2018 International Conference on Defence Technology Proceedings

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Energetic material

New energetic graphene oxide frameworks (GOFs) for combustion of han-based monopropellant

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KEYWORDS

Graphene oxide frameworks;
Hydroxylammonium nitrate;
Burning rate;
Thermal analysis;
Mass spectrometry

ABSTRACT

In this paper, reports on the thermal decomposition of 95 wt.-% hydroxylammonium nitrate in presence of microporous graphene oxide frameworks (GOFs) based on carbonized rise husk. The thermal decomposition of HAN spiked with GOFs was assessed by DTA – TG method. Shown, that the high specific surface area GOFs, the ability to trigger the decomposition of HAN at a lower temperature (92 ℃ Vs 185 ℃) was observed. The gaseous products formed in the course of thermal decomposition of HAN, in the presence of GOFs were characterized by electron ionization mass spectrometry analysis. Results show significant reduction of NO*x* emissions during thermal decomposition of HAN 95 wt.-% solution.

1. Introduction

HAN - is inorganic high-energy substance, which widely pursue as a liquid gun and rocket propellant [1]. The aqueous compounds such as HAN, NH_3OHNO_3 - hydroxymammonium nitrate were proposed as one of the most promising a "green" alternative for hydrazine to use in satellite control elements [2-3]. However, for the effective combustion of HAN, the introduction of energy-intensive additives is required.

Metal-organic frameworks (MOF) - one of the interesting substances with a wide field of applications, including as technological additives to the combustion reactions [4-10]. Porous crystalline structure is attracting an attention due to their high surface area and easily controllable structures. Unfortunately, the process for preparing these bulk polymers is expensive and multistage. Thus, the high cost of raw materials of production of MOFs pose a major challenge for creation of new, lower-cost high performance materials [11-12]. One of the perspective alternative materials is graphene oxides (GO). The GOs take a high interest [13-19], and they have a complicated structure, which consist graphene sheets with functional groups on their ends, corners and planes.

In this work, we used GOFs based on rice husk with a high specific surface area. Rice husk is a large-scale vegetable waste and green material with low commercial value [20]. The surface area of GOF, S_{bet} =1200 m^2/g and have a developed microporous structure consisting: macro pores up to < 50 nm, mesopores pores between 2nm and 50 nm and micropores >2 nm [21]. Obtaining GOFs from rice husks is a simple and cost-effective process. The analysis showed that the GO based on rice husk has 5–10 sheets of graphene [22-29], which can be considered as a bulk material with a framework structure with the possibility of introducing ions or small clusters of metal oxides.

2. Experimental

2.1. *The differential thermal analysis*

A modulated DTA-TG device “RIGAKU TG8120” was operated in the temperature ranging from –180 ℃ to +725 ℃ , with an accuracy of ± 0.05 ℃ and a heating rate of 0.1~25 ℃ /min, with an error of ± 0.3 ℃ and ± 0.2 mg, with a maximum working weight of up to 200 mg with vertical loading of the samples. The heating rate in the instrument varied from 5 to 10 ℃ /min.

2.2. *Electron ionization – mass spectrometry (ei-ms) analysis*

Agilent 7890A standard mass spectrometer, which ensures the analysis in the electron ionization (EI) mode and the pyrolysis installation with a controlled heating rate system. Ionization by electron impact was performed at 70 eV, 200 mA, the ion source temperature was 150 ℃ , and the scan range was m/z = 0-300 with 0.001 a.m.u. an error. The probe temperature was ramped from 25 ℃ to 600 ℃ at different heating rate 16~128 K/min.

3. Material properties and characterization

3.1. *Graphene oxide frameworks*

The characteristic of morphology of used GOFs was shown in Fig. 1. According to the images of scanning electron microscopy, the material has a characteristic surface morphology defined by the initial raw material (RH) and has a developed surface with a large number of micro- and mesopores.

