45–48 h), the NO conversion and N₂ selectivity of MnCe-HTM catalyst were recovered to some extent. Thus, the MnCe-HTM catalyst exhibited nearly 100% NO conversion in the range 100–325 °C, above 70% N₂ selectivity in the range 50–200 °C, and good H₂O resistance at 200 °C for the selective catalytic reduction of NO by NH₃. These results indicate that the hydrothermal treatment is an effective method for preparing MnO_x-CeO₂ catalysts for low-temperature *de*NO_x processes. To gain further insight into the catalytic performance of the MnCe-HTM catalyst and to understand the differences in the performance of catalysts produced by different methods, we characterized their structural and morphological properties.

3.2. Structural characteristics

Fig. 3(a) shows the XRD patterns of the MnO_x-CeO₂ catalysts obtained by different preparation methods. The results of the MnO_x and CeO₂ catalysts are also shown in this figure for comparison. Diffraction peaks were detected in MnO_x, which were attributed to a large amount of Mn₂O₃ (PDF-ICDD 41-1442) and a small amount of MnO₂ (PDF-ICDD 44-0141). The CeO₂ samples showed a typical cubic fluorite structure (PDF-ICDD 34-0394) with several characteristic diffraction peaks. The results of the MnO_x-CeO₂ catalysts showed some interesting phenomena. For the MnCe-MMM catalyst, strong diffraction peaks assigned to CeO₂ and several weaker characteristic peaks attributed to Mn₂O₃ were detected. These resulted from the mechanical mixing of CeO₂ and MnO_x. However, a weak diffraction peak from MnO₂ appeared at 37.3° instead of that of Mn₂O₃, which was detected in the MnCe-IM catalyst. We attribute this to Mn species on the surface of CeO₂ that were fully oxidized during the calcination process. Interestingly, only weakened and broadened diffraction peaks from CeO₂ were observed from MnCe-HTM, MnCe-CPM, and MnCe-SGM catalysts. The absence of MnO_x diffraction peaks indicated that Mn species were highly dispersed on the CeO₂ surface and/or incorporated into the CeO₂ lattice. Moreover, we found that the diffraction peaks from the MnCe-HTM, MnCe-CPM, and MnCe-SGM catalysts shifted to slightly higher diffraction angles, compared with those in CeO₂. This result further confirmed that Mn species were partially incorporated into the CeO₂ lattice forming a uniform ceria-based solid solution (containing a Mn-O-Ce structure) [34–36].

The structural data of these synthesized catalysts are summarized in Table 1. The lattice parameters of CeO₂, MnCe-MMM, and MnCe-IM catalysts were very close, indicating that the mechanical mixing and impregnation methods had a similar influence on the bulk structure of the CeO₂. Interestingly, the lattice parameters of MnCe-HTM, MnCe-CPM, and

Fig. 3. (a) XRD patterns and (b) Raman spectra of the synthesized catalysts.

Table 1

Textural data, crystallite size, lattice parameter, the position and FWHM of the main Raman line (F_{2g}), and the peak area ratio in Raman spectra of the synthesized catalysts.

Catalyst	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Crystallite size (nm)	Lattice parameter (Å)	Position of F_{2g} (cm ⁻¹)	FWHM of F_{2g} (cm ⁻¹)	S_{II}/S_I
CeO ₂	68.5	0.1972	14.4	5.4149	463	22.9	0.0295
MnCe-MMM	59.7	0.1594	14.2	5.4145	463	25.5	0.0381
MnCe-IM	48.5	0.1468	15.1	5.4143	460	29.3	0.0663
MnCe-HTM	81.6	0.2368	13.5	5.3904	448	42.7	0.6945
MnCe-CPM	97.8	0.2502	9.6	5.3862	459	45.4	0.4291
MnCe-SGM	115.7	0.2609	7.1	5.3819	448	47.1	0.4471

MnCe-SGM catalysts were smaller than those of bulk CeO₂. This was likely because the ionic radii of Mn⁴⁺ (0.54 Å), Mn³⁺ (0.66 Å), and Mn²⁺ (0.80 Å) are smaller than that of Ce⁴⁺ (0.92 Å). Incorporation of these Mn ions into the CeO₂ lattice led to lattice contraction and distortion [37–39]. The crystallite size of these synthesized catalysts was also studied. Both CeO₂ and MnCe-MMM showed similar crystallite sizes, while the MnCe-IM catalyst was larger than that of CeO₂ due to the second calcination. Notably, the MnCe-HTM, MnCe-CPM, and MnCe-SGM catalysts exhibited crystallite sizes that were smaller than those of bulk CeO₂, which suggests that the incorporation of Mnⁿ⁺ inhibited the grain growth of CeO₂ [37,40].

