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Novel CeMn_aO_x catalyst for highly efficient catalytic decomposition of ozone



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ABSTRACT

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Novel CeMn_aO_x (a is the molar ratio of Mn to Ce) catalysts for catalytic decomposition of ozone (O₃) under high GHSV conditions were successfully synthesized by a facile homogeneous precipitation method. CeMn₁₀O_x showed ozone conversion of 96 % for 40 ppm O₃ under relative humidity (RH) of 65 % and space velocity of $840 \text{ Lyg}^{-1} \text{ h}^{-1}$ after 6 h at room temperature, which is far superior to the performance of the α -Mn₂O₃ (38 %). The ozone decomposition activity of α -Mn₂O₃ increased by a factor of 2.5 with the addition of Ce. XRD, XPS, H₂-TPR, O₂-TPD, EXAFS and DFT calculations data confirmed that cerium-manganese complex oxides with enhanced surface area were formed, which played a key role in the decomposition that can be prepared by a simple method, and promoting the performance of manganese oxides for practical ozone elimination.

1. Introduction

Tropospheric ozone is one of the most widespread global air pollution problems today. As a highly reactive oxidant, it is harmful to human health and crop production [1-5]. Therefore, the World Health Organization set the guideline value (WHO2005) for ozone at 50 ppb for an 8-h daily average. Tropospheric ozone is formed mainly by the interaction of sunlight with volatile organic compounds (VOCs) and nitrogen oxides (NO_x) . In recent years, the concentration of ozone in the troposphere has increased in the most populous countries or regions [4,6-8]. The increase of outdoor ozone will lead to an increase in indoor ozone, because of the air exchange between the indoor and outdoor air. Ionizing or ozonolysis air cleaners are the main sources of indoor ozone [9]. The concentration of ozone in aircraft cabins could be significantly higher than the recommended exposure limit. Besides its direct effects on health, ozone can react with VOCs to produce more toxic oxidation products [10,11]. Therefore, the study of ozone decomposition is urgent for the protection of environmental and human health.

Catalytic decomposition is the most effective method to remove ozone at present. Catalysts for ozone decomposition include noble metals and transition metal oxides [12–15]. Among these catalysts, manganese oxides are a highly efficient and economical catalysts for ozone decomposition, especially MnO_2 [16–25]. Recent studies have

found that modification with another transition metal, especially Ce, can effectively improve the ozone catalytic decomposition activity of MnO₂ [26-35]. For example, Liu et al. [28] found that Ce modification of todorokite-type MnO₂ changes the morphology from agglomerated particles to small sheets, increasing the surface area and oxygen vacancies due to the crystal boundaries between MnO2 and CeO2, which act as the active sites for ozone decomposition. Ma et al. [30] found that the replacement of K^+ in the tunnel and Mn^{4+} in the framework of MnO_2 (OMS-2) by Ce^{3+} can increase the content of Mn^{3+} (along with oxygen vacancies) and surface defects, which is favorable for ozone decomposition. Li et al. [31] found that the formation of mixed crystals consisting of α -MnO₂ and γ -MnO₂ after doping with Ce increased the surface area and surface defects of γ -MnO₂, which play a key role during the decomposition of ozone. These results indicate that Ce modification is an effective means to improving the catalytic activity of manganese oxides for ozone decomposition. However, it should be pointed out that all these catalysts are prepared by complex hydrothermal methods, which is time-consuming, energy-consuming and produces a large amount of waste liquid.

In this study, a series of novel CeMn_aO_x catalysts for highly efficient catalytic decomposition of ozone were successfully synthesized by a facile homogeneous precipitation method. The ozone decomposition activity of α -Mn₂O₃ increased by a factor of 2.5 with the addition of Ce. With characterization by XRD, XPS, H₂-TPR, O₂-TPD and EXAFS, the

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high performance was found to be related to the formation of ceriummanganese complex oxides at the interface between CeO₂ and α -Mn₂O₃. Unwashed catalysts had the same activity as catalysts washed to neutral, which solves the problem of producing large amounts of wastewater in the process of catalyst production. This study provides important insights for developing improved catalysts for gaseous ozone decomposition that can be prepared by a simple method, and promoting the performance of manganese oxide for practical ozone elimination.

