Enhancing Oxygen Vacancies of Ce-OMS-2 via Optimized Hydrothermal Conditions to Improve Catalytic Ozone Decomposition

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S Supporting Information

ABSTRACT: In this study, a series of Ce-OMS-2 catalysts were synthesized by a hydrothermal method, their physicochemical properties and catalytic activity for ozone decomposition were evaluated. The results show that suitable grain size and morphology can be formed as needed by tuning the hydrothermal conditions. In this way, the content of surface oxygen in the catalyst can be increased to enhance the reduction performance of the samples. At the same time, the quantity of low-valent manganese (Mn²⁺ and Mn³⁺) can be increased to raise the oxygen vacancy concentration, and finally improve the O₃ elimination performance of the catalyst. On the basis of this study, we screened out a suitable range of



hydrothermal conditions, namely 95-100 °C and 8-24 h, which showed a higher ozone conversion rate than manganese oxide catalysts reported to date. The durability of the preferred catalyst under harsh conditions shows that preferred Ce-OMS-2 catalysts can meet the requirements of engineering applications.

1. INTRODUCTION

Compared with the "bare teeth and claws" of haze, ozone pollution is "hidden" in the clear sky, and has become a culprit in air pollution as well as a "health killer" of human beings. Outdoor O_3 mostly results from the reactions of nitrogen oxides (NO_r) and volatile organic compounds (VOCs) with solar illumination.^{1,2} Ozone is considered to be a typical secondary pollutant with plant toxicity, which is harmful to land vegetation and crop yield to a certain extent.^{3,4} In addition, indoor ozone produced by electrostatic precipitator, ozone air cleaner, ionic wind, and photocopiers also causes serious air pollution,^{5,6} threatens human health, and leads to respiratory and cardiovascular diseases, permanent lung injury, and even DNA damage in organisms and premature death.⁷ Nowadays, public attention to ozone has been rising. The World Health Organization (WHO, 2000) reports that the 8 h average ozone concentration be less than 50 ppb. On October 1, 2015, the National Environmental Protection Agency (EPA) upgraded the national ambient air quality standard for surface O₃ from 75 to 70 ppb. Therefore, it is urgent to develop effective methods to eliminate O₃ pollution so as to improve air quality.

At present, many methods have been exploited to eliminate O_{3} , such as adsorption by carbon composite catalysts,¹⁰ photocatalytic decomposition,¹¹ thermal decomposition,¹² and catalytic decomposition.^{13,14} The catalytic decomposition method, with its high efficiency and low energy consumption, has attracted more and more attention because the catalyst can quickly decompose ozone to oxygen and requires no energy consumption. The conditions for the treatment of ozonecontaining gases are demanding, such as high ozone concentration, high humidity, high space velocity, and even low temperatures, so it is important to prepare high-efficiency catalysts. Catalysts for O₃ elimination involve noble metals, transition metals,^{16,17} and their derived mixed oxides.^{18–20} Because of the high cost and limited resources of noble metals, manganese oxides are widely used.^{21,22} Among them, cryptomelane-type manganese oxide (OMS-2) is an efficient and economical catalyst, $^{23-25}$ and its activity is higher after

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doping with other metals.^{26–29} Ma et al.¹⁹ tuned the trivalent manganese (oxygen vacancy) content of OMS-2 by metal doping, and found that cerium doping distorted the structure of the OMS-2 catalyst, exposed more surface active sites, and promoted the elimination of O₃. OMS-2 doped with Ce showed a high ozone conversion of 90% under humidity of 90% and GHSV of 600 000 h⁻¹. The Ce-OMS-2 catalyst has good application prospects for the catalytic decomposition of ozone.

Furthermore, another study found that different synthesis methods (microwave-assisted synthesis, conventional reflux method, hydrothermal method) can affect the properties of OMS-2, and in the process of rapid microwave heating, the performance of the catalysts depends on accurately controlling the reaction temperature.³⁰ In addition, it is considered that the reaction temperature would affect the interaction between MnO_x and CeO_2 , which is the key factor determining the catalytic activity of samples.³¹ Also, at different hydrothermal treatment times, the size and morphology of samples can change, which leads to alteration of the catalyst activity.^{24,32} Thus, the catalyst morphology,^{33,34} crystal structure,³⁵ and surface oxygen vacancy concentration^{24,36} can be tuned by changing the preparation method and optimizing the preparation conditions. However, for the Ce-OMS-2 catalyst, the relationship between ozone decomposition and the parameters of the hydrothermal synthesis process is not clear, especially regarding hydrothermal temperature and time.

In this study, a series of Ce-OMS-2 materials were synthesized by a hydrothermal method, and ozone decomposition experiments were carried out at high relative humidity (RH). The Ce-OMS-2 samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Brunauer-Emmett-Teller (BET), and H₂-TPR, and the humidity resistance and durability performances of the catalysts were investigated. For the first time, the relationship between catalyst activity and hydrothermal temperature and time was established based on the characterization results and catalytic activity data. An optimized Ce-OMS-2 catalyst was obtained with high ozone decomposition activity at room temperature under high humidity and high space velocity. The promoted catalytic activity should be attributed to the enhancement of the oxygen vacancies of Ce-OMS-2.

