



Synthesis and thermal behavior of Cu₂O flower-like, Cu₂O-C₆₀ and Al/Cu₂O-C₆₀ as catalysts on the thermal decomposition of ammonium perchlorate



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ABSTRACT

Microparticles Cu₂O flower-like, new Cu₂O-C₆₀ composite and energetic composite Al/Cu₂O-C₆₀ were successfully synthesized. The morphology, structure, and chemical composition of these additives were observed by using SEM, XRD, EDS and FTIR analysis. Non-isothermal DSC/TGA measurements were performed to study the thermal behavior of these additives at different heating rates. From the comparison of DSC and TGA plots, it has been clearly noticed the catalytic effect of Cu₂O and Cu₂O-C₆₀ where, the LTD of AP was decreased from 331 °C to 315 °C, 310 °C and 303 °C (in presence of Cu₂O, Cu₂O-C₆₀ and Al/Cu₂O-C₆₀ respectively) and the HTD was dropped from 430 °C (pure AP) to 384 °C, 375 °C and 350 °C (for the compounds AP/Cu₂O, AP/Cu₂O-C₆₀ and AP/Al/Cu₂O-C₆₀ respectively). The kinetics of the different samples were studied by isoconversional models, Friedman, OFW, and KAS methods, and then compared to those obtained by an iterative procedure using MATLAB R2016a as platform of computations. The pure AP kinetic results indicated that the decomposition process is complex and involves different stages with different reaction mechanisms. The additives incorporated in the AP have influenced its decomposition process by modifying the reaction mechanisms and the number of involved stages.

1. Introduction

Ammonium Perchlorate (AP) is one of the most common energetic material and oxidizer in composite solid propellants. The thermal decomposition of AP plays a significant role in the burning behavior of propellants [1]. At present time, one effective solution to tune the propellant reactivity is to combine several chemicals for the sake of obtaining a composition with adequate properties. Aiming to improve the combustion rate and the ballistic performances of solid propellants, nanosized materials are utilized as catalytic additives in virtue of their large reactive surface. There are a panoply of nanocompounds that have been investigated in the recent decades, which include metal based composites, nanometal particles, metal oxides, energetic nanocatalysts, organometallic compounds, and carbon nanomaterials. These additives play an important role in the amelioration of both thermal decomposition and burning rate as well as augment the combustion efficiency of the corresponding solid propellants by enhancing the thermal conductivity, the rate of reaction, modifying the diffusivity of gas-phase reaction and the decomposition mechanisms of the main constituents.

Carbon nanomaterials, such as carbon nanotubes [2,3], and

graphenes [4,5], have been widely investigated in many fields of research, on account for their various intrinsic properties, for instance, the thermal and electrical conductivities, mechanical strength and lightness features that range of usually materials do not possess [6]. Relying on the diversity of their structure, the above characteristic values could be entangled over an extremely wide range of conditions. Hence, a multitude of elaboration methods has been intended to obtain a variety of metal matrix composites containing carbon nanomaterials by utilizing both liquid-state techniques [7–10] and solid-state techniques [11]. Since carbon nanomaterials for their most part are agglomerated via Van Der Waals bonds, as a result, their dispersion in a melt matrix is quite difficult. Thus, solid-state routes have been considered as more likely interesting techniques, enabling mechanical dispersion of these nanoscale materials into metals via rigorous plastic deformation of the metal matrix [12].

According to the previous scope, fullerenes as a new comer form of carbon material with a spherical shape structure, might be of great interest as reinforcements due to their zero dimensional geometric characteristics. They have a facile dispersion in the metal matrix and they are hardly distorted during extreme mechanical excitation

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processes. The formulation of fullerene (C_{60}) derivatives has drawn considerable attention in an array of fields such as semiconductor and optoelectronic devices due to their individual structural, electrical and optical properties [13]. They are renowned for their excellent electron affinities, which are highly efficient for electron transfer [14]. When combining C_{60} with a semiconductor photocatalyst, it will bring an improved photo-induced charge separation and transfer, thereby enhancing the photocatalytic activity [15,16]. The C_{60} based materials present a crucial importance as candidates for the development of solar cells technology and renewable sources of electrical energy due to their semiconductor band gap energy which is around 1.6–1.9 eV [17].

There are different approaches for the synthesis of nanodimensional systems, such as the solvothermal method [18], hydrothermal route [19], sonochemical technique, single source precursor routes [20], sol–gel method [21], in-situ [22], ion exchange technique [23]. Recently, several new methods of preparing easy and environment friendly synthesis protocols for nanoparticles were developed and appeared promising [24]. A clean, and industrial electrochemical process for production of high pure nano-copper oxides (Cu_2O) was successfully achieved with fast occurring reaction time [25]. Synthesis of Cu_2O nanowires by controlling calcination environment of electrospun polymeric nanowires and its charge storage properties showed higher surface area and the electrospun electrodes delivered high discharge capacity [26].

With the advances in fullerene preparation techniques, availability and moderate-priced fullerenes are now largely provided. We propose in this study the use of C_{60} combined with Cu_2O microparticles as a new catalyst to study the effect it provides as additive on the thermal decomposition of AP, which is not attended before to the best of our knowledge. Based on the valence variations of cuprous ions, Cu_2O is considered as one of the most potential burning rate catalysts because it tends to seize or release surface lattice oxygen in the redox reaction, accordingly. As a result, the catalytic activity of Cu_2O is closely correlated to its surface state. Heng et al. have found that Cu_2O microcrystals exhibit facet dependent activities in the thermal decomposition of AP [27]. However, most of studies have paid more attention to the scale-related or facet-dependent activities of Cu_2O on AP thermal decomposition, than to the special structures of Cu_2O . Taking into account the excellent individual properties of C_{60} and Cu_2O [28], the combination of the two components could give enhanced performances [29] and we assume that it may provide an increase in the thermal decomposition of AP by influencing the triplet kinetic parameters (Activation Energy (E), Pre-exponential Factor (A) and reaction order).

