

Preparation of NiO nanoparticles and their catalytic activity in the thermal decomposition of ammonium perchlorate

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Abstract

NiO nanoparticles with an average size of 10 nm were prepared by a solid-state reaction using nickel acetate and sodium hydroxide as the raw materials and the Tween 80 as dispersant. The reaction was studied by DTA, TG, XRD and FTIR. The size and morphology of NiO nanoparticles were characterized by TEM. The catalytic effect of the NiO nanoparticles for thermal decomposition of ammonium perchlorate (AP) was investigated by DTA and TG. The catalytic performance of NiO nanoparticles is superior to that of bulk NiO particles. Adding 2% of NiO nanoparticles to AP decreases the decomposition temperature by 93 °C and increases the heat of decomposition from 590 to 1490 J g⁻¹. © 2005 Elsevier B.V. All rights reserved.

Keywords: NiO nanoparticles; Solid-state reaction; Ammonium perchlorate; Catalytic performance; Thermal decomposition

1. Introduction

Nickel oxide (NiO) has received a considerable amount of attention in recent years for its catalytic, electronic and magnetic properties [1–3]. Nanometer-sized NiO is expected to possess many better properties than those of bulk NiO [4–7]. Carnes et al. [5] reported that NiO nanoparticles are much more effective catalysts than commercial NiO powder for catalytic reduction of carbon dioxide to methanol.

There are many different methods reported for the synthesis of nanometer-sized nickel oxide [8–12]. Among these methods, the solid-state reaction exhibits many advantages, no need for solvent, high yield, low energy consumption and simple reaction technology. In this work, the preparation of NiO nanoparticles was carried out via solid-state reaction of Ni(OAc)₂·4H₂O and NaOH with Tween 80 as dispersant.

Ammonium perchlorate (AP) is the most common oxidizer in composite solid propellants. The thermal decomposition characteristics influence the combustion behavior of the propellant [13]. The catalytic activities of transition

metal oxides in the thermal decomposition of AP have been reported [13–15]; nanometer-scale Cu₂O, CuO and Fe₂O₃ as catalysts in the thermal decomposition of AP have been reported [16–18]. Use of NiO and nanometer-scale NiO have not been reported for this use. This paper describes the preparation of ~10 nm NiO nanoparticles by solid-state reaction and the role of NiO nanoparticles as a catalyst in thermal decomposition of AP.

2. Experimental

2.1. Materials

Bulk NiO was spectrograde and other reagents were analytical grade chemicals. All were obtained from the Shanghai chemical factory; Bulk NiO, NiO nanoparticles and AP were mixed in 2:98 (wt%) respectively to prepare the samples for the thermal analyses experiment.

2.2. Preparation of NiO nanoparticles

NiO nanoparticles were prepared by grinding a stoichiometric amount of Ni(OAc)₂·4H₂O with NaOH and the

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appropriate amount of Tween 80 in an agate mortar at room temperature for about half an hour. Then the products were washed with distilled water, treated in an ultrasonic bath with absolute ethanol and centrifuged. After that, the samples were dried in desiccators at 80 °C for 4 h, a light green powder was obtained which was then sintered at 400 °C for 2 h.

2.3. Instrumentation

X-ray diffraction (XRD) was carried out on a Bruker D8 Advance X-ray diffraction instrument (Cu K α), the diffraction angle (2θ) from 25 to 80° was scanned. Transmission electron microscopy (TEM) images were taken with a JEM-200CX electron microscope, the sample was dispersed in aqueous ethanol by ultrasonic stirring. FTIR spectra were recorded from 400 to 4000 cm^{-1} with a Bruker vector-22 Fourier transform infrared using the KBr pellet technique. Shimadzu DTA-50 and Beijing WCT-2A thermal analyzers were used at a heating rate of 20 °C/min in N₂ atmosphere over the range 20–500 °C with Al₂O₃ as reference.

3. Results and discussion

3.1. The feasibility of solid-state reaction

Ni(OAc)₂·4H₂O reacts with NaOH during the process of grinding. A black powder was obtained after the precursor was sintered at 400 °C for 2 h.

TG and DTA measurements were performed to study the thermal behavior of the precursor. The weight loss starts from room temperature, and there is a sharp weight loss between 230 and 300 °C due to the decomposition of hydroxide phase to NiO. DTA shows two endothermic peaks, a weak endothermic peak at ~75 °C associated with the loss of physically absorbed water and a strong endothermic peak at ~270 °C caused by dehydration of Ni(OH)₂ [11]. The theoretical weight loss for the formation of NiO from the Ni(OH)₂ is 19.4% while experimental value is about 30% which shows there is some water and Tween not completely removed in washing and drying.