2. EXPERIMENTAL SECTION

2.1. Chemicals. All chemical reagents were obtained commercially. Chemicals including $MnAC_2 \cdot 4H_2O$ (AR, $\geq 99.0\%$), KMnO₄ (GR, $\geq 99.5\%$), and HAC (GR, $\geq 99.8\%$), were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ce(NH₄)₂(NO₃)₆ (AR, 99%) was obtained from Innochem Co., Ltd. (Beijing, China). All chemical reagents were directly used in the preparation of catalysts without further purification.

2.2. Preparation of Catalysts. Ce-OMS-2 catalysts were synthesized using the reaction of $MnAC_2$ and $KMnO_4$ in acid solution via a hydrothermal method with different treatment temperatures and times. Typically, 14.82 mmol Mn- $(CH_3COO)_2$ · $4H_2O$ and 18.60 mmol Ce $(NH_4)_2(NO_3)_6$ were dissolved in deionized water under vigorous stirring, adding 2.5 mL CH₃COOH to adjust the solution to an acidic environment. Then, 13.65 mmol KMnO₄ aqueous solution was added into the above mixture at room temperature under vigorous

stirring. The solution was transferred to a 100 mL Teflon-lined autoclave and maintained at designated temperatures (i.e., 70, 80, 90, 95, 100, 110, and 120 $^{\circ}$ C) and times (i.e., 2, 4, 8, 14, 24, 30, and 36 h). The obtained resultant precipitate was then filtered and washed with deionized water thoroughly and dried at 100 $^{\circ}$ C. The reference catalyst without Ce was also prepared, denoted as OMS-2 and confirmed by XRD as shown in Figure S1.

2.3. Catalyst Characterization. The phase structures of the samples were studied by X-ray powder diffraction (XRD, Bruker D8A A25) with Cu K α radiation (λ = 0.15418 nm) at 40 kV and 40 mA and scanning range from 5 to 90°. Lattice parameter and grain size calculations were performed using DIFFRAC. EVA and Topas software. For the morphology analyses of the samples, field-emission scanning electron microscopy (FE-SEM, Hitachi SU 8020, Japan) and transmission electron microscopy (TEM, Hitachi H-7500, Japan) were carried out. The nitrogen adsorption/desorption isotherms and specific surface areas (S_{BET}) were determined by applying an automated gas sorption analyzer (Quantachrome, Boynton Beach, FL). The S_{BET} was obtained by the Brunauer-Emmett-Teller method, and the pore size distribution was plotted based on the Barrett-Joyner-Halenda (BJH) method. All catalysts were degassed for 12 h at 90 °C before nitrogen adsorption to eliminate physisorbed moisture. To study the reducibility of the catalysts, H₂-TPR experiments were carried out using an automatic temperature-programmed chemisorption analyzer (AutoChem II 2920, Micromeritics) with a thermal conductivity detector (TCD). Prior to the test, 80 mg samples of the catalysts were treated at 300 °C in Ar. Subsequently, the catalysts were cooled to 25 °C and saturated with H_2/Ar (10 vol %) for half an hour. Finally, the catalysts were heated to 850 °C with a heating rate of 10 °C/min. The signal was monitored by TCD. X-ray photoelectron spectroscopy (XPS) of catalysts was carried out using a surface analysis system (AXIS Supra, Shimadzu, U.K.). The binding energies were standardized based on the 284.8 eV C 1s peaks for all catalysts. The Raman spectra were measured by a confocalmicro-Raman spectrometer (Invia plus, Renishaw, U.K.) at 532 nm with a range of 100-1000 cm⁻¹. The chemical compositions of catalysts were obtained by inductively coupled plasma-optical emission spectrometry (ICP-OES) (OPTIMA 8300).

2.4. Evaluation of Ozone Decomposition Activity. The catalytic performance measurements of Ce-OMS-2 catalysts (40–60 mesh) for ozone elimination were performed in a fixed-bed continuous flow microreactor (4 mm) at 30 °C. A low-pressure ultraviolet lamp was used to generate ozone and the total gas flow rate was kept at 1.4 L/min. The GHSV was about 600 000 h⁻¹. The concentration of reactant gas was 40 \pm 2 ppm and detected by an O₃ monitor (Model 202, 2B Technologies). The relative humidity (RH) was monitored by a humidity monitor (HMP 110, VAISALA) and the RH was adjusted by a constant temperature water bath bubbler. To eliminate the effect of the reaction system, the blank test was conducted and the result was shown in Figure S1. The O₃ conversion was defined as

$$O_3 \text{ conversion } (\%) = \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}} \times 100\%$$

where C_{in} and C_{out} are the inlet and outlet concentrations of ozone accordingly.