2. Experimental

2.1. Preparation of catalysts

The CeMn_aO_x (a is the molar ratio of Mn to Ce) catalysts were prepared by the homogeneous precipitation method. Aqueous solutions of Mn(AC)₂·4H₂O as Mn precursor and Ce(NO₃)₃·6H₂O as Ce precursor were mixed in the required molar ratios (the molar ratios of Ce and Mn were 1:6, 1:8, 1:10 and 1:15). An excess of urea enough to precipitate all precursors was then added into the mixed solution. The solution was heated to 90°C with a plastic film cover and held there for 12 h under vigorous stirring. After filtration and washing with deionized water, the resulting precipitate was dried at 100°C overnight and subsequently calcined at 600°C for 3 h in air (the heating rate was controlled at 5°C/ min). The synthetic procedure for unwashed sample was similar to that for CeMn_aO_x without washing with deionized water. The synthetic procedure for MnO_x (CeO₂) was similar to that for CeMn_aO_x without the addition of Ce(NO₃)₃·6H₂O (Mn(AC)₂·4H₂O) in the initial solution. In order to determine the optimal calcination temperature, we also prepared CeMn₁₀O_x at different temperatures (300, 400, 500 and 700°C). A catalyst having the same molar ratio of Ce and Mn as CeMn₁₀O_x was prepared by mechanical mixing of the appropriate amount of CeO₂ and MnOx.

2.2. Catalyst characterization

The phase structures of the catalysts were studied by X-ray powder diffraction (XRD, Bruker D8A A25) with Cu Ka radiation $(\lambda = 0.15418 \text{ nm})$ at 40 kV and 40 mA and scanning range from 5-90° with a step of 0.02° and a scan rate of 1.5° min⁻¹. Raman spectra were measured with a laser microconfocal Raman spectrometer (InVia Reflex, Renishaw). The morphologies were observed with a SU8020 field emission scanning electron microscope (FESEM) at an accelerating voltage of 3 kV. Nitrogen adsorption-desorption isotherms were obtained using a Quantachrome physisorption analyzer at 77 K. H₂-TPR and O2-TPD experiments were conducted using an AutoChemII 2920 Chemisorption Analyzer (Micromeritics) equipped with a TCD detector and MS, respectively. X-ray photoelectron spectroscopy (XPS) measurements were carried out using an Imaging X-ray Photoelectron Spectrometer (Axis Ultra, Kratos Analytical Ltd.). The XANES and EXAFS of Ce-L3 and Mn-K edges were measured at room temperature on the BL14W1beam line, Shanghai Synchrotron Radiation Facility (SSRF), Shanghai China.

2.3. Catalytic activity

The activity of the catalysts for ozone decomposition was measured in a fixed-bed continuous flow quartz reactor (4 mm i.d.) using about 150 mg of catalyst with size of 40–60 mesh at room temperature (30 °C). The gas flow passing through the reactor was 1400 mL/min, and the weight space velocity was calculated to be $560 \text{ L·g}^{-1} \cdot \text{h}^{-1}$. Activity testing at higher weight space velocity (840 L·g⁻¹ ·h⁻¹) conditions was carried out by reducing the amount of catalyst to 100 mg. The relative humidity of the gas stream was maintained at 65 % by controlling the flow of wet gas, and measured with a humidity probe (HMP110, Vaisala OYJ). The ozone was generated by exposing the air to low-pressure ultraviolet lamps, and the concentration was maintained at 40 \pm 2 ppm. An ozone monitor (Model 202, 2B Technologies) was used to monitor the inlet and outlet ozone concentrations. The ozone conversion was calculated by the following equation:

$$D_3 \text{ conversion} = \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}} \times 100\%$$

where $C_{\rm in}$ and $C_{\rm out}$ are inlet and outlet concentrations of ozone, respectively.

2.4. DFT calculations

All calculations were performed using the Perdew-Burke-Ernzerhof (PBE) functional [36] with van der Waals correction proposed by Becke-Jonson (i.e., DFT-D3 method) [37] as implemented in the Vienna ab initio simulation package (VASP 5.4.4) [38]. The projector augmented wave method (PAW) was used to describe the interaction between the ions and the electrons [39]. To properly describe the localization of electrons on Mn_{3d} and Ce_{4f} levels, a Coulomb U of 1.6 eV and 4.5 eV for Mn_{3d} and Ce_{4f} respectively was introduced, which was consistent with the values used in the literature [40,41]. The energy cutoff of the plane wave was set to 400 eV. The unit cell of α -Mn₂O₃ was modeled using the cubic bixbyite structure (lattice constants: a =9.4157 Å, b =9.4233 Å, c =9.4047 Å) [42]. According to previous research [40], the (001) and (111) crystal facets are the predominantly exposed facts of α -Mn₂O₃, therefore we constructed 7-layer p(1 × 1) (001) plane and 9-layer p(1 \times 1) (111) plane models of α -Mn₂O₃. A vacuum gap of 12 Å thickness was adopted so that self-interactions among the adsorbates could be ignored. During the geometrical optimization, the top O-Mn-O layers were allowed to relax, while all other atoms were fixed at their bulk positions until the forces on each atom were smaller than 0.02 eV/Å. Only the Gamma point of the Brillouin zone was sampled. The Gaussian smearing method with a smearing width of 0.2 eV was employed to accelerate the convergence of integration at the Brillouin zone. The energetic convergence threshold for the self-consistent field (SCF) is 1.0×10^{-5} eV/atom. One Mn atom on the top surface was replaced by a Ce atom for the Ce-Mn₂O₃ model.

