

Synthesis of hierarchical flower-like Co_3O_4 superstructure and its excellent catalytic property for ammonium perchlorate decomposition

Gang Li ^{a,b,*}, Weiyang Bai ^b

^a College of Materials Science and Engineering, Chongqing University, Chongqing 400044, PR China

^b School of Chemistry and Chemical Engineering, Chongqing University of Technology, Chongqing 400054, PR China

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ABSTRACT

Hierarchical flower-like cobalt tetroxide (Co_3O_4) was successfully synthesized via a facile precipitation method in combination with heat treatment of the cobalt oxalate precursor. The samples were systematically characterized by thermo gravimetric analysis and derivative thermo gravimetric analysis (TGA-DTG), X-ray powder diffraction (XRD), field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and N_2 adsorption-desorption measurements. The results indicate that the as-fabricated Co_3O_4 exhibits uniform flower-like morphologies with diameters of 8–12 μm , which are constructed by one-dimensional nanowires. Furthermore, catalytic effect of this hierarchical porous Co_3O_4 on ammonium perchlorate (AP) pyrolysis was investigated using differential scanning calorimetry (DSC) techniques. It is found that the pyrolysis temperature of AP shifts 142 °C downward with a 2 wt% addition content of Co_3O_4 . Meanwhile, the addition of Co_3O_4 results in a dramatic reduction of the apparent activation energy of AP pyrolysis from 216 kJ mol^{-1} to 152 kJ mol^{-1} , determined by the Kissinger correlation. The results endorse this material as a potential catalyst in AP decomposition.

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1. Introduction

Ammonium perchlorate (AP) is a commonly used oxidizer in the composite solid propellants, and its pyrolysis characteristic has a dramatic effect on the burning behavior of the propellant [1,2]. It has been widely known that the overall burning property of the propellant will be boosted as the AP pyrolysis temperature decreases. In other words, with the decreasing of the pyrolysis temperature of AP, the delay time of propellant ignition will be shorten and thus a higher burning rate as well as a better performance of the composite solid propellants will be achieved [3].

To lower the AP thermal decomposition temperature, two types of methods have been developed. One is reduction of the particle size of AP, and the other is introduction of a small amount of catalysts. There is no doubt that the burning velocity of propellants can be improved to a certain degree by decreasing AP's particle size, but the effectiveness is quite limited. Moreover, the ultra-finishing process for AP is very dangerous [4,5]. Therefore, more and more attention has been paid to hunting catalysts with high performance towards AP pyrolysis.

In the past decades, numerous catalysts, particularly transition metal oxides and their composites, such as NiO [6], CeO_2 [7], CdO [8], Cu_2O [9], Fe_3O_4 [10], MnO_2 [11], $\text{Fe}_2\text{O}_3/\text{Co}_3\text{O}_4$ [12], $g\text{-C}_3\text{N}_4/\text{CeO}_2$ [7], and so on, have been studied by researchers for promoting AP pyrolysis. Among these catalysts, Co_3O_4 has drawn particular attention due to its stable spinel crystal structure, rich abundance, environmental friendliness and high efficiency in catalyzing decomposition of AP. For instance, it was reported by Alizadeh-Gheshlaghi et al. that the pyrolysis temperature of AP could shift 92 °C downward with nano-sized Co_3O_4 synthesized via sol-gel method as catalyst [13]. Zhang et al. described that urchin-like Co_3O_4 played a catalytic role on the decrease of the pyrolysis temperature of AP by 120 °C [14]. Zhang and co-workers demonstrated that Co_3O_4 nanoflakes obtained through hydrothermal reaction and subsequent calcination process showed an excellent catalytic effect for AP pyrolysis, which allowed the decomposition temperature of AP decrease by 122 °C [15]. In Zhou's work, reduction of the AP pyrolysis temperature by 137 °C using Co_3O_4 single-crystalline octahedron-like nanoparticle exposed (1 1 1) facets as additive was represented [16].

From the literature, it is clear that the catalytic performances of Co_3O_4 are highly sensitive to their morphologies, microstructures, crystal defects, and so on. To date, Co_3O_4 catalysts, including nanoparticles [1,13], nanoflakes [17], nanocubes [18], nanowires

* Corresponding author at: College of Materials Science and Engineering, Chongqing University, Chongqing 400044, PR China.

E-mail address: 47922138@163.com (G. Li).

[19], and so forth, has been prepared for the AP thermal decomposition. Although much progress has been made, viable and facile routes to synthesize Co_3O_4 with specific morphology and high catalytic activity are still lacking. Thereby, in the present study, we attempt to fabricate Co_3O_4 with novel hierarchical porous flower-like superstructure through a facile precipitation method combined with subsequent thermal treatment of the oxalate precursors, during which CoSO_4 and $\text{Na}_2\text{C}_2\text{O}_4$ are used as raw materials. Meanwhile, the catalytic properties of the as-fabricated Co_3O_4 towards AP pyrolysis will be investigated.

2. Experimental sections

2.1. Material synthesis

In a typical synthesis, 100 mL of 0.1 M CoSO_4 aqueous solution and 70 mL of ethanol were mixed firstly at room temperature. Then, under magnetic stirring, 105 mL of 0.1 M $\text{Na}_2\text{C}_2\text{O}_4$ solution was quickly poured into the aforementioned solution. After that, the reaction mixture was stirred continuously for another 2 h. Subsequently, the precipitate was collected, rinsed and dried. Finally, the precipitate was heat treated at 350 °C for 90 min with a heating rate of 5 °C min^{-1} in air atmosphere.

