



Catalytic activities of two different morphological nano-MnO₂ on the thermal decomposition of ammonium perchlorate

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ARTICLE INFO

Keywords:

Nano-MnO₂
Ammonium perchlorate
Catalysis
Thermal decomposition

ABSTRACT

In order to investigate the catalytic activity of nano-MnO₂ on the thermal decomposition of ammonium perchlorate, two different shapes of nano-MnO₂ (sea-urchin and linear) were prepared by the hydrothermal method with MnSO₄·H₂O and Na₂S₂O₈, MnSO₄·H₂O and (NH₄)₂S₂O₈, respectively. X-ray diffraction, scanning electron microscopy and the nitrogen adsorption/desorption analysis were used to characterize the structure of the nanocomposites. The sea-urchin nano-MnO₂ possesses a greater specific surface area than the linear nano-MnO₂. The catalytic properties of nano-MnO₂ on the thermal decomposition of ammonium perchlorate (AP) were demonstrated by differential scanning calorimeter (DSC). As shown in the DSC curves, the addition of the sea-urchin nano-MnO₂ got the thermal decomposition peak temperature of AP reduced much more than the addition of the linear nano-MnO₂, the low-temperature decomposition process even disappeared, and the high-temperature pyrolysis peak temperature decreased by 94.6 °C. All evidences indicated that the sea-urchin nano-MnO₂ is a better catalytic than the linear one.

1. Introduction

Ammonium perchlorate (AP) is the most commonly used oxidant for composite solid propellants [1–3], whose combustion behaviors can be affected by its thermal decomposition characteristics [4–6]. The combustion process of the solid propellant can be promoted by the refinement of AP, but it is limited to the danger of the ultrafine AP [7]. At present, the academia mainly chooses a safe method by adding different kinds of thermal decomposition catalysts [8–10] to AP in order to improve the combustion properties of solid propellants. Nowadays, the transition-metal oxides (TMOs), such as nanosized TiO₂ [11], V₂O₅ [12], Fe₂O₃ [13,14], CuO [15,16], Co₃O₄ [17,18] and so on, have caught most attentions due to their fascinating properties in stability and catalysis. However, the catalytic activities of the most reported metal oxide nanoparticles, whose addition could not make the pyrolysis temperature decrease in a large scale [11–19], were not satisfactory.

Among those TMOs, Mn-based oxides can undergo a variety of reactions due to the wide range of accessible oxidation states of Mn (Mn⁰, Mn²⁺, Mn³⁺, and Mn⁴⁺), which are endowed with many potential applications, including energy storages [20,21], magnetic materials [22], sensors [23], and catalysis [24,25]. However, compared with the

investigation of other TMOs, only a few hydrothermal methodologies starting from different manganese salts have been developed for the preparation of manganese oxides with different morphologies and dimensions [20–25]. Therefore, a synthetic method for nano- or micro-sized manganese oxide particles with a specific morphology is still essential and significant. Moreover, manganese dioxide is a non-stoichiometric compound that can exist in plenty of polymorphs including α -, β -, γ - and δ -MnO₂ and the catalytic activity of MnO₂ is phase selective so the preparation of single-phase MnO₂ is necessary.

Here, we use hydrothermal methods to prepare two kinds of nanosized β -MnO₂ with different microscopic morphologies in order to investigate their catalytic activities on the thermal decomposition of AP. Their thermographies from differential scanning calorimeter (DSC) show that the catalytic activity of our obtained sea-urchin nano-MnO₂ is good enough to reduce the peak temperature of the high-temperature pyrolysis by almost 100 °C, which is much larger than the above-mentioned other metal oxide nanoparticles do. Furthermore, in combination with the results of the nitrogen adsorption/desorption analyses, it can be inferred that the specific surface area is a significant factor to influence the decomposition behavior of AP.

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2. Experiments

2.1. Reagents

The chemical reagents of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, $\text{Na}_2\text{S}_2\text{O}_8$, anhydrous ethanol were purchased from Sinopharm Chemical Reagent Co. Ltd. All the chemicals are of analytical grade and used without further purification.

2.2. Controlled synthesis of nano- MnO_2 by a simple hydrothermal reduction method

2.2.1. Preparations of the linear nano- MnO_2

The concentration of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was 0.1 mol/L and 0.15 mol/L in deionized water, respectively. Magnetic stirring was performed to completely dissolve the reaction mixture, which subsequently was transferred to a 50 mL polytetrafluoroethylene liner in a hydrothermal reactor and incubated in an oven at 140 °C for ca. 12 h. The product was then obtained by a centrifugal separation after cooling down naturally at room temperature, washed for three to four times by deionized water and absolute ethanol, and finally dried at 70 °C under normal pressure.

2.2.2. Preparations of the urchin nano- MnO_2

The concentration of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ and $\text{Na}_2\text{S}_2\text{O}_8$ was 0.05 mol/L and 0.25 mol/L in deionized water, respectively. The mixed dissolution was put into 2.5 mL concentrated sulfuric acid before being stirred for ca. 10 min with a magnetic stirrer. After the reaction mixture was completely dissolved, it was transferred to a 50 mL polytetrafluoroethylene liner in a hydrothermal reactor and incubated in an oven at 110 °C for ca. 1 h. The product was then obtained by a centrifugal separation after naturally cooling down at room temperature, washed repeatedly for three or four times by deionized water and absolute alcohol, and finally dried at 60 °C under normal pressure.