The adsorption energy of the adsorbate (O_3) is defined as follows:

 $E_{ads} = E_{total} - E_{basic} - E_{adsorbate}$

where E_{ads} is the binding energy of the adsorbed molecule to the surface, E_{total} is the total energy of the adsorption model, E_{basic} is the energy of the surface and $E_{adsorbate}$ is the energy of an isolated molecule of the adsorbate.

3. Results and discussion

3.1. Effect of calcination temperature and water washing on the ozone decomposition over $CeMn_{10}O_x$

Fig. 1A shows the catalytic activity for ozone decomposition on CeMn₁₀O_x catalysts calcined at different temperatures. The activity of CeMn₁₀O_x catalysts prepared at 300, 400 and 700°C dropped sharply within 6 h. The CeMn₁₀O_x catalysts prepared at 500 and 600°C dropped only slightly to 97.9 % and 99.5 % ozone conversion after 6 h, respectively. The XRD patterns of the as-prepared catalysts are shown in Fig. 1B. The uncalcined materials were composed of MnCO₃ and Ce₂O $(CO_3)_2$ ·H₂O. Ce₂O $(CO_3)_2$ ·H₂O was decomposed into CeO₂ by calcining at 300°C (Fig. 1B), which was also confirmed by an obvious desorption peak of H₂O before 300°C in the TG-DSC-MS results (Figure S1) and consistent with a previous study [43]. MnCO₃ also began to decompose at 300°C, but did not decompose completely until 500°C, which was consistent with previous results [25,44]. After calcination at 300°C and 400°C, the two most intense XRD peaks of MnCO3 (20 = 24.3° and 31.4°) were still observed, while the characteristic peaks of MnO2 also appeared. Further increasing the calcination temperature to 500°C, the



Fig. 1. (A) The conversion of ozone over $CeMn_{10}O_x$ catalysts calcined at different temperatures. Conditions: ozone inlet concentration 40 ppm, temperature 30 °C, RH = 65 %, weight space velocity = $560 L g^{-1} h^{-1}$; (B) XRD patterns of $CeMn_{10}O_x$ catalysts calcined at different temperatures.

diffraction peaks of MnCO₃ disappeared, which means that MnCO₃ was decomposed completely. When the temperature was increased to 600°C, the diffraction peaks of Mn₂O₃ could be detected, which is ascribed to the thermal decomposition of MnO₂ to Mn₂O₃. The decrease of the half-width of peak at 23.24° indicating that the crystallinity of Mn₂O₃ was further increased by increasing the calcination temperature to 700°C. No peaks for other crystal phases were observed in the XRD pattern. Therefore, the CeMn₁₀O_x catalyst prepared at 500°C consisted mainly of MnO₂ and CeO₂. The CeMn₁₀O_x catalyst prepared at 600°C consisted mainly of Mn₂O₃ and CeO₂. Because the decomposition performance of ozone over CeO₂ is very poor (Figure S2), the high ozone decomposition activity of the CeMn₁₀O_x catalyst prepared at 600°C appears at first glance to be attributable to the formation of Mn₂O₃. However, this is inconsistent with the reported ozone decomposition activity of Mn₂O₃, which is significantly lower than that of MnO₂ [25].