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Figure 1. Ozone conversion over Ce-OMS-2 samples prepared at different (A) and (C) hydrothermal temperature and 24 h treatment time, (B) and (D) hydrothermal time at 95 °C treatment temperature. All reactions were carried out at $O_3 = 40 \pm 2$ ppm, Temp. = 30 °C, RH = 90% and GHSV = 600 000 h⁻¹.



Figure 2. Refined XRD patterns of the Ce-OMS-2 samples prepared at different (A) hydrothermal temperatures at 24 h and (B) hydrothermal time at 95 °C. L is the crystallite size of catalysts.

3. RESULTS AND DISCUSSION

3.1. Ozone Decomposition Performance. In our experiment, we wondered whether the performance of Ce-OMS-2 samples for O_3 elimination was dependent on the hydrothermal temperature and time or not, and if so, to what extent. To seek answers, the impacts of hydrothermal temperature and time on the ozone elimination of the catalysts were studied. The ozone conversion of the Ce-OMS-2 catalyst shows that the performance is strongly dependent on hydrothermal temperature and time (Figure 1). The ozone decomposition activity of the Ce-OMS-2 catalysts shows a volcano-shaped dependence on hydrothermal temperature and

time. The 6 h ozone conversion of the catalyst prepared at 70 °C was 57%. As the hydrothermal temperature increased to 100 °C with increments of 10 °C, the ozone conversion significantly increased from 57 to 63, 70, and 90%. Notably, when the temperature reached 95 °C, the ozone conversion rate reached 90%. After raising the hydrothermal temperature to 110 °C, the activity of the catalyst decreased rapidly to 41%, and the catalyst was almost completely deactivated when the hydrothermal temperature was raised further to 120 °C. The influence of hydrothermal time on the activity of the samples was similar to that of hydrothermal temperature. With increasing hydrothermal time, the 6 h ozone conversion increased from 61% (2 h hydrothermal time) to 93% (14 h)



Figure 3. FE-SEM (up) and TEM images (down) of Ce-OMS-2 catalysts prepared at different hydrothermal temperatures and times.

and then decreased to 74% (36 h). The results show that a hydrothermal temperature that is too high or hydrothermal time that is too long will lead to a decrease in the ozone decomposition performance. Generally, the use of high hydrothermal temperature and long hydrothermal treatment time would be more favorable for improving the crystallinity and reducing lattice defects, which is not conducive to good ozone decomposition activity. Based on the above results, we obtained the optimum ranges for the hydrothermal temperature and time for the Ce-OMS-2 catalyst of 95–100 °C and 8–24 h, and the Ce-OMS-2 sample prepared at 95 °C and 14 h had the best decomposition performance.

3.2. Structure and Morphology of the Catalysts. To verify the effect of hydrothermal temperature and time on the phase composition of the catalysts, the materials were characterized by XRD. Figures S2 and 2 show the XRD diffraction patterns of OMS-2 and Ce-OMS-2 materials synthesized at different hydrothermal temperatures and times. The sample obtained at 95 °C and 2 h is amorphous, indicating that the hydrothermal time is too short to form crystals, and the subsequent discussion on XRD data does not include this sample. The characteristic peaks of the diffraction spectra of other samples are consistent with the standard spectrum of OMS-2 (JCPDS 29-1020), indicating that the sample is pure-phase cryptomelane-type manganese oxide. Compared with OMS-2, no diffraction peaks of Ce species were observed in the pattern of Ce-OMS-2, which indicates that the Ce species were highly dispersed or incorporated into the structure. No new diffraction peaks appear in the diffraction patterns of samples prepared with increasing hydrothermal temperature and prolonged hydrothermal time. As can be seen, changing the hydrothermal temperature and time (except for the 2 h sample) did not change the crystal structure or produce other crystal phases in the process of hydrothermal synthesis. However, as the hydrothermal temperature and time increase, the diffraction peak intensities of the samples increase, and the intensity increases slowly in the range of 70-100 °C or 4-24 h. After that, once the temperature is above 100 °C or the time is longer than 24 h, the diffraction peak intensities of samples increase sharply, indicating that the crystallinity of the sample increases rapidly if the temperature is above 100 °C or the time is longer than 24 h. A catalyst with overly high crystallinity is not conducive to the exposure of plentiful defects and active sites on the samples, so this is disadvantageous to the decomposition of ozone. Rietveld structure refinement of OMS-2 and Ce-OMS-2 samples was conducted by TOPAS software based on the standard cryptomelane-type structure with the tetragonal system (I4/m). The c/a ratios of all Ce-OMS-2 catalysts

were 0.290–0.291, which is smaller than that of OMS-2 (0.292). Theoretically, the catalyst crystal parameters would remain unchanged if the Ce ion was only dispersed on the external surfaces of OMS-2. Therefore, Ce was deduced to be inserted into the OMS-2 catalyst tunnels. If the smaller Ce³⁺ ions (1.14 Å) or Ce⁴⁺ ions (0.87 Å) are substituted for K⁺ ions (1.65 Å), the tunnel would be expected to be slightly distorted. The grain sizes of the samples range from 5.4 to 28.6 nm. With rising hydrothermal temperature or time, the grain size of the Ce-OMS-2 catalysts increased gradually and rapidly after 100 °C or 24 h. Combined with the ozone decomposition activity data of Ce-OMS-2, there is an optimal crystallinity and grain size (9.7–12.2 nm) that is beneficial to the catalytic decomposition of O₃.