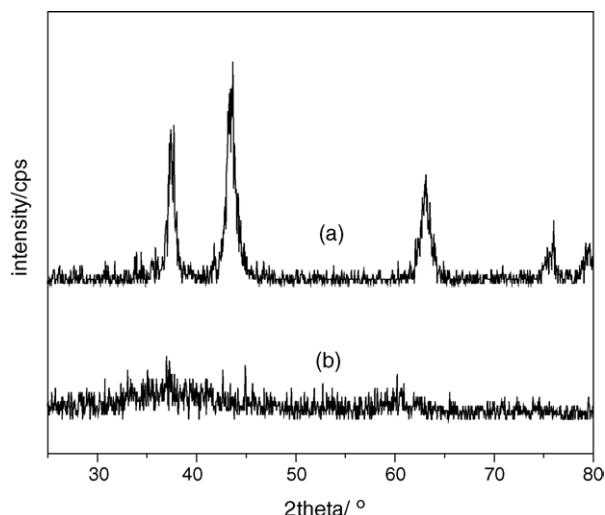


Fig. 1. XRD pattern of: (a) as-prepared product; (b) precursors.

The NiO product was characterized by XRD, TEM and FTIR. The XRD measurement (Fig. 1a) shows the product is single-phase NiO with a cubic structure, the diffraction data are in good agreement with JCPDS card of NiO (JCPDS no.: 01-1239), No impure peaks are observed in the XRD pattern. The average particle size was ~10 nm determined from the XRD pattern parameters of the NiO powder according to the Scherrer equation [19]. The TEM image in Fig. 2 verifies this result and shows a homogenous particle distribution. The diffuse nature of the electron diffraction pattern is attributed to the contribution from the disordered grain boundary.

Fig. 3 shows the FTIR spectrum of the NiO product and bulk NiO. The Ni–O band appears at 482 cm^{-1} . In Fig. 3a, the Ni–O has an absorption band at 437 cm^{-1} [20] which is red-shifted about 45 cm^{-1} compared with Fig. 3b, this is caused by the nanometer-scale surface properties. Based on the XRD, TEM and FTIR, the NiO nanoparticles were obtained.

3.2. Catalytic effect

The DTA curves for pure AP, AP in presence of bulk NiO and AP in presence of NiO nanoparticles are shown in Fig. 4.

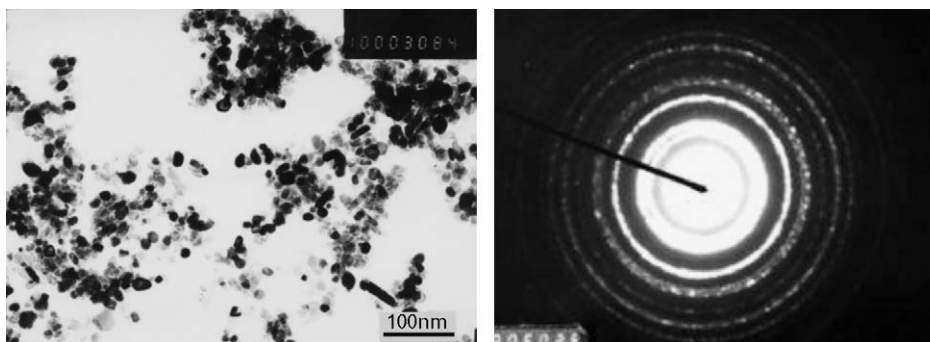


Fig. 2. TEM images and ED pattern of the NiO nanoparticles.

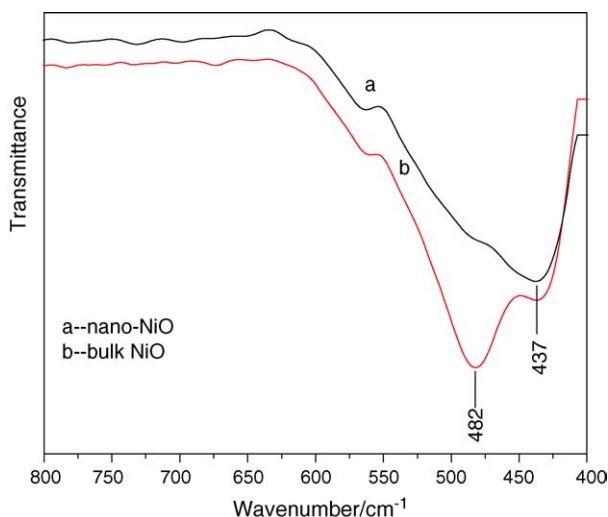


Fig. 3. FTIR spectra of: (a) NiO nanoparticles; (b) bulk NiO.