The structures of the different MnO_x-CeO₂, MnO_x, and CeO₂ catalysts were further characterized by Raman spectroscopy, and the corresponding results are shown in Fig. 3(b). Two weak Raman bands were observed at 310 and 702 cm⁻¹ for MnO_x, which were attributed to out-of-plane bending and symmetric stretching modes of Mn₂O₃, respectively [41,42]. CeO₂ exhibited a strong Raman band at 463 cm⁻¹ and a shoulder at ~600 cm⁻¹, which were assigned to the F_{2g} vibration (labeled as I) and defect-induced modes (D band, labeled as II) of the cubic fluorite structure, respectively [43–45]. The D band is related to oxygen vacancies in ceria-based materials, the area ratio of F_{2g} and D (*i.e.*, S_{II}/S_I) reflects oxygen vacancy concentration [19,23,45]. The F_{2g} vibration mode and defect-induced mode (D band) of CeO₂ were also detected in the MnO_x-CeO₂ catalysts, as shown in Fig. 3(b). The F_{2g} band of the MnCe-MMM catalysts was not shifted with respect to that of CeO₂, while that of the MnCe-IM catalyst shifted slightly from 463 to 460 cm⁻¹, owing to electronic interactions between MnO_x and CeO₂ (Table 1). Table 1 and Fig. 3(b) show that the F_{2g} band of MnCe-HTM, MnCe-CPM, and MnCe-SGM catalysts also clearly shifted to 448, 459, and 448 cm⁻¹, respectively. This shift was accompanied by an enhancement of the D band, which further indicated that Mn species were incorporated into the CeO₂ lattice to form a uniform ceria-based solid solution (containing Mn-O-Ce structures). The substitution of Ce⁴⁺ by Mnⁿ⁺ (such as Mn⁴⁺, Mn³⁺, and Mn²⁺) into the CeO₂ lattice induced additional lattice perturbations and structural strain, which generated surface defects (*e.g.*, oxygen vacancy). The FWHM values of F_{2g} for the synthesized catalysts are listed in Table 1. The FWHM of F_{2g} for the MnCe-HTM, MnCe-CPM, and MnCe-SGM catalysts were larger than those of CeO₂, MnCe-MMM and MnCe-IM catalysts. This may be partially related to the crystallite size and oxygen vacancies in these samples. Importantly, oxygen vacancies (V_O) can lead to transformation of $V_O + O_2 + e^- \rightarrow$ adsorbed oxygen

species (including O₂⁻, O₂²⁻, and O⁻). This improved oxygen migration ability was beneficial for the oxidation of NO to NO₂, and enhanced the NH₃-SCR catalytic performance by introducing a “fast NH₃-SCR” route [19]. The oxygen vacancy concentration for these MnO_x-CeO₂ catalysts is also summarized in Table 1, and followed the trend: MnCe-HTM > MnCe-SGM > MnCe-CPM > MnCe-IM > MnCe-MMM. This pattern corresponds with the catalytic performance results for the NH₃-SCR model reaction. The MnCe-HTM catalyst exhibited the largest oxygen vacancy concentration among the synthesized samples because of incorporation of Mnⁿ⁺ into the CeO₂ lattice. This sample formed a uniform ceria-based solid solution (containing the Mn-O-Ce structure), which strengthened electronic interactions between MnO_x and CeO₂, driven by the high-temperature and high-pressure conditions during the hydrothermal treatment process.

The BET specific surface area and pore volume of the synthesized catalysts measured from N₂ physisorption are listed in Table 1. The MnCe-MMM and MnCe-IM catalysts exhibited a smaller BET specific surface area and pore volume than those of CeO₂, likely because MnO_x particles blocked pores in the CeO₂. However, the BET specific surface area and pore volume of MnCe-HTM, MnCe-CPM, and MnCe-SGM catalysts were obviously larger than those of CeO₂, which is partially related to the crystallite size of these samples. The CeO₂ crystallite size was decreased by incorporation of Mnⁿ⁺ into the CeO₂ lattice, which resulted in an increased BET specific surface area and pore volume. These features also likely contributed to the enhanced catalytic performance by increasing the number of reaction sites on the catalysts.

3.3. Reduction properties and surface acidity (H₂-TPR and NH₃-TPD)

The reduction properties of the catalysts were investigated by H₂-TPR, as shown in Fig. 4(a). The H₂-TPR profile of CeO₂ as a function of reduction temperature is also included in this figure, and presents two reduction peaks at 510 and 816 °C corresponding to reduction of CeO₂ surfaces and bulk CeO₂, respectively [24,40,46]. All of the MnO_x-CeO₂ catalysts exhibited two broad reduction peaks (a low-temperature peak labeled I, and a high-temperature peak labeled II) in the range 100–550 °C, which are attributed to stepwise reduction of MnO_x, *i.e.*, MnO₂/Mn₂O₃ → Mn₃O₄ → MnO, overlapped by reduction of surface Ce⁴⁺ [19,35,36]. Compared with the MnCe-MMM catalyst, the reduction peaks of the MnCe-IMM, MnCe-HTM,

Fig. 4. (a) H_2 -TPR profiles and (b) NH_3 -TPD profiles of the synthesized catalysts.

MnCe-CPM, and MnCe-SGM catalysts shifted to lower temperatures, which indicated that some electronic interactions existed between MnO_x and CeO_2 for these samples. This phenomenon is very similar to the findings of He *et al.* [47,48] in cerium-gold oxide and cerium-vanadium oxide systems. Quantitative analysis of the H_2 -TPR data of the synthesized catalysts are summarized in Table 2. The total H_2 consumption (peaks I + II) of the MnCe-IM, MnCe-HTM, MnCe-CPM, and MnCe-SGM catalysts were larger than that of the MnCe-MMM catalyst, which suggests that the electronic interactions between MnO_x and CeO_2 promoted the reduction of surface Ce^{4+} . The total H_2 consumption of these MnO_x - CeO_2 catalysts followed the order: MnCe-HTM > MnCe-SGM > MnCe-CPM > MnCe-IM > MnCe-MMM. On the basis of these results and the XRD and Raman findings, it is likely that incorporation of Mn^{n+} into the CeO_2 lattice generated a uniform ceria-based solid solution (containing Mn-O-Ce structures). This promoted the reduction of surface Ce^{4+} more effectively than simple surface loading of MnO_x to form a supported catalyst, as is the case for the MnCe-IM catalyst. Furthermore, it has been widely reported that Mn^{4+} is the most effective redox state of manganese-based catalysts and is beneficial for NO conversion [19,49]. Therefore, we focused on the low-temperature reduction peak I of these MnO_x - CeO_2 catalysts and found that the corresponding H_2 consumption could be ranked in the order: MnCe-HTM >

MnCe-SGM > MnCe-CPM > MnCe-IM > MnCe-MMM, while the peak temperature exhibited the reverse order. This relationship was also consistent with our NH_3 -SCR results.

