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Inhibition effect of ammonium dihydrogen phosphate on the thermal decomposition characteristics and thermal sensitivity of ammonium nitrate

Man Yang[a,b], Xianfeng Chen[a,*], Bihe Yuan[a,*], Yujie Wang[a], Ali S. Rangwala[c], Huiqi Cao[a], Yi Niu[a], Ying Zhang[a], Ao Fan[a], Shuhui Yin[a]

[a] School of Resources and Environmental Engineering, Wuhan University of Technology, Luoshi Road 122, Wuhan 430070, China
[b] School of Architectural Engineering, Wuhan polytechnic, Guanshan Avenue 463, Wuhan 430074, China
[c] Department of Fire Protection Engineering, Worcester Polytechnic Institute, 100 Institute Road, Worcester, United States

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ABSTRACT

In order to analyze the inhibition effect of the additive on the thermal decomposition characteristics of ammonium nitrate (AN), thermal stability and thermal decomposition behavior of AN and its mixtures with various concentrations of ammonium dihydrogen phosphate (ADP) are systematically investigated by DSC-TG, DSC-TG-QMS and TG-FTIR. Breaking point value of the samples is obtained as an evaluation parameter for thermal safety. Experimental results show that the AN-ADP mixtures show higher onset decomposition temperatures, narrower reaction temperature region and lower enthalpy values than those of pure AN. The main evolved decomposition gases of AN are NH_3, H_2O, NO, N_2O, NO_2 and HNO_3, while the major gaseous products of the AN mixture with ADP are NH_3, H_2O, NO, N_2O and NO_2. Furthermore, the generation of NO and NO_2 is obviously postponed in the AN mixture. In addition, the breaking point value of AN is markedly improved by ADP. The decomposition mechanism of AN-ADP mixture is concluded and the inhibition mechanism of ADP is proposed. It is concluded that ADP is an effective inhibitor for AN and its thermal stability is effectively enhanced.

1. Introduction

As an important and widely-used chemical reagent, ammonium nitrate (AN) is used as a common fertilizer and an important ingredient for explosives and solid propellants [1–4]. As is well known, pure AN is relatively safe and stable, as compared with other hazardous chemicals [5]. Furthermore, AN is a strong oxidizer, and it can detonate in the presence of impurities which act as promoters [6]. Usually, AN explosion accidents cause great calamity. For example, one of the latest extremely large AN explosion accidents happened in a chemical storage warehouse in Tianjin harbor, China, in 2015. This explosive accident caused 8 disappearances, 165 fatalities and more than 798 injuries. The explosion risk of AN is due to the contamination by the impurities, resulting in many tragic explosion accidents [7–10]. One of the recent explosion incidents occurred in storage facility of West Fertilizer Company in Texas, in 2013. It has been reported that the possible cause of this accident is the contamination of AN by the chloride element from PVC pipe [11].

Thermal stability and thermal sensitivity of AN are greatly influenced by the additives. The effects of several metal oxides, acids, organic and inorganic salts on the thermal behavior and thermal risk of AN have been extensively investigated [12–18]. As just aforementioned, under acidic condition, chloride can promote the decomposition of AN. Han et al. [6] found that the onset decomposition temperature of AN is decreased by potassium chloride. The destabilization effect of chloride is attributed to the reaction between Cl^- and NO_2^+, which is the intermediate of AN decomposition [19]. Furthermore, the decomposition of AN can be accelerated by several inorganic acids, such as sulfuric acid and phosphoric acid [20–22]. However, some metal carbonates exhibit inhibiting influence on AN. The addition of $CaCO_3$ makes AN less sensitive to detonation [23,24]. According to stabilization and destabilization performances, these additives can be classified as inhibitors and promoters. For the safe use of AN-containing products, it is essential to study the decomposition mechanism of AN and its mixtures. In our previous work, we studied the thermal decomposition characteristics of AN under different atmospheres, heating rates and gas flow rates [25]. The decomposition modes of AN under air and nitrogen atmospheres are proposed and its thermal safety is evaluated. Although the inhibition decomposition of AN has been widely investigated, only few detailed decomposition modes have been presented on the basis of solid experimental results.

In this work, ammonium dihydrogen phosphate (ADP), which is a

* Corresponding authors.
E-mail addresses: cxf618@whut.edu.cn (X. Chen), yuanbh@whut.edu.cn (B. Yuan).

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common fertilizer, was mixed with AN. The effect of ADP on the thermal stability and thermal decomposition of AN was systematically explored. The thermal decomposition products were analyzed with differential scanning calorimeter interfaced with a mass spectrometer and thermogravimetric analysis-infrared spectrometry. The decomposition mechanisms of AN-ADP mixture were investigated and the inhibition mechanisms were proposed.

2. Experimental

2.1. Materials

AN (purity ≥ 99.0 wt%, Tianjin Fengchuan Chemical Reagent Co., Ltd.) and $NH_4H_2PO_4$ (purity ≥ 99.0 wt%, Sinopharm Chemical Reagent Co., Ltd.) were used without further purification. AN and ADP samples were grinded and mixed uniformly for different ratios, then dewatered in an electro-thermal drying oven for 2 h until the constant weight.

2.2. Differential scanning calorimetry (DSC)

DSC (STA6000 simultaneous thermal analyzer) was used to examine the thermal behavior of pure AN, ADP and AN-ADP mixture with different concentrations of ADP. The mass of pure AN and ADP samples were approximately 10 mg. The samples of AN-ADP mixtures were 10 mg of pure AN mixed with various concentrations of ADP, including 1 wt% (0.1 mg), 5 wt% (0.53 mg), 10 wt% (1.1 mg), 15 wt% (1.8 mg) and 20 wt% (2.5 mg). The above samples were placed in open aluminum pans, and then they were heated from 30 to 450 ℃ at a heating rate of 10℃·min^{-1} in air flow, and the gas flow rate was maintained at 20 mL·min^{-1}.

