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Effect of MnC_2O_4 nanoparticles on the thermal decomposition of TEGDN/NC propellant

Yanchun Li · Kou Chenxia · Chuan Huang · Yi Cheng

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Abstract The effect of MnC_2O_4 nanoparticles on the thermal decomposition of double-base propellant composed of nitrocellulose (NC) and triethylene glycol dinitrate (TEGDN) has been investigated by TG/DSC–MS–FTIR coupling technique. The results show that the decomposition of TEGDN/NC propellant has two stages, the first stage is the volatility and decomposition of TEGDN, the second is the decomposition of NC. The addition of MnC_2O_4 nanoparticles gets the onset temperature of first stage higher, and makes the activation energy of decomposition of TEGDN grow by about 20–30 kJ/mol. The catalytic also accelerates the total weight loss, and makes the peak temperatures of DSC curves higher. The activation energy of the second stage has a decrease of 20–40 kJ/mol. MS and FTIR analysis show that the catalyst gets the gas products of macromolecular significantly reduce, while small molecules increase significantly. It also results in the decrease of H_2O, N_2O, and NO_2, and the increase of NO and HCN. Above all, the catalytic improves the thermal stability of TEGDN/NC propellant, make it more safety in storage, and make the decomposition easier and more thorough in main reaction zone.

Keywords MnC_2O_4 nanoparticles · TEGDN/NC propellant · TG/DSC–MS–FTIR · Thermal decomposition

Introduction

Triethylene glycol dinitrate (TEGDN) is a nitrated alcohol ester of triethylene glycol. It is used as an energetic plasticizer in explosives and propellants. Its chemical formula is $O_2N–O–CH_2CH_2–O–CH_2CH_2–O–CH_2CH_2–O–NO_2$ [1]. TEGDN has good dissolving capacity to nitrocellulose (NC). The thermal stability of TEGDN is better than nitroglycerine (NG). The toxicity and volatility of TEGDN are smaller than NG [2]. So TEGDN is being considered as replacements for NG in propellants.

TEGDN/NC propellant is double-base propellant composed of TEGDN and NC. The addition of catalyst can effectively improve the combustion performance of propellant. Many researches have been done in this field. With the method of volume closed bomb, Kaishu Huang [3] studied the influences of the different catalysts on the combustion of TEGDN gun propellant. Results showed that nickel oxalate can reduce the gun propellant pressure index obviously. Wei [4, 5] used TG–MS coupling technique to study the catalytic effect of NiO nanoparticles on the thermal decomposition of EGDN/NC propellant. It was shown that adding 2% of NiO nanoparticles to TEGDN/NC propellant can accelerate the thermal decomposition process after around 188 °C. Yi [6] studied effects of pressure and TEGDN content on decomposition reaction mechanism and kinetics of DB gun propellant containing the mixed ester of TEGDN and NG.

In this article, the double-base propellant composed of TEGDN and NC will be studied under nonisothermal methods by combined TG/DSC–QMS–FTIR, the gas products will be detected, and the activation energy will also be calculated by Friedman method. The object is to gain insights into the effect of MnC_2O_4 nanoparticles on the thermal decomposition of TEGDN/NC propellant. It is hoped that this study will be helpful for further investigations on the properties of TGEDN/NC system propellants. It is hoped that this study will be helpful for further investigations on the properties of TGEDN/NC propellants.

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Experimental

Sample

All the reagents were of analytical grade. The MnC_2O_4 nanoparticles used inTEGDN/NC propellant was prepared as reported in Ref. [16].The sample used in the experiment is a DB gun propellant composed of 58% (mass fraction) of NC, 40.8% of TEGDN, and 1.2% of *N*,*N*′-Dimethyl-*N*,*N*′-diphenylurea. The sample with MnC_2O_4 was added extra 1% MnC_2O_4 nanoparticles.