For this investigation, Cu_2O particles, a new Cu_2O - C_{60} and Al/ Cu_2O - C_{60} were carefully prepared using the well-known hydrothermal method. The as prepared products were subsequently used as nanoadditives in the thermal decomposition of AP. From the comparison of DSC and TGA plots, it has been clearly noticed the catalytic effect of Cu_2O and Cu_2O - C_{60} where, the Lower Temperature Decomposition (LTD) of AP was decreased from 331 °C to 315 °C, 310 °C and 303 °C, in presence of Cu_2O , Cu_2O - C_{60} and Al/ Cu_2O - C_{60} respectively, and the High Temperature Decomposition (HTD) was dropped from 430 °C (pure AP) to 384 °C, 375 °C and 350 °C, for the compounds AP/ Cu_2O , AP/ Cu_2O - C_{60} and AP/Al/ Cu_2O - C_{60} , respectively. Non-isothermal DSC/TGA measurements were performed to study the thermal behavior of these additives at different heating rates (10, 15 and 20 K/min). Isoconversional models, Friedman, OFW, and KAS methods were used to study the kinetics of the different samples. The results of pure AP indicated that the decomposition process is complex and involves different stages with different reaction mechanisms. The additives incorporated in the AP have influenced its decomposition process by modifying the reaction mechanism and the number of stages involved in the process of decomposition.

2. Experimental procedure

2.1. Materials

Pure C_{60} was purchased from J&K Scientific, LTD. Cupric acetate $Cu(CH_3COO)_2 \cdot H_2O$ was obtained from Tianjin chemical reagents Limited Company. Nano-aluminum powder was provided by Tianjin Zhiyuan Chemical Reagent Co., Ltd. AP was purchased from Sinopharm Chemical Reagent Co., Ltd. All the reagents are of analytically pure grade (AR) and they were used without further purification.

2.2. Preparation of the samples

There is a multitude of methods used for the preparation of metal oxide particles. In this study, we have opted for the hydrothermal method, since, it is a simple, safe, efficient, and not much material demanding.

2.2.1. Preparation of Cu_2O microparticles

In a typical experiment, 0.005 mol $Cu(CH_3COO)_2 \cdot H_2O$ and 0.01 mol $C_6H_{12}O_6$ were dissolved in 100 ml distilled water in a 250 ml round-bottomed flask with magnetic stirring, then the mixed transparent solution was heated to 90 °C and kept for 5 h. After heating for the desired time, the product was separated by centrifugation, washed with water and ethanol several times, and dried at 70 °C under vacuum.

2.2.2. Preparation of Cu_2O - C_{60} composite

0.005 mol $Cu(CH_3COO)_2 \cdot H_2O$, 0.01 mol $C_6H_{12}O_6$ and 0.27 mg of C_{60} were dissolved in 100 ml distilled water in a 250 ml round-bottomed flask with magnetic stirring, then the mixed solution was heated to 90 °C and kept for 10 h. After heating for the desired time, the product was separated by centrifugation, washed with water and ethanol several times, and dried at 70 °C in vacuum.

2.2.3. Preparation of Al/ Cu_2O - C_{60}

The energetic material Al/ Cu_2O - C_{60} , was prepared by physical mixing of Cu_2O - C_{60} composite in an agate mortar for 15 min in presence of ethanol, followed by sonication and dispersion of the mixture of Al powder and Cu_2O - C_{60} composite for 30 min. After that, the excess ethanol was removed by heating. The samples were prepared with a stoichiometric weight ratio of Al: additives (67%:33%).

2.2.4. Preparation of AP/(Cu_2O , Cu_2O - C_{60} , Al/ Cu_2O - C_{60}) mixtures

To prepare the DSC/TGA samples: 0.03 g (Cu_2O , Cu_2O - C_{60} or Al/ Cu_2O - C_{60}) was mixed with 0.47 g of AP, and ground in an agate mortar, meanwhile, a little ethanol was added into the mixtures during the grinding. Then, the mixtures were dried in a vacuum oven at 60 °C over night.

2.3. Characterization of the materials

The crystal structure of the prepared samples was characterized by Powder X-ray diffraction (XRD) analysis using a Rigaku TTR-III equipped with $CuK \alpha$ radiation ($\lambda = 0.15406$ nm). The different morphologies, sizes and composition of the samples were observed by SEM coupled with Energy Dispersive X-ray (EDS), using Model (JEM-2100). The chemical structure of the powders was depicted by Fourier Transform Infrared Spectroscopy (FTIR) (Perkin Elmer Spectrum 100) in the data range of 500–4000 cm^{-1} . The catalytic effect of the synthesized additives on the thermal behavior of AP was detected by DSC/TGA (German NETZSCH-STA409C thermal analyzer) in a dynamic (50 ml/min) atmosphere of static N_2 . Samples mass of 8 ± 0.5 mg are put in a crucible Al_2O_3 pan, with heating rate of 20 °C/min over the interval of 50–600 °C.

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