3.2. Effect of Ce/Mn ratio on the ozone decomposition over $CeMn_aO_x$

Since the $CeMn_{10}O_x$ catalyst prepared at 600°C possessed the best performance for ozone decomposition, the effect of the Ce/Mn ratio on the catalytic activity for ozone decomposition over CeMn_aO_x catalysts prepared at 600°C was further investigated, and the results are shown in

Fig. 2A. The activity of MnO_x was only about 40 % after 6 h and the XRD results confirmed that the material was Mn₂O₃ (Fig. 2B). This is consistent with previous work showing that Mn₂O₃ is a poor ozone decomposition catalyst [25]. It can be seen from Fig. 2B that the addition of Ce reduces the crystallinity and crystal size of Mn₂O₃, and also leads to the formation of CeO2. Raman spectroscopy also confirmed that the catalyst surface was also a mixture of CeO₂ and Mn₂O₃ (Figure S3). A catalyst with poor crystallinity can generate more defects, which is favorable to the adsorption and decomposition of ozone molecules [31]. The crystallinity of CeMn₈O_x, CeMn₁₀O_x and CeMn₁₅O_x catalysts was similar, but the activity of the CeMn₁₀O_x catalysts was superior to that of the $CeMn_8O_x$ and $CeMn_{15}O_x$ catalysts. This indicates that besides crystallinity, there are other factors that determine the activity of the catalyst, which will be discussed in the following sections. It was noted that the activity of CeMn₆O_x was only about 60 % after 6 h, which may be due to the presence of too much inactive CeO₂ component. The ozone decomposition rate of $CeMn_aO_x$ catalyst was calculated to be 0.0095, 0.0225, 0.0230, 0.0205 and 0.0135 mmol g^{-1} min $^{-1}$ for MnO_x, CeMn₁₅O_x, CeMn₁₀O_x, CeMn₈O_x and CeMn₆O_x, respectively. In order to compare the activity with MnO₂, a precipitated MnO_x catalyst that has been calcined at lower temperature in order not to decompose the Mn (IV) containing phase. It can be seen that calcined at low temperature



Fig. 2. (A) The conversion of ozone over CeMn_aO_x catalysts prepared at 600°C. Conditions: ozone inlet concentration 40 ppm, temperature 30 °C, RH = 65 %, weight space velocity = $840 \text{ Lg}^{-1} \cdot \text{h}^{-1}$; (B) XRD patterns of CeMn_aO_x catalysts prepared at 600°C.

(400 °C) leads to the formation of MnO₂ (Figure S4), which is the main active component of commercial catalyst. Although the activity of MnO_x samples calcined at 400 °C is better than that of MnO_x samples calcined at 600 °C, both of them are lower than that of $CeMn_{10}O_x$ catalysts prepared at 600 °C under our test conditions. Therefore, CeMn₁₀O_x catalyst is superior to Mn₂O₃ and MnO₂. The ozone decomposition efficiency of physically mixed catalyst is much lower than that of $CeMn_{10}O_x$ (Figure S5), which indicates the importance of the interaction between Ce and Mn. Due to the competitive adsorption of water and ozone molecules, humidity inhibits the decomposition of ozone. However, compared with MnOx, CeMn10Ox has a better ability to resist the decrease of activity caused by humidity (Figure S6). The crystal structure and valence state of the CeMn₁₀O_x catalyst have not changed obviously (Figure S7 and S8), which shows that the $CeMn_{10}O_x$ catalyst has good stability. Water washing is a typical post-treatment process of catalyst preparation that can improve the activity of the catalysts, however, causing large amount of sewage. Figure S9 shows the unwashed catalyst had the same superior activity as the washed catalyst, which indicating that CeMn₁₀O_x catalyst prepared in this work has very high practical value and is very conducive to industrial application.

3.3. Effect of Ce on the structure and properties of $CeMn_aO_x$

Rietveld structure refinement of CeMn_aO_x catalysts were conducted by TOPAS software based on the standard fluorite structure (CeO₂) with a space group Fm3m and bixbyite-type structure (α -Mn₂O₃) with a space group (Ia3) (Figure S10). The values of the lattice parameters and grain size for all the catalysts are listed in Table 1. A decrease in the lattice parameter from 5.410 Å (CeO₂) to 5.391–5.408 Å (CeMn_aO_x catalysts) confirming that some Mn ions are incorporated in the CeO₂ lattice forming homogeneous Ce-Mn solid solutions [45]. However, it can be seen that this CeMn₆O_x catalyst with the most Ce-Mn solid solution content has poor ozone decomposition activity (Fig. 2A), so the Ce-Mn solid solution may not play a key role in ozone decomposition. As can be seen from Table 1, for catalysts with high ozone conversion rate, the main phase structure is α -Mn₂O₃. An increase in the lattice parameter from 9.404 Å (α-Mn₂O₃) to 9.416 Å (CeMn₁₀O_x catalysts) confirming that some Ce ions are incorporated in the α -Mn₂O₃ lattice, because the ionic radius of Ce^{3+} (1.14 Å) or Ce^{4+} (0.87 Å) is bigger that of Mn^{n+} ($Mn^{2+} = 0.83$ Å, $Mn^{3+} = 0.645$ Å, and $Mn^{4+} = 0.53$ Å). Therefore, Ce doped α -Mn₂O₃ is the main active site for ozone decomposition. On the other hand, it can also be seen from Table 1 that the grain size of the CeMn_aO_x catalysts is significantly smaller than that of the pure oxide, which may also be a factor in the improvement of ozone decomposition activity. FESEM images confirmed (Figure S11) that the morphology and size of the mixed oxide is obviously different from that of the pure MnOx and CeO2, indicating the formation of cerium-manganese complex oxide.