The adsorption and activation of NH_3 at active sites of the catalysts play an important role in the NH_3 -SCR model reaction. Therefore, NH_3 -TPD was used to probe the amount of acid sites and their acidic strength in the MnO_x - CeO_2 catalysts. The corresponding results are shown in Fig. 4(b). The NH_3 -TPD profile of CeO_2 as a function of desorption temperature is also shown in this figure for comparison. The area and position of these desorption peaks directly relate to the amount of acidic sites and their acidic strength, respectively [26,50]. Fig. 4(b) presents the NH_3 desorption signals of the catalysts over a wide temperature range. Differences in the peak positions and heights are caused by variations in the thermal stability of adsorbed NH_3 species. All the samples exhibited a narrow peak around 100 °C (labeled as α), and a broad peak between 150 and 550 °C (labeled as β). The former (α) at low temperature was attributed to desorption of physisorbed NH_3 and NH_3 at weak acidic sites, while the latter (β) at high temperature resulted from NH_3 adsorbed to strong acid sites of the catalysts [2,19,26,50]. The NH_4^+ ions anchored at Brønsted acid sites were less thermally stable than NH_3 species bonded at Lewis acid sites. This suggests that the desorption peak (α) at low temperature was related to NH_4^+ ions anchored at Brønsted

Table 2

The quantitative analysis data of H_2 -TPR and NH_3 -TPD for the synthesized catalysts.

Catalyst	H_2 -TPR					NH_3 -TPD		
	Peak temperature (°C)		H_2 consumption (a.u.)			Acid amount (a.u.)		
	I	II	I	II	I+II	α	β	$\alpha+\beta$
CeO_2	—	—	—	—	—	1179	498	1677
MnCe-MMM	385	472	1035	1387	2422	1397	581	1978
MnCe-IM	260	346	1813	1523	3336	1435	1522	2957
MnCe-HTM	216	302	2772	1527	4299	1831	4190	6021
MnCe-CPM	242	352	1905	1821	3726	1520	2091	3611
MnCe-SGM	235	339	2059	1779	3838	1691	2784	4475

acid sites, while the desorption peak (β) at high temperature was related to NH_3 species bonded at Lewis acid sites [26,50,51]. The temperatures of the β desorption peak of the MnCe-HTM, MnCe-CPM, and MnCe-SGM catalysts were obviously higher than those of the MnCe-MMM and MnCe-IM catalysts, as shown in Fig. 4(b). This indicates that the first three catalysts were more strongly acidic than the latter two catalysts. This phenomenon suggests that incorporation of Mn^{n+} into the CeO_2 lattice generated a uniform ceria-based solid solution (containing Mn-O-Ce structure), which enhanced the acidic strength of the MnO_x - CeO_2 catalysts. Quantitative analysis of the NH_3 -TPD data from the synthesized catalysts are listed in Table 2. These data show that the total amount of acidic sites in the MnCe-IM, MnCe-HTM, MnCe-CPM, and MnCe-SGM catalysts was considerably larger than those in the CeO_2 and MnCe-MMM samples owing to electronic interactions between MnO_x and CeO_2 . The total amount of acid sites followed the order: MnCe-HTM > MnCe-SGM > MnCe-CPM > MnCe-IM > MnCe-MMM, which corresponded with the order of catalytic performances in the NH_3 -SCR model reaction. The MnCe-HTM catalyst exhibited the largest amount of acidic sites and the strongest acidic strength among the synthesized samples. The acidity was increased by strengthening of the electron interactions between MnO_x and CeO_2 driven by the high-temperature and high-pressure conditions during the hydrothermal treatment process.

3.4. Surface analysis of the catalysts (XPS)

The surface chemical composition and oxidation states of these synthesized catalysts were measured by XPS. High resolution spectra from Ce 3d, Mn 2p, and O 1s are displayed in Fig. 5. For the Ce 3d spectrum (Fig. 5(a)), all samples exhibited eight characteristic peaks in the range 880–920 eV, which are labeled as u''' , u'' , u' , u^0 (u), v''' , v'' , v' , and v^0 (v). The u' and v' peaks can be attributed to Ce^{3+} species, while the u''' , u'' , u^0 (u), v''' , v'' , and v^0 (v) peaks can be assigned to Ce^{4+} species. The spectra indicate that Ce was mainly in the +4 oxidation state, with some Ce^{3+} present in the synthesized catalysts [40,46,52, 53]. The relative content of surface Ce^{3+} (i.e., $\text{Ce}^{3+}/(\text{Ce}^{3+}+\text{Ce}^{4+})$)

was calculated as shown in Table 3. This was determined by the following formula based on the area of the u' and v' peaks [24,54]:

