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Abstract

In this paper, the catalytic effect of Zn nanopowders on thermal decomposition of ammonium perchlorate (AP) as well as those of Zn micropowders has been investigated using differential thermal analysis (DTA). The results show that both nanometer and micrometer Zn powders show similar excellent catalytic effect on the decomposition of AP, while the total heat releases of AP added by Zn nanopowders are generally higher than those of AP added by Zn micropowders. In addition, an attempt has been made to explain the observed results with the help of theoretical considerations and data generated during this work.

Keywords: Ammonium Perchlorate, Micropowders, Nanopowders, Thermal Decomposition, Zn
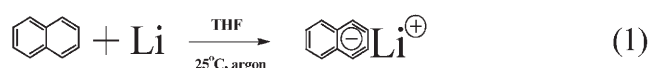
1 Introduction

More recently, the study of nanosized materials as components for high energy systems attracts strong interest due to the recognition that their specific properties, such as huge surface areas and extraordinary chemical activity, could have significant impact on energy-release characteristics [1]. For example, it has been demonstrated by many researchers that Alex aluminum nanopowders can increase burning rates and decrease the ignition time compared to propellants with standard grade aluminum when mixed with solid oxidizer powder [2–5]. At the same time recent studies reveal that the presence of nanosized metals in propellants does not necessarily lead to an increased burning rate [6, 7]. The reasons of this effect are not clear.

The thermal decomposition of ammonium perchlorate (AP), the most common oxidizer and an important energetic material in solid rocket propellant, is believed to influence the performance of solid rocket propellants [8]. Liu et al. [8–10] reported that nanosized metals such as Ni, Cu, Co, Al, and NiCu powders have better catalytic effect on the main exothermic decomposition of AP than that of microsized powders. The catalytic mechanism of nanosized metallic powders is due to the following four points: efficient heat transfer, huge surface area, the coordination ability, and the reactivity of metal with the decomposition products of AP. The transitional metals show better catalytic effect than the active metal Al in that they have stronger coordination ability with the decomposition products of AP.

Zn is not only an active but also a transitional metal, indicating it has a higher reactivity and its ion has certain coordination ability. However, Zn is rarely used as an additive in AP. In this paper, Zn nanoparticles were prepared via lithium reduction of the corresponding zinc salt in tetrahydrofuran (THF) [11]. The reactions are illustrated as follows:

 (1)

 (2)

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Polyethylene glycol (PEG) was added to protect the particles from being oxidized in air. The catalytic performance of the as-prepared Zn nanopowders on the thermal decomposition of AP was investigated by differential thermal analysis (DTA), and their effect has been compared with that of Zn micropowders. An attempt has been made to explain the observed results with the help of theoretical considerations and data generated during this work.

2 Experimental Part

2.1 Materials

Lithium (99.9%), PEG with a molecular weight in the range of 285 – 315, and analytical grade naphthalene were used as received. THF was distilled from its Na/benzophenone solution. The ultra dry $ZnCl_2$ was purchased from Aldrich, AP was presented by Nanjing Science and Technology University in China. Micrometer Zn powders were purchased from Tianjin Kermel Chemical Reagents Development Centre.

2.2 Preparation of Nanometer Zn Powders

In a typical preparation, the procedure is as follows: a 100 mL flask was equipped with a Teflon-coated magnetic stirring bar, rubber septum, and a condenser connected to an argon inlet. The flask was charged with 0.12 g of lithium, 0.2 g of naphthalene, and 50 mL of THF. The mixture was stirred vigorously at room temperature for 1 h, and then 1 g of zinc chlorides was added. The reaction was allowed to continue for 18 h for complete reaction. The highly reactive Zn appeared as blue – black colloidal solution. Subsequently, 3 mL of PEG was injected into the flask and the reaction was allowed to continue for another 5 h. The resultant black product was filtered in the air using millipore filter, washed with ethanol, and dried under ambient conditions. The product was found to be stable in air in that it was not pyrophoric and its appearance did not change with storage under ambient conditions.

2.3 Preparation of Samples Containing AP and Metal Powders for DTA Studies

To prepare the samples for the thermal decomposition experiments, metal powders and AP were dispersed in ethanol by supersonic wave for several minutes, and then filtered and dried in vacuum desiccators. The result mixtures were ground and finally the samples comprising AP and metal powders were obtained.

