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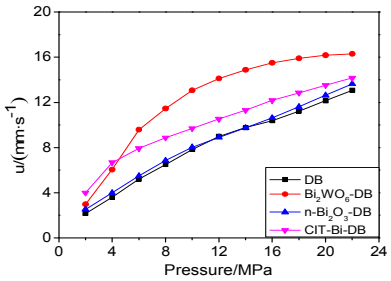

Nano Bi_2WO_6 used as burning catalyst of NG/NC propellant increase burning rate, decrease pressure exponent and form specific high-pressure platform.

Catalytic action of nano Bi_2WO_6 on thermal decompositions of AP, RDX, HMX and combustion of NG/NC propellant

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Abstract: Nano Bi_2WO_6 was prepared by hydrothermal method and characterized by XRD, SEM and EDS. Catalytic decomposition effects of nano-Bi_2WO_6 on AP, RDX and HMX were studied by DSC method. Nano Bi_2WO_6 can reduce the decomposition temperature and apparent activation energy of decomposition process. The thermal behaviors of Bi_2WO_6-DB propellant were studied. The self-accelerating decomposition temperature and critical temperature of thermal explosion are 168.3 and 178.1 °C, respectively. Nano Bi_2WO_6 used as burning catalyst of NG/NC propellant can greatly increase the burning rate, decrease the pressure exponent and form specific high-pressure "platform" at 16-22 MPa. Nano Bi_2WO_6 exhibits good application performance in solid propellant.

Keywords: Nano Bi_2WO_6; Metal composite oxide; Solid propellant; Thermal decomposition; Catalytic combustion.

1. Introduction

The combustion of solid propellant is a complicated transfer process of mass and energy. The burning rate mainly depends on the contact area of oxidizers and combustibles as well as the effect of combustion catalysts. Although the dosage of combustion catalysts used is small (about 2 %-5 %), which can greatly affect the burning rate and burning performance of solid propellant [1-5]. Metal oxides or nanosized metal oxides, such as CuO, PbO and Bi_2O_3, are often used as burning catalysts in the solid propellant [6-8]. Meanwhile, the physical mixtures of two metal

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oxides have better application properties than single metal oxide [9-11]. The particle sizes of metal oxides are smaller, and the application properties are better.

However, those active nano metal oxides present bad compatibility with some acidic components of solid propellant, on the contrary, which limits their application. Nano metal composite oxides possess specific structure properties and higher chemical stability (acid and alkali resistance), and two kinds of metals can form "synergistic effect" [12,13], so they have been largely reported in recent years and used in many high and new fields, such as photoelectric materials, magnetic materials, and photocatalysis [14-16]. In our work, we hope that metal composite oxides are used as burning catalysts in the special field of solid propellant and exhibit better catalytic burning performances, instead of single metal oxide and their physical mixtures.

Metal composite oxide Bi_2WO_6, as one of the simplest numbers of Aurivillius oxide family of layered perovskite, has a stable skeleton structure and presents good chemical stability. The cation can be replaced to generate oxygen vacancy. Valence state of transition metal changes to form defect, leading to change the stripping absorption properties of oxygen and improve the catalytic performance. Bi_2WO_6 has been largely reported in solar-energy-transfer and photocatalytic fields recently. For example, Sebastián et al carried out the photoconversion of methane into methanol with Bi_2WO_6 [17]. Nithya et al used nanosized Bi_2WO_6 particles to develop an inexpensive and eco-friendly electrode material for supercapacitors [18]. Šalkus et al prepared Bi_2WO_6 ceramics [19]. Based on the good properties of Bi_2WO_6, we design to substitute Bi_2WO_6 for Bi_2O_3 to be used as burning catalyst of solid propellant, which will be a first report. Meanwhile, Bi_2WO_6 is a green catalyst substitute for the most common lead compounds.

Ammonium perchlorate (AP), cyclotrimethylene trinitramine (RDX) and cyclotetramethylene tetranitramine (HMX) are three frequently-used high-energy explosives (oxidants) in solid propellant. NG/NC double-base propellant is the most common solid propellant [20]. In this paper, we will report the preparation of nano

Bi_2WO_6, explore its catalytic decomposition action on AP, RDX and HMX, and study its catalytic combustion properties in NG/NC propellant.