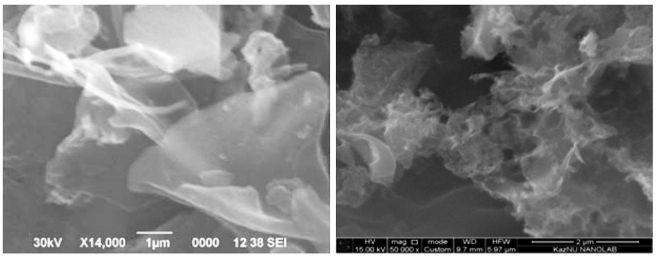


Fig. 1. SEM image of GOFs based on carbonized rise husk.

It is possible to observe the graphene structure based on sets of transparent graphene layers, the presence of chemical impurities and defects.

Raman spectra (Fig. 2) of graphene oxide showed multiple structure. The intensity of peaks “G” and “2D” indicates that the GOFs based on rise husk consists up to 4 - layers of graphene films (IG / I2D = 1.57 and ID / IG = 0.39).

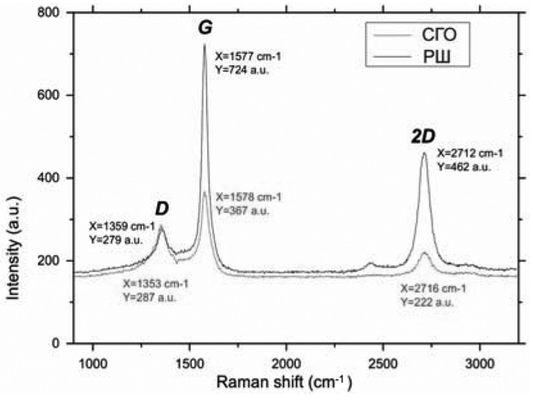


Fig. 2. Raman spectra of GOFs based on rise husk

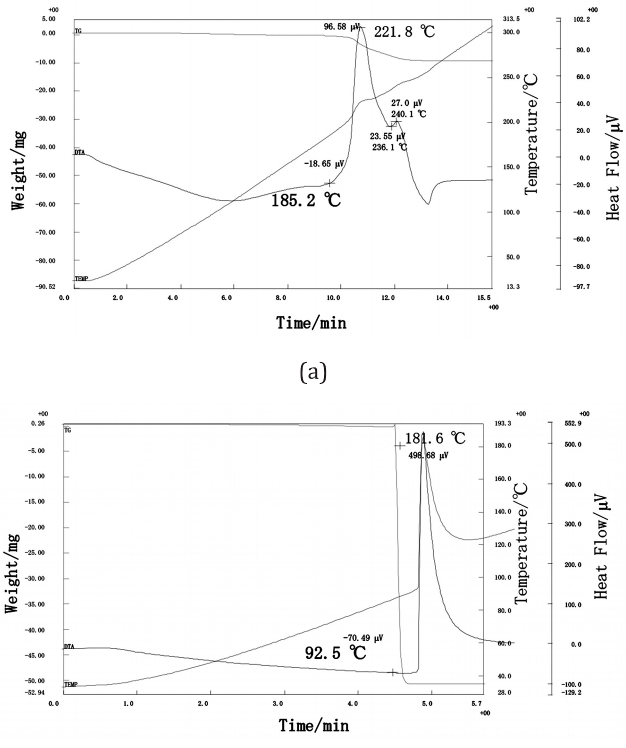
3.2. *Hydroxymammonium nitrate*

HAN is well-known chemical propulsion and many of the important thermodynamic and fluid dynamic characteristics have been characterized [30–33].

4. Results and discussion

4.1. *Experimental studies of thermal analysis of decomposition HAN with GOFs based on Carbonized Rice Husk by DTA-TG*

The decomposition of HAN in the presence of GOFs has been carried out and an example of DTA-TG comparable results is presented in Fig. 3. DTA-TGA analysis of 100% HAN decomposition (a), 99 % HAN and 1% GOFs decomposition (b). The DTA curve shows large endothermic peak with conversion into the soft exothermic peak in pure HAN water solution (a) and strong exothermic peaks at the presence of GOFs (b).