Generally, the specific surface area plays an important role in catalyst activity. Figure S12 shows the N₂ adsorption-desorption isotherms of the CeMn_aO_x catalysts. The catalysts have similar N₂ adsorption/

Table 1

The lattice parameters and	grain	size	of	CeMn _a O _x	cataly	sts
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Catalysts	CeO ₂			α -Mn ₂ O ₃		
	Phase content (%)	Grain size (nm)	Lattice parameters (a)	Phase content (%)	Grain size (nm)	Lattice parameters (a)
MnO _x	0	-	-	100	35.4	9.404
CeMn ₁₅ O _x	19.9	3.7	5.401	80.1	22.5	9.409
CeMn ₁₀ O _x	23.9	6.3	5.404	76.1	22.3	9.416
CeMn ₈ O _x	28.0	7.8	5.408	72.0	23.2	9.409
CeMn ₆ O _x	33.8	8.2	5.403	66.2	22.7	9.404
CeO ₂	100	9.4	5.410	0	-	-

desorption isotherms, showing the characteristics of mesoporous materials. The specific surface areas, average pore diameters and pore volumes are shown in Table S1. Compared with pure MnO_x , the addition of Ce doubled the specific surface area of the $CeMn_aO_x$ catalysts. The specific surface areas of the $CeMn_15O_x$, $CeMn_10O_x$, $CeMn_8O_x$ and $CeMn_6O_x$ catalysts were 89, 75, 84 and 76 m²/g, respectively. The enhanced surface area is beneficial to the increase of ozone decomposition. The pore distribution of the MnO_x catalyst shows a maximum at 30.6 nm as shown in Figure S13. With the substitution of Ce, the pore size became smaller and adopts a bimodal pattern (with peaks at 3.8 and 17 nm). These results also show that the particle size of the catalyst decreases, which is consistent with the XRD results.

The valence state of Ce ions in the catalysts was characterized by analyzing their Ce 3d XPS spectra (Figure S14). The Ce³⁺/(Ce³⁺ + Ce⁴⁺) ratio in CeMn₁₅O_x, CeMn₁₀O_x, CeMn₈O_x and CeMn₆O_x catalysts was estimated by the deconvolution of their Ce 3d XPS spectra to be 0.17, 0.16, 0.16 and 0.14 (Table S2), respectively, indicating that most of the Ce ions exist in the form of Ce⁴⁺. The actual atomic ratios of Ce to Mn are 2.8–5.7 times higher than the nominal values (Table S2), which indicates that Ce aggregates on the catalyst surface.

The XPS spectra of Mn 2p and O 1s are shown in Fig. 3. For the MnO_x catalyst without Ce substitution, the binding energies of Mn $2p_{3/2}$ and Mn 2p_{1/2} peaks were located at 641.7 and 653.5 eV, respectively, which indicated that the majority of manganese species in this catalyst were in the Mn^{3+} oxidation state, similar to those in Mn_2O_3 [46,47]. In addition, a small fraction of the manganese species in this catalyst were in the Mn⁴⁺ oxidation state, thus the overall manganese species in MnO_x showed slightly higher binding energies than those in Mn_2O_3 , which was also reported in the literature (Mn $2p_{3/2}$ at 641.3 \pm 0.2 eV) [46]. With increasing Ce substitution amounts, the intensities of Mn $2p_{3/2}$ and Mn $2p_{1/2}$ peaks gradually weakened due to decrease in the concentration of surface manganese species. At the same time, the corresponding binding energies also showed variation, with Mn 2p_{3/2} shifting from 641.7–641.2 eV and Mn $2p_{1/2}$ shifting from 653.5–653.0 eV. This result showed that the Mn^{4+}/Mn^{3+} ratio in CeMn_aO_x catalysts became smaller when the Ce substitution amount was higher. Fig. 3B shows that the O 1s peaks also shifted from 529.8-529.3 eV. These results indicated that the electron cloud density of Mn and O on the surface increases and the reduction ability increases.