$$\text{Ce}^{3+} = \frac{S_{u'} + S_{v'}}{\sum (S_u + S_v)} \times 100\%$$

The data in Table 3 show that the relative content of surface Ce^{3+} in the MnCe-MMM catalyst was very close to that of CeO_2 , while the MnCe-IM catalyst exhibited a higher relative surface Ce^{3+} content than the CeO_2 and MnCe-MMM samples. This was attributed to electronic interactions between MnO_x and CeO_2 . Interestingly, the relative contents of surface Ce^{3+} in the MnCe-HTM, MnCe-CPM, and MnCe-SGM catalysts were clearly larger than those of CeO_2 , MnCe-MMM, and MnCe-IM samples. This is also related to the incorporation of Mn^{n+} into the CeO_2 lattice to form a uniform ceria-based solid solution (containing Mn-O-Ce structures) and electron interactions between MnO_x and CeO_2 . The relative surface Ce^{3+} content is another widely used indicator for defect structures (e.g., oxygen vacancy) in ceria-based materials [44]. The surface Ce^{3+} content for the MnO_x - CeO_2 catalysts varied in the order MnCe-HTM > MnCe-SGM > MnCe-CPM > MnCe-IM > MnCe-MMM. This also followed the order of oxygen vacancy concentrations determined by Raman analysis. Oxygen vacancies driven by the transformation of Ce^{4+} to Ce^{3+} can promote activation and migration of oxygen molecules, which is beneficial to the oxidation of NO to NO_2 , and further enhances the catalytic performance through a “fast NH_3 -SCR” route [19].

The Mn 2p spectrum (Fig. 5(b)) suggested that Mn species existed in a mixture of valence states on the surface of the MnO_x - CeO_2 catalysts. By performing peak-fitting deconvolution, we divided the Mn 2p_{3/2} signal into three characteristic peaks, which were assigned to Mn^{4+} (643.3 eV), Mn^{3+} (641.3 eV), and Mn^{2+} (639.6 eV), respectively [40,46]. The Mn 2p_{1/2} signal exhibited corresponding peaks from three Mn species in the binding energy range 650–660 eV. Previous studies have shown that Mn^{4+} species have favorable redox properties for NO conversion [19,49]. Therefore, the relative content of surface Mn^{4+} (i.e., $\text{Mn}^{4+}/(\text{Mn}^{2+}+\text{Mn}^{3+}+\text{Mn}^{4+})$) of these MnO_x - CeO_2 catalysts was calculated, and listed in Table 3. We found that the surface Mn^{4+} content of the MnCe-IM, MnCe-HTM,

Fig. 5. XPS spectra of the synthesized catalysts. (a) Ce 3d; (b) Mn 2p; (c) O 1s.

Table 3

The surface composition of the synthesized catalysts.

Catalyst	Atomic concentration (at%)			Atomic ratio (%)			
	Ce	Mn	O	Mn/Ce	Ce ³⁺ /(Ce ³⁺ +Ce ⁴⁺)	Mn ⁴⁺ /(Mn ²⁺ +Mn ³⁺ +Mn ⁴⁺)	O ^{''} /(O'+O'')
CeO ₂	19.75	—	80.25	—	13.53	—	29.30
MnCe-MMM	18.53	1.52	79.95	8.20 (42.86)	13.98	22.93	30.02
MnCe-IM	17.48	4.69	77.83	26.83 (42.86)	15.42	31.62	31.38
MnCe-HTM	14.63	9.24	76.13	63.16 (42.86)	18.67	41.65	36.50
MnCe-CPM	17.36	7.64	75.00	44.01 (42.86)	16.29	28.13	32.19
MnCe-SGM	17.24	8.74	74.02	50.70 (42.86)	17.57	29.80	33.79

MnCe-CPM, and MnCe-SGM catalysts was larger than that of the MnCe-MMM catalyst. This was attributed to electronic interactions between MnO_x and CeO₂, which resulted in the redox equilibrium of Mn³⁺ + Ce⁴⁺ ↔ Mn⁴⁺ + Ce³⁺ shifting to right [19]. The surface composition of these synthesized catalysts is summarized in Table 3. The surface Mn/Ce molar ratios of MnCe-MMM and MnCe-IM catalysts were clear smaller than their respective theoretical values (given in the parentheses) because of the occurrence of crystalline Mn₂O₃ and MnO₂ (as determined by XRD). However, the surface Mn/Ce molar ratios of the MnCe-HTM, MnCe-CPM and MnCe-SGM catalysts were larger than the theoretical values, indicating that the Mn species were highly dispersed on the surface of the catalysts. The surface Mn/Ce molar ratio of these MnO_x-CeO₂ catalysts was ranked as MnCe-HTM > MnCe-SGM > MnCe-CPM > MnCe-IM > MnCe-MMM, which was in agreement with the NH₃-SCR results.

