Full Length Article

Nitric acid-treated birnessite-type MnO₂: An efficient and hydrophobic material for humid ozone decomposition

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A B S T R A C T

MnO₂ catalysts are important for low-temperature removal of air pollutants. Sometimes the unavoidable moisture is not conductive to the desired reactions, therefore, water-resistant materials are desirable. However, the reported methods are not easily fulfilled for practical applications and the underlying mechanism for the improved hydrophobicity has not been clarified. In this study, highly water-resistant birnessite-type MnO₂ was designed for humid ozone (O₃) decomposition, which is important for alleviating global O₃ pollution. The sample treated by nitric acid (H-MnO₂) exhibited stable O₃ conversion of ~50% within 24 h under 50% of relative humidity (115 ppm of O₃, 600 $L·g^{-1}·h^{-1}$ of space velocity, 25 °C). However, the pristine MnO₂ was quickly deactivated with O₃ conversion dropping to ~10% within 30 min. Detailed characterizations show that higher amount of acid sites and oxygen vacancies together with their improved water-resistant properties facilitates adsorption and subsequent decomposition of humid O₃ over the H-MnO₂. DFT calculations demonstrate that compared with the pristine MnO₂, oxygen vacancies were more easily formed over the H-MnO₂, and the surface of the H-MnO₂ was more hydrophobic and more attractive to O₃ adsorption. Finally, a mechanism involving acid sites and oxygen vacancies for gaseous O₃ decomposition was proposed.

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1. Introduction

As a strong oxidizing agent, ozone (O₃) plays an important role in many chemical processes in the troposphere and is the main secondary pollutant of photochemical reaction [1]. Besides outdoor O₃ exposure, nowadays people are also susceptible to indoor O₃ pollution since a lot of office and household appliances, such as printer, copier, O₃ disinfection cabinet and O₃ air purifier, can release O₃. O₃ pollution is detrimental to human health, as reported by the US [2–4], European [5] and Asian [6] scientists in recent publications. Inhalation of O₃ at concentrations as low as ppb level will worsen the respiratory system and cause damage to lung function [3].

Catalytic decomposition has been considered as an effective method for gaseous O₃ removal [7]. Transitional metal oxides are usually used for gaseous O₃ decomposition, such as Ag [8–10], Ni [11,12], Co [13], Ce [14], Cu [15] and Mn [12,16,17]. MnO₂ catalysts are very active for O₃ decomposition and frequently used in gaseous O₃ removal. However, the coexistence of water vapor in real environment can easily lead to significant deactivation of the MnO₂-containing catalysts [18–20], which is one of the main obstacles impeding their practical use. Moreover, the combination of transitional metal oxide with precious metal did not have prolonged activity either. According to Kameya and Urano [21], the activity of the γ-MnO₂ supported Pd catalyst also decreased gradually with reaction time. He et al. [18,22] reported that Fe or Ce doped α-MnO₂ exhibited stable O₃ removal efficiency under humid condition; however, the adopted hydrothermal synthesis of catalyst is not conducive to mass production, and the underlying mechanism for the improvement of water resistance has not been clarified yet.

Therefore, in order to effectively reduce the detrimental impact of indoor O₃ on human health and improve the safety of indoor air purification appliances, it is of great importance and urgency to develop an easy way to design water-resistant O₃ decomposition

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catalyst with long-term stability and high efficiency at ambient temperature.

Birnessite-type MnO_2 is one of the common manganese oxide minerals in terrestrial deposits and ocean nodules. The basic structural unit of birnessite-type MnO_2 is a sheet of MnO_6 octahedra with cations and water molecules occupying the interlayer positions [23]. There has been considerable interest in its possible uses as catalysts [24–29]. However, to the best of our knowledge, very few studies have been reported focusing on catalytic decomposition of gaseous O_3 over birnessite-type MnO_2, which, however, is of great significance to scientific research and practical application due to its abundance in nature. Recently, Gopi et al. [30] reported the improvement of gaseous O_3 decomposition by proton exchange over birnessite-type MnO_2; however, they did not investigate the effect of humidity on the catalyst performance. Of course the effect of acid treatment on the water-resistant property was not investigated either. Herein, gaseous O_3 decomposition in humid stream over birnessite-type MnO_2 is reported. The promoting effect of nitric acid treatment on the water-resistant property of MnO_2 was observed and further elaborated by various characterizations, deliberately designed experiments and the density functional theory (DFT) calculations. An acid sites and oxygen vacancies involved mechanism for gaseous O_3 decomposition was finally proposed. The present study provides scientific insights on rational designs of affordable and efficient catalysts for environmental application.

2. Experimental and computational

2.1. Catalyst preparation & characterization and activity tests

The birnessite-type MnO_2 was prepared by the redox reaction between $KMnO_4$ and CH_3OH solution. Briefly, an appropriate amount of $KMnO_4$ solid was dissolved in deionized water. Then CH_3OH was added into the $KMnO_4$ solution and the mixture was kept stirring for 12 h. After filtration and washing with deionized water, the obtained solid was dried at 105 °C overnight in an oven. The pristine MnO_2 was obtained.

