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Insight into cooling agent addition on combustion activity and mechanism of catalyzed 5AT-$Sr(NO_3)_2$ based propellant

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ABSTRACT

Thermal decomposition characteristics and combustion behaviors of 5-amino-1H-tetrazole-strontium nitrate (5AT-$Sr(NO_3)_2$) propellant are of great essence in determining fire-fighting efficiency of the novel Halon alternative technology-solid propellant gas generators (SPGGs). This study will seek to find the impacts on combustion mechanism of adding two kinds of coolants, aluminum hydroxide ($Al(OH)_3$) and calcium carbonate ($CaCO_3$) into 5AT-$Sr(NO_3)_2$ based propellant with the employments of experimental measurement and theoretical analysis. Results show that apart from three similar reactions occurring around the close temperature ranges for three different propellants, an endothermic reaction stemming from the breakdown of $Al(OH)_3$ forms when adding $Al(OH)_3$, and two extra exothermic reactions representing the reaction between $CaCO_3$ and HCN, and the generation of isocyanato exist with $CaCO_3$ addition. Especially, according to traditional Kissinger method calculation, great variations can be seen in the activation energy except for the 5AT decomposition reaction. With the presence of $Al(OH)_3$ or $CaCO_3$, the propellant's theoretical outlet temperature has been reduced by ~300 °C, while experimental combustion temperature at different sampling points are lowered approximately by 342–417 °C. With the employment of closed-bomb test, it is discovered that the burning rate in the relatively-low pressure zone is mastered by condensed-phase thermal decomposition reaction of 5AT, whereas that in the relatively-high pressure area is dominant by the redox reaction. Unlike $Al(OH)_3$, addition of $CaCO_3$ could reduce the pressure exponent effectively. The specific shapes of burning surface are found to determine the flame shapes for three 5AT-$Sr(NO_3)_2$ based propellants, which turn out be parallel, divergent, and converging profile, respectively. Besides, a gas flow model for 5AT-$Sr(NO_3)_2$ based propellant is proposed in this study, which can well illustrate the burning rate differences from the perspective of porous structure for propellant particles. Results of this study have implications concerning designs for 5AT-$Sr(NO_3)_2$-based propellants widely used in SPGGs apparatus, which can provide a potential approach for making a novel 5AT-$Sr(NO_3)_2$-based propellant with low combustion temperature as well as low burning rate pressure exponent.

1. Introduction

Considering Halon 1301 fire suppressant has a great damage to the ozonosphere and environmental pollution [1], “Montreal Protocol on Substances that Deplete the Ozone Layer” [2] has been published to limit the production and use of Halon 1301 in fire protection engineering, motivating researchers to develop Halon-alternative products. A series of new fire-fighting techniques have been created, including heptafluoropropane (HFC-227ea) [3], water mist system [4], superfine powder [5], etc., among which solid propellant gas generator (SPGG) is firstly proposed in Next Generation Fire Suppression Technology Program [6]. SPGG is composed by solid propellant and chamber system. Once solid propellant is ignited inside the chamber, large amounts of gases (nitrogen, carbon dioxide, water vapour, etc.) will be generated and released quickly, then pushing the fire-fighting agents forward outside [7]. This SPGG technology has the advantages of large amounts generation of inert volatile products, co-usage along with high-boiling point extinguishing agents [8] (including 2-bromo-3,3,3-trifluoropropene, dodecafluoro-2-methylpentan-3-one, etc.), and ease to storage. The solid propellants components in SPGGs are usually composed of fuels, oxidants, and additives. Therein, the reductant 5-amino-1H-tetrazole (5AT/CH_3N_5) is a potential environmental-friendly energetic compound [9,10], which only produces non-poisonous volatile products after full oxidation, and the oxidant strontium nitrate ($Sr(NO_3)_2$) has no corrosiveness and proper thermal stability [11],

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which makes 5AT-$Sr(NO_3)_2$ becoming the most widely used formulations in SPGGs. Redox reaction between 5AT and $Sr(NO_3)_2$ is shown as *Scheme* 1, of which ideal nitrogen production is 0.308 L g^{-1}.

$$CH_3N_5+0.7Sr(NO_3)_2 \rightarrow 0.7SrO + 3.2N_2+CO_2+1.5H_2O \quad \text{(Scheme 1)}$$

Despite the above mentioned advantages, there still exists several shortcomings severely limiting the implement and development of SPGGs. Especially, its high ejected gas temperature and unstable burning rate under high pressures are not desirable considering the needs of fire-fighting technology [12–14], conversely a stable and fast ejecting rate with low temperature is expected for such 5AT-$Sr(NO_3)_2$ based propellants. Therefore, researchers have conducted experiments to optimize the propellants burning characteristics by adding flammable inhibitors, or burning rate modifiers. Zhang et al. [15] have added calcium carbonate ($CaCO_3$) with 20% mass fraction into 5AT-$Sr(NO_3)_2$ based propellants, and found that the combustion temperature was reduced from 1564 to 976 K, whereas burning rate was cut down by more than half. Ghorpade et al. [16] have applied melamine into nitrogen-generating formulations, and it worked to reduce thermal decomposition temperature effectively, but bring the burning rate down along with more sensitive friction/impact sensitivity undesirably. Gann [17] has studied propellants with 40% mass fraction magnesium carbonate ($MgCO_3$) addition, and ejecting temperature turned out to be 1450 K. Sun et al. [18] has investigated modifying effect of strontium carbonate ($SrCO_3$) for AP/HTPB propellants, and found that the $SrCO_3$ addition could decrease burning rate significantly, increase the activation energy, and reduce pressure exponent. Three kinds of transition metal oxides (nanosized Fe_2O_3, CuO, and NiO) have been used as burning rate modifiers into 5AT-$Sr(NO_3)_2$ based propellants by Zhang et al. [19], and have been found to elevate burning rate as well as reduce combustion temperature. They also noted that thermal conductivity coefficient of transition metal oxide was a core factor mastering burning rate. Puccio et al. [20] have added 25% mass fraction silicon dioxide (SiO_2) into sodium azide propellants, and found combustion temperature reduced by 100 °C, but ignition difficulty increased.