(a)

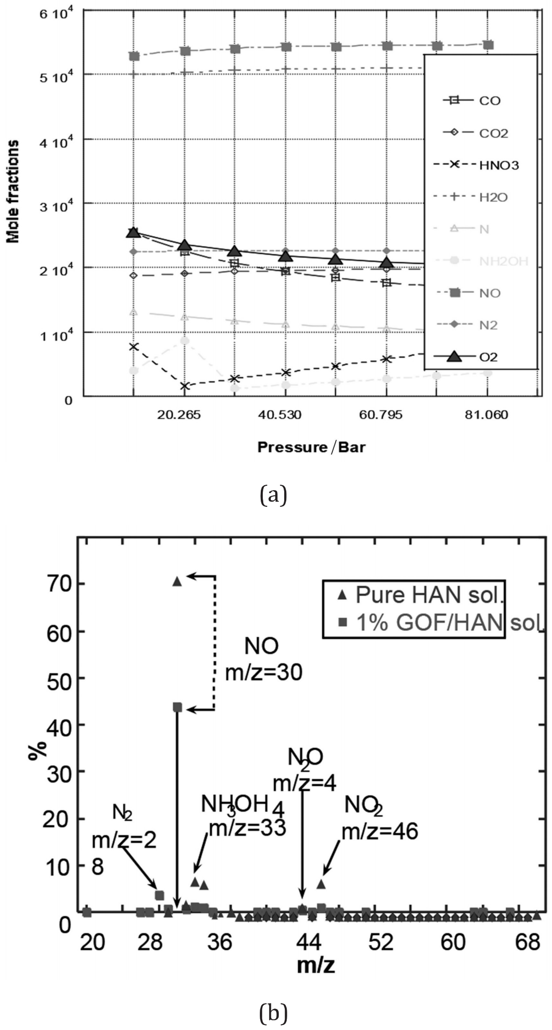
(b)

Fig. 3. DTA-TG results of HAN decomposition at 20 °C/min heating rate:(a) pure HAN sol.,(b) 1% GOFs/HAN sol.

The thermal decomposition of HAN admixed with 1% GOFs has been started around 92 ℃ and has highly exothermic reaction with a maximum at 181.6 ℃ . HAN decomposition with GOFs is occurred by one step and observed between 90 and 200 ℃ . Basically, the decomposition of pure HAN occurs in two-stage mechanism, but including a catalyst in the mixture, change the mechanism in single step. This phenomenon has been reposted in the previous studies [2, 34, 35]. In accordance with the DTA-TG profiles, the HAN decomposition in presence of GOFs proceeds rapidly with realization of high decomposition temperature.

4.2. *Gaseous Products from Decomposition of HAN in presence of high SSA GOFs by EI - Mass Spectrometry*

Fig. 4.(a) represents the calculated equilibrium products by chemical equilibrium analysis software (NASA-CEA) for the HAN samples in presence of GOFs under consideration. The results show calculations of the combustion products of 95% water solution of HAN with graphitized carbon at a ratio of 90/10 in the pressure range from 10 to 80 bar. The equilibrium calculations indicate the products to be CO, CO_2, H_2O, HNO_3, NH_2OH, NO, N_2, etc. It is noted that concentration of NO (nitric oxide) and H2O (waste) is significantly high than other products. Also, as can be seen, all components have weak but noticeable dependence on the value of the initial pressure.

