

# Structural manipulation of manganese oxides for enhanced catalytic decomposition of ozone

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**Abstract:** Manganese oxides with tailored structure, i.e., abundant surface oxygen vacancy, enhanced electron transfer ability and/or large surface area, were facilely prepared via facile redox method by modulating the addition sequence of the precursors and tuning the calcination temperature, and directly used for catalytic decomposition of ozone. The as prepared manganese oxides exhibited superior activity and stability for ozone decomposition. The structure-activity relationship was established by combining kinetics study and catalysts characterization. These results may shed new light on the design of novel manganese oxides based catalysts for ozone decomposition.

**Keywords:** Ozone decomposition, Manganese oxides, Structural manipulation.

## 1. Introduction

Ground level ozone (O<sub>3</sub>) is a regulated air pollutant that damages human health, reduces crop yields, changes the climate system, and is also an important greenhouse gas<sup>1</sup>. Several methods have been developed to remove ozone, including adsorption, absorption, passive removal, and catalytic decomposition<sup>2</sup>. Among these approaches, catalytic decomposition of ozone has attracted considerable interests due to its high effectiveness and economical potential, especially over manganese based oxides in terms of the relatively high performance and the low cost<sup>3</sup>. The surface oxygen vacancy as well as the electron transfer ability of manganese oxides were suggested strongly influencing the ozone decomposition behavior, possibly by modulating the adsorption of ozone and acting as the probable active sites<sup>4,5</sup>.

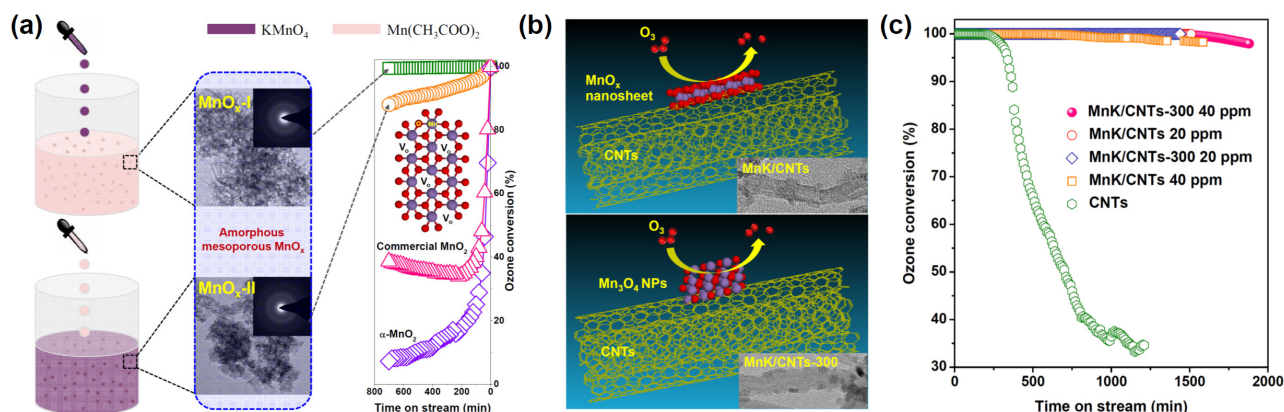
Herein, we fabricated amorphous mesoporous manganese oxides, and manganese oxides-CNTs composites by facile redox reaction approach, and applied these catalysts for ozone decomposition. The catalyst structure-performance relationship was correlated by using multiple techniques, combining with the kinetic study. Subsequently, the stability test over the manganese oxides for ozone decomposition was performed.