Aluminum hydroxide ($Al(OH)_3$) and calcium carbonate ($CaCO_3$) are good candidates as coolants for 5AT-$Sr(NO_3)_2$ based propellant considering their low price, ease to preparation, heat absorption of thermal decomposition, and inert gas generation. This paper will study the impacts of above mentioned two coolants on combustion characteristics of 5AT-$Sr(NO_3)_2$ based propellant and their catalytic mechanisms. Thermogravimetric-differential scanning calorimetry-fourier transform infrared analysis (TG-DSC-FTIR) is employed to investigate their thermal pyrolysis behaviors and mechanism under particular heating program. Then peak temperatures are recognized and selected to calculate activation energies by Kissinger method. Characteristic combustion temperature is captured using thermocouple matrix. Propellant burning rate and pressure exponent are acquired through formula derivation, while flame shape under inert atmosphere is captured with the employment of visible combustion chamber. Lastly, scanning electron microscope (SEM) and pore radius analysis are performed to reveal combustion mechanism from the perspective of morphology. In the light of the promising usage prospect of SPGG as a Halon-alternative technology, the study concerning about the combustion characteristic of 5AT-$Sr(NO_3)_2$ based propellant used inside the SPGG technique certainly will be of great value, which is bound to make up SPGG's disadvantages and contribute to its application. Results of this study will be conducive to the simulation on combustion or ignition process for the novel 5AT-$Sr(NO_3)_2$ based propellant.

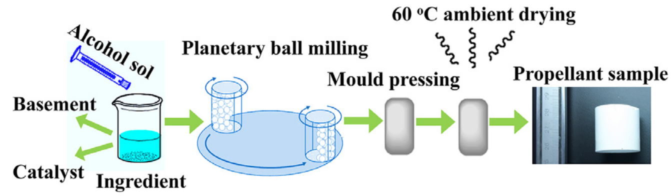

Fig. 1. Experimental procedure for the preparation of 5AT-$Sr(NO_3)_2$ based propellant.

2. Materials and methods

2.1. Propellant preparation and characterization

Based on the zero oxygen balance principle [21], the ingredients used for basement preparation are 5AT (36.48% mass fraction, melting point: 206 °C [22], supplied by Dongyang Tianyu Chemical Co., Ltd.) and $Sr(NO_3)_2$ (63.52%, melting point: 570 °C, supplied by Sinopharm Chemical Reagent Co., Ltd.). Other coolants $Al(OH)_3$ (10%, melting point: 300 °C) and $CaCO_3$ (10%, melting point: 825 °C) are purchased from Sinopharm Chemical Reagent Co., Ltd., and all reagents are used at analysis level. The stepwise experimental scheme is shown in Fig. 1. The basements (5AT and $Sr(NO_3)_2$) and catalysts ($Al(OH)_3$ or $CaCO_3$) are mixed with alcohol solvent, with a volume ratio of 1:3, and then grounded inside a planetary ball mill, at 150 rpm for 24 h. The solution is put in a vacuum oven for 8 h to evaporate the solvents. Before burning tests, the obtained powders are compression molded into a cylinder with the diameter of 25.5 mm. Finally, sample strands are placed in the laboratory oven at 60 °C for 48 h at vacuum pressure. Three 5AT-$Sr(NO_3)_2$ based propellants are denoted as CSP0 (5AT-$Sr(NO_3)_2$ basement), CSP1 ($Al(OH)_3$ addition with 10% mass fraction), and CSP2 ($CaCO_3$ addition with 10%).

Pore radius analysis is performed with Barrett–Joyner–Halenda (BJH) method (Tristar II 3020M Surface Area Analyzer, Micromeritics Instrument Corporation, America), while the static microstructures of propellants are observed by a SIRION200 SEM (FEI, Netherlands).

2.2. TG-DSC-FTIR test

TG-DSC analysis is carried out with a SDT-Q600 simultaneous analyzer (TA Instruments, USA) at three linear heating rates (5, 10, and 15 °C min^{-1}) from 25 to 800 °C. A powder sample of ~5 mg is distributed in an open alumina crucible under a purge flow of a 100 mL min^{-1} N_2. A TG-FTIR (PerkinElmer TL8000, USA) technique is employed to evaluate catalytic effects of additives on pyrolysis gaseous products. To prevent the condensation of volatile gases, a stainless steel transfer line maintaining at 280 °C is applied to connect the TG and FTIR analyzer. FTIR analysis is conducted with a purge flow of 35 mL min^{-1} N_2 at the heating rate of 20 °C min^{-1}.

2.3. Combustion temperature measurement

A thermocouple matrix composed of three self-made micro-thermocouples (Pt/Pt-Rh13%, time constant: 0.008 s) is assembled to measure burning temperature. One is placed above the propellant surface at distance of 1.5 cm, one on the burning surface, and one below the surface at distance of 1.5 cm. An Agilent 34970A instrument is used to collect the temperature signals.

2.4. Burning rate test

The burning rate and its pressure exponent are the critical parameters for evaluating the efficiency of expelling extinguishing