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Effect of particle size on thermal decomposition of alkali metal picrates

Rui Liu, Tonglai Zhang*, Li Yang, Zunning Zhou

State Key Laboratory of Explosion Science and Technology, School of Mechatronic Engineering, Beijing Institute of Technology, Beijing 100081, China

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ABSTRACT

Three alkali metal picrates, KPA, RbPA and CsPA, were prepared into three micron sizes by microemulsion synthesis, and their thermal decomposition behaviors were investigated by DPTA at different temperatures and by DSC at different heating rates. The smaller-sized picrate has greater gas emission and smaller kinetic and thermodynamic parameters than do its larger counterpart. It can be attributed to the decreasing particle size which leads to the high surface energy, the fast mass and heat transfer, and the increasing active sites on the reaction interface. The small size effect and surface effect cause the autocatalysis which reduces the activation energy and promotes the reaction activity. The particle size does not affect the reaction mechanism. However, the picrates with different central alkali metals exhibit different reaction mechanisms even though they are of the same size. This is because the central metal determines the bond energy and consequently affects the stability of picrate.

1. Introduction

Granularity refinement has been applied widely in preparing and modifying the micro- and nano materials and devices with a wide range of applications in medicines, biomaterials and energy resources [1–3]. Refinement to ultrafines has become one of the hottest topics with great expectation of bringing revolutionary changes to material science [4–6]. The ultrafine materials show many special properties in chemistry, mechanics, electrics, magnetism, and optics [7–14], compared to their large-sized counterparts. The distinctive excellences have opened up new applications for the ultrafines especially in the field of high-performance energetic materials in munitions and aerospace [15–22].

Picric acid (2,4,6-trinitrophenol, HPA) is an important raw material for preparing explosives and dyes [23,24]. It reacts with the alkali metals to form the alkali metal picrates (MPAs) which are used as heat-resisting explosives, delay compositions, and ignition charges. Current researches of MPAs are focused on exploring the new preparation methods of their ultrafine particles and briefly analyzing some properties [25–29]. There are many feasible methods of refinement such as mechanical grinding method [30], sol–gel method [31–33], solvent-non-solvent recrystallization [34–37], chemical vapor deposition [38,39] and microemulsion synthesis [40,41]. The microemulsion synthesis is the most appropriate method for refining the energetic materials, because the processes of synthesis and refinement are completed synchronously, which is safe and convenient. Researches on the thermal decomposition kinetics and thermodynamics of MPAs are of great significance to evaluate their thermal safety, using performance and storage life [42,43]. However, the particular properties of the ultrafine MPAs in different sizes have not been studied. In this work, three kinds of picrates combined with different alkali metals were prepared and refined to three micron sizes. The effect of particle size on thermal decomposition behaviors, thermal stability, thermal decomposition kinetics and thermodynamics was investigated by dynamic pressure measuring thermal analysis (DPTA) and differential scanning calorimetry (DSC).

2. Experimental

2.1. Preparation and refinement

Three kinds of MPAs, KPA, RbPA and CsPA, were prepared by microemulsion synthesis according to the following steps:

$$2HPA + MgO \rightarrow Mg(PA)_2 + H_2O$$

$$2MNO_3 + Mg(PA)_2 \rightarrow Mg(NO_3)_2 + 2MPA$$

$$M = K, Rb, Cs$$

* Corresponding author. Tel.: +86 10 68911202; fax: +86 10 68911202.
E-mail addresses: ztlbit@bit.edu.cn, ztlbit@163.com (T. Zhang).

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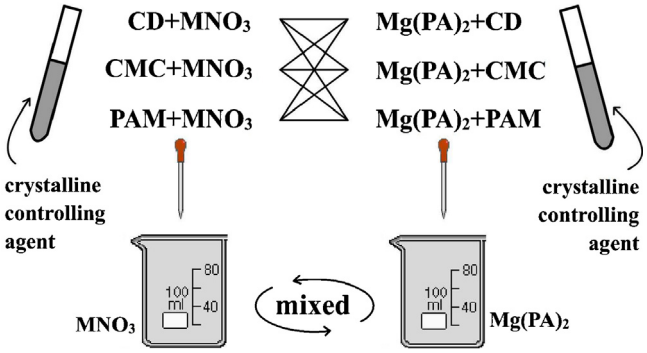

Fig. 1. Method of determining crystalline controlling agent.

9.20 g (0.04 mol) HPA (solid, water content: ≥30%, Sinopharm Chemical Reagent Co., Ltd.) and 0.81 g (0.02 mol) magnesium oxide (MgO, solid, purity ≥98.5%, Sinopharm Chemical Reagent Co., Ltd.) were mixed and added into 300 ml distilled water. The mixture solution was stirred at 60 °C until a dark brown solution was formed, and the $Mg(PA)_2$ solution was obtained by instant filtration. Then, 4.05 g (0.04 mol) potassium nitrate (KNO_3, solid, purity ≥99.0%, Sinopharm Chemical Reagent Co., Ltd.) or 5.90 g (0.04 mol) rubidium nitrate ($RbNO_3$, solid, purity ≥99.5%, Sinopharm Chemical Reagent Co., Ltd.) or 7.80 g (0.04 mol) cesium nitrate ($CsNO_3$, solid, purity ≥99.5%, Sinopharm Chemical Reagent Co.,Ltd) was dissolved in 60 ml distilled water. Such solution was added slowly into $Mg(PA)_2$ solution under the constant stirring at 60 °C. When the mixture solution became turbid, it was rapidly moved into a low-temperature chemical reaction apparatus. After the yellow crystals were precipitated, the product was obtained through filtration, washing with distilled water and anhydrous ethyl alcohol, and drying at 55 °C. The yields of different MPAs ranged from 70 to 85%.

