



Feature Article

Catalytic decomposition of gaseous ozone over todorokite-type manganese dioxides at room temperature: Effects of cerium modification



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ABSTRACT

Catalytic decomposition of gaseous ozone (O_3) over todorokite-type manganese dioxides (T- MnO_2) at room temperature and the effects of cerium modification were investigated. Catalytic activity and stability were greatly improved over Ce-modified MnO_2 (Ce- MnO_2), which increased with the increase of Ce/Mn atomic ratios from 0.06 to 0.28. The cerium modification made agglomerated MnO_2 particles transformed into small sheets of Ce- MnO_2 catalyst with Ce/Mn ratio of 0.28, accordingly increasing the specific surface area. Moreover, the crystal boundaries between MnO_2 and CeO_2 formed at high ratios of Ce/Mn. Larger surface area and the crystal boundaries between MnO_2 and CeO_2 resulted in the formation of more oxygen vacancies, which act as the active sites for O_3 decomposition. Besides, we found the improved catalytic stability was associated with the desorption of oxygen species occupying the positions of oxygen vacancies.

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1. Introduction

Ozone (O_3) is a unique species whose chemistry has a profound impact in many areas of our society. It is well known that O_3 layer in the stratosphere prevents short wavelength UV light from reaching the Earth surface [1]. However, tropospheric O_3 is a common pollutant detrimental to human health [2]. Due to its strong oxidizing ability, O_3 is widely used in water [3,4] and air [5–12] purification, and the residual O_3 in the stream usually exceeds the allowable concentration. In addition, the chemical interactions between indoor O_3 and organic molecules can produce short-lived products that may be highly irritative with adverse health effects [13].

Catalytic decomposition technique has been generally adopted for O_3 removal at low temperatures [14]. Among various catalysts, MnO_x -based materials are mostly used due to its high activity [15]. Generally, MnO_x is supported on the carriers with high surface area to improve its activity [16–18]. Recently, the effects of crystal structure and morphology of MnO_x on its activity have been investigated. Jia et al. [19] reported that among three kinds of MnO_2 (α -, β - and γ -) with different tunnel structures, α - MnO_2 with tunnel size of $0.46\text{ nm} \times 0.46\text{ nm}$ possessed the highest activity. In addition, α - MnO_2 nanofiber exhibited better activity than other two α - MnO_2 samples with nanorod and nanotube morphologies, which

is ascribed to its highest content of oxygen vacancies caused by its exposed (211) facet and largest specific surface area [20]. Mn-Fe mixed oxide exhibited $\sim 100\%$ removal efficiency for $\sim 10,000$ ppm of O_3 within 66 h under the space velocity of $12\text{ L g}^{-1}\text{ h}^{-1}$ and relative humidity of 40% at 25°C [21].

Todorokite-type MnO_2 is consisted of triple chains of edge-sharing MnO_6 octahedra with a tunnel size of $0.69\text{ nm} \times 0.69\text{ nm}$ [22], which widely exists in terrestrial deposits and ocean nodules [23]. There has been considerable interest in its possible uses as catalysts due to its unique tunnel structure [22,24–28]. However, to the best of our knowledge, no study has been reported focusing on catalytic decomposition of gaseous O_3 over todorokite-type MnO_2 , which, however, is of great significance to scientific research and practical application due to its special structure and abundance in nature. Herein, we report the study on gaseous O_3 decomposition over the todorokite-type MnO_2 catalyst for the first time, and the effects of cerium modification on the formation of oxygen vacancies and accordingly on the O_3 decomposition performance are also clarified.

2. Experimental

2.1. Catalyst preparation

Todorokite-type MnO_2 were obtained by autoclaving layer-structured MnO_2 (i.e., birnessite), which was synthesized by reactions of MnO_4^- and Mn^{2+} under strong alkaline conditions

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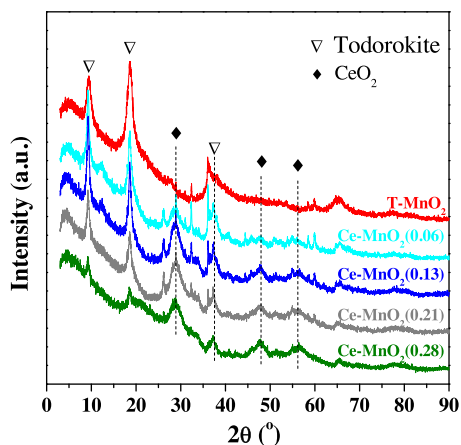


Fig. 1. XRD patterns of the T-MnO₂ and Ce-MnO₂ catalysts.

as reported in literature [24]. The preparation procedures are as follows.