2.4 Characterization

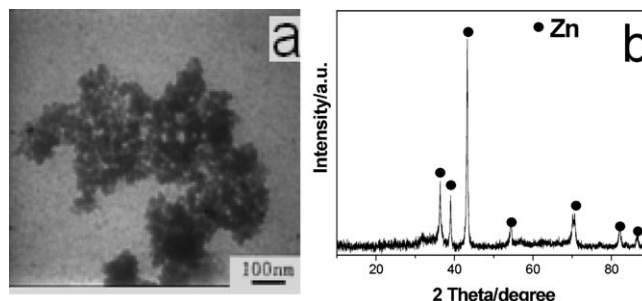X-ray powder diffraction (XRD) experiments were performed on the X′ pert Philips diffractometer using Cu

K_α radiation. The morphology of the particles was observed on a JSM-5600 scanning electron microscope (SEM) and a JEM 100CX-α transmission electron microscope (TEM). Thermalgravimetric (TG) analysis and DTA studies were performed with Mettler Toledo TGA/SDTA851^e at a heating rate of $20\ K \cdot min^{-1}$ and under a nitrogen flow of $20\ mL \cdot min^{-1}$.
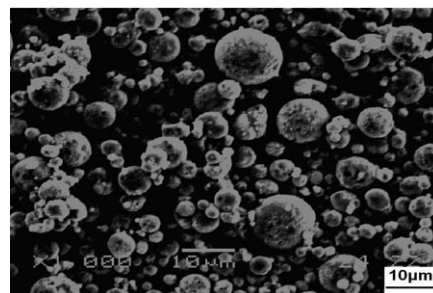
3 Results and Discussion

Figure 1 shows TEM and XRD results of Zn nanoparticles. The shape of the particles is irregular, and the average size is 25 nm (Figure 1a). There are only diffraction peaks of Zn ascribed to hexagonal Zn (JCPDS 04-0831) in the XRD pattern of the as-prepared nanoparticles as Figure 1b shows, indicating the product is of high purity. The crystal size calculated from XRD according to Scherrer's equation is 24 nm which is close to the result of TEM, suggesting that the as-prepared particles are composed of Zn single crystal.

Figure 2 gives the SEM image of the micrometer Zn particles. The particle is of spherical shape with a wide size distribution between 1 and 15 μm.
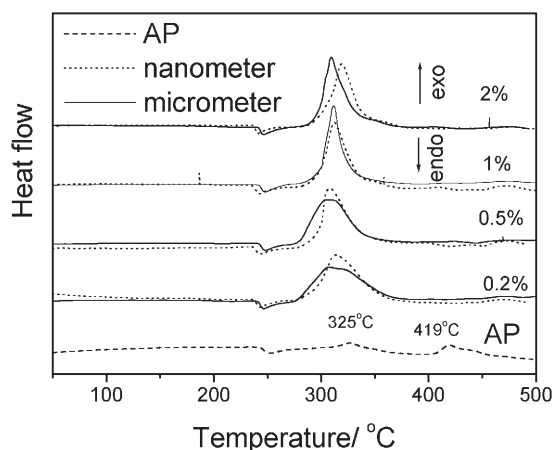
Figure 3 shows DTA curves of AP in the absence and presence of different contents of Zn powders. The thermal decomposition of pure AP is characterized by three events. First, the endothermic peak at around 250 °C is ascribed to the transition from the orthorhombic to the cubic phase. Second, the exothermic peak at low temperature 325 °C corresponds to the partial decomposition of AP and

Figure 1. TEM and XRD pattern of the as-prepared Zn nanoparticles.

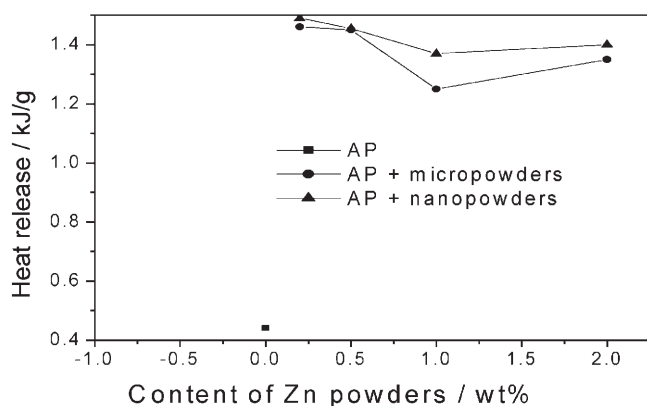**Figure 2.** SEM micrograph of micrometer Zn powders.