Subsequently, the pristine MnO_2 powder was soaked in HNO_3 solution in a beaker and constantly stirred in a water bath for 6 h. The mass ratio of solid to liquid was kept at 1:20. Three HNO_3 aqueous concentrations (0.1, 0.2 and 0.4 M) and three treatment temperatures (30, 50 and 70 °C) were investigated. After acid treatment, the suspension was filtered and repeatedly washed with deionized water until the pH of the eluate was about 7. The resultant solid was then dried at 105 °C overnight in an oven. The obtained powder was grounded, tableted, crushed and sieved to 40–60 mesh. For convenience, the acid-treated MnO_2 was denoted as H-MnO_2.

For details of the instruments, procedures and parameters used for catalyst characterization, see the electronic supplementary information.

The catalysts were tested for humid O_3 decomposition. The detailed procedures and parameters, and the definition of O_3 conversion were described in the electronic supplementary information.

2.2. DFT calculations

The formation energy of oxygen vacancy (E_{vo}) and the adsorption energies of gaseous O_3 ($E_{ads}^{O_3}$) and H_2O ($E_{ads}^{H_2O}$) molecules onto the catalyst surface were calculated according to Eqn. (S2)–(S4), respectively. For details of DFT calculations, see the electronic supplementary information.

3. Results and discussion

3.1. Comparison of O_3 decomposition over the pristine and acid-treated MnO_2

Fig. 1A shows the variations of O_3 conversion with reaction time over the pristine MnO_2 and H-MnO_2. The H-MnO_2 was obtained by treating the pristine MnO_2 in 0.2 M of HNO_3 solution at 50 °C for 6 h. The O_3 decomposition efficiency was much higher over the H-MnO_2 than the pristine MnO_2, which indicates that acid treatment could greatly enhance O_3 decomposition.

In terms of catalyst stability, O_3 conversion decreased fast from an initial conversion of ~59% to ~8% within 30 min over the pristine MnO_2. After about 2-h reaction, the pristine MnO_2 almost lost its activity for O_3 decomposition. However, the O_3 conversion dropped quickly from ~98% to ~66% in the first 30 min and kept almost stable around 60% thereafter over the H-MnO_2. These results demonstrate that acid treatment greatly suppressed catalyst deactivation and enhanced the catalyst stability.

3.2. Characterization studies

The acid-treated sample obtained under the conditions of 0.2 M of HNO_3 solution at 50 °C was chosen for further characterizations since the sample obtained in these conditions resulted in the best O_3 decomposition performance, as shown in Fig. S1A and B.

3.2.1. Crystal structure, element contents and textural properties

XRD patterns of the pristine and acid-treated MnO_2 are displayed in Fig. 2. The layered structure was observed, as indicated by the diffraction peaks around 12.0° {0 0 1}, 25.2° {0 0 2}, 37.6° {−1 1 1}, 42.3° {−1 1 2} and 66.5° {0 0 5}, which are consistent with the standard information of birnessite MnO_2 (JCPDS 80-1098). However, the crystallinity was poor. Besides, no phase changes could be detected after acid treatment, although the relative intensities are slightly different. This could be due to partial destabilization of the layered structure from the leaching of K^+ cations [31], which will be discussed in the next paragraph.

Compared with the pristine MnO_2, the K content of the H-MnO_2 dropped significantly, as can be seen from the ICP-OES results in Table 1. About 5.5 mmol of K^+ was lost after 2 g of the pristine MnO_2 powder was treated in HNO_3 solution. Besides, the pH value of the supernatant after acid treatment was increased to ~0.9 and the consumption of H^+ was calculated to be about 4 mmol, which is nearly equal to the loss of K^+. It is also found that the K content of the sample treated in deionized water (H_2O-MnO_2) decreased very slightly from the pristine MnO_2, which means that the loss of K^+ was not caused by water washing. Therefore, we ascribe the loss of K^+ to the exchange of H^+ into the layers. This deduction is further supported by the NMR characterization (Fig. S2). K^+ ions act as layer adhesive, so the loss of K^+ by H^+ exchange would cause destabilization of the layered structure. This phenomenon was also observed by other authors [32–34].

The isotherms of N_2 adsorption are shown in Fig. S3 and the calculated BET specific surface area (S_{BET}), pore diameter (D_{pore}) and pore volume (V_{pore}) are compared in Table 1. The S_{BET} of the pristine MnO_2 was only 40 $m^2 \cdot g^{-1}$; however, HNO_3 treatment greatly increased the S_{BET} to 228 $m^2 \cdot g^{-1}$, which might also be caused by the destabilization of the layered structure after proton exchange [31]. Besides, the D_{pore} became smaller and the V_{pore} became twice larger after acid treatment. The large S_{BET} and V_{pore} and small D_{pore} are beneficial for O_3 decomposition, as reported by Lian et al. [18]. The S_{BET}-normalized reaction rate was also calculated, and the time dependence of the S_{BET}-normalized reaction rate over the pristine and acid-treated MnO_2 was compared in Fig. 1B. The O_3