Preparation of the ultrafine particles should add the crystalline controlling agents in right reaction steps. β-Cyclodextrin (CD, solid, purity ≥98.0%, Sigma–Aldrich Co. LLC.), sodium carboxymethylcellulose (CMC, average M_w = 250,000, Sigma–Aldrich Co. LLC.), and polyacrylamide (PAM, liquid, 15 wt.% in H_2O, Sigma–Aldrich Co. LLC.) were selected as the crystalline controlling agents. The ultrafine MPAs of different particle sizes were obtained by altering the kinds and concentrations of crystalline controlling agents through orthogonal tests as shown in Fig. 1. There were 9 groups of tests. Each agent made in different concentrations reacted with $Mg(PA)_2$ and MNO_3, respectively. The other operations were same as mentioned above. Then, the yellow precipitates were collected by filtration, washing and drying. The yields of the refined products in different particle sizes range from 75 to 90%. The recrystalization improved the purities more than 99%.

To avoid the effects of adsorbed gaseous impurities the prepared samples were vacuum-dried at 40 °C for 12 h and stored in a desiccator below room temperature until use.

2.2. Apparatus and methods

The morphology of sample was observed by Olympus BX51-P polarizing microscope under transmitted light. Sample was dispersed in the anhydrous ethanol and placed on a slide.

The particle size was determined by Mettler Toledo FBRM-V6.7.0 online particle size analyzer with dynamic air pressure of 0.4 MPa. Sample was dispersed in hexane dispersant before test.

DPTA, formerly known as dynamic vacuum stability test (DVST), is a novel thermal analysis method established by our lab based on the principle of vacuum stability test (VST) [44,45]. All operations were in strict accordance with current National Military Standards [46,47]. DPTA was used to study the initial decomposition at low temperatures ranging from 25 to 200 °C. Sample was weighed 1.0000 ± 0.0010 g and loaded in the explosion-proof glass test tube. The tube was sealed and evacuated bellow 0.10 kPa before being put in to the thermostat. The reaction unit was heated from room temperature to target temperature at ≤3 °C min^{-1} then kept isothermal for 48 h. The target temperatures were set to 60, 80, 100, 120 and 140 °C, respectively.

Perkin-Elmer Pyris-1 DSC was loaded 0.5 mg sample which was distributed evenly in an uncovered aluminum crucible. Sample was heated from 50 to 500 °C at 5, 10, 15 and 20 °C min^{-1}, respectively, in dynamic nitrogen atmosphere with the flow rate of 20 ml min^{-1}.

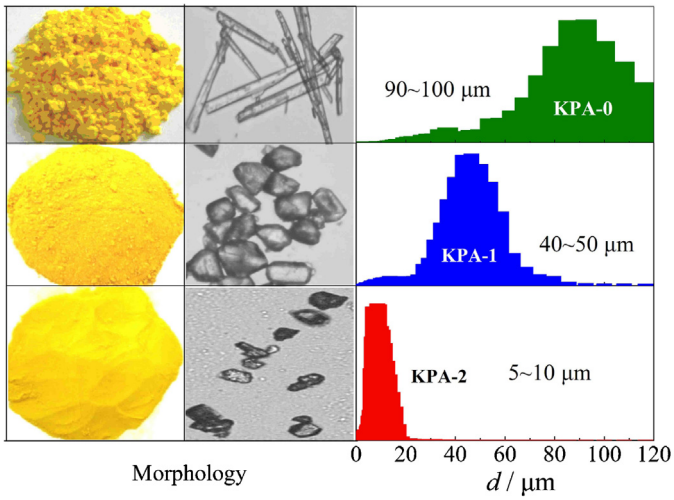

Fig. 2. Morphologies and particle size distributions of KPA.

3. Results and discussion

3.1. Particle size distribution

The raw MPA without the action of crystalline controlling agent (labeled MPA-0) has the particle size of 90–100 μm. A mixture of 2% CD and 30% $Mg(PA)_2$ reacted with a mixture of 0.1% PAM and 30% MNO_3, producing the refined MPA (labeled MPA-1) with the particle size of 40–50 μm. (2% CD and 15% $Mg(PA)_2$) reacted with (0.1% PAM and 15%MNO_3) to form the smaller refined MPA (labeled MPA-2) with the particle size of 5–10 μm. The MPAs of different central metals have the similar particle size when the same crystalline controlling agents are applied. Take the morphologies and particle size distributions of KPA as an example as shown in Fig. 2.

3.2. DPTA analysis

DPTA records the apparent evolved gas pressure (p_{ap}) changing with the time. Errors due to thermal expansion and sensor drift/lag were corrected by standardization to obtain the net pressure at the conditions of 1.0 g sample mass, 25 mL volume and 273.15 K temperature. The time dependences of net decomposition gas pressure and temperature (p & T vs. t) of three samples in different sizes at 100 °C are shown in Fig. 3.

The DPTA curves of three samples show the similar trends: the pressure increases in approximately parabolic fashion with heating time. At early non-isothermal stage, the decomposition gas pressure increases rapidly with increasing temperature. The smaller-sized sample has higher pressure growth rate. At the following isothermal stage, the pressure grows gradually but the growth rate then slows. The decomposition proceeds slowly and smoothly in a long duration. The total gas pressure increases as the