Fig. 5(c) shows the O 1s spectrum of these synthesized catalysts, which exhibited a strong peak at 529.1 eV (labeled as O'), and a shoulder at a higher binding energy of 531.2 eV (labeled as O''), which can be attributed to lattice oxygen and adsorbed oxygen on the surface of these samples, respectively [1,55]. It has been widely reported that oxygen in the gas phase can be activated by oxygen vacancies on the surface of *de*NO_x catalysts to form surface adsorbed oxygen. This effect may also enhance catalytic performance in the NH₃-SCR model reaction [19,56]. Furthermore, a process of oxygen storage/release between Ce³⁺ and Ce⁴⁺ has been proposed in the following equations: (a) 2CeO₂ → Ce₂O₃ + O* (adsorbed oxygen) and (b) Ce₂O₃ + 1/2O₂ → 2CeO₂ [19]. The increase of O'' content can promote the oxidation of NO to NO₂ and enhance the catalytic performance of the low-temperature *de*NO_x catalysts through a "fast NH₃-SCR" route [19,57]. The relative content of O'' (*i.e.*, O''/(O'+O'')) of these synthesized catalysts was calculated, and is given in Table 3. The O'' content of the MnO_x-CeO₂ catalysts was higher than that in CeO₂ owing to the higher of oxygen vacancy concentration in the MnO_x-CeO₂ catalysts. The O'' content followed the order MnCe-HTM > MnCe-SGM > MnCe-CPM > MnCe-IM > MnCe-MMM, which was consistent with the catalytic performance of the catalysts in the NH₃-SCR model reaction. To summarize, the MnCe-HTM catalyst exhibited the highest surface Ce³⁺, Mn⁴⁺ and adsorbed O'' contents among the synthesized samples. This was attributed to the incorporation of Mnⁿ⁺ into the CeO₂ lattice to form a uniform ceria-based solid solution (containing Mn-O-Ce structures). Furthermore this catalyst featured a strong electron interaction between MnO_x and CeO₂ (*i.e.*, Mn³⁺ + Ce⁴⁺ ↔ Mn⁴⁺ + Ce³⁺) driven by the high-tempera-

ture and high-pressure conditions during the hydrothermal treatment process.

3.5. NH₃ or/and NO+O₂ interactions with the catalysts (*in situ* DRIFTS)

The MnCe-HTM catalyst exhibited excellent physicochemical properties and optimal catalytic performance for the low-temperature NH₃-SCR model reaction. Thus, the MnCe-HTM catalyst and CeO₂ (for comparison) were chosen as representative samples to investigate interactions between low-temperature *de*NO_x catalysts and reactant molecules. The *in situ* DRIFTS technique is a useful tool for this purpose. NH₃ adsorption measurements by *in situ* DRIFTS were performed on representative samples, and the results as a function of temperature are shown in Fig. 6. For CeO₂ (Fig. 6(a)), several characteristic bands were observed at 1560, 1299, 1140, and 1051 cm⁻¹ at room temperature (25 °C), which were attributed to the vibration modes of coordinated NH₃ adsorbed to Lewis acid sites (labeled as L acid) [58,59]. The bands at 1641 and 1430 cm⁻¹ were assigned to symmetric and asymmetric bending vibration modes of NH₄⁺ species adsorbed to Brønsted acid sites (labeled as B acid) [19,60]. Some interesting phenomena were observed as temperature was increased. At 100 °C, the bands from the B acid disappeared completely due to the poor thermal stability of these species. Furthermore, the intensity of the L acid band weakened at higher temperature, but the band remained even at 350 °C, which was consistent with the results of NH₃-TPD. A new band was detected at 1320 cm⁻¹ at 200 °C, which was attributed to adsorbed -NH₂ species, resulting from dissociation of NH₃ coordinated to L acid sites [59,61]. For the MnCe-HTM catalyst (Fig. 6(b)), the L acid bands were observed at 1604, 1167, and 1051 cm⁻¹ at room temperature (25 °C), and the B acid exhibited two bands at 1668 and 1404 cm⁻¹. Compared with CeO₂, we found that the B acid bands of the MnCe-HTM catalyst disappeared at 200 °C. The intensity decrease of the L acid bands in the MnCe-HTM catalyst was considerably slower than that in CeO₂. Furthermore, the L acid band had a considerable intensity up to 350 °C. The adsorbed -NH₂ species appeared as two bands at 1428 and 1357 cm⁻¹ at a lower temperature of 150 °C. The corresponding intensity of these bands was clearly much stronger than those in CeO₂. Fig. 6(a) and (b) show that the intensity of the L acid and B acid bands of the MnCe-HTM catalyst was stronger than that of CeO₂ at all temperatures. In summary, these observations indicated that the amount of acidic sites and the acidic strength of the

Fig. 6. NH_3 adsorption *in situ* DRIFTS of (a) CeO_2 and (b) MnCe-HTM catalyst.

MnCe-HTM catalyst were larger and stronger than those of CeO_2 . This was attributed to the incorporation of Mn^{n+} into the CeO_2 lattice to form a uniform ceria-based solid solution (containing Mn-O-Ce structures). Strengthening of the electron interaction between MnO_x and CeO_2 (*i.e.*, $\text{Mn}^{3+} + \text{Ce}^{4+} \leftrightarrow \text{Mn}^{4+} + \text{Ce}^{3+}$) driven by the high-temperature and high-pressure conditions during the hydrothermal treatment process, was also beneficial for the adsorption and activation of NH_3 molecules.

