The critical role of oxygen atom adsorption capacity of oxygen vacancies for the ozone decomposition over manganese oxides

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Abstract: Catalytic decomposition of ozone at room temperature was achieved using manganese oxide in four crystal structures: α-, β-, γ- and δ-phase MnO_2 catalysts. The catalytic activities followed the sequence γ- > α- > δ- > β-MnO_2. γ-MnO_2 showed the best catalytic activity among the four samples and 66% ozone decomposition was obtained under 40 ppm ozone and space velocity of 600,000 h^{-1} after 6h. Characteristic results reveal that moderate oxidation state of Mn and the dissociate ability of ozone molecules of oxygen vacancies determines the ozone decomposition activity for different crystal type MnO_2.

Keywords: Manganese dioxide, Ozone decomposition, Oxygen vacancies.

1. Introduction (11-point boldface)

High concentrations of ozone can cause detrimental effects on human health and ecosystem [1]. Hence, effective abatement of ozone is urgently needed in order to improve air quality and reduce the public health risk. Catalytic decomposition is a common method to remove ozone, and manganese oxide is the most effective catalysts [2]. MnO_2 shows great structures flexibility and appears in a number of crystallographic polymorphs. The α-, β-, γ- and δ-MnO_2 structures are all constructed from chains of MnO_6 octahedra, which link in different ways[3]. Only a few work have investigated the activity of MnO_2 with specific crystal phase for ozone decomposition[4], and the relationship between structure of MnO_2 and their catalytic property for ozone decomposition is still not clear. Previous studies found that the content of Mn^{3+} or the content of oxygen vacancies determine the ozone decomposition activity, but the role of the property of oxygen vacancy in the ozone decomposition has not been reported. Due to the different link mode of the MnO_6 octahedra, the property of oxygen vacancies for the different types of manganese oxides have obvious differences. Therefore, it would be worth exploring the effect of MnO_2 structures on ozone decomposition to understand the mechanism on how oxygen vacancy influencing the MnO_2 activity.

In this study, α-, β-, γ- and δ-phase MnO_2 catalysts were synthesized by a hydrothermal process. The effects of the crystal phase of the MnO_2 catalysts on ozone decomposition were investigated at room temperature.

2. Experimental (or Theoretical)

α-, β-, γ- and δ-phase MnO_2 catalysts were prepared by a hydrothermal method similar with our previous work[5].

The catalyst were characterized by XRD, physisorption analyzer, FE-SEM, TEM, and XPS. Density functional theory (DFT) calculations were performed using CASTEP package on the basis of the plane-wave-pseudo-potential approach. The ozone decomposition texts were conducted in a fixed bed continuous flow quartz reactor (4 mm i.d.) at temperature 30 ^oC, and the space velocity in all experiments was 600,000 h^{-1}. The relative humidity (RH = 45%) of the feed gas stream was maintained by changing the gas flow through a bubbler. The concentration of inlet ozone, which was generated by low-pressure ultraviolet lamps, was 40 ± 2 ppm. Inlet and outlet ozone concentrations were monitored online with an ozone monitor (Model 202, 2B Technologies).

3. Results and discussion

Figure 1 shows the XRD patterns of the MnO_2 catalysts. All of the four catalysts could be well indexed and were in good agreement with the lattice constants of constants of α-MnO_2 (JCPDS 44-0141), β-MnO_2 (JCPDS 24-0735), γ-MnO_2 (JCPDS14-0644) and δ-MnO_2 (JCPDS 80-1098), confirming the successful preparation of MnO_2 with four types of crystal structures. The BET surface areas of α-, β-, γ- and δ-phase MnO_2 catalysts were 80.8, 23.3, 85.3, and 108.4 $m^2\ g^{-1}$, respectively.

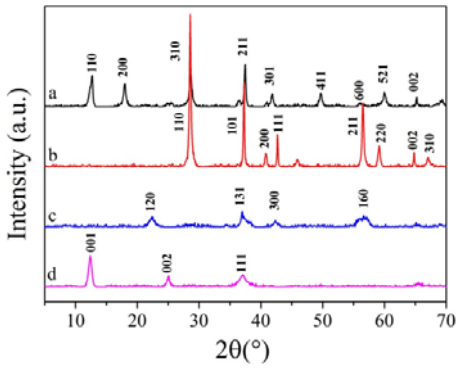

Figure 1. XRD patterns of (a) α- MnO_2, (b) β- MnO_2, (c) γ- MnO_2 and (d) δ- MnO_2 catalysts.