The H₂-TPR profiles (Fig. 4A) of the CeMn_aO_x catalysts were measured to evaluate their reducibility. The MnOx and CeMnaOx catalysts all exhibited two principal reduction peaks (peak II and III). As shown in Table S3, the H₂ consumption of peak III is about twice that of peak II, so the catalysts could mainly follow a reduction route such that Mn₂O₃ firstly transforms into Mn₃O₄, then to MnO. The reduction peaks of MnO_x appeared at 288 and 385 °C. The shift of the two reduction peaks of CeMn_aO_x to lower temperature indicates that they have higher reducibility, which is consistent with the XPS results. It is noteworthy that a new reduction peak (peak I) appears between 100 and 250 °C for CeMn_aO_x catalysts. This peak is not caused by the reduction of CeO₂, because only a weak reduction peak between 300 and 500 °C was observed for CeO₂, which is consistent with the results in the literature [48–50]. This peak may be due to the formation of cerium-manganese complex oxides. According to previous reference [51], the reductive step of the ozone decomposition catalytic cycle is rate limiting, therefore the promoted reducibility for the mixed oxide catalysts caused the promoted ozone decomposition. The oxygen storage capacity (OSC) of the catalysts were calculated and shown in Table S1. With the increase of Ce content, the OSC of the catalyst decreased, which was consistent with the decrease of surface oxygen content in XPS. For further investigation of the oxygen mobility of the catalysts, O2-TPD tests were carried out and the results are shown in Fig. 4B. It can be seen that all catalysts exhibited prominent desorption peak at around 800 °C which is attributed to lattice oxygen [40]. For the CeMn_aO_x catalyst, new desorption peaks appeared over a rather broad temperature range



Fig. 3. (A) Mn 2p and (B) O 1s XPS spectra of the CeMn_aO_x catalysts.

(200-700 °C) with three maxima at 327, 594 and 654 °C. These results indicate that the oxygen mobility in the CeMn_aO_x catalyst is stronger than that in either CeO₂ or MnO_x, which is consistent with the TPR results, indicating the formation of cerium-manganese complex oxides.

X-ray absorption fine structure spectroscopy (XAFS) is a suitable tool to characterize structural information because it can be used to determine the local environment around specific atoms, irrespective of the crystallinity or dimensionality of the target materials. Fig. 5 A presents the normalized XANES of the Ce-L₃-edge in the Ce-containing catalysts. It can be seen that the CeMn_aO_x catalysts exhibit a split double peak structure at the threshold, similar to CeO₂. This indicates that cerium in the CeMn_aO_x catalysts was mainly in the Ce⁴⁺ oxidation state. Although all the catalysts exhibit a split double peak, subtle but clear differences can be seen in the XANES of the CeMn_aO_x samples when compared to CeO2. The four features present in the XANES of CeO₂ are marked in Fig. 5A. It is generally accepted now that the peaks a and b can be attributed to many-body final state effects [52]. Note that the intensity of peak b is larger than that of peak a in CeO₂. However, in the CeMn_aO_x catalysts the relative intensity of these two peaks is changed, i.e. the intensity ratio of peak b to peak a becomes smaller (Fig. 5B). This was caused by the different long-range crystal structures, although the local structure is the same as in CeO₂. These results indicate that Ce-Mn solid solution have been formed in the catalyst, which is consistent with the XRD results. As shown in Fig. 5C,

both the pre-edge peaks and the post-edge regions of the Mn-K-edge XANES in CeMn_aO_x catalysts were similar to the reference spectrum of Mn₂O₃. Afterwards, to further determine the average valence of Mn species in our catalysts, the first-order derivatives of the Mn-K-edge XANES in the series of CeMn_aO_x catalysts were taken and compared with those in the reference samples. As shown in Fig. 5D, the Mn K-edge absorption energy (E₀) of the CeMn_aO_x catalysts was determined to be 6548.1 eV, which was identical to the reference α -Mn₂O₃, indicating that the Mn species in our catalysts were mainly in Mn³⁺ oxidation state. These results indicate that the electronic and local structure of our CeMn_aO_x catalysts is similar to that of Mn₂O₃, which is in good accordance with the XRD results.