The morphology and microstructure of the catalysts were obtained by FE-SEM and TEM (as shown in Figures 3 and S3). The Ce-OMS-2 catalysts mainly appeared in the form of honeycomb-like and rod structures. The catalyst adopts a honeycomb-like structure when the hydrothermal temperature is lower than 100 °C or hydrothermal time is less than 24 h, and the proportion of honeycomb-like structure increases with the rise in hydrothermal temperature or time. The content of the honeycomb-like structure for the catalyst reached the maximum when the hydrothermal temperature was 95-100 °C and the hydrothermal time was 8-24 h. If the hydrothermal temperature was above 100 °C or the time was longer than 24 h, the catalyst gradually changed into a rod structure, and with the rise of hydrothermal temperature or time, the rod structure became more and more prevalent while the honeycomb-like structure was less and less apparent. Compared with the rod structure, a catalyst with the honeycomb-like structure has more surface defects and more active sites, which is beneficial for the adsorption and decomposition of ozone molecules, consistent with the activity trend of Ce-OMS-2 catalysts.

To confirm the position of the added Ce, the chemical compositions of catalysts were obtained by ICP-OES. From Table S1, confirming the incorporation of Ce in the structure compared the ion concentration of Ce-OMS-2 samples with OMS-2. The bulk K/(Mn + M + K) mass ratio and Mn/(Mn + M + K) mass ratios of Ce-OMS-2 samples were all lower than those of the pure OMS-2, which means that the substitution of both Mn ions in the framework and K⁺ in the tunnel sites of OMS-2 by the added Ce took place. Furthermore, the final ion contents in the prepared Ce-OMS-2 samples were not exactly the same despite the fact that the initial mass ratios of Ce in the reactant mixtures were the same. As the hydrothermal temperature and time increase, the Ce/(Mn + M + K) mass ratio of these samples increase with



Figure 4. Raman spectra of Ce-OMS-2 catalysts prepared at different (A) hydrothermal temperature and (B) hydrothermal time.



Figure 5. Pore size distribution plots of the Ce-OMS-2 catalysts prepared at different (A) hydrothermal temperature and (B) hydrothermal time.

Mn/(Mn + M + K) mass ratio and K/(Mn + M + K) mass ratio decrease in the range of 70–95 °C or 2–8 h. After that, the ion concentrations were almost not changed, indicating that Ce was completely doped when hydrothermal temperature over 95 °C or time more than 8 h. Ce concentration is not the main factor for the difference in the apparent activity of the catalyst.

Raman scattering is a powerful technique for analyzing the structure of manganese oxides, especially for samples with poor crystallinity. To further confirm the effect of hydrothermal temperature and hydrothermal time on the crystal structure, Raman spectra were measured and the results are shown in Figure 4. Fifteen lines of Raman spectral activity model $(6A_g +$ $6B_g + 3E_g$) were predicted by group theory. However, it is difficult to observe all the predicted Raman in the sample in practice, because some of these models have low polarizability and the overlap of incomplete analytical models. In addition, due to the low Raman activity of manganese oxides, some Raman modes may have too little strength to be observed.³ For the Ce-OMS-2 catalysts obtained at different hydrothermal temperatures and times, the two strong and sharp peaks at 640 and 580 cm^{-1} correspond to the A_{1g} spectral mode, while the peaks at 517 and 478 cm^{-1} correspond to F_{2g} spectral species.³⁸ The two sharp high-frequency Raman bands at 640 and 580 cm⁻¹ show a well-developed tetragonal structure with 2×2 tunnels.³⁹ The strong peaks at 640 and 580 cm⁻¹ belong to the Mn-O symmetric stretching vibration perpendicular to the double-stranded direction of MnO₆ octahedron and the displacement of the oxygen atom connected to the manganese atom along the octahedral chain, respectively.^{37,39} Bands at

185, 288, and 395 cm⁻¹ correspond to the deformation mode of a metal—oxygen chain of Mn-O-Mn.⁴⁰ The Raman band at 750 cm⁻¹ is related to the antisymmetric Mn-O stretching vibration.³⁷ Since no spectral bands were detected at 465 cm⁻¹, it was proved again that there was no single crystal or polycrystal of Ce. From Figure 4, the Raman pattern of Ce-OMS-2 changes regularly with the change of reaction temperature and time. Increasing the hydrothermal temperature or time (except for 2 h, it has been proved in XRD that the sample is amorphous), the Raman peak gradually becomes sharper and the intensity becomes stronger. Increasing the hydrothermal temperature or time lead to the ordering of the internal lattice structure increases, resulting in the improvement of crystal quality and the increase in particle size, which is consistent with the results of XRD.