Equipment and conditions

All the tests were performed on a NETZSCH STA449C (DSC/TG), NETESCH-QMS403C, and NICOLET6700 FTIR. All samples were placed in closed crucibles made from aluminum with a pinhole in the cap. Experiments were performed, using sample weight of 2 ± 0.2 mg. High-purity nitrogen (>99.999%) was used as purge gas with a gas flow rate of 20 mL/min. NETESCH-QMS403C conditions: ionizing electron energy of 70 eV, quartz capillary gas connector, pressure injection 1000 mbar, and capillary temperature 200 °C. NICOLET6700 FTIR conditions: resolution of 4 cm^{-1}, the gas cell and the gas tube between the TG/DSC and the FTIR stay at 200 °C. The experiments were performed under non-isothermal conditions with constant heating rates of 2, 5, 10, and 15 K/min.

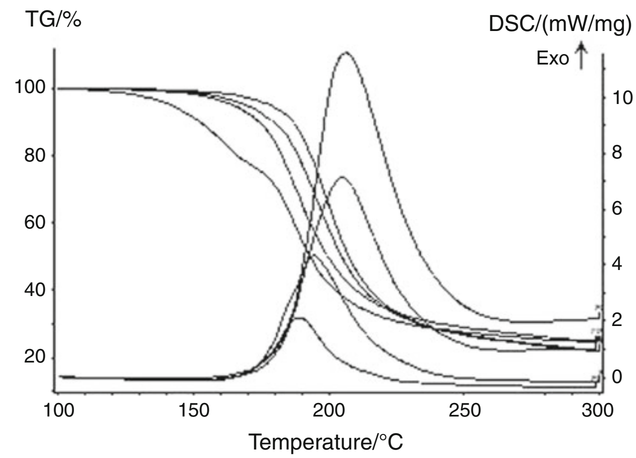

Fig. 1 TG-DSC curves of TEGDN/NC propellant at different heating rates (2, 5, 10, and 15 K/min)

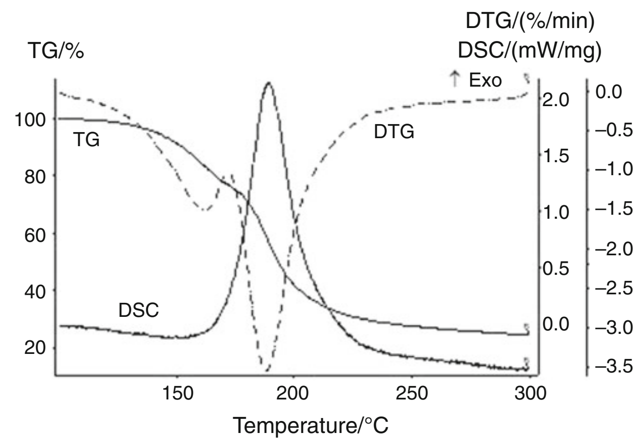

Fig. 2 TG-DTG-DSC curves of TEGDN/NC propellant at 2 K/min

Results and discussion

TG-DSC analysis on the thermal decomposition of the catalyzed TEGDN/NC propellant

The TG-DSC curves for TEGDN/NC Propellant are shown in Fig. 1. The TG-DTG-DSC curves of TEGDN/NC Propellant at 2 K/min are shown in Fig. 2. At 2 K/min the total mass loss has two stages: the first stage starts from 117° to 172°, the mass loss of first stage is about 22.48%; the second stage is from 172° to 250°, the mass loss of this stage is about 50.51%. The first stage accounts for 31% of the total mass loss. At 5, 10, and 15 K/min there is just one mass loss stage, it is from about 140° to 250°, and the global mass loss is about 72%. On the DSC curves there is just one exothermic peak from 170° to 250°. While from 120° to 175° there is no endothermic or exothermic peak, but here the mass loss is obvious. According to the thermal behavior of NC and TEGDN [6, 7] and as reported in Ref. [9], it is believed that the initial decomposition is mainly induced from the volatility and decomposition of TEGDN. The evaporation and decomposition of TEGDN occur at the same time, the exothermic process of TEGDN decomposition conceals the endothermic process of its evaporation, exothermic reaction occurred in the gas phase.

The TG-DSC curves for TEGDN/NC propellant with MnC_2O_4 are shown in Fig. 3. The TG-DTG-DSC curves of TEGDN/NC Propellant with MnC_2O_4 at 2 K/min are shown in Fig. 4. The TG-DTG-DSC data of TEGDN/NC propellant without and with MnC_2O_4 are listed in Table 1. After adding catalyst, it can be found that: at 2 K/min, the onset temperature of TG has an increase of 11 °C. As the increase of heating rate, the increase of onset temperature becomes less obvious; at 2 K/min, the two mass loss stages almost become one stage after adding catalyst; the total mass loss also has a significant increase; the peak temperatures of DSC curves also become higher than TEGDN/NC propellant without MnC_2O_4. But the decomposition enthalpies decrease slightly.