Figure 3. DSC curves of the pure AP and AP in the presence of Zn powders.

formation of an intermediate product. Finally, the main exothermic peak at higher temperature 419 °C corresponds to the complete decomposition of the intermediate product into the volatile product.

Addition of small amounts of Zn powders will not change the phase transition peak but remarkably influence the exothermic decomposition peaks. For mixtures containing Zn powders, there is only one exothermic decomposition peak located between 300 and 315 °C in their DTA curves. With the increase in the Zn content, the exothermic peak becomes narrower, while the peak depositions experience little changes. In the presence of 0.2 and 0.5% Zn powders, the exothermic peaks of nanopowders are more prominent than that of micropowders. However, in general, the effect of nanometer Zn powders on the thermal decomposition is similar to that of micrometer Zn powders especially for the mixtures with the 1 wt.-% content of Zn powders. Therefore, both Zn nanopowders and micropowders show excellent catalytic effect on the thermal decomposition of AP by significantly lowering the decomposition temperature.

More noticeably, the addition of Zn powders greatly increases the heat release of AP as shown in Figure 4. The

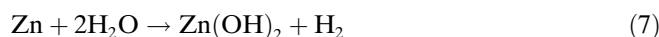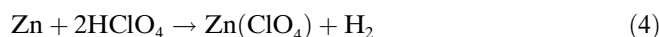**Figure 4.** The comparison of heat releases of pure AP and AP in the presence of Zn powders.

heat release of pure AP is only 0.44 kJ g^{-1}. However, in the presence of Zn powders, it jumps to a higher value between 1.25 and 1.49 kJ g^{-1}. With the increase in the Zn content, the heat release is reduced gradually. The heat release of AP added by Zn nanopowders is generally higher than that of AP added by Zn micropowders except the mixtures with the 0.5 wt.-% content of Zn powders, which have nearly equal heat releases. The maximum heat release is found for the mixture containing 0.2% Zn nanopowders, i.e., 1.49 kJ g^{-1}.

The thermal behavior of AP in the presence of Zn powders indicates that the thermal decomposition mechanism has been changed. It is well known that the first decomposition step is a solid–gas multiphase reaction including decomposition and sublimation as shown in the following:
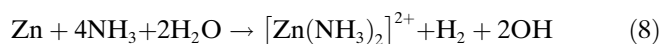
$$NH_4^+ + ClO_4^- \rightarrow NH_3(s) + HClO_4(s)$$
$$\rightarrow NH_3(g) + HClO_4(g) \quad (3)$$

Simultaneously a series of reactions happen to gaseous $NH_3(g)$ and $HClO_4(g)$. The products are N_2O, O_2, Cl_2, H_2O, and a small amount of NO. The catalytic mechanism of Zn nanoparticles is probably attributed to the following five points:

- Zn is an active metal, namely, it can react with most products of the first decomposition of AP such as $HClO_4$, O_2, Cl_2, and H_2O, the reactions are illustrated as follows:

$$Zn + 2HClO_4 \rightarrow Zn(ClO_4) + H_2 \quad (4)$$

$$Zn + Cl_2 \rightarrow ZnCl_2 \quad (5)$$

$$2Zn + O_2 \rightarrow 2ZnO \quad (6)$$

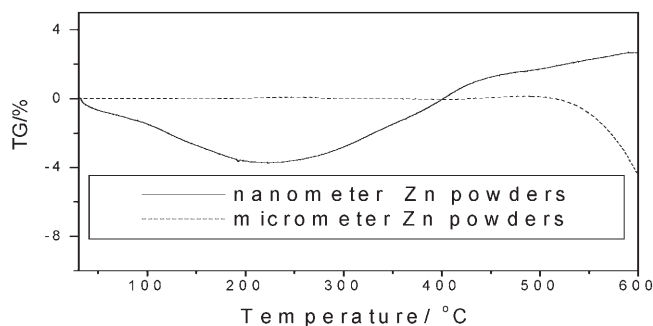$$Zn + 2H_2O \rightarrow Zn(OH)_2 + H_2 \quad (7)$$

In addition, Zn is also a transitional metal, so its ion has a tendency to coordinate with species containing atoms with surplus electrons such as NH_3. The following reaction is an example:

$$Zn + 4NH_3 + 2H_2O \rightarrow \left[Zn(NH_3)_2\right]^{2+} + H_2 + 2OH \quad (8)$$

As a result, the first decomposition of AP is promoted greatly.