As shown in Fig. 6A, the Ce-L₃-edge $k^2\chi(k)$ oscillation curve for the CeMn_aO_x catalysts displayed noticeable differences compared with that of CeO₂. This was further verified by comparing their corresponding Fourier transformed (FT) $k^2\chi(k)$ functions in Fig. 6B, which displayed two main peaks at 1.93, and 3.59 Å, corresponding to the Ce-O, and Ce-Ce coordination shells, respectively. For the CeMn_aO_x catalysts, the Ce-O and Ce-Ce peak gradually shifted to the low R direction along with decreased intensities, qualitatively revealing their distinct local atomic arrangements compared with the CeO₂ bulk counterpart. For the Mn-K-edge, there are two main peaks at 1.53, and 2.70 Å, corresponding to the Mn-O, peak shifted to the high R direction along with increased intensities, and the



Fig. 4. (A) H₂-TPR (B) O₂-TPD profiles of the CeMn_aO_x catalysts.



Fig. 5. (A) Ce-L₃-edge XANES of CeMn_aO_x catalysts and Ce-containing reference samples. (B) I_b/I_a of CeMn_aO_x catalysts (C) Mn-K-edge XANES and (D) first-order derivatives of Mn-K-edge XANES of CeMn_aO_x catalysts and Mn-containing reference samples.

Mn-Mn peak shifted to the high R direction along with decreased intensities, qualitatively revealing their different local atomic arrangements compared with the α -Mn₂O₃ bulk counterpart.

In order to explain the shift of the peak position and change of the peak intensity observed in the XAFS results, the local structures of standard α -Mn₂O₃ and CeO₂ were analyzed, as shown in Fig. 7 A and B. The bond lengths and coordination numbers of different coordination

shells are shown in Table S4. The Mn-O and Mn-Mn coordination shells at *ca*.2.003 and 3.104 Å of α -Mn₂O₃ have coordination numbers of 6 and 6, respectively. The Ce-O and Ce-Ce coordination shells at *ca*.2.343 and 3.826 Å of CeO₂ have coordination numbers of 8 and 12, respectively. If a composite oxide structure is formed between Ce and Mn as shown in Fig. 7 C, then the Mn-O peak will shift to the high R direction along with increased intensities, the Ce-O peak shifted to the low R



Fig. 6. Synchrotron radiation XAFS measurements. (A) Ce-L₃-edge extended XAFS oscillation function $k^2\chi(k)$, (B) the corresponding Fourier transforms FT ($k^2\chi(k)$) (R space, phase shift uncorrected), (C) Mn-K-edge extended XAFS oscillation function $k^3\chi(k)$, (D) the corresponding Fourier transforms FT ($k^3\chi(k)$) (R space, phase shift uncorrected) for CeMn_aO_x catalysts and Ce or Mn-containing reference samples.



Fig. 7. (A) local structure model of α -Mn₂O₃, (B) local structure model of CeO₂, (C) schematic diagram of local structure of cerium-manganese complex oxides.

direction along with decreased intensities. Furthermore, the Mn-Mn and Ce-Ce peak will shift to the high R direction and low R direction, respectively, along with decreased intensities, because of the replacement of a Mn atom by a Ce atom or vice versa. These results confirmed the formation of Ce doped α -Mn₂O₃, which can effectively decompose ozone.

Fig. 8 shows schematic drawings of the possible formation process of $CeMn_aO_x$ during calcination. With the hydrolysis of urea, the pH of the solution increases gradually to basic, and the Ce^{3+} or Mn^{2+} in the aqueous solution will precipitate. For pure Ce^{3+} or Mn^{2+} , a carbonate precipitate is first formed and then decomposed into oxides under high temperature calcination, resulting in CeO_2 or α -Mn₂O₃ with large

particle size. For the combined system of Ce³⁺ and Mn²⁺, two kinds of carbonate precipitate were formed at the same time, which were converted into CeO₂ and α -Mn₂O₃ under calcination, resulting in CeO₂ and α -Mn₂O₃ with small particle size. In the calcination process, Ce-Mn solid solution and Ce doped α -Mn₂O₃ were formed.