Figure S4 shows the adsorption/desorption isotherms of Ce-OMS-2 samples. For Ce-OMS-2 catalysts prepared at different hydrothermal temperatures, on the basis of the IUPAC classification, the isotherms of the samples prepared below 100 °C show a type IV isotherm model and H2 type hysteresis loop. This type of isotherm is correlated with the formation of particles and fissured pores, indicating that the catalysts have a rich heterogeneous mesoporous structure.^{41,42} The isotherms of catalysts prepared at hydrothermal temperatures higher than 100 °C show a type II isotherm pattern and H3 type hysteresis loop. The isotherms of all samples synthesized at different hydrothermal times were similar to those prepared at different hydrothermal temperatures. With increasing hydrothermal time, the isotherm of the catalyst changed from type IV to type II, and when the hydrothermal time was more than 24 h,

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samples	${surface area \atop (m^2 \cdot g^{-1})}$	$\begin{array}{c} 6 \ h \ O_3 \ decomposition \ rate \\ (mmol \cdot g^{-1} \cdot min^{-1}) \end{array}$	surface-specific activity $(\mu \text{mol} \cdot \text{m}^{-2} \cdot \text{min}^{-1})$	samples	$\substack{ surface area \\ (m^2 \cdot g^{-1}) }$	$\begin{array}{c} 6 \ h \ O_3 \ decomposition \ rate \\ (mmol \cdot g^{-1} \cdot min^{-1}) \end{array}$	surface-specific activity $(\mu \text{mol} \cdot \text{m}^{-2} \cdot \text{min}^{-1})$
70 °C	364	0.0102	0.0279	2 h	411	0.0109	0.0265
80 °C	311	0.0113	0.0362	4 h	312	0.0152	0.0486
90 °C	244	0.0125	0.0513	8 h	222	0.0163	0.0733
95 °C	171	0.0161	0.0937	14 h	186	0.0166	0.0894
100 °C	168	0.0161	0.0959	24 h	171	0.0161	0.0937
110 °C	155	0.0073	0.0472	30 h	141	0.0154	0.1091
120 °C	125	0.0020	0.0157	36 h	119	0.0134	0.1123





Figure 6. H₂-TPR profiles of Ce-OMS-2 samples prepared at different (A) hydrothermal temperatures and (B) hydrothermal times.

the isotherms of the catalysts showed a type II isotherm model. The pore diameter distribution is shown in Figure 5, with data calculated by the BJH method, which is usually used to estimate the structural characteristics of mesoporous materials to indicate the nature of the packing of anisotropic particles and their agglomerates. For the catalysts prepared under different conditions, the pore size distribution of Ce-OMS-2 materials tended to change from narrow to wide with the increase in hydrothermal temperature or time, which may be related to the particle size and particle accumulation. As shown in Table 1, the S_{BET} of Ce-OMS-2 materials varied from 119 to 412 $m^2 \cdot g^{-1}$, decreasing with the rise in hydrothermal temperature or time. Ce-OMS-2 samples with low specific surface area (such as the samples at prepared at 120 °C with 24 h hydrothermal time and 95 °C with 36 h) show high crystallinity, which may be attributed to the existence of large particles. The 6 h ozone decomposition rate of Ce-OMS-2 catalysts ranged from 0.0102 to 0.0166 mmol·g⁻¹·min⁻¹. The 6 h ozone elimination rate increased at first and then decreased with the rise in hydrothermal temperature or time. The maximum value was reached when the temperature was 95-100 °C and the time was 8-24 h. The changing trend of the specific surface area is not consistent with that of the ozone decomposition rate. Referring to the previous literature, $^{43}S_{\text{BET}}$ is not the main factor for the difference in the apparent activity of the catalyst. Furthermore, the influence of hydrothermal temperature on the surface-specific activity of the samples was similar to that on the ozone decomposition rate. The surfacespecific activity of the Ce-OMS-2 catalysts shows a volcanoshaped dependence on hydrothermal temperature and the maximum value was reached when the temperature was 95-100 °C. For hydrothermal times, although the surface-specific activities of 30 and 36 h seem to be satisfying, considering the industrial application, the hydrothermal time of 8-24 h is more reasonable.