The decomposition of ozone was negligible without catalysts. Figure 2 shows the ozone decomposition activity over α-, β-, γ- and δ-MnO_2 catalysts at RH=45% with an inlet ozone concentration of 40 ppm. The activity were distinctly related to the phase structures of MnO_2. The catalytic activities followed the sequence γ- > α- > δ- > β-MnO_2. γ-MnO_2 showed the best catalytic activity among the four samples and 66% ozone decomposition was obtained after 6h. The above findings clearly showed that the catalytic activity of MnO_2 for the ozone decomposition was in tight correlation with the crystal structures.

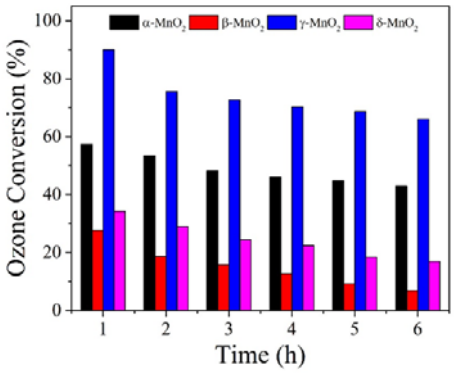

Figure 2. Conversion of ozone on α-, β-, γ- and δ-MnO_2 catalysts at RH = 45%. (Ozone inlet concentration 40 ppm, 20% O_2, N_2 balance, temperature 30 °C, relative humidity 45%, GHSV: 600,000 h^{-1})..

The adsorption of oxygen atom on the vacancy of the catalyst were calculated using density functional theory (DFT). The calculated $E_{O,\,ads}$ was -2.49 eV, -1.39 eV, -2.74 eV and -2.19 eV for α-MnO_2, β-MnO_2, γ-MnO_2 and δ-MnO_2, respectively. The energy decreased in the order γ- > α- > δ- > β-MnO_2. The relationship between the between the calculated adsorption energy ($E_{O,\,ads}$) and the ozone conversion rate is plotted in Figure 3. It is obvious that the adsorption of oxygen atom on the vacancy of MnO_2 greatly influences the catalytic activity and γ-MnO_2 which has the highest adsorption energy (-2.74 eV) shows the highest ozone conversion rate. This theoretical result further reveals that the catalytic activities of ozone decomposition was depend on the adsorption of oxygen atom on the oxygen vacancy of the catalyst, that is, the dissociate ability of ozone molecules on the vacancy.

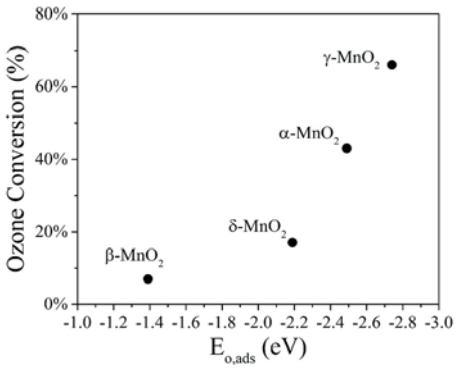

Figure 3 Relationship between the calculated adsorption energy ($E_{O,\,ads}$) and the ozone conversion rate.

4. Conclusions

α-, β-, γ- and δ-phase MnO_2 catalysts were synthesized by hydrothermal method and tested for ozone decomposition. The catalytic activities followed the sequence γ- > α- > δ- > β-MnO_2. γ-MnO_2 showed the best catalytic activity among the four samples and 66% ozone decomposition was obtained under 40ppm ozone and space velocity of 600,000 h^{-1} even after 6h. The dissociate ability of ozone molecules on the oxygen vacancy of the catalyst determine the catalytic activity of MnO_2 were confirmed by DFT calculations. These findings are helpful for understanding the key factor that determine the catalytic activity and designing more effective catalyst for ozone removal.

References

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