It is obviously that MnC_2O_4 nanoparticles have apparent positive effect on the thermal decomposition of TEGDN/

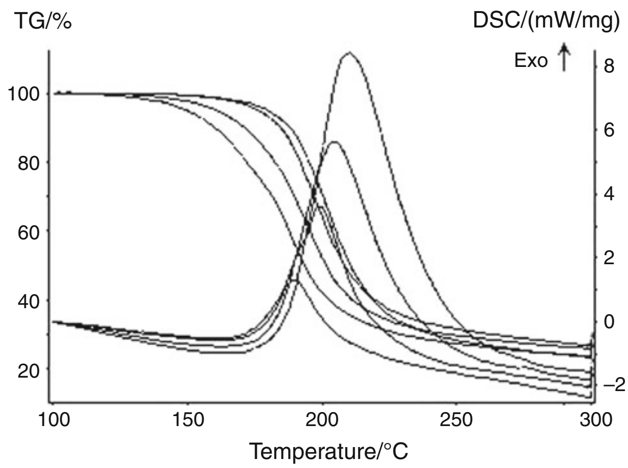

Fig. 3 TG-DSC curves of TEGDN/NC Propellant with MnC_2O_4 at different heating rates (2, 5, 10 and 15 K/min)

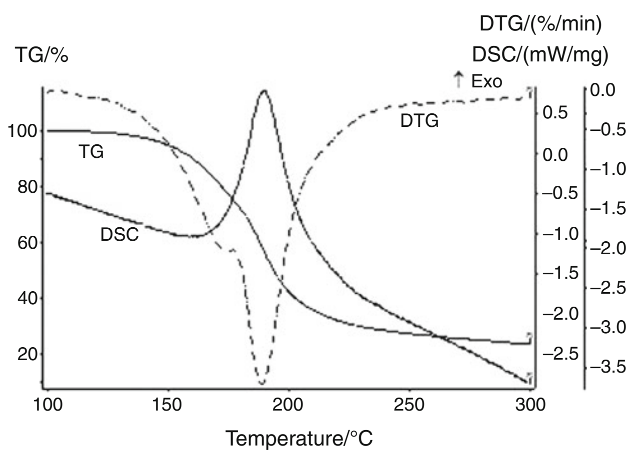

Fig. 4 TG-DTG-DSC curves of TEGDN/NC propellant with MnC_2O_4 at 2 K/min

NC propellant. Therefore, the mass spectrometer and FTIR were applied to monitor the evolved gases in order to investigate the detailed changes of gaseous products during the thermal decomposition process.

MS and FTIR analysis on the thermal decomposition of the catalyzed TEGDN/NC propellant

The evolution of gases could provide information on the chemical reactions during thermal decomposition [5, 8–10], and the thermal decomposition process was monitored by MS and FTIR online. The evolution curves of the gaseous products released in argon are shown as ion current versus temperature curves in Fig. 5.

It can be found that the ion fragments curves of $m/z = 18$, 30, 46 have two peaks, The first peak is 120–170 °C, the second is from 170 to 250 °C corresponding to the two stage of TG curve. Ion current of $m/z = 46$ still has one peak after 250 °C. After adding 1% MnC_2O_4 nanoparticles, the peak temperature of first peak becomes higher, while that of second peak doesn't have obviously changes.

The ion current of $m/z = 27$, 44, 52, 73 just have one peak, $m/z = 27$ and 44 is from 140 to 250 °C, most area of the peak is from 170 to 250 °C corresponding to the second TG stage, the first TG stage release little. $m/z = 52$ is from 170 to 250 °C corresponding to the second TG stage. $m/z = 73$ is from 110 to 200 °C corresponding to the first TG stage.