3.3. Redox Properties and Surface Oxygen Vacancies of the Catalysts. The ozone decomposition activity on manganese oxide is closely related to the reduction of manganese oxide and the density of surface oxygen vacancies. The reduction performance of the Ce-OMS-2 samples was evaluated by an H2-TPR experiment. From the H2-TPR data (Figure 6), the Ce-OMS-2 catalyst showed a weak peak at about 224 °C and two strong peaks at 274 and 308 °C. If the hydrothermal temperature is too low (70 °C) or the hydrothermal time is too short (4 or 2 h), peak I appears as the surface oxygen consumption peak. Here, some explanation is needed: although the catalysts with a high specific surface area prepared by hydrothermal treatment at 70 °C or 2-4 h are easier to reduce, this is due to the imperfect crystal formation caused by the temperature being too low and the time too short during the crystal growth process. Combined with the activity data in Figure 1, this is not beneficial to ozone decomposition. Once the hydrothermal temperature is higher than 95 °C and hydrothermal time is more than 8 h, the peak gradually disappears. For other Ce-OMS-2 catalysts, in the reduction path of MnO₂, first reduction to Mn₂O₃ and then to MnO, corresponding to peaks II and III, respectively. The reduction peaks of the catalyst have a tendency to move to the

sample	Ce ³⁺ (%)	Mn ²⁺ (%)	Mn ³⁺ (%)	$(Mn^{2+} + Mn^{3+})/Mn^{4+}$	AOS	O _{sur} (%)
70 °C	32.49	3.52	29.99	0.50	3.60	28.55
80 °C	34.84	4.37	32.56	0.59	3.55	32.82
90 °C	37.47	4.48	37.33	0.72	3.51	36.47
95 °C	41.61	6.25	48.97	1.23	3.34	43.58
100 °C	41.40	6.35	47.20	1.15	3.44	42.34
110 °C	31.43	7.92	20.51	0.40	3.58	25.30
120 °C	30.18	6.17	14.92	0.27	3.62	14.84
2 h	33.55	3.66	30.90	0.53	3.56	30.19
4 h	40.18	3.90	48.83	1.12	3.43	41.92
8 h	42.05	5.20	52.70	1.38	3.33	43.88
14 h	42.64	5.32	54.56	1.49	3.21	48.24
24 h	41.61	6.25	48.97	1.23	3.34	43.58
30 h	40.72	5.66	47.79	1.14	3.38	42.32
36 h	38.60	5.32	39.82	0.82	3.49	38.06

Tal	ole	2.	XPS	Results	of	the	Ce-OMS-2	Cata	lysts
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high-temperature region with increasing hydrothermal temperature or time beyond 95-100 °C and 8-24 h, indicating that the reducibility of catalysts will be reduced if the hydrothermal temperature is too high or the hydrothermal time is too long.

As shown in the XPS results of Figure S5, the oxidation state of Ce in the Ce-OMS-2 samples was characterized by analyzing the Ce 3d spectrum. For the Ce 3d spectrum, the identified peaks at 916.8, 908.4, 903.3, 901.1, 896.5, and 885.5 eV correspond to the Ce⁴⁺ oxidation state, while the peaks at 906.1, 898.8, 889.4, and 882.6 eV correspond to Ce^{3+,4+} The percentage of Ce³⁺ in the catalyst is between 30.18 and 42.64%, indicating that Ce⁴⁺ is the main oxidation state of Ce ion in these catalysts.

As can be seen in the spectrum of Mn $2p_{3/2}$, the peaks at about 640.7, 642.3, and 643.4 eV are assigned to Mn^{2+} , Mn^{3+} , and Mn⁴⁺, respectively (Figure S6).³⁵ The existence of lowvalent manganese in the catalyst crystal promotes the formation of oxygen vacancies, so that for charge conservation, at the same time, samples rich in low-valent manganese are conducive to the redox reaction, thus promoting the catalytic decomposition of ozone.^{41,45,46} According to Table 2, the hydrothermal temperature and time have significant effects on the formation of low-valent manganese. Once the temperature rises to 95 °C, the molar ratio of low-valent manganese ((Mn²⁺ + Mn^{3+}/Mn^{4+} increases significantly to 1.23 and then decreases to 0.29 when the temperature continues to rise to 120 °C. The changes with hydrothermal time were similar, and the molar ratio $(Mn^{2+} + Mn^{3+})/Mn^{4+}$ increased at first as a function of hydrothermal time and then decreased sharply, reaching a maximum at 14 h (1.49). Combined with the above information, the change in the catalyst activity with hydrothermal temperature and time is largely due to the formation of low-valent manganese, which is associated with an increase in oxygen vacancies.

In addition, the average oxidation state (AOS) of manganese oxide can be obtained from the Mn 3s spectrum. The energy difference (E_s) between the main peak and the edge peak of Mn 3s decreases with the increase in the average oxidation state.⁴⁷ According to the Mn 3s spectrum (Figure S7), the surface average oxidation state (AOS) of Mn is accurately estimated by using the following formula

 $AOS = 8.956 - 1.126\Delta E_s$

where ΔE_s is the binding energy difference between the doublet Mn 3s peaks. As shown in Figure S7, with rising

hydrothermal temperature or time, the calculated AOS decreased first and then increased, and reached the lowest value when the hydrothermal temperature was 95 °C and the hydrothermal time was 8 h. These results further confirm that the oxygen vacancy concentration of the catalysts prepared at 95–100 °C for 8–24 h treatment time is higher than that of the other catalysts, which is consistent with the Mn $2p_{3/2}$ XPS results.