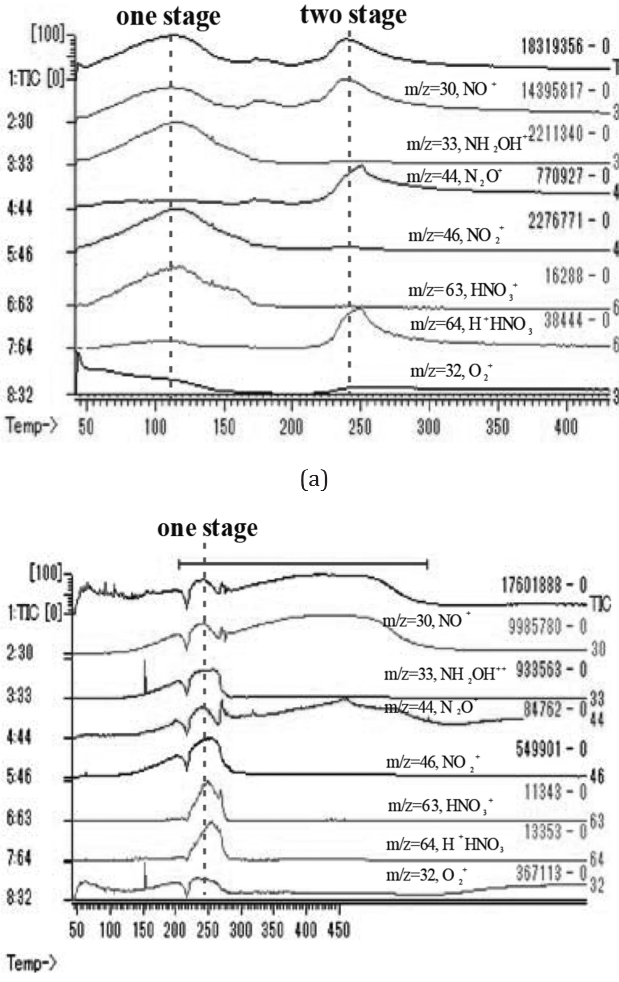


(a)

(b)

Fig. 4. Theoretical (a) and experimental (b) products of HAN decomposition in the presence of GOFs.

In the Fig.4(b) shown experimental data of HAN decomposition product distribution assessed by EI-MS. Analysis of HAN decomposition showed two different pictures, i.e.: intensity of the formation of major gas products: NO, NO_2 and H_2O.



(a)

(b)

Fig. 5. MS analysis of Gaseous Products from Decomposition of pure HAN (a) and HAN with GOFs (b).

Fig. 5 shows all detected products at the HAN decomposition. Peak 33 m / z indicates the formation of HO_2. It should be noted that the substance is always backed up by a peak 16 m / z and 32 m / z peaks (oxygen) and 17 m / z, 18 m / z 19 and m / z, which indicates the water course.

The major species were found to be H_2O, N_2O, NO, NO_2 and HNO_3 [36]. In this case the main products of the decomposition of hydroxylamine nitrate with GOFs are H_2O, N, NO, O_2, H_3NO, N_2O and NO_2. Presented the results of a comparison of the intensity of the formation of NO gas, NO_2 and H_2O in the thermal decomposition of hydroxylamine nitrate with carbon additives.

Fig. 6 shows different pictures of combustion tests of HAN/CMC with addition of GOFs taken by high speed video camera.

As seen in bottom images, with the addition of GOFs at an initial pressure of 5 MPa burning rate is increase and take a place stable combustion with burning rate up to 20 mm · s^{-1}. Also, it was observed that the addition of GOFs on the combustion of HAN-based propellant increases the concentration of the black smoke. This is may be explained by the formation of carbon oxides CO and CO_2.