The endothermic peak at 243 °C in Fig. 4 is due to a crystallographic transition [21]. The NiO additives have no effects on the crystallographic transition temperature. The exothermic peak at 347 °C in Fig. 4c is attributed to the partial decomposition of AP and formation of some intermediate NH_3 and HClO_4 by dissociation and sublimation [14,22,23]. The exothermic peak at about 450 °C is caused by the complete decomposition to volatile products. The heat of decomposition of pure AP is 590 J g^{-1} . Noticeable changes can be seen in Fig. 4b. The two exothermic peaks come closer and the temperatures are lower. The heat of decomposition in presence of bulk NiO is increased to 932 J g^{-1} .

From Fig. 4a, with NiO nanoparticles added, one sharp exothermic peak occurs at 357 °C with a heat of decomposition of 1490 J g^{-1} .

The TG curves for pure AP, AP in presence of bulk NiO and AP in presence of NiO nanoparticles are shown in Fig. 5. Fig. 5c and b exhibit two weight loss steps, Fig. 5a exhibits

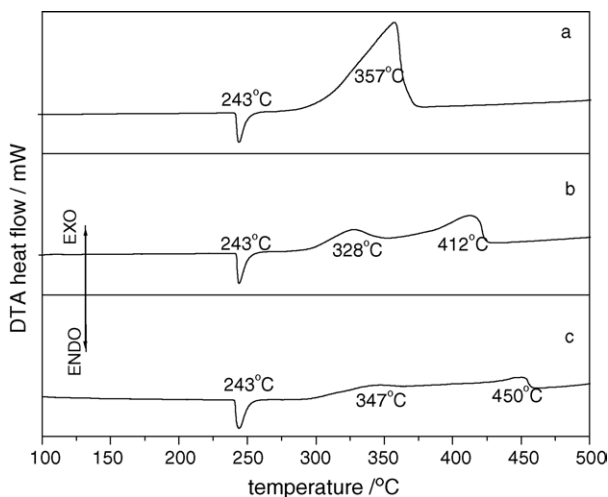


Fig. 4. DTA curves for: (a) AP + NiO nanoparticles; (b) AP + bulk NiO; (c) pure AP.

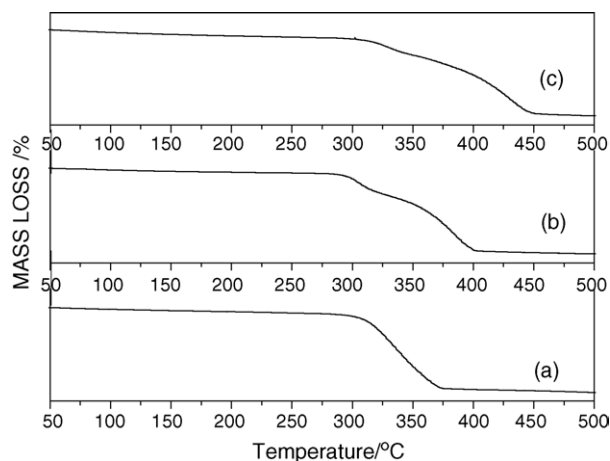


Fig. 5. TG curves for: (a) AP + NiO nanoparticles; (b) AP + bulk NiO; (c) pure AP.

only one weight loss step, corresponding to the exothermic peaks of the DTA curves. The onsets of thermal decomposition of the three samples are all at about 300 °C, while the end temperatures are about 450, 400 and 370 °C, respectively. The thermal decomposition rate of AP in presence of NiO nanoparticles is the fastest, AP in presence of bulk NiO is slower, pure AP is the slowest.

Adding 2% of NiO nanoparticles to AP decreases the temperature of thermal decomposition by 93 °C and increases the heat of decomposition from 590 J g^{-1} (sublimation) to 1490 J g^{-1} (redox decomposition of AP).

Acknowledgements

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