The chemical bonding of oxygen in Ce-OMS-2 catalysts was characterized by XPS. The O 1s spectrum (Figure 7) shows



Figure 7. XPS deconvolution spectra of O 1s peak of Ce-OMS-2 samples prepared at different (A) hydrothermal temperature and (B) hydrothermal time.

that two different oxygen species can be distinguished, in which the peak at 529.8 eV is related to lattice oxygen (O_{latt}) , and the peak of 530.7 eV to surface oxygen (O_{sur}) .⁴⁸ The content of surface oxygen has an important effect on the catalytic elimination of O_3 . If the content of surface oxygen is high, O_2^* is prone to desorb, giving a faster rate of ozone decomposition. The content of surface oxygen obtained by peak-differentiation analysis of the O 1s spectrum is listed in Table 2. It can be seen that the content of O_{sur} increases at first

and then decreases with the increase in the hydrothermal temperature or time, indicating that suitable hydrothermal temperature (95–100 °C) and time (8–24 h) are beneficial for the formation of surface oxygen vacancies, which are considered to be the active sites for O₃ elimination.^{35,46,49–51} This is consistent with the oxidation state of Mn and explains the high ozone removal activity of the catalysts prepared at 95 °C and 14 h.

The reaction mechanism of ozone decomposition mainly includes redox steps on oxygen vacancy: adsorption of ozone in oxygen vacancy and desorption of intermediates. The reaction scheme for ozone decomposition is presented as follows

$$O_{3} + [Mn^{3+}] \rightarrow O_{2} + O_{sur}^{-}[Mn^{4+}]$$

$$O_{3} + O_{sur}^{-}[Mn^{4+}] \rightarrow 2O_{2} + [Mn^{3+}]$$

$$O_{3} + [Mn^{2+}] \rightarrow O_{2} + O_{sur}^{-}[Mn^{3+}]$$

$$O_{3} + O_{sur}^{-}[Mn^{3+}] \rightarrow 2O_{2} + [Mn^{2+}]$$

Ozone is adsorbed on oxygen vacancy where the position of low-valence manganese (Mn^{3+} and Mn^{2+}) and then decomposes to an O₂ molecule with produce one intermediate. These intermediates form O₂ in a reduction process in which when electrons are transformed to the Mn center, the intermediates combine with another O₃ molecule to form gaseous oxygen and low valence states of manganese (Mn^{3+} or Mn^{2+}). At the same time, oxygen vacancies are restored and complete a cycle of ozone decomposition.

3.4. Durability Performance under Harsh Conditions. In actual ozone decomposition, moisture resistance, high space velocity resistance, and stability are very important factors to consider. To further analyze the stability of the materials at high GHSV and high humidity, a continuously alternating humidity experiment was carried out for the Ce-OMS-2 prepared at 95 °C and 14 h (Ce-OMS-2 (95 °C, 14 h)), which exhibited the highest O₃ conversion, under the conditions of GHSV = 1 400 000 h^{-1} and RH = 90% or dry air (RH < 5%). As shown in Figure 8, the ozone removal activity of Ce-OMS-2 (95 °C,14 h) catalyst remains at 100% under dry gas conditions, and decreases to 40-56% under wet gas conditions of RH = 90%. The results show that the deactivation of the catalyst at high humidity is mainly caused by the competitive adsorption of O₃ molecules and water molecules. In the alternating humidity experiment, the ozone decomposition



Figure 8. Durability testing of the catalyst prepared at 95 °C and 14 h carried out at $O_3 = 40 \pm 2$ ppm, Temp. = 30 °C, RH = 90%, and GHSV = 1 400 000 h⁻¹.

activity of Ce-OMS-2 (95 $^{\circ}$ C, 14 h) in the first wet flow (RH = 90%) was about 56%. Once switching to dry flow, the ozone decomposition activity quickly returned to 100%, indicating that the adsorption of water molecules on the material was very weak and could be blown off by dry gas flow. In the wet flow of the second cycle, the ozone conversion of Ce-OMS-2 (95 °C, 14 h) decreased to 50%, which was slightly lower than that in the first cycle. Similarly, the O_3 conversion for the wet airflow in the subsequent cycle decreased slightly compared with the previous cycle, and by the sixth cycle, the O_3 conversion in the wet airflow decreased to 40%. This may be due to the fact that some of the less easily desorbed oxygen species from ozone molecules are adsorbed on the oxygen vacancies during the ozone decomposition process, resulting in a decrease in the number of oxygen vacancies that can be used for ozone decomposition.^{20,35} An ozone converter is currently used in modern commercial aircraft to protect passengers from ozone exposure during cruising and to protect other elements in the Nitrogen-Generation system from oxidation. A catalyst with ozone conversion over 90% at the ultra-high airspeed and below 0 °C is desired for O3 converters installed on commercial passenger aircraft. Our preferred Ce-OMS-2 catalyst shows high catalytic activity at low temperatures (-5)°C) (Figure 9), achieving a 100% conversion of 1.8 ppm ozone



Figure 9. Low temperature ozone conversion of the catalyst prepared at 100 °C and 24 h carried out at different GHSV, $O_3 = 1.8$ ppm and Temp. = -5 °C.