According to the characteristic ion fragments of $m/z = 26$, 27 can be ascribed to the evolution of HCN^+. The ion currents of $m/z = 16$, 17, and 18 could be mainly ascribed to the evolution of H_2O^+. Considering the isotope effects and according to the MS curves for $m/z = 29$ and 30, the ion currents of $m/z = 29$ could be mainly ascribed to the evolution of HCO^+, that of $m/z = 30$ could be the evolution of NO^+ and CH_2O^+. $m/z = 44$ could be mainly ascribed to the evolution of ${CO_2}^+$ and N_2O^+.

As it is shown, there is still one peak on the MS curves for $m/z = 46$ after 250 °C. It is known that NO is the most intense fragment of NO_2 according to the reference mass spectra in NIST database [11]. Therefore, from the profile of MS curves for $m/z = 30$, it is believed that the first two peaks on the MS curves for $m/z = 46$ is attributed to the evolution of NO_2, while the peak after 250 °C is caused by the evolution of HCOOH gas.

Table 1 TG-DTG-DSC data of TEGDN/NC propellant without and with MnC_2O_4

β/K/min	TEGDN/NC propellant/TEGDN/NC propellant with MnC_2O_4					
	TG		DTG		DSC	
	T_o/°C	Mass lose/%	T_o/°C	T_p/°C	T_p/°C	H/J g^{-1}
2	98/109	75.5/76.4	131/143	188/189	188/190	1615/1347
5	115/118	76.3/77.26	162/167	189/194	194/199	1627/1489
10	123/124	73.5/78	169/172	196/198	204/203	1420/1371
15	132/134	76.8/78.39	175/176	199/202	206/210	1523/1428