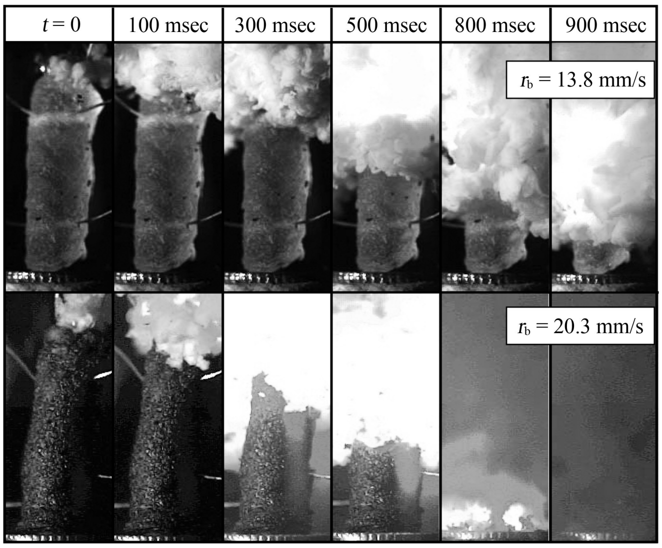
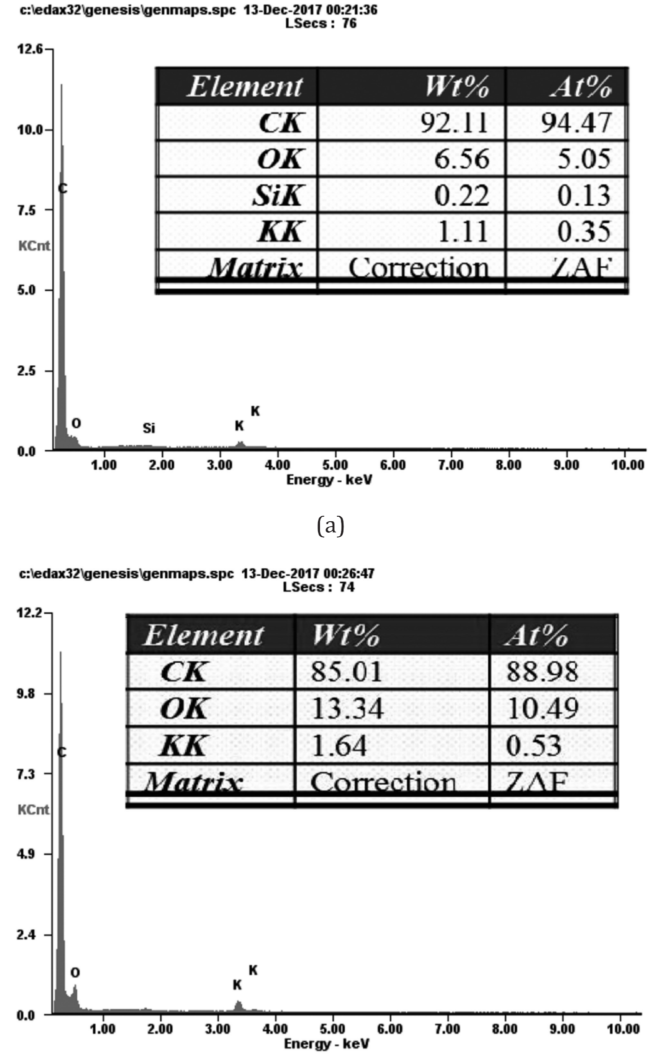


Fig. 6. Captured images of the combustion process of (a) 10 % CMC-gel/HAN sol. (b) 1 % GOFs/9 % CMC-gel/HAN sol., (P_{init} = 5 MPa).



Element	Wt%	At%
CK	92.11	94.47
OK	6.56	5.05
SiK	0.22	0.13
KK	1.11	0.35
Matrix	Correction	ZAF

(a)

Element	Wt%	At%
CK	85.01	88.98
OK	13.34	10.49
KK	1.64	0.53
Matrix	Correction	ZAF

(b)

Fig. 7. EDAX analysis of GOFs before (a) and after (b) combustion with 95% HAN water solution.

5. Conclusion

The synthesized GOF based on rice husk is graphen oxides framworks – SiO_2/K_2O_3. The developed additive is commercial cheap material and significantly effective for reaching the burning rate. The results of HAN decomposition with GOFs shows that propellant destruction mechanism is modified. EI-MS and DTA-TG results show acceleration of reaction rate, decreasing of ignition temperature, going down of activation energy and increasing of intensity of formation of gas products of propellant.

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