The critical role of Ce doped α -Mn₂O₃ on the ozone decomposition was further investigated by DFT calculations. Firstly, we optimized the pure and Ce-substituted crystal planes of (001) and (111) of α -Mn₂O₃ (Figure S15 and Figure S16). The substitution of Ce led to prominent surface reconstruction for both (001) and (111) facets after Ce substitution, resulting in a rougher surface, which may be beneficial to the adsorption of molecules on the surface. Based on the results, the adsorption of O₃ molecules on the surface was optimized (Figure S17) and the calculated adsorption energy results are shown in Fig. 9 and Table 2, where a more negative adsorption energy means stronger adsorption. The adsorption energy of ozone on all surfaces is negative, which proves that ozone is easily adsorbed on these surfaces. When ozone is adsorbed on the (001) surface of Mn₂O₃, the O₁-O₂ bond is shortened from 1.29 Å to 1.24 Å, which is consistent with the gaseous oxygen molecule, and the O2-O3 bond is elongated from 1.29 Å to 1.53 Å, which indicates that ozone can be decomposed into oxygen and surface oxygen atoms after adsorption. On the (001) surface of Ce-Mn₂O₃, the stretching of O₂-O₃ after ozone adsorption is greater than that on Mn_2O_3 (1.58 Å vs.1.53 Å), which indicates that ozone is easier to decompose on the Ce-doped surface. When ozone is adsorbed on the (111) surface of Mn₂O₃, the O₁-O₂ bond and the O₂-O₃ bond are elongated from 1.29 Å to 1.40 Å and from 1.29 Å to 1.38 Å, respectively. However, a relatively stable ring-shaped adsorption structure is formed, which indicates that ozone is not easy to decompose on the (111) surface of Mn₂O₃. The linear adsorption of O₃ on the (111) surface of $Ce-Mn_2O_3$ indicates that it is easier to decompose than on the (111) surface of Mn_2O_3 . These results show that the (001) surface has higher activity for the ozone decomposition reaction compared to the (111) surface, and Ce doping can further improve the ozone decomposition activity of Mn₂O₃. These results suggest that Mn₂O₃-phase catalysts with improved ozone decomposition activity can be obtained by controlling the crystal surface. We further calculated the adsorption of water molecules on both the (001) and (111) surface of α -Mn₂O₃ and



Fig. 8. Schematic drawings of the possible formation process of CeMn_aO_x during calcination.



Fig. 9. The calculated adsorption energy of ozone on the (001) and (111) surface of α -Mn₂O₃ and Ce-Mn₂O₃.

Table 2	
The calculated bond length and adsorption energy on the surface.	

$\begin{array}{cccccccccccccccccccccccccccccccccccc$	models	0 ₁ -0 ₂ (Å)	O ₂ -O ₃ (Å)	DS ^a (Å)	E _{ads} (eV)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O ₃ O ₂ O ₃ on Mn ₂ O ₃ (001) O ₃ on Ce-Mn ₂ O ₃ (001) O ₃ on Mn ₂ O ₃ (111) O ₃ on Ce-Mn ₂ O ₃ (111)	1.29 1.24 1.24 1.24 1.24 1.40 1.37	1.29 - 1.53 1.58 1.38 1.39	- 1.86 1.82 1.99/2.05 2.25	- - 0.43 - 0.86 - 1.35 - 5.58

^a DS represents the distance between adsorption atom and surface.

Ce- Mn_2O_3 . The calculated bond length and adsorption energy results are shown in Table S5 in the SI. It can be seen that water is not dissociation but molecular adsorption on the surface. Therefore, water and ozone will compete for adsorption on the surface and inhibit ozone decomposition under high humidity, which is consistent with our experimental results.

4. Conclusions

In this work, a series of novel CeMn_aO_x catalysts with high activity and high thermal stability for catalytic decomposition of ozone under high GHSV conditions were successfully synthesized by a facile homogeneous precipitation method. The ozone decomposition activity of $CeMn_{10}O_x$ was 2.5 times higher than that of α -Mn₂O₃ for 40 ppm O₃ under relative humidity (RH) of 65 % and space velocity of 840 $\text{L}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ ¹ after 6 h at room temperature, indicating that it is a promising material for ozone decomposition. Unwashed catalysts had the same activity as catalysts washed to neutral, which solves the problem of producing large amounts of wastewater in the process of catalyst production. With characterization by XRD, XPS, H2-TPR, O2-TPD, EXAFS and DFT calculations, the high performance was related to the formation of Ce doped α -Mn₂O₃. This study provides important insights for developing improved catalysts for gaseous ozone decomposition that can be prepared by a simple method, and promoting the performance of manganese oxides for practical ozone elimination.

CRediT authorship contribution statement

Jinzhu Ma: Conceptualization, Investigation, Data curation, Writing - original draft. Xiaotong Li: Investigation, Writing - review & editing. **Changbin Zhang:** Writing - review & editing. **Qingxin Ma:** Conceptualization, Writing - review & editing. **Hong He:** Writing - review & editing, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.apcatb.2019.118498.

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