2. Experimental section

2.1 Samples

Nano Bi_2WO_6 was prepared according to the following method [21,22]: $Na_2WO_4{\cdot}2H_2O$ (AR grade) was dissolved into ethylene glycol under stirring. Poly(vinyl pyrrolidone) (PVP) was added to the Na_2WO_4 glycol solution to form a homogeneous mixtures, and then $Bi(NO_3)_3{\cdot}5H_2O$ (AR grade) was put into the homogeneous solution to form plenty of precipitation. Mole ratio of $Na_2WO_4{\cdot}2H_2O$ and $Bi(NO_3)_3{\cdot}5H_2O$ was 1:2. NaOH (AR grade) solution was employed to adjust the pH value under stirring. The resulting precursor was transferred into a teflon-lined stainless steel autoclave (V=50 mL) after stirring for 2 h. The autoclave was sealed and maintained at different temperatures for different reaction times, and cooled to ambient temperature naturally. The products were filtrated, washed and dried at 60 ℃ for 12 hours.

The Bi_2WO_6-NG/NC double-base propellant (Bi_2WO_6-DB) used in this research was prepared as follows: NG/NC double-base propellant was composed of 59 % (mass fraction) of nitrocotton (NC), 30 % of nitroglycerin (NG), 8.5 % of DEP, 2% of centralite II (C_2) and 0.5 % of other auxiliaries. The Bi_2WO_6-DB propellant consisted of the above components (500 g) and nano-Bi_2WO_6 (15 g, 40 nm) was prepared by a solventless extrusion technique, including slurry mixing, rolling and extruding.

2.2 Equipments and Conditions

XRD was analyzed by a 6100 X-ray diffractometer (Shimadzu, Japan) and the conditions were: Cu Kα radiation; Current, 30.0 mA; Scan range, 2θ = 20-80 °; Scan speed, 6 deg min^{-1}. SEM and EDS graphs were obtained with a Carl Zeiss SIGMA field emission scanning electron microscope. DSC was determined with a 200F3 differential scanning calorimeter (Netzsch, Germany) and the conditions were: nitrogen gas purity, 99.999 %; N_2 flowing rate, 40 mL min^{-1}; sample mass, about 0.5

mg; heating rate (β), 5.0, 10.0, 15.0, and 20.0 °C min^{-1}. The burning rates of solid propellant were measured in a standard burner filled with nitrogen at different pressures, and the samples prepared were the Φ5×100 mm cylinder coated with polyvinyl formal.

2.3 XRD, SEM and EDS characterization of nano Bi_2WO_6

XRD patterns were used to characterize Bi_2WO_6. The results of different preparation conditions (pH, temperature and time) are shown in **Fig. 1**. Herein, the pH is the most important factor. Only pH=10, the product presents a higher crystallization degree (JCPDS 39-0256), otherwise the signals of impurities (Bi_2O_3 and WO_3) will appear. The effects of hydrothermal temperature and hydrothermal time are not obvious to the purity of product. Considering energy consumption and ensuring product purity and good morphology, the optimal conditions for preparation of nano Bi_2WO_6 are as follows: pH of 10, hydrothermal time of 20 h and temperature of 160 °C.