T_o the onset temperature, T_p the peak temperature

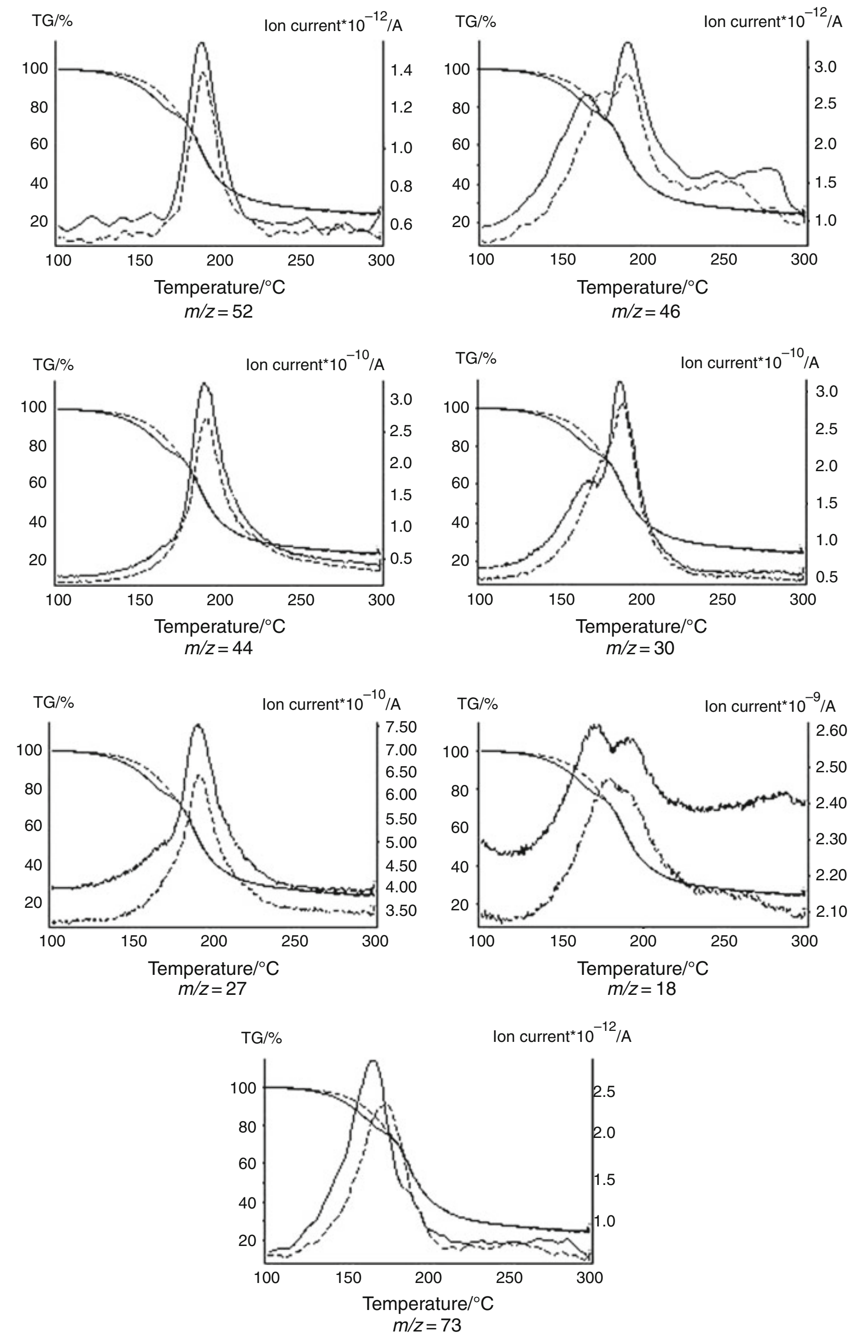

Fig. 5 The Mass spectra of the gas products of TEGDN/NC propellant without and with MnC_2O_4 at 2 K/min (*solid line* is TEGDN/NC propellant, *dashed line* is TEGDN/NC propellant with MnC_2O_4)

In order to avoid complexity and to conveniently compare relative quantities of volatiles, the relative intensity values (peak area) of individual ions of TEGDN/NC propellant are designed as 100%, while the relative intensity values of individual ions with MnC_2O_4 nanoparticles are based on those of corresponding ions of TEGDN/NC propellant. Although the intensity data must not be compared between the different compounds due to the different sensitivities of the mass spectrometer, the intensity values of a given ion are comparable between the samples because they were normalized to the carrier gas and the sample mass [5, 12].

As shown in Table 2, adding 1% MnC_2O_4 can result in the decrease of m/z = 18, 43, 44, 45, 46, 52, 73. However, the intensities of m/z = 16, 17, 26, 27, 29, 30, 31 are increased with the catalysis of MnC_2O_4 nanoparticles on the decomposition of TEGDN/NC propellant. It can also be found that among the gas products, the amount of m/z = 29(HCO+) increases most evidently. As reported in [13], HCHO is an important product during the thermal

Table 2 Relative peak of individual irons of the TEGDN/NC propellant without and with MnC_2O_4

Ion /*m/z*	16	17	18	26	27	29	30	31	43	44	45	46	52	73
TEGDN/NC propellant /%	100	100	100	100	100	100	100	100	100	100	100	100	100	100
TEGDN/NC propellant with 1% MnC_2O_4 /%	118	115.6	91.2	122.7	131.1	149.2	110.6	113.9	98.9	84	95.8	73.5	78	81.3

decomposition which will participate in the production of other gaseous products. Reference [5] considered that HCHO is suppressed to take part in reaction as below:

$$8NO_2 + 6HCHO = 8NO + 2CO_2 + 3CO + 5H_2O + HCOOH \quad (1)$$

It is obvious that after adding 1% MnC_2O_4 nanoparticles, the amount of H_2O, N_2O, and NO_2 decrease while the amount of NO and HCN decrease, our supposition is that with catalysis of MnC_2O_4, the reaction below is promoted.

$$2H_2O + 2CO_2 + 4N_2O = 4HCN + 4NO + 3O_2 \quad (2)$$

It can be concluded that after addition of catalyst, the gas products of macromolecular significantly reduce, while small molecules increase significantly. It indicates that the addition of catalyst make the decomposition of TEGDN/NC propellant more thorough.

After the addition of catalyst, the FTIR spectra don't have obvious change except the absorbance. Figure 6 represents the FTIR spectra of gas products of TEGDN/NC propellant at 2 K/min. It is certain that there are N_2O (2238 cm^{-1}), CO (2176 cm^{-1}), CO_2 (2368 cm^{-1}), NO_2 (1658–1549 cm^{-1}), NO (1965–1762 cm^{-1}) [14], H_2O. The main gas product is N_2O. In addition, by comparison with the standard spectra, there must be 4-amino benzoic acid in gas products from the decomposition of *N*,*N*′-Dimethyl-*N*,*N*′-diphenylurea. 2-methyl succinate and octanoic acid ethyl ester may also exit in the gas products.