First, Mn(OH)₂ sol was obtained by adding 50 mL of 5 M NaOH solution into 40 mL of 0.5 M MnCl₂ solution under vigorous stirring. Then 40 mL of 0.2 M KMnO₄ solution was added dropwise

into the above mixture under vigorous stirring and dark precipitates were formed. The MnO₄⁻/Mn²⁺ mole ratio was set at ~0.4. This suspension was aged at room temperature for 2 days, then filtered and washed with deionized water for 6 times. In order to fully remove the residual Cl⁻, the solid was further mixed with 200 mL of deionized water under mild stirring for another 2 days, which was proposed as the “double-aging method” [29]. The layered phase thus obtained (Na-birnessite) was then filtered and washed with deionized water for 3 times.

Then, wet Na-birnessite sample was transferred into 200 mL of 1 M Mg(CH₃COO)₂ solution and stirred for 12 h for ion exchange of sodium ion with magnesium ion. After washed with deionized water for 6 times, the ion-exchanged sample was kept in the Teflon-lined autoclave at 125 °C for 2 days to form tunnel structure. The resultant solid product was filtered, washed with deionized water for 3 times and dried at 105 °C in an oven overnight. The obtained powder was grounded, tableted, crushed and sieved to 40–60 mesh, and is denoted as T-MnO₂.

For cerium modification, Ce(NO₃)₃·6H₂O and MnCl₂·4H₂O were added into 40 mL of deionized water from the beginning of the above preparation procedure. The subsequent steps were the same as those of the pure todorokite MnO₂. Four nominal Ce/Mn atomic ratios of 0.1, 0.2, 0.3 and 0.4 in the starting mixture were chosen. For convenience, the Ce-modified MnO₂ samples were denoted as

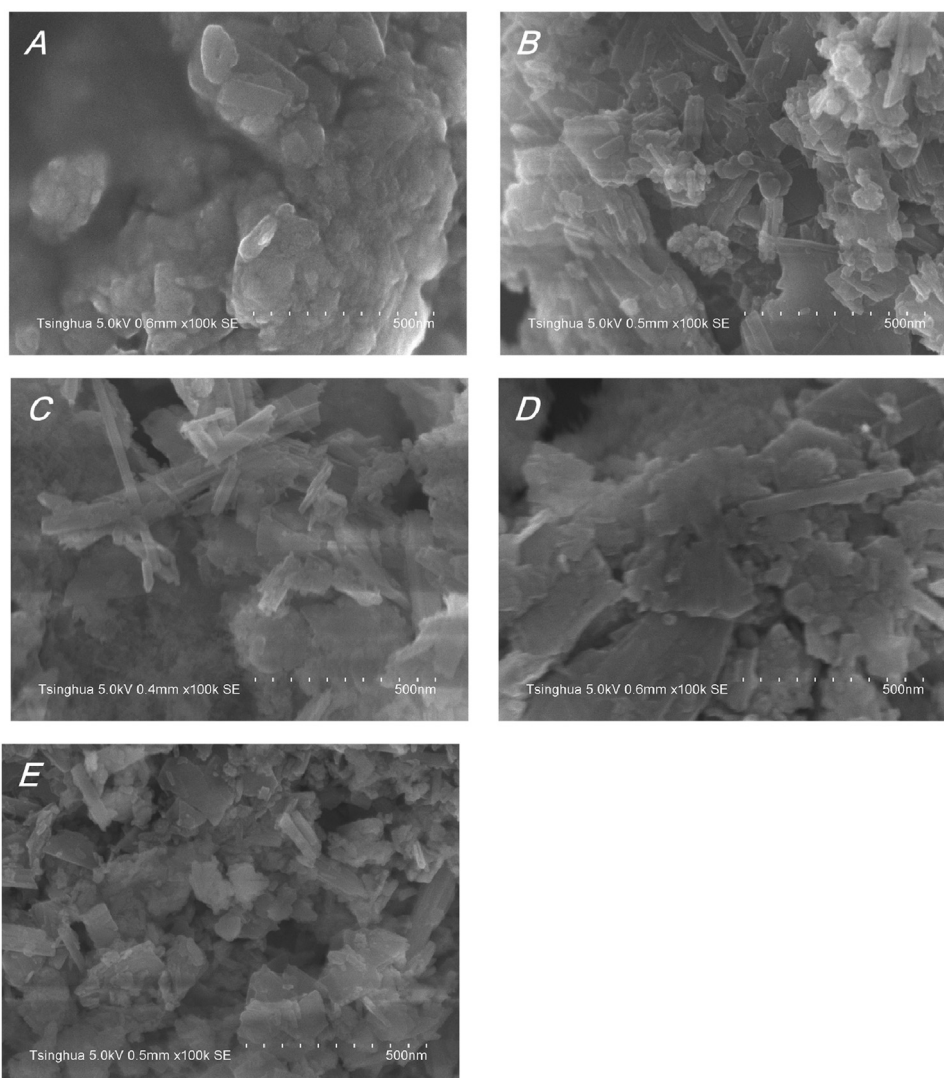


Fig. 2. SEM images of the samples: (A) T-MnO₂, (B) Ce-MnO₂(0.06), (C) Ce-MnO₂(0.13), (D) Ce-MnO₂(0.21) and (E) Ce-MnO₂(0.28).

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