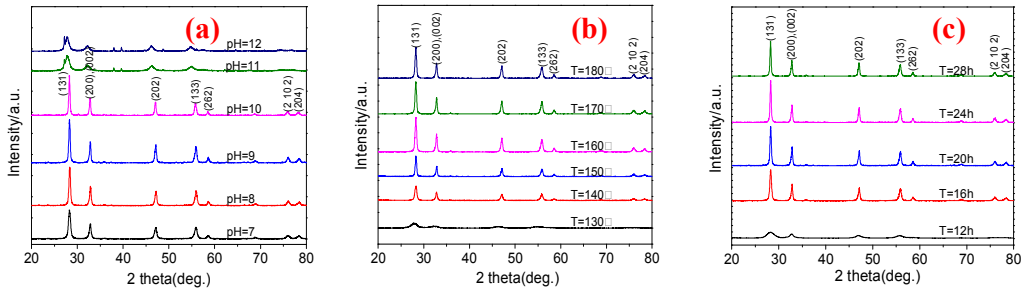

Fig. 1 XRD results for Bi_2WO_6 at different conditions

Fig. 2 shows three microstructural features of nano Bi_2WO_6 prepared at 160 °C for 20 h with pH=8, 9 and 10, respectively. The powder prepared at pH=9 presents large irregular sheet particles. The powder at pH=8 is relatively homogeneous with a particle size of about 100 nm. When the value of pH is 10, the product exhibits similar microstructure with a spherical shape, good homogeneity as well as a fine and uniform particle size. The results revealed an average grain size on a nanometric scale of about 40 nm. EDS result showed that the typical signals of element Bi and W appeared, and the ratio of the two elements is about 2:1, also indicating that the sample is Bi_2WO_6. The products prepared at 160 °C for 20 h with pH=10 were used to

the subsequent experimental studies.