## 2. Experimental

Two types of amorphous mesoporous manganese oxides were prepared by a redox method ( $3\text{Mn}^{2+} + 2\text{Mn}^{7+} \rightarrow 5\text{Mn}^{4+}$ , and  $\text{Mn}^{4+} + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2 + 4\text{H}^+$ ) by tuning the solution adding sequence (MnO<sub>x</sub>-I KMnO<sub>4</sub> to Mn(CH<sub>3</sub>COO)<sub>2</sub>, and MnO<sub>x</sub>-II, Mn(CH<sub>3</sub>COO)<sub>2</sub> to KMnO<sub>4</sub>)<sup>6</sup>. A reference sample was also prepared from MnO<sub>x</sub>-I calcined at 500 °C for 3 h in a muffle furnace, which was denoted as MnO<sub>x</sub>-I-C. All the samples were compressed, crushed and sieved through 40-60 mesh sieves before the activity evaluation. Manganese oxides-CNTs composites were prepared following the chimeric reaction equation  $4\text{MnO}_4^- + 3\text{C} + \text{H}_2\text{O} \rightarrow 4\text{MnO}_2 + \text{CO}_3^{2-} + 2\text{HCO}_3^-$  between KMnO<sub>4</sub> and acid pretreated CNTs, denoted as MnK/CNTs. The as prepared sample was further calcined at 300 °C under nitrogen atmosphere, names as MnK/CNTs-300. Ozone decomposition over the as-prepared catalysts (ca. 0.1 g) was conducted in a fixed bed continuous flow quartz reactor (8 mm inner diameter) with GHSV (i.e., gas hourly space velocity) of 600,000 mL/(g·h) at 25 °C. The relative humidity (RH) of the feed gas was maintained at 50% during the tests. Ozone was generated by passing filtered clean air through a vacuum ultraviolet lamp (10 W, Cnlight, China). The ozone concentration inlet and outlet has been measured by ozone detector (model 106-L, 2B Technologies, USA).

### 3. Results and discussion

Amorphous mesoporous manganese oxides prepared from redox method between  $\text{KMnO}_4$  and  $\text{Mn}(\text{CH}_3\text{COO})_2$  with different synthesis routes, were active for ozone decomposition (Fig. 1a). The morphology, textural property and surface chemistry of  $\text{MnO}_x$ -I and  $\text{MnO}_x$ -II were significantly affected by the addition sequence of the precursors. Both  $\text{MnO}_x$ -I and  $\text{MnO}_x$ -II exhibited higher activity than the referenced  $\text{MnO}_x$ -I-C ( $\alpha$ - $\text{MnO}_2$ ) owing to their more surface oxygen vacancies as well as larger specific surface area and ease reducibility, which can provide more active sites.  $\text{MnO}_x$ -I was not only much more readily to catalytically activate ozone, but also was more stable than  $\text{MnO}_x$ -II under different concentration of ozone. The more adsorbed water molecule were proposed probably to account for the deactivation of  $\text{MnO}_x$ -II while the oxidation state change of Mn may not contribute to the stability change.



**Figure 1.** (a) TEM images and the ozone conversion of  $\text{MnO}_x$ -I and  $\text{MnO}_x$ -II, (b) scheme of MnK/CNTs and MnK/CNTs-300 and (c) ozone conversion over MnK/CNTs and MnK/CNTs-300 at different ozone concentration.

Manganese oxides with different morphologies (Fig. 1b, nanosheet and nanoparticles) supported on CNTs were well manipulated by tuning the calcination temperature. Manganese oxides were highly dispersed on the support and showed superior activity for ozone decomposition, even at higher ozone concentration for ca. 24 h (Fig. 1c, 40 ppm). Either supported manganese nanosheets or NPs was rich in surface oxygen vacancy due to the amorphous structure and multiple oxidation state, respectively. In addition, the electron transfer from manganese oxides to CNTs which was derived by the work function difference are favorable for the oxygen desorption reaction ( $\text{O}_2^{2-} \rightarrow \text{O}_2 + 2e^-$ ) and thus enhance the decomposition of ozone.

### 4. Conclusions

Manganese oxides with amorphous state or multiple oxidation state are rich in surface oxygen vacancies and are favorable for ozone decomposition. Both the activity and stability can be facilitated by the enhanced electron transfer ability between the metal oxides and the support. The conclusions here may direct the rational design of highly active manganese oxide-based catalysts.

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