$\text{NO} + \text{O}_2$ co-adsorption *in situ* DRIFTS studies were performed on these representative samples to investigate their oxidation ability for NO to NO_2 and the adsorption behavior of NO species, as shown in Fig. 7. For CeO_2 (Fig. 7(a)), following introduction of $\text{NO} + \text{O}_2$ mixed gases into the *in situ* DRIFTS cell at room temperature (25 °C), several vibration bands appeared in the range of 900–1700 cm^{-1} . Bridging bidentate nitrate ex-

hibited an N=O stretching vibration band at 1611 cm^{-1} , and a NO_2 symmetric vibration mode at 1006 cm^{-1} ; the linear nitrite displayed a vibrational band at 1278 cm^{-1} ; moreover, the chelating bidentate nitrate showed a vibration mode at 1229 cm^{-1} [2,62,63]. As temperature was increased, the band of the linear nitrite weakened and disappeared at 350 °C due to desorption/decomposition/transformation during the heating process. We found that the bands of the bridging bidentate nitrate and chelating bidentate nitrate increased in intensity as the temperature was increased owing to oxidation of NO to NO_2 . The NO_2 was adsorbed to the CeO_2 surface and formed different kinds of nitrates. With regard to the MnCe-HTM catalyst (Fig. 7(b)), all the vibrational bands of bridging bidentate nitrate, linear nitrite, and chelating bidentate nitrate were also detected at the same corresponding positions at 25 °C. The changes of

Fig. 7. $\text{NO} + \text{O}_2$ co-adsorption *in situ* DRIFTS of (a) CeO_2 and (b) MnCe-HTM catalyst.

these bands with temperature for the MnCe-HTM catalyst were similar to those which occurred for CeO₂. Interestingly, compared with CeO₂, the linear nitrite band for the MnCe-HTM catalyst disappeared at a lower temperature of 200 °C. This indicates that the desorption/decomposition/transformation of linear nitrite was promoted by the electronic interaction between MnO_x and CeO₂. Fig. 7(a) and (b) show that bands of bridging bidentate nitrate and chelating bidentate nitrate on the surface of the MnCe-HTM catalyst were stronger than those on the CeO₂ surface at all temperatures. Moreover, the intensity of these bands increased more rapidly for the MnCe-HTM catalyst than CeO₂ as temperature was increased. These phenomena may be attributed to the incorporation of Mnⁿ⁺ into the CeO₂ lattice to form a uniform ceria-based solid solution (containing Mn-O-Ce structures). The strengthening of the electronic interaction between MnO_x and CeO₂ (*i.e.*, Mn³⁺ + Ce⁴⁺ ↔ Mn⁴⁺ + Ce³⁺), driven by the high-temperature and high-pressure conditions during the hydrothermal treatment process, also effectively improved adsorption of NO species and the ability of the catalyst to oxidize NO to NO₂. This was attributed to good migration ability of oxygen, which resulted from the high oxygen vacancy concentration in the MnCe-HTM catalyst. This effect enhanced the catalytic performance for selective catalytic reduction of NO by NH₃ through a “fast NH₃-SCR” route.

To explore the reaction mechanism of the selective catalytic reduction of NO by NH₃ over MnO_x-CeO₂ catalysts, NO+NH₃+O₂ co-adsorption was measured by *in situ* DRIFTS under the reaction conditions for these representative samples, and the corresponding results are presented in Fig. 8. When CeO₂ was exposed to NO+NH₃+O₂ mixed gases at 25 °C, bridging bidentate nitrate and linear nitrite were observed at 1605 and 1284 cm⁻¹, respectively [62,63]. Furthermore, NH₄⁺ species adsorbed to B acid sites and NH₃ species coordinated to L acid sites were also detected at 1435 and 1200 cm⁻¹, respectively [59,60]. Compared with the *in situ* DRIFTS results for NH₃ adsorption (Fig. 6(a)), the B and L acid bands were more intense in the reaction

mixture because the presence of NO+O₂ increased the amount of acidic sites in CeO₂. However, as the temperature was increased, the B and L acid bands disappeared at 100 and 300 °C, respectively. Bands of chelating bidentate nitrate appeared at 1530 and 1220 cm⁻¹, and the bridging bidentate nitrate exhibited a NO₂ symmetric vibrational band at 1017 cm⁻¹ [62]. For the MnCe-HTM catalyst (Fig. 8(b)), in the presence of the mixed gases in the *in situ* DRIFTS cell at room temperature (25 °C), bridging bidentate nitrate (1605 and 1023 cm⁻¹), chelating bidentate nitrate (1542 and 1266 cm⁻¹), monodentate nitrate (1495 cm⁻¹), linear nitrite (1301 cm⁻¹), B acid (1435 cm⁻¹), and L acid (1188 cm⁻¹) bands were detected [23,59,60,62]. These results suggested that both of NO and NH₃ were simultaneously adsorbed on the surface of MnCe-HTM catalyst. This indicated that selective catalytic reduction of NO by NH₃ over the MnCe-HTM catalyst followed a Langmuir-Hinshelwood (L-H) mechanism. Furthermore, we found that the intensity of bands from adsorbed NO species on the MnCe-HTM catalyst were stronger than that on CeO₂. This can again be attributed to the introduction of MnO_x. This observation is supported by reports from Li *et al.* [64], who reported that Mn species can improve the adsorption of NO species to CeO₂ catalysts. At elevated temperatures, the B and L acid band disappeared at 200 and 300 °C, respectively. Changes in the bands of the adsorbed NO species were not obviously owing to the balance between NO conversion and NO adsorption. However, the bands for adsorbed NO species became more intense above 300 °C owing to declining NO conversion. These findings are also supported by the results of the NH₃-SCR model reaction.

3.6. Possible reaction mechanism for NH₃-SCR over MnO_x-CeO₂ catalysts

On the basis of our characterizations, we propose a possible reaction mechanism (schematic diagram) for the selective catalytic reduction of NO by NH₃ under the current reaction condi-

Fig. 8. NO+NH₃+O₂ co-adsorption *in situ* DRIFTS of (a) CeO₂ and (b) MnCe-HTM catalyst.