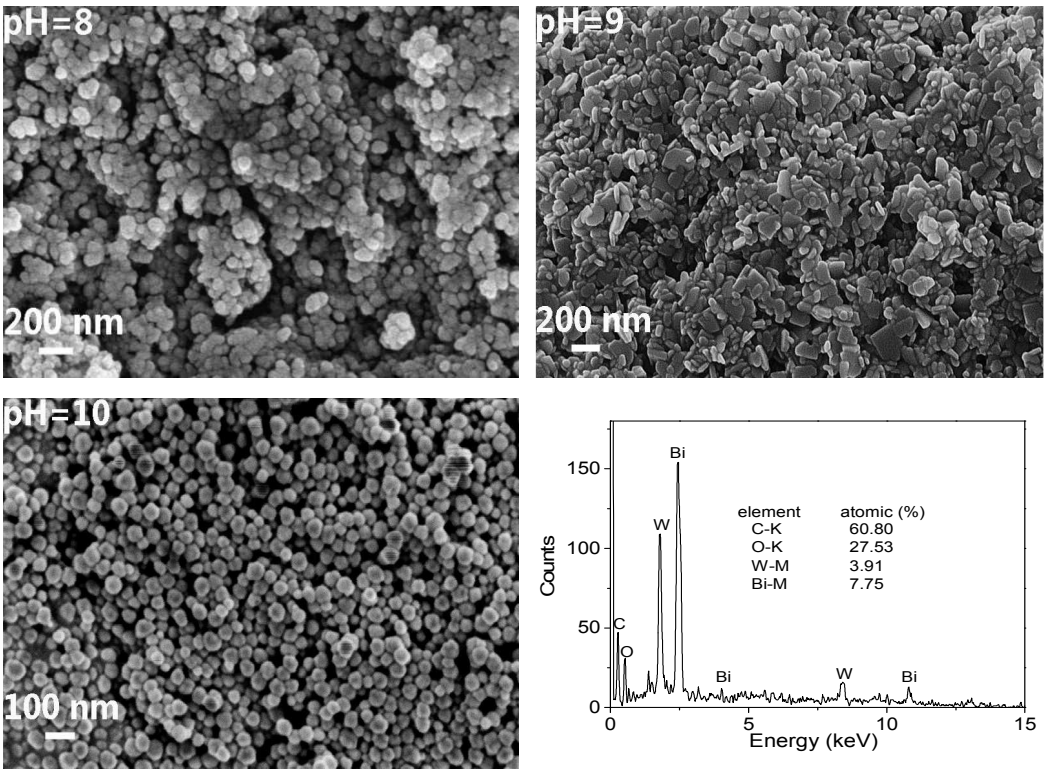

Fig. 2 SEM and EDS results of Bi_2WO_6 samples

3. Results and Discussion

3.1. Effects of Bi_2WO_6 on thermal decompositions of AP, RDX and HMX

Two nano Bi_2WO_6 samples with different particle sizes (100 nm and 40 nm) were used to explore the catalytic decomposition action on AP, RDX and HMX. The investigations were carried out by DSC method at a heating rate of 10 °C min^{-1}. Nano Bi_2WO_6 and pure AP/RDX/HMX were mixed at a mass radio of 1:4, respectively [23]. The results (**Fig. 3**) indicate that nano Bi_2WO_6 exhibits obvious catalytic actions on the thermal decompositions of AP, RDX and HMX. Peak temperatures of exothermic decomposition are ahead of 8.9 (100 nm) and 20.2 °C (40 nm) for AP, 0.6 (100 nm) and 1.7 °C (40 nm) for RDX, and 13.5 (100 nm) and 24.7 °C (40 nm) for HMX, respectively. Corresponding decomposition enthalpies increase about 20 (100 nm) and 76 J g^{-1} (40 nm) for AP, 16 (100 nm) and 56 J g^{-1} (40 nm) for RDX, and 249 (100 nm) and 381 J g^{-1} (40 nm) for HMX, respectively. Influence of Bi_2WO_6 on thermal

decomposition of HMX is very obvious, but is small to RDX. The peak shape of HMX also changes greatly from a sharp peak to a broad one. The smaller particle size has the bigger effect and exhibits the better catalytic action.

Apparent activation energy of decomposition process was studied by Kissinger method with DSC data from different heating rates (5.0, 10.0, 15.0 and 20.0 °C min^{-1}) [24]. Apparent activation energies of decomposition process for three mixtures (Bi_2WO_6 +AP, Bi_2WO_6+RDX and Bi_2WO_6+HMX, Bi_2WO_6 with particle size of 40 nm) were obtained to be 139, 175 and 155 kJ mol^{-1}, respectively. Comparing with literature values of pure compounds, they decreased by 8, 12 and 20 kJ mol^{-1} respectively [25-27], also indicating that nano Bi_2WO_6 possesses big catalytic decomposition action on energetic materials.

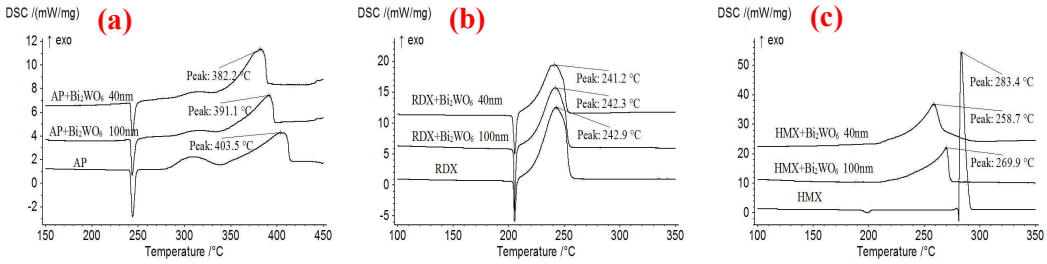

Fig. 3 DSC curves of AP (a) /RDX (b) /HMX (c) and their mixtures with Bi_2WO_6

3.2 *Thermal behaviors of Bi_2WO_6-DB propellant*

DSC curves (**Fig. 4**) at different heating rates indicate that the thermal decomposition behavior of Bi_2WO_6-DB propellant presents a large exothermic process, which is consistent with that of DB propellant without Bi_2WO_6 catalyst, but the peak temperature is ahead of about 1.5 °C from 208.8 °C to 207.3 °C at the heating rate of 10.0 °C min^{-1} [23,28].

