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Thermal decomposition of ammonium perchlorate in the presence of $Cu(OH)_2 \cdot 2Cr(OH)_3$ nanoparticles

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A B S T R A C T

The $Cu(OH)_2 \cdot 2Cr(OH)_3$ nanoparticle preparation procedure and its accelerating effect and accelerating mechanism on thermal decomposition of ammonium perchlorate (AP) were investigated using transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), selected area electron diffraction (SAED), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis and differential scanning calorimetry (TG–DSC), X-ray photoelectron spectroscopy (XPS), and thermogravimetric analysis and mass spectroscopy (TG-MS). In the preparation procedure, TEM, SAED, and EDS showed that the $Cu(OH)_2 \cdot 2Cr(OH)_3$ particles were amorphous with nanometer size under the controllable preparation conditions. When the amorphous $Cu(OH)_2 \cdot 2Cr(OH)_3$ nanoparticles were used as additives for the thermal decomposition of AP, the TG–DSC results showed that the addition of $Cu(OH)_2 \cdot 2Cr(OH)_3$ nanoparticles to AP remarkably decreased the onset temperature of AP decomposition from approximately 450 °C to 259 °C. The XRD and FT-IR results confirmed that the $Cu(OH)_2 \cdot 2Cr(OH)_3$ nanoparticles were transformed from amorphous form to Cr_2O_3 and $CuCr_2O_4$ phases after being used as additives for the AP thermal decomposition. The XPS results indicated that Cu^{2+} of the $Cu(OH)_2 \cdot 2Cr(OH)_3$ surface gained the electron from the perchlorate ion of AP, and the Cu ions were enriched on the $Cu(OH)_2 \cdot 2Cr(OH)_3$ surface in the AP decomposition. The electron transfer process plays a major role in the decrease of the onset temperature of AP decomposition, while the nano-effect is beneficial to easier enrichment of Cu ions on the surface of $Cu(OH)_2 \cdot 2Cr(OH)_3$ nanoparticles.

1. Introduction

Ammonium perchlorate (AP) is the most common oxidizer used in composite solid propellants [1,2]. The characteristics of its thermal decomposition influence the combustion of these propellants: lower high-temperature thermal decomposition temperature results in a shorter ignition delay time and a higher burning rate of these propellants [3–5].

A specific feature of the AP thermal decomposition is its extreme sensitivity to metal oxide additives [6,7]. The most commonly used additives are p-type metal oxides, such as CuO, MnO_2, Nd_2O_3 and $CuCr_2O_4$. The $CuCr_2O_4$, as the best metal oxide additive, decreases the onset temperature of the AP decomposition from about 450 °C to 273 °C [8–10]. The thermal decomposition of AP catalyzed by the p-type metal oxides can be widely interpreted by the electron transfer process. In the electron transfer process, the rate-controlling step of the thermal decomposition of AP is the transfer of an electron from the perchlorate ion to the positive hole in p-type metal oxide additives. The annihilation of the positive hole in the valence band of a metal oxide enhances the thermal decomposition of AP.

Recent investigations have shown that understanding of the behavior of AP thermal decomposition accelerated by nanoparticles is changing due to the particles' nano-effect. Nansized Fe_2O_3, CuO nanorod, NiO nanoparticle and Cu–Cr–O nanocomposite [1,11–13], have been shown to be efficient additives for the thermal decomposition of AP. However, interpretation of the relative accelerating behavior is still confusing, for example, the accelerating behavior of the CuO nanorod additive in AP decomposition is associated with a proton transfer process, while the accelerating behavior of the nanosized Fe_2O_3 and Cu–Cr–O nanocomposite additives is explained by the electron transfer process. Nanosized $Cr(OH)_3$ [14] and $Cr(OH)_3 \cdot Al(OH)_3$ [15] additives prepared by this laboratory are benefits to accelerating the oxidation of NH_3 in the AP decomposition due to their surface hydroxyl and amorphous form. The accelerating behavior of the nanosized $Cr(OH)_3$ and $Cr(OH)_3 \cdot Al(OH)_3$ additives can be explained by the proton transfer process.

This study thus aimed to study the thermal decomposition of AP in the presence of prepared nanosized $Cu(OH)_2 \cdot 2Cr(OH)_3$ which possessed electron transfer and nano-effect characteristics. The preparation procedure of $Cu(OH)_2 \cdot 2Cr(OH)_3$ nanoparticles was studied. The effect of the prepared $Cu(OH)_2 \cdot 2Cr(OH)_3$ nanoparticles used as

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Table 1
Effects of the reagent concentrations and SO_4^{2-}/Cr^{3+} molar ratios on the morphological characteristics of the precipitates prepared by aging solutions of $CuSO_4$ and $Cr(NO_3)_3$ at 100 °C for 20 h in the presence of sulfate, urea, and PVP.

Precipitate	$CuSO_4$ (M)	$Cr(NO_3)_3$ (M)	PVP (g dm^{-3})	Urea (M)	SO_4^{2-}/Cr^{3+}	Particle shape	Mean size
S1	0.0005	0.001	20	0.02	0.5	Spheres	100–300 nm
S2	0.0015	0.003	20	0.02	0.5	Spheres	150–600 nm
S3	0.0025	0.005	20	0.02	0.5	Spheres	70 nm
S4	0.01	0.02	20	0.02	0.5	Agglomerates	–
S5	0.0025	0.005	–	0.02	0.5	Agglomerates	–
S6	0.0025	0.005	20	–	0.5	No precipitation	–
S7	0.0025	0.005	20	0.02	2	Spheres	120-350 nm
S8	0.0025	0.005	20	0.02	5	Spheres	130-400 nm
S9	0.0025	0.005	20	0.02	20	Agglomerates	–

additives on the thermal decomposition of AP was studied in detail, and its related accelerating mechanism was also discussed.