- If the reaction of Zn and $HClO_4$ is very rapid, the decomposition of $HClO_4$ will turn into the decomposition of $ZnClO_4$ which occurs around 300 °C [12, 13]. The products of ZnO and $Zn(OH)_2$ can react with $HClO_4$ to form $ZnClO_4$, and thus the decomposition repeats. As a result, the first decomposition of AP is advanced to be close to 300 °C and the second decomposition disappears.
- Most reactions of Zn with the decomposition products of AP described above are exothermic, which might be responsible for the significant increase in the heat release. In addition, since the decomposition of AP in the

Figure 5. TG comparisons of nanosized Zn powders and micro-sized Zn powders.

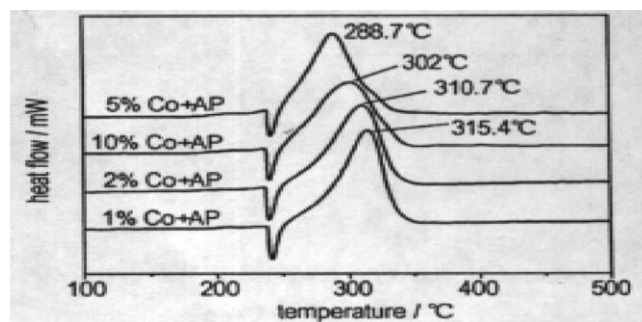**Figure 6.** DTA curves of AP in the presence of nanometer Co powders [10].

presence of Zn powders is more concentrated than that of pure AP, in one stage, the heat loss would be effectively restrained. As a result, the heat release in the presence of Zn powders increases significantly.

● Figure 5 shows the TG comparison of nanometer and micrometer Zn powders. There is nearly no weight change until 500 °C for micrometer Zn powders, and after that there is a sudden weight loss which might be caused by sublimation of Zn. However, there are obvious weight changes in the TG curve of Zn nanopowders before 500 °C. First, a weight loss about 3.7 wt.-% before 212 °C might be caused by the decomposition of PEG on the surface of the particles. Subsequently, the weight gain process above 212 °C results from the reaction of Zn with the atmosphere. These results indicate that nanometer Zn powders have a higher reactivity than micrometer Zn powders, and thus their reactions with decomposition products of AP might be faster and more concentrated. Therefore, the total heat release increased by nanometer Zn powders is higher than that increased by micrometer Zn powders.

At the same time, the higher reactivity of Zn nanopowders results in the oxidation of the particles before the decomposition of AP and hence the decrease in effective Zn content, which leads to a negative influence on the catalytic effect. Therefore, the advantage of nanopowders is restrained in the DTA measurement.

● In the mixture of AP and metal powders, metal powders maybe mostly absorbed on the surface of AP particles, thus the course of AP sublimation to go into gas phase was obstructed, resulting in hindering the decomposition of AP at first stage. In the case of nanometer Zn powders, they will cover much more surface of AP particles and thus this effect will be enhanced. Therefore, the advantage of nanometer Zn powders is not obvious in a comparison with the effect of micrometer Zn powders although the nanopowders have huge surface areas or higher reactivity which might be helpful to the decomposition process.

With the increase in Zn content, the reactions (4–8) involving Zn, will be promoted, but the obstruction effect on

the sublimation will be also enhanced. As a result, the exothermic peak becomes narrower and the heat release reduces with increase in Zn content.

In all, the thermal behavior of AP in the presence of Zn powders is the integrative result of the above factors.

In addition, the catalytic effect of Zn particles is similar to that of Co nanoparticles reported by Yang et al. as shown in Figure 6 [10]. However, Zn as catalyst for AP is better than Co because it is cheaper.

4 Conclusions

Zn nanoparticles with an average size of 25 nm were prepared under ambient conditions by a solution method. They show excellent catalytic effect on the decomposition of AP via lowering the decomposition temperature and enhancing the total heat release. In a comparison with the effect of micrometer powders, the advantage of nanometer Zn powders is not obvious except the higher heat release, which might be caused by the decrease in effective metallic Zn content and the enhanced obstruction of the sublimation of AP at the first decomposition step by nanopowders. The excellent catalytic effect of Zn powders is mainly caused by its reactivity.

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