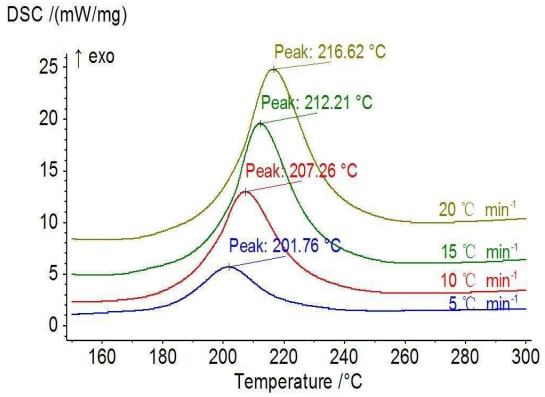

Fig. 4 DSC curves of Bi_2WO_6-DB propellant at different heating rates

From DSC data at different heating rates, apparent activation energy (E_a) and pre-exponential constant (A) of the exothermic decomposition process by Kissinger method and Ozawa method are obtained and shown in **Table 1**[24,29]. The most probable mechanism function of decomposition process was obtained by putting DSC data and 41 types of kinetic model functions into five integral equation (The general integral equation, the universal integral equation, MacCallum-Tanner equation, Šatava-Šesták equation and Agrawal equation) for calculating [30,31]. Comparing with apparent activation energies obtained by Kissinger method and Ozawa method, the most probable mechanism function for the Bi_2WO_6-DB propellant is Avrami-Erofeev equation with n=3/4 and $f(\alpha)=3(1-\alpha)[-\ln(1-\alpha)]^{1/4}/4$, according to the unanimity rule of calculation results from each model equation [24,29,30,32]. So the kinetic equation of the exothermic decomposition process for Bi_2WO_6-DB propellant can be described as:

$$\frac{d\alpha}{dt}=\frac{10^{16.9}}{4\beta}3(1-\alpha)[-\ln(1-\alpha)]^{1/4}\exp(-1.726\times10^{5}/RT) \quad (1)$$

Table 1 DSC data and kinetic parameters of the exothermic decomposition process of Bi_2WO_6-DB propellant

β/(°C min^{-1})	T_e/°C	T_p/°C	E_k/ (kJ mol^{-1})	log (A_k/s^{-1})	r_k	E_O/ (kJ mol^{-1})	r_O
5.0	181.3	201.8	172.6	16.9	0.989	171.7	0.990
10.0	189.5	207.3					
15.0	196.9	212.2					
20.0	198.2	216.6					

Subscript k, data obtained by Kissinger method; subscript o, data obtained by Ozawa method; r is the linear correlation coefficient.

The self-accelerating decomposition temperature (T_{SADT}) and critical temperature of thermal explosion (T_b) are two important parameters required to ensure safe storage and process operations for energetic materials and then to evaluate the thermal stability. T_{SADT} and T_b can be obtained by Eqs (2) and (3) [30,31], respectively.

$$T_{SADT} = T_{e0} = T_{ei} - a\beta_i - b\beta_i^2 \qquad i=1 - 4 \tag{2}$$

$$T_b = \frac{E_O - \sqrt{E_O^2 - 4E_O R T_{e0}}}{2R} \tag{3}$$

where E_o is the apparent activation energy obtained by Ozawa method, a and b are coefficients.

T_{SADT} and T_b for Bi_2WO_6-DB propellant are 168.3 and 178.1 °C respectively, indicating that the thermal stability of Bi_2WO_6-DB propellant is good.

3.3. Combustion properties of Bi_2WO_6-DB propellant

Burning rate (u), catalysis efficiency (η) and pressure exponent (n) are three important factors to characterize application performance of solid propellant [33,34]. The relationships between u, n, and η are shown in Eqs. (4) and (5).

$$u=cP_i^n \qquad i=1\text{-}11 \tag{4}$$

$$\eta_i = u_i / u_{0,i} \tag{5}$$

The determination results of burning rate for Bi_2WO_6-DB propellant were shown in **Fig. 5(a)**, which included the burning rates of different DB propellants for comparison (DB, NG/NC double-base propellant with no any catalyst; Bi_2WO_6-DB, NG/NC double-base propellant with Bi_2WO_6 catalyst; n-Bi_2O_3-DB, NG/NC

double-base propellant with nano Bi_2O_3 catalyst; CIT-Bi-DB, NG/NC double-base propellant with bismuth citrate catalyst) [35,36]. We can see that the burning rate of Bi_2WO_6-DB propellant increases rapidly with the rise of pressure at 2-12 MPa, and then the increase becomes slow. The burning rate presents an approximate "platform" in the high pressure range of 16-22 MPa, which is a rather rare result in solid propellant. Moreover, Bi_2WO_6-DB propellant has the highest burning rates after 6 MPa among the four DB propellants, which even can reach the double of DB and n-Bi_2O_3-DB at 6-12 MPa. **Fig. 5(b)** indicates that the catalytic efficiency of Bi_2WO_6 increases at first and then decreases, and reaches the biggest values at 6 MPa. But the catalytic efficiency of Bi_2WO_6 is much higher than that of n-Bi_2O_3 and Bi salt (> 6MPa). Even, the value of η is higher than 1.5 at 4-14 MPa.

