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Particle size effects on thermal kinetics and pyrolysis mechanisms of energetic 5-amino-1h-tetrazole

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ABSTRACT

Thermal stability, kinetics, and dynamics data of the novel energetic material 5-amino-1h-tetrazole (5AT) are of the essence to obtain safety information for safety storage, handling, and even demilitarization. This study will seek to find particle size effects on thermal kinetics and pyrolysis mechanisms of 5AT with the employments of model-free and model-fitting methods. Results showed that a significant variation existed in thermal hazards of 5AT for different particle sizes. As the particle diameter increased from 70.9 to 236.5 μm, a monotonous increase in activation energy occurred from 276.4 to 313.2 kJ mol^{-1}. Particularly, the smallest average particle size 70.9 μm was the most sensitive with self-accelerating temperature 200.6 °C, critical ignition temperature 201.8 °C, and thermal explosion temperature 203.1 °C. When 5AT particle diameter reduced, there was a distinct decrease on enthalpy of activation by 36.7 kJ mol^{-1}, and entropy of activation by 75.5 J mol^{-1}. Decomposition mechanisms of four 5AT samples were all found to be mastered by third-order (F3) model. Results of this study have implications concerning designs for 5AT storage and transportation, which can help to get better understandings of particle size effects on 5AT pyrolysis kinetics and mechanism.

1. Introduction

As an environmentally friendly green energetic material, 5-amino-1h-tetrazole (5AT/CH_3N_5) has attracted more and more attentions in solid propellants, rocket engines, airbags, and fire extinguishing areas [1,2]. What makes 5AT extremely attractive is its surprisingly potential energy property, e.g. high nitrogen content (82.3%), high formation enthalpy (208.7 kJ mol^{-1}), moderate mechanical, and thermal sensitivity [3,4]. The chemical structure of 5AT is listed in Scheme 1. Once the mixtures of 5AT and oxidizers (strontium nitrate, potassium nitrate, etc.) are ignited, violent redox reactions will immediately take place with the generation of large amounts of gases and heats, creating desirable impetus. Undoubtedly, pyrolysis behavior of thermal hazard substance usually plays a crucial role in burning rate and gas production performance for propellants, pyrotechnics, and explosives [5]. Pyrolysis of 5AT is also regarded as the fundamental step to generate gaseous product which supports fuel ignition, burning, and releasing energy. To elucidate the mechanism governing propulsive performance, it appears essential to analyze the thermal degradation behavior of 5AT.

Most work investigating pyrolysis influence factors and gas generating properties of 5AT has focused on different oxidizers, catalyst effects, and reaction with hydrohalide. Zhang et al. [2] calculated the thermal kinetics triplets of 5AT-based propellants with different nano-sized metal oxides (Fe_2O_3, CuO, and NiO) as catalysts, and illustrated the differences in pyrolysis parameter, and burning rate from the perspective of thermal conductivity. Wang et al. [6] analyzed the combustion behavior of gas-generating mixtures comprised of 5AT as fuel and CuO as catalyst. They found that the addition of CuO catalyst could reduce the formation of some harmful gases (CO and NH_3), but increase the content of NO_x. The flash pyrolysis of hydrohalide (HCl, HBr, and HI) salts of 5AT were studied by T-jump/FTIR spectrum technology to explore the evolved gas production [7], and the important role of acidity coefficient for three hydrohalide salts played in the burning rate and pressure exponent was noted. Miyata and Hasue [8] selected 5AT as fuel and KNO_3/$NaNO_3$ as oxidizers, then they examined the effects of different oxidizers on 5AT thermal decomposition characteristics and heat transfer process. Compared with 5AT/KNO_3 mixtures, 5AT/$NaNO_3$ showed a slower burning rate while adiabatic flame temperature increased. Zhang et al. [4] examined the thermal decomposition characteristic of 5AT-based propellants with calcium carbonate addition, and revealed its catalytic effect on activation energy, pre-exponential factor, and decomposition temperature.

Above reviewed literatures have mentioned that the pyrolysis kinetics, reaction mechanisms, and burning characteristics of 5AT and its mixtures with oxidizer could be influenced by multiple factors. Among these are oxidizer and catalyst species, hydrohalide salt, and even

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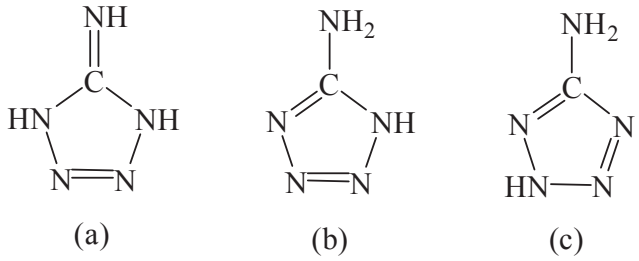

Scheme 1. Chemical structure of 5AT (a) imino; (b) amino 1-H isomer; (c) amino 2-H isomer.

particle size. Especially for solid hazardous material like propellants and explosives, particle size is an essential element that must be considered inevitably during pyrolysis characteristics study, which is concerned with material safety storage, transportation, and design for maximum propulsive performance and brisance. Particle size can influence material pyrolysis kinetics and rate since each particle diameter has different specific surface area, namely surface-to-mass ratio. In previous studies, researchers have investigated the particle geometrical size effects on thermal decomposition behaviors of some typical energetic materials, such as octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) [9], nitrocellulose [10], and ammonium perchlorate (AP) [11]. Results showed that size effects indeed can influence pyrolysis behavior of energetic materials.