2.3. Differential scanning calorimetry-thermogravimetric-quadrupole mass spectrometer (DSC-TG-QMS)

Differential scanning calorimetry (STA449F3 simultaneous thermal analyzer) equipment interfaced with a mass spectrometer (QMS 403 D Aëolos) was used to investigate the thermal decomposition behavior of AN, ADP, AN mixtures with ADP. It was employed for non-isothermal evolved gas study of samples in air flows. AN (sample mass: approximately 10 mg) and its mixture with 10 wt% ADP (sample mass: approximately 11.1 mg) were placed in aluminum pans and rid with pinhole. The samples were heated from 30 to 450 ℃ at a heating rate of 10 ℃·min^{-1} in air flow, and the evolved gases from DSC-TG instrument were transported to mass spectrometer by the purge gas. The system was purged with 20 mL·min^{-1} air in the whole experiment. The mass spectrometer was operated in electron impact ionization mode, with selected ion monitoring for the mass-to-charge (m/z) ratios: 17 (NH_3), 18 (H_2O), 28 (N_2), 30 (NO), 32 (O_2), 44 (N_2O), 46 (NO_2) and 63 (HNO_3).

2.4. Thermogravimetry-Fourier transform infrared spectrometer (TG-FTIR)

Nicolet-6700 Fourier Transform Infrared Spectrometer (FTIR) (Thermo Electron Scientific Instruments) was used to identify the gaseous products during the thermal decomposition. The samples of AN and its mixture with 10 wt% ADP were heated from 30 to 450 ℃ at a heating rate of 10 ℃·min^{-1} in air flow, and the evolved gases from thermogravimetry instrument were transported to FTIR by the purge gas.

2.5. Breaking point tester

LBFY-3 Breaking Point Tester (Hebi Hongke Coal Testing Equipment Factory) was used to obtain the breaking point value and five seconds delay time to ignition of AN (sample mass: approximately 35 mg) and its mixture with 10 wt% of ADP (sample mass: 39 mg). Temperature ranges of temperature controller and thermos-detector were 15–600 ℃. The breaking point was tested according to the Chinese standard of AQ/T 4119-2011 (Fireworks and firecrackers—breaking point test method for pyrotechnics).

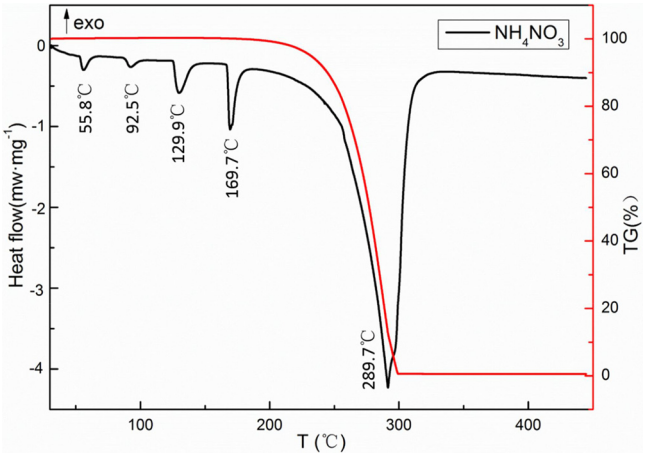

Fig. 1. DSC-TG curves of AN in air atmosphere.

Table 1
DSC-TG results of pure AN and pure ADP.

Sample	Onset temperature (℃)	Peak temperature (℃)	End temperature (℃)	Weight loss (wt %)	Decomposition enthalpy (J·g^{-1})
AN	265.9	289.7	294.7	98.7	1684.9
ADP	198.5	206.2	216.3	26.0	217.0

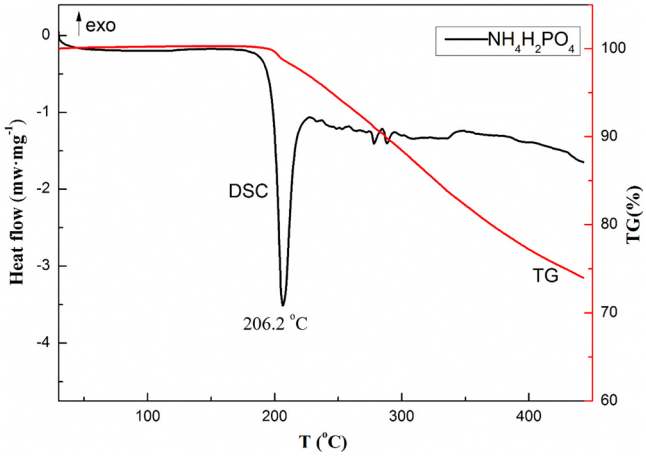

Fig. 2. DSC-TG curves of ADP in air atmosphere.

3. Results and discussion

3.1. DSC-TG analysis

DSC-TG curves of AN in air atmosphere are shown in Fig. 1. The main characteristic parameters determined by DSC-TG are shown in Table 1. As show in Fig. 1, there are five main endothermic peaks in the DSC curve and one weight loss stage in TG curve of AN. The first three peaks in the DSC curve are attributed to crystal transformation involving non-chemical reaction and the fourth peak is assigned to the melting process. The last endothermic peak is due to the thermal decomposition [2]. The thermal decomposition of AN is highly dependent on the experimental conditions, such as pressure, sample weight, confinement and heating rates [26,27]. For example, the endothermic