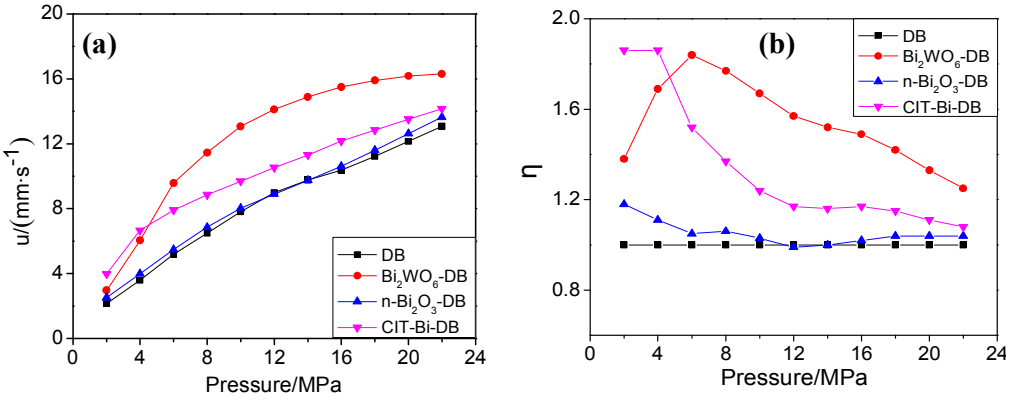

Fig. 5 Burning rate curves (a) and catalytic efficiency curves (b) of different DB propellants

The pressure exponent (n) for Bi_2WO_6-DB can be fitted according to Eq. (4), and the result is shown in **Fig.6**, which also included the pressure exponents of different DB propellants for comparison. We can see that the pressure exponent of Bi_2WO_6-DB propellant rises at first and then rapidly declines with the rise of pressure (>8 MPa). And the pressure exponent at each experimental pressure is lower than the available value (0.6) after 8 MPa. The pressure exponent of Bi_2WO_6-DB propellant is the lowest among the four DB propellants after 12 MPa and reaches 0.11 at the pressure of 22 MPa. Thus nano Bi_2WO_6 can reduce the pressure exponent of NG/NC propellant dramatically. The above three indicators illustrate that nano Bi_2WO_6 exhibits good application performance in solid propellant, which is much more suited

to the special high pressure burning solid propellant.

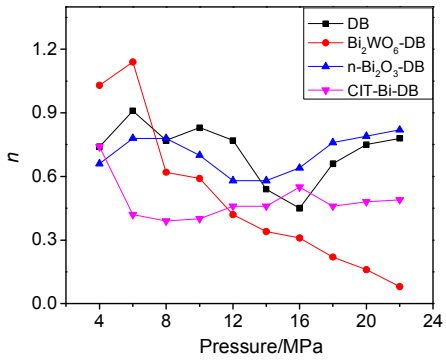

Fig. 6 Pressure exponents of different DB propellants

4. Conclusions

Nano Bi_2WO_6 with particle size of 40 and 100 nm were prepared and characterized. Effects of nano Bi_2WO_6 on the thermal decomposition of AP, RDX and HMX were investigated with DSC method. Nano Bi_2WO_6 can reduce the decomposition temperature and apparent activation energy of decomposition process. The smaller particle size sample has the better catalytic action. The thermal behavior of Bi_2WO_6-DB propellant was studied, and kinetic equation of decomposition process is: $\frac{d\alpha}{dt}=\frac{10^{16.9}}{4\beta}3(1-\alpha)[-\ln(1-\alpha)]^{1/4}\exp(-1.726\times10^5/RT)$. The self-accelerating decomposition temperature and critical temperature of thermal explosion are 168.3 and 178.1 °C, respectively. Nano Bi_2WO_6 used as burning catalyst of NG/NC propellant can greatly increase the burning rate, decrease the pressure exponent, and form a specific high-pressure "platform" at 16-22 MPa. Nano Bi_2WO_6 exhibits good application performance in solid propellant.

Acknowledgments

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