2.3. Characterizations of nano- MnO_2

The morphology characterizations of as-prepared samples were taken on scanning electron microscope (SEM, Hitachi S-4800). The powder X-ray diffraction (XRD) patterns of the samples were carried out on a Bruker AXS D8 ADVANCE X-ray diffractometer equipped with Cu K α source ($\lambda = 0.15406$ nm) within the range of $2\theta = 10\text{--}80^\circ$. Nitrogen adsorption/desorption isotherms of the samples at -196°C were recorded using Micromeritics TriStar II 3020 porosimetry analyzer and surface areas were calculated according to the Brunauer-Emmett-Teller (BET) method.

2.4. Thermal catalytic decomposition of AP on the nano- MnO_2

The thermal catalytic decomposition experiments were performed as follows: the mixture of the two as-synthesized nano- MnO_2 with AP was ground in a glass mortar for 30 min to ensure the homo-dispersion of as-obtained samples. The weight ratios of nano- MnO_2 to AP were 1, 2, and 5%, respectively. After one drying procedure about 5 h at 50 °C, the pure AP followed the same steps as references.

The catalytic effect of the as-synthesized nano- MnO_2 on the thermal decomposition of AP has been demonstrated by differential scanning calorimetry (DSC, Mettler -Toledo) experiments at a heating rate of 20 K min^{-1} in a temperature range of 50–450 °C.

3. Results and discussion

3.1. Characterizations of structures and morphologies

As seen from Fig. 1a–b, the morphology of the prepared linear nano- MnO_2 by the hydrothermal method is clear and uniform with ca. 2 μm

in the particle size. From Fig. 1c–d, it can be seen that the surface of the sea-urchin nano- MnO_2 , whose spherical diameter is about 2 μm , is covered with nano-rods in a uniform length. and the morphology of sea-urchin nano- MnO_2 is assembled from numerous tiny nanocrystals. In addition, the dispersion of the sea-urchin nano- MnO_2 is so good that there is no accumulation phenomenon.

3.2. X-ray diffractions

Fig. 2 shows the XRD patterns of two different morphological nano- MnO_2 composites which have been prepared by two sets of raw materials. The XRD pattern in Fig. 2 curve (a) shows the phase of linear nano- MnO_2 obtained at a reaction time of 12 h. The well-resolved diffraction peaks at 28.70°, 37.33°, 56.65°, 59.37° and 72.38°, which correspond to the (110), (101), (211), (220) and (112) planes of $\beta\text{-MnO}_2$ (JCPDS File no. 24-0735). No other peaks of impurities are detected, indicating that the product has been completely transformed into MnO_2 during the hydrothermal reaction. The XRD pattern in Fig. 2 curve (b) illustrates the phase of sea-urchin nano- MnO_2 obtained at a reaction time of 1 h. The diffraction peaks at 28.70°, 37.33° and 56.65°, which correspond to the (110), (101) and (211) planes of $\beta\text{-MnO}_2$ (JCPDS File no. 24-0735). Since no characteristic peak for other materials is detected, it suggests no impurity in the sample. By increasing the hydrothermal time from 1 h to 12 h, excess peaks at 59.37° and 72.38° in curve (a) [26]. Compared to curve (b), the narrower and stronger peaks in curve a suggest the higher purity of the $\beta\text{-MnO}_2$ phase, which is due to increasing the hydrothermal temperature from 110 °C to 140 °C.

3.3. Specific surface area analyses

The results of the nitrogen adsorption/desorption analysis for the linear and sea-urchin nano- MnO_2 are given in Fig. 3. As shown in Fig. 3, the adsorption–desorption curves of the sea-urchin nano- MnO_2 exhibit type IV isotherm with a H3 hysteresis loop [27], suggesting a characteristic of mesoporous structure. By the calculations with the BET (Brunauer-Emmett-Teller) method, the specific surface area of the sea-urchin nano- MnO_2 is 55.22 $\text{m}^2 \text{g}^{-1}$. However, the adsorption–desorption curves of the linear nano- MnO_2 almost overlap each other, exhibit type II isotherm with a H3 hysteresis loop and it can be considered that there is no adsorption hysteresis which is characteristic of nonporous materials. The specific surface area of the linear nano- MnO_2 is 11.93 $\text{m}^2 \text{g}^{-1}$, which is much lower than that of the sea-urchin nano- MnO_2 . The specific surface area of the sea-urchin nano- MnO_2 is consistent with the analysis of SEM above, which may improve the catalytic performance.

3.4. Thermal analyses

In order to study the catalytic effect of the nano- MnO_2 on AP, the neat AP was first analyzed by DSC without an addition of nano- MnO_2 (Fig. 4). It can be seen from the DSC curve of the neat AP that the thermal decomposition process of AP can be divided into three processes with increasing temperature. The first is the endothermic process, which occurs at around 244 °C. It is a crystalline transformation process of AP for a solid-solid endothermic reaction in which AP changes from orthorhombic to cubic [28]. The second is the low temperature exothermic process, in which the pyrolysis reaction of AP occurs for its low temperature decomposition temperature at 305.4 °C. The third is the high temperature exothermic process, in which the decomposition of AP happens in the peak temperature of decomposition at 380.8 °C.

As seen from Fig. 4a, the linear nano- MnO_2 catalysts with different mass fractions are of no detected effect on the crystalline transformation temperature (about 244 °C) of AP. When the mass fraction of the linear nano- MnO_2 is 1%, the peak temperatures of the low-temperature

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