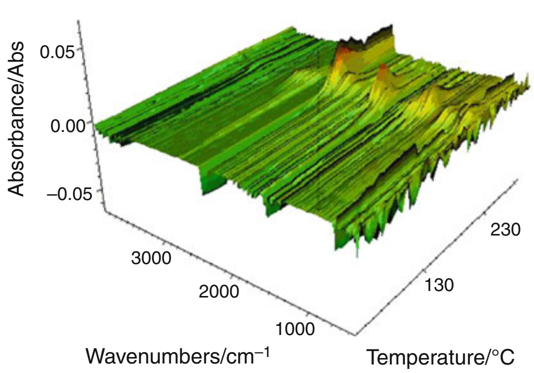

Fig. 6 The FTIR spectra of gas products of TEGDN/NC propellant at 2 K/min

Kinetic analysis on the thermal decomposition of the catalyzed TEGDN/NC propellant

For the further understanding to catalysis process, the activation energy of TEGDN/NC propellant without and with MnC_2O_4 was also calculated by Friedman method [15]. The results are shown in Fig. 7.

Figure 7 shows that the activation energy curves have two stages, the first stage is before 30%, and here the activation energy dependence of conversion is linear, the activation energy is from 80 to 210 kJ/mol, this stage must be the vapor and decomposition of TEGDN; the second stage is after 30%, and here the activation energy doesn't change significantly with conversion. This stage must be mainly the decomposition of NC.

After the addition of MnC_2O_4, the activation energy for the first stage has an average increase of 20–30 kJ/mol, and the second stage has an average decrease of 20–40 kJ/mol. It can be concluded that: the addition of MnC_2O_4 gets the decomposition of TEGDN harder. MnC_2O_4 improves the thermal stability of TEGDN/NC propellant. It makes the TEGDN/NC propellant more safety in the storage; while the addition of MnC_2O_4 gets the decomposition of NC more easily. It also gets the decomposition of NC more thorough.

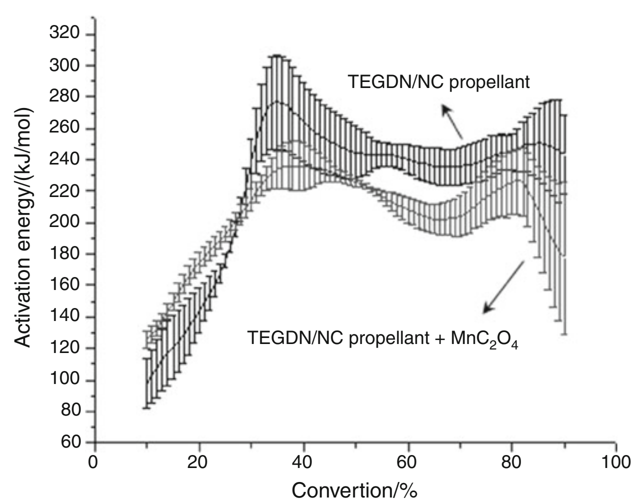

Fig. 7 The activation energy of TEGDN/NC propellant without and with MnC_2O_4

Conclusions

MnC_2O_4 nanoparticles have a positive effect on the thermal decomposition of TEGDN/NC propellant. Adding 1% MnC_2O_4 nanoparticles to the TEGDN/NC propellant can get the onset temperature become higher, accelerate the total weight loss rate of the thermal decomposition, and also make the peak temperatures of DSC curves higher.

MS and FTIR analysis shows that the catalyst gets the gas products of macromolecular significantly reduce, while small molecules increase significantly. It also results in the decrease of H_2O, N_2O, and NO_2, and the increase of NO and HCN. The catalyst results in the decomposition more thorough.

The kinetic calculation shows that MnC_2O_4 makes the activation energy of decomposition of TEGDN increase by about 20–30 kJ/mol. It improves the thermal stability of TEGDN/NC propellant. It makes the TEGDN/NC propellant more safety in the storage; while the addition of MnC_2O_4 gets the decomposition of NC easier. It also makes the decomposition of NC more thorough.

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