Fig. 9. Possible reaction mechanism (schematic diagram) of NH_3 -SCR over MnO_x - CeO_2 catalysts.

tions, as shown in Fig. 9. The results obtained indicated that the MnCe-HTM catalyst exhibited excellent physicochemical properties, optimal catalytic performance, and good H_2O resistance during a low-temperature NH_3 -SCR model reaction. The reaction mechanism over the MnCe-HTM catalyst was examined. When exposed to a mixture of $\text{NO}+\text{NH}_3+\text{O}_2$ gases, the reactant molecules can simultaneously adsorb to the MnCe-HTM catalyst surface, and the selective catalytic reduction of NO by NH_3 over MnCe-HTM catalyst follows a L-H mechanism. This is supported by the results of our *in situ* DRIFTS studies. First, oxygen vacancies associated with Ce^{3+} enhanced the migration abilities of oxygen and activated O_2 molecules to generate surface adsorbed oxygen species (such as $\text{O}^-(\text{ad})$), as confirmed from our Raman and XPS results. Second, it has been reported that Mn species promote adsorption of NO species to these catalysts [64]. Any NO molecules adsorbed to Mn species can be transformed into $\text{NO}^+(\text{ad})$ by donation of electrons to Mn^{4+} . The oxidized species can then further react with surface adsorbed oxygen species to form NO_2 or adsorbed nitrate (ad-NO_3^-). These findings are consistent with the results of our *in situ* DRIFTS studies. The intensities of the vibration bands for NH_4^+ and NH_3 at B and L acid sites, respectively, were clearly stronger for the MnCe-HTM than those for CeO_2 , indicating that the adsorption of NH_3 molecules occurred mainly on Mn species. Adsorbed NH_3 species (NH_4^+ and $\text{NH}_3(\text{ad})$) react with surface adsorbed oxygen species to generate adsorbed $-\text{NH}_2$ (ad-NH_2). Finally, NO_2 or ad-NO_3^- reacts with ad-NH_2 to form the final products, N_2 and H_2O . To summarize, the redox interaction between $\text{Mn}^{3+} + \text{Ce}^{4+} \leftrightarrow \text{Mn}^{4+} + \text{Ce}^{3+}$ can remarkably increase Ce^{3+} , Mn^{4+} , oxygen vacancies, the amount of acidic sites and their acidic strength. These features enhance the catalytic performance of MnO_x - CeO_2 catalysts in the NH_3 -SCR model reaction. The MnCe-HTM catalyst exhibited the best catalytic performance owing to the strongest electron interaction between MnO_x and CeO_2 .

4. Conclusions

In the present work, a series of MnO_x - CeO_2 catalysts were synthesized by different preparation methods to explore the effects on physicochemical properties and catalytic perfor-

mance for the selective catalytic reduction of NO by NH_3 at low temperature. Several conclusions can be drawn as follows:

(1) Mn^{n+} species can be incorporated into the lattice of CeO_2 . The presence of these cations inhibits the grain growth, resulting in smaller crystallite sizes and larger BET specific surface areas for the MnO_x - CeO_2 catalysts prepared by the hydrothermal treatment method, co-precipitation method, and sol-gel method.

(2) The MnCe-HTM catalyst exhibited the best catalytic performance and good H_2O resistance for the low-temperature NH_3 -SCR model reaction. This was attributed to the high content of surface Ce^{3+} , Mn^{4+} , and adsorbed oxygen species, as well as a high concentration of oxygen vacancies and a large amount of acidic sites with high acidic strength. These effects resulted from incorporation of Mn^{n+} ($n = 2-4$) into the CeO_2 lattice to form a uniform ceria-based solid solution (containing Mn-O-Ce structures). Furthermore, these features were linked to strengthening of the electronic interaction between MnO_x and CeO_2 (i.e., $\text{Mn}^{3+} + \text{Ce}^{4+} \leftrightarrow \text{Mn}^{4+} + \text{Ce}^{3+}$) driven by the high-temperature and high-pressure conditions during the hydrothermal treatment process.

(3) NO, NH_3 , and O_2 can interact with MnCe-HTM catalyst simultaneously, which indicates that the selective catalytic reduction of NO by NH_3 over MnCe-HTM catalyst follows a L-H mechanism.

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Graphical Abstract

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Influence of preparation methods on the physicochemical properties and catalytic performance of $\text{MnO}_x\text{-CeO}_2$ catalysts for $\text{NH}_3\text{-SCR}$ at low temperature

Xiaojiang Yao *, Kaili Ma, Weixin Zou, Shenggui He, Jibin An, Fumo Yang *, Lin Dong *

Chongqing Institute of Green and Intelligent Technology, Chinese Academy of Sciences; Nanjing University; Institute of Chemistry, Chinese Academy of Sciences; Chongqing University of Arts and Sciences; Institute of Urban Environment, Chinese Academy of Sciences

Electron interaction between MnO_x and CeO_2 is influenced by the preparation methods, which can improve the physicochemical properties of $\text{MnO}_x\text{-CeO}_2$ catalysts, and promote the adsorption/activation of reactant molecules to result in excellent catalytic performance.