So the work reported here was motivated by a study of particle size effects on thermal kinetics and pyrolysis mechanisms of 5AT. For this investigation, four different particle sizes were prepared and conducted by thermogravity experiments for determinations of kinetics and pyrolysis mechanism. Advanced Vyazovkin method was employed to obtain kinetics with higher accuracy compared with traditional iso-conversional methods. Also the pyrolysis mechanism of 5AT was explored by Coats-Redfern and Kennedy-Clark methods. 5AT is an environmentally friendly green energetic material, which can generate large amounts of gases once being mixed with oxidizer and then ignited, and therefore the results of this study will be valuable in 5AT material storage safety problems and 5AT-based solid propellant gas generator design.

2. Theoretical consideration

According to Arrhenius equation [12], the decomposition rate of heterogeneous system under non-isothermal condition can be written as Eq. (1),

$$\beta\frac{d\alpha}{dT} = Af(\alpha)\exp\left(-\frac{E_a}{RT}\right) \tag{1}$$

where A is pre-exponential factor, E_a is activation energy, R is molar gas constant (8.314 J mol^{-1} K^{-1}), T is thermodynamic temperature, α is conversion of reaction, and β is linear heating rate. Generally, the aim of studying kinetics is to obtain the dynamic model, and calculate kinetic triplets, A, E_a, and f (α). Therein, f (α) is the differential form of kinetic mechanism function, representing the functional relationship between reaction rate and conversion, as listed in Table 1 [13]. In the following analysis, both model-free and model-fitting methods will be applied to analyze 5AT pyrolysis kinetics.

2.1. Model-free approach

2.1.1. Kissinger method

Kissinger method (Eq. (2)) can be used to calculate E_a, and A from peak temperature. The plot of the $\ln(\beta/T_p^2)$ against $1/T_p$ could generate a linear relationship with a slope $-E_a/R$ by which active energy can be obtained [14].

Table 1
Algebraic expressions for f (α) and g (α) for the kinetic models commonly used.

Reaction model	Symbol	f (α)	g (α)
One-dimensional diffusion	D1	$1/2\alpha$	α^2
Two-dimensional diffusion	D2	$[-\ln(1-\alpha)]^{-1}$	$[(1-\alpha)\ln(1-\alpha)]+\alpha$
Three-dimensional diffusion	D3	$3(1-\alpha)^{1/3}/[2(1-\alpha)^{-1/3}-1]$	$[1-(1-\alpha)^{1/3}]^2$
Three-dimensional diffusion	D4	$3/2[(1-\alpha)^{-1/3}-1]^{-1}$	$1-2\alpha/3-(1-\alpha)^{2/3}$
First-order	F1	$(1-\alpha)$	$-\ln(1-\alpha)$
Three-halves order	F3/2	$(1-\alpha)^{3/2}$	$2[(1-\alpha)^{-1/2}-1]$
Second-order	F2	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$
Third-order	F3	$(1-\alpha)^3$	$(1/2)[(1-\alpha)^{-2}-1]$
Zero-order	R1	1	α
Contracting area	R2	$2(1-\alpha)^{0.5}$	$1-(1-\alpha)^{1/2}$
Contracting volume	R3	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
Avrami-Erofeev (n = 1.5)	A3/2	$(3/2)(1-\alpha)[-\ln(1-\alpha)]^{1/3}$	$[-\ln(1-\alpha)]^{2/3}$
Avrami-Erofeev (n = 2)	A2	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
Avrami-Erofeev (n = 3)	A3	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
Avrami-Erofeev (n = 4)	A4	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
Power law	P1	$4\alpha^{3/4}$	$\alpha^{1/4}$
Power law	P2	$3\alpha^{2/3}$	$\alpha^{1/3}$
Power law	P3	$2\alpha^{1/2}$	$\alpha^{1/2}$
Power law	P4	$2/3\alpha^{-1/2}$	$\alpha^{3/2}$

Note: g (α) is the integral form of f (α).

$$\ln\frac{\beta}{T_p^2} = \ln\frac{RA}{E_a} - \frac{E_a}{RT_p} \tag{2}$$

2.1.2. Advanced Vyazovkin method

More accuracy of kinetics calculation can be acquired through numerical integration. Vyazovkin [15] proposed an advanced iso-conversional method which contains integration as:

$$I(E_\alpha, T_\alpha) = \int_0^{T_\alpha} \exp\left(\frac{-E_a}{RT}\right)dT \tag{3}$$

$$I = \frac{E_a}{R}p(x) \tag{4}$$

As shown in Eq. (5), the value of apparent active energy at a certain conversion can be obtained by minimizing the following formula,

$$\Omega(E_\alpha) = \sum_{i=1}^{n}\sum_{i\neq j}^{n}\frac{I(E_\alpha, T_{\alpha,i})\beta_j}{I(E_\alpha, T_{\alpha,j})\beta_i} \tag{5}$$

The temperature integration can be calculated by an approximation after a series of transforms. Farjas and Roura derived the six-order Pade' approximation which can give an absolute error less than 10^{-16} for x > 12:

$$p(x) \approx \frac{\exp(-x)}{x} \times \left(\frac{x^5 + 40x^4 + 552x^3 + 3168x^2 + 7092x + 4320}{x^6 + 42x^5 + 630x^4 + 4200x^3 + 12600x^2 + 15120x + 5040}\right) \tag{6}$$

Minimization can be repeated for every conversion through Eqs. (3)–(6), then dependency between activation energy and conversion extent can be obtained.

2.1.3. Kissinger-Akahira-Sunose (KAS) method

KAS method is an integral method [16]. Plotting $\ln(\beta/T^2)$ against $1/T$ allows E_a to be calculated for each extent of conversion values,