2.2. Material characterization

Thermo gravimetric analysis (TGA) and derivative thermo gravimetric analysis (DTG) of the precursor was performed on a NEZSCH STA 449C thermal analyzer in air. The heating rate was 10 °C min^{-1} and the temperature range was 30–700 °C. The crystal structure and phase purity of the samples were detected on a Philip X' pert PRO diffractometer equipped with Cu $K\alpha$ radiation in the 2θ range of 15–85°. The morphologies of the samples were observed using a Quanta F250 field emission scanning electron microscope (FESEM, FEI, American) and by a JEM-2100F transmission electron microscope (TEM, JEOL, Japan). The N_2 adsorption and desorption isotherms were obtained on a Quantachrome NOVA 2000e nitrogen adsorption apparatus at 77.35 K.

2.3. Catalytic activity measurement

Catalytic performances of the as-obtained product on AP thermal decomposition were studied using differential scanning calorimetry (DSC) on a NEZSCH STA 449C thermal analyzer in N_2 atmosphere with working temperature between 30 and 600 °C. Prior to the experiments, 98 wt% of AP and 2 wt% of Co_3O_4 were thoroughly blended. DSC tests were carried out under an open aluminum crucible and samples with a total weight of approximately 3 mg were used in all runs. For comparison, neat AP without addition of Co_3O_4 was also put into the measurements.

3. Results and discussion

3.1. Thermal behavior of the precursor

To choose an appropriate heat treatment temperature of the as-synthesized $\text{CoC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$ to Co_3O_4 , the pyrolysis behavior of the precursor was investigated using TGA-DTG technique in air. As depicted in Fig. 1, two distinguished weight loss steps can be observed. Weight loss in the first-step takes place at the temperature ranges 140–180 °C, with a maximum loss temperature of 167 °C, which should be attributed to the liberation of crystallized water ($\text{CoC}_2\text{O}_4 \cdot n\text{H}_2\text{O} \rightarrow \text{CoC}_2\text{O}_4 + n\text{H}_2\text{O}$). The weight loss of this step is approximately 20%, thus it is easy to determine the precursor as $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. The second-step weight loss occurs at the tempera-

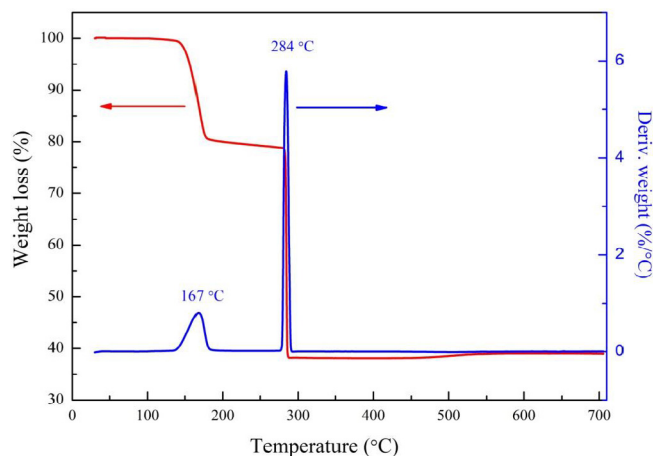


Fig. 1. TGA-DTG curves of the precursor.

ture ranges 270–295 °C, with a maximum loss temperature of 284 °C, which should be due to the transformation of CoC_2O_4 into Co_3O_4 ($3\text{CoC}_2\text{O}_4 + 2\text{O}_2 \rightarrow \text{Co}_3\text{O}_4 + 6\text{CO}_2$). The weight loss in this procedure is approximately 43%, which is consistent with the theoretical values of 45.4% calculated from the above-mentioned equation. After 300 °C, no distinct weight loss is watched from the TGA curve, which suggests the decomposition of the precursor has finished. Thus, 350 °C was chosen as the thermal treatment temperature for the precursor to ensure its complete pyrolysis in this work.

3.2. XRD analysis

Fig. 2 displays the XRD patterns of the precursor and the final product. As for precursor, the pattern shows seven major characteristic diffraction peaks located at approximately $2\theta = 18.40^\circ$, 21.18° , 22.74° , 29.18° , 35.00° , 43.23° and 48.44° , which can be indexed to the (2 0 2), (1 1 2), (0 0 4), (1 1 4), (0 2 2), (2 2 4) and (0 2 6) planes of $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (JCPDS card No.25–0250). It is evident that the XRD result is coincident with that of TGA shown above. After calcination, the as-obtained sample exhibits eight major peaks located at approximately $2\theta = 19.00^\circ$, 31.27° , 36.85° , 38.55° , 44.81° , 55.66° , 59.35° and 65.23° , which can be assigned to (1 1 1), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (5 1 1) and

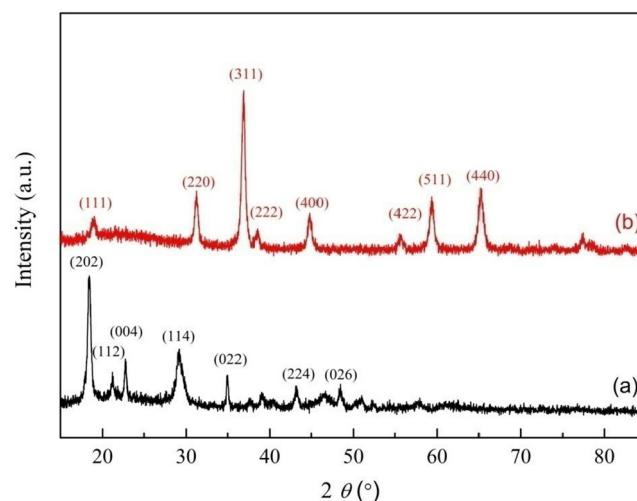


Fig. 2. XRD patterns of the precursor (a) and the final product (b).

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