(typical ozone concentration at flight altitude) even at the high GHSV of 2 400 000 h^{-1} , during a 180 h test. This means that the preferred Ce-OMS-2 catalysts can be used for O₃ converters installed on commercial passenger aircraft. To further confirm the stability of catalyst after ozone reaction, we test the XRD and Raman of the catalyst (95 °C, 14 h) after reaction with ozone for 100 h, XRD and Raman results are shown in Figures S8 and S9. The catalyst crystal parameters and surface structure remain unchanged, which means this catalyst is stable during the ozone decomposition process. In addition, Table 3 shows a summary comparing the ozone decomposition activities of manganese oxides in the literature. As can be seen, among these catalysts, the Ce-OMS-2 catalysts prepared at 95-100 °C for 8-24 h have outstanding comprehensive performance in terms of catalytic efficiency, RH value, and GHSV value, and have good potential for industrial application.

4. CONCLUSIONS

In this study, a series of Ce-OMS-2 catalysts were synthesized by hydrothermal synthesis at different hydrothermal temper-

catalysts	ozone concentration (ppm)	temperature (°C)	GHSV $(mL \cdot g^{-1} \cdot h^{-1})$	RH (%)	6 h O ₃ decomposition rate $(\text{mmol} \cdot \text{g}^{-1} \cdot \text{min}^{-1})$	references
Ce-OMS-2 (95 °C, 14 h)	40	30	$600\ 000\ (600\ 000\ h^{-1})$	90	0.0166	this work
Ce-OMS-2 (95 °C, 8 h)	40	30	$600\ 000\ (600\ 000\ h^{-1})$	90	0.0163	this work
Ce-OMS-2 (95 °C, 24 h)	40	30	$600\ 000\ (600\ 000\ h^{-1})$	90	0.0161	this work
Ce-OMS-2 (100 °C, 24 h)	40	30	600 000 (600 000 h^{-1})	90	0.0161	this work
OMS-2-Ac	40	30	$600\ 000\ (600\ 000\ h^{-1})$	90	0.0133	43
α-MnO ₂ (vac-200-4 h)	20	25	540 000 $(126\ 000\ h^{-1})$	90	0.0032	23
α -MnO ₂ (KOH-4 h)	50	25	540 000	50	0.0106	24
$Co-MnO_x(0.36)-Al$	1000	25	48 000	95	0.0114	52
MnO_x/AC (1.1%)	43-48	25	$180\ 000\ (82\ 000\ h^{-1})$	60	0.005	53
MnCO ₃ (S-300)	110-120	25	600 000	75	0.005	54

Table 3. Summary of Catalytic Activity of Various Catalysts for Ozone Decomposition

atures and times. The effects of hydrothermal temperature and time on the concentration of oxygen vacancy and ozone decomposition are investigated for the first time in this work. Raising the hydrothermal temperature and time will increase the crystallinity and grain size of samples, broadening the pore size distribution, and decreasing the specific surface area. The results of further analysis showed that the honeycomb-like structure is most prevalent for the preparation at 95 °C and 14 h, which is beneficial for ozone decomposition. In addition, the redox properties of the catalysts were studied, and a hydrothermal temperature that is too high or a hydrothermal time that is too long will reduce the reducibility of the catalyst. The results of the oxidation state analysis of Ce and Mn showed that Ce4+ is the main oxidation state of Ce ions in the material. The hydrothermal temperature and time had remarkable effects on the formation of low-valent manganese. The manganese with the lowest valence will be produced at 95-100 °C and 8-24 h, resulting in more oxygen vacancies being produced to balance the charge, which explains the higher ozone decomposition activity of catalysts prepared under these conditions. Combining the ozone decomposition test data and the above analysis results, we showed that the crystallinity and grain size of the catalyst can be controlled by tuning the hydrothermal temperature and time. In this way, the content of low valence manganese $(Mn^{2+} + Mn^{3+})$ can be increased to raise the oxygen vacancy concentration, and finally improve the ozone decomposition performance of the catalyst. On the basis of this study, we screened out the suitable range of hydrothermal temperature of 95-100 °C and hydrothermal time of 8-24 h. The preferred catalyst shows excellent activity and stability at low temperatures $(-5 \ ^{\circ}C)$, high GHSV (1 400 000 h^{-1}), and high RH (90%), which means that it can meet the requirements of engineering applications. In addition, this work also provides technical parameters for the industrial production and application of ozone decomposition catalysts.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.9b05967.

Refined XRD patterns; FE-SEM and TEM images; N_2 adsorption/desorption isotherms; Raman spectra; XPS deconvolution spectra of Ce 3d peak, Mn 2p peak and Mn 3s peak (PDF)

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Notes

The authors declare no competing financial interest.

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