2. Experimental section

All chemicals were analytical-grade reagents and used as received without further purification. $Cr(NO_3)_3$, $CuSO_4$, Na_2SO_4, urea, and polyvinylpyrrolidone (PVP) were dissolved in distilled water to prepare aqueous solutions.

In a typical synthesis, 20 mL 0.0025 M $CuSO_4$ and 0.005 M $Cr(NO_3)_3$, 40 mL 0.02 M urea and 40 mL 20 g dm^{-3} PVP, and 100 mL 0.18 M Na_2SO_4 were added to Pyrex test tubes (250 cm^3), which were tightly sealed with Teflon caps and placed in a preheated oven at 100 °C for 20 h. After aging, the dispersions were cooled naturally and then centrifuged at 8000 rpm. The obtained precipitates were washed several times with distilled water, filtered, and freeze-dried at −50 °C for 20 h. The concentrations of reagents and Na_2SO_4 in the starting solutions were systematically varied to analyze morphological characteristics (shape and size) of the precipitates.

To study the accelerating effect of the prepared precipitates on the thermal decomposition of AP, different amounts of the precipitates were mixed with an ethanol solution of AP, and then dried in an oven at 40 °C for 10 h. The obtained samples were sintered in a nitrogen atmosphere in a furnace at 10 °C min^{-1} from ambient temperature to 500 °C.

The crystal structure of the precipitates and samples was characterized by powder X-ray diffraction (XRD) at diffraction angles (2θ) ranging from 5 to 90° and Fourier Transform Infrared Spectroscopy (FT-IR) on a Spectrum GX spectrophotometer. The morphological characterization and quantitative analysis of the powders were performed by transmission electron microscopy (TEM), selected area electron diffraction (SAED) and energy dispersive spectroscopy (EDS) on a JEOL JEM 2100 (UHR) instrument operated at an acceleration voltage of 200 kV. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the precipitates and samples were performed at a heating rate of 10 °C min^{-1} with Al_2O_3 as the reference on a Mettler- Toledo TGA/DSC 1 instrument. X-ray photoelectron spectroscopy (XPS) data of the powders were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300-W Al Kα radiation. TG-MS analyses were performed in a nitrogen atmosphere at a heating rate of 10 °C min^{-1} from 50 to 500 °C, using a NETZSCH STA449C instrument.

3. Results and discussion

3.1. Preparation of $Cu(OH)_2 \cdot 2Cr(OH)_3$ nanoparticles

Table 1 summarizes the effects of the reagent concentrations, SO_4^{2-}/Cr^{3+} molar ratios, urea and PVP on the morphological characteristics of the particles precipitated after aging at 100 °C for 20 h. As observed, low SO_4^{2-}/Cr^{3+} molar ratio and suitable reagent concentrations contributed to preparing spherical particles of different sizes. Typically, spherical nanoparticles (S3) with a diameter of 70 nm were synthesized through the aging of solutions with a SO_4^{2-}/Cr^{3+} molar ratio of 1:2, the $CuSO_4$ concentration maintained at 0.0025 M, and the $Cr(NO_3)_3$ concentration maintained at 0.005 M. The SO_4^{2-}/Cr^{3+} molar ratio required for the formation of such uniform dispersions was even more restrictive, since for values higher than 0.5 either inhomogeneous precipitates (SO_4^{2-}/Cr^{3+} molar ratio = 2, 5) or ill-defined precipitates (SO_4^{2-}/Cr^{3+} molar ratio = 20) were observed. The addition of urea to the starting solutions is observed to be essential in producing precipitates in the above-described systems. No precipitates were obtained without this compound addition. When the above solutions were aged in the absence of PVP, ill-defined precipitates were formed, indicating that the PVP addition was also needed to form the regular particles.

The composition of S3 prepared in this study was confirmed by EDS, as shown in the attached EDS of Fig. 1. The nanoparticles (S3) consisted

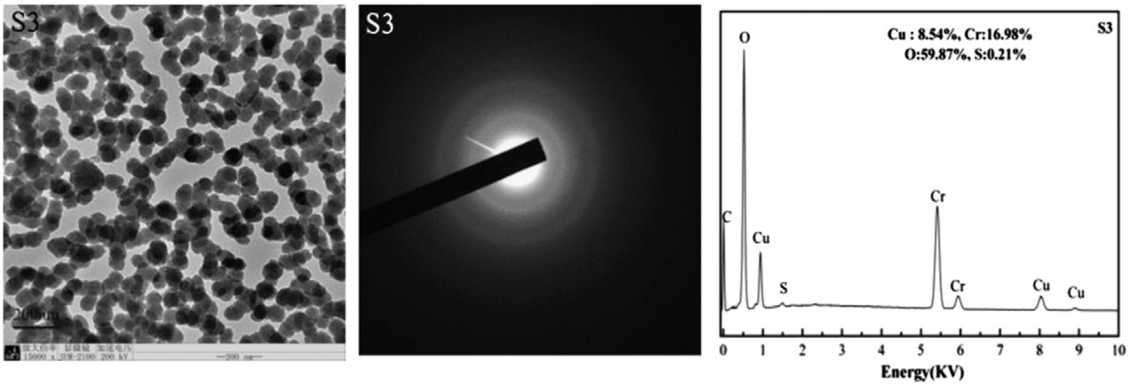

Fig. 1. TEM image of S3, EDS mapping and SAED pattern of S3.