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制备方法对 $\text{MnO}_x\text{-CeO}_2$ 催化剂理化性质及低温 $\text{NH}_3\text{-SCR}$ 脱硝性能的影响

姚小江^{a,*}, 马凯莉^b, 邹伟欣^b, 何圣贵^c, 安继斌^d, 杨复沐^{a,e,#}, 董林^{b,\$}

^a中国科学院重庆绿色智能技术研究院, 中国科学院水库水环境重点实验室, 重庆400714

^b南京大学化学化工学院, 介观化学教育部重点实验室, 江苏南京210093

^c中国科学院化学研究所, 北京分子科学国家实验室, 北京100190

^d重庆文理学院, 环境材料与修复技术重庆市重点实验室, 重庆402160

^e中国科学院城市环境研究所, 中国科学院区域大气环境研究卓越创新中心, 福建厦门361021

摘要: 随着人们环保意识的增强, 氮氧化物(NO_x)的危害引起广泛关注. NO_x 作为首要的大气污染物之一, 主要来源于以燃煤电厂为代表的固定源和以机动车为代表的移动源. 它不仅能够导致酸雨和光化学烟雾, 而且还是 $\text{PM}_{2.5}$ 的重要前驱体, 严重危害人类健康和植物生长. 因此, NO_x 的治理迫在眉睫. 研究表明, 氨选择性催化还原($\text{NH}_3\text{-SCR}$)技术是控制固定源 NO_x 排放最经济有效的方法.

商业化 $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ 和 $\text{V}_2\text{O}_5\text{-MoO}_3/\text{TiO}_2$ 脱硝催化剂的最佳工作温度窗口为300–400 °C. 因此, $\text{NH}_3\text{-SCR}$ 脱硝设施通常安装在除尘器和脱硫装置之前以满足最佳工作温度需要. 然而, 在这种情况下, 脱硝催化剂容易因烟气中的飞灰和含硫化化合物堵塞、中毒而失活. 此外, 对于老电厂增加脱硝设施的改造工程, 在除尘器和脱硫装置之前没有足够的空间用于安装脱硝设施. 因此, 开发环境友好型低温 $\text{NH}_3\text{-SCR}$ 脱硝催化剂显得尤为重要, 因为它可以直接安装在除尘器和脱硫装置之后, 从而有效减缓脱硝催化剂失活, 有利于改造工程的施工.

研究表明, 锰基催化剂由于其优异的氧化还原性能和氧迁移能力有利于氧化 NO 为 NO_2 , 促进反应沿着“快速 $\text{NH}_3\text{-SCR}$ ”途径进行, 从而表现出优异的低温脱硝性能. 然而, 其 N_2 选择性、抗水性能和工作温度窗口还有待改善. 因此, 开发既具有高催化活性又具有宽工作温度窗口、优异抗水性能以及理想 N_2 选择性的低温脱硝催化剂仍是一个富有挑战性的课题.

二氧化铈(CeO_2)由于具有优异的氧化还原性能、良好的储/释氧能力、丰富的氧空位以及 $\text{Ce}^{4+}/\text{Ce}^{3+}$ 的轻易切换而被广泛用于 $\text{NH}_3\text{-SCR}$ 反应. 因此, 将锰氧化物(MnO_x)与 CeO_2 相结合而制备的 $\text{MnO}_x\text{-CeO}_2$ 催化剂可能会表现出优异的低温脱硝性能. 而催化剂的理化性质和催化性能还强烈地依赖于其制备方法. 因此, 本文采用不同方法(机械混合法、浸渍法、水热法、共沉淀法以及溶胶-凝胶法)制备了一系列 $\text{MnO}_x\text{-CeO}_2$ 催化剂用于低温 $\text{NH}_3\text{-SCR}$ 反应, 并运用X射线衍射(XRD)、拉曼光谱(Raman)、氮气物理吸附、氢气程序升温还原($\text{H}_2\text{-TPR}$)、氨气程序升温脱附($\text{NH}_3\text{-TPD}$)、X射线光电子能谱(XPS)以及原位漫反射红外光谱(*in situ* DRIFTS)等表征技术对催化剂进行了系统分析. 重点考察了制备方法对 $\text{MnO}_x\text{-CeO}_2$ 催化剂理化性质和催化性能的影响.

结果表明, 低温脱硝性能有如下顺序: 水热法 > 溶胶-凝胶法 > 共沉淀法 > 浸渍法 > 机械混合法. 这与催化剂表面 Ce^{3+} 和 Mn^{4+} 含量、氧空位和表面吸附氧物种浓度以及酸量和酸强度顺序一致. 这些性质都与 MnO_x 和 CeO_2 之间的电子相互作用(即 $\text{Mn}^{3+} + \text{Ce}^{4+} \leftrightarrow \text{Mn}^{4+} + \text{Ce}^{3+}$)密切相关. 特别是水热法制备的 $\text{MnO}_x\text{-CeO}_2$ 催化剂(MnCe-HTM)由于 Mn^{n+} 掺入到 CeO_2 晶格形成铈基固溶体(含 Mn-O-Ce 结构)以及水热过程中的高温高压环境加强了 MnO_x 和 CeO_2 之间的电子相互作用, 从而表现出优异的理化性质、最佳的低温脱硝性能以及理想的抗水性能.

关键词: $\text{MnO}_x\text{-CeO}_2$ 催化剂; 制备方法; 氮氧化物; 低温氨选择性催化还原; 电子相互作用; 表面酸性

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*通讯联系人. 电话: (023)65935909; 传真: (023)65935924; 电子信箱: yaoxj@cigit.ac.cn;

#通讯联系人. 电话: (023)65935909; 传真: (023)65935924; 电子信箱: fmyang@cigit.ac.cn

\$通讯联系人. 电话: (025)83592290; 传真: (025)83317761; 电子信箱: donglin@nju.edu.cn

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