

Study on the catalytic effect of NiO nanoparticles on the thermal decomposition of TEGDN/NC propellant

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ARTICLE INFO

Article history:

Received 3 December 2008

Received in revised form 17 February 2009

Accepted 17 February 2009

Available online 26 February 2009

Keywords:

NiO nanoparticles

TEGDN/NC propellant

TG–MS

Thermal decomposition

ABSTRACT

The catalytic effect of NiO nanoparticles on the thermal decomposition of double-base propellant composed of nitrocellulose (NC) and triethylene glycol dinitrate (TEGDN) has been investigated by thermogravimetry–mass spectrometry (TG–MS) coupling technique. It was shown that adding 2% of NiO nanoparticles to TEGDN/NC propellant can accelerate the thermal decomposition process after around 188 °C TG–MS analysis indicated that NiO nanoparticles have resulted in the increase in intensity (peak area) of $m/z = 27, 28,$ and 29 MS signals, but the decrease in the intensity of $m/z = 18, 30, 44$ and 46 (peak 2) MS signals during the thermal decomposition. The catalytic mechanism was also discussed in this paper.

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1. Introduction

The thermal decomposition processes of energetic materials and its ingredients have been studied for long years [1–6]. As well known, nanomaterials possess unique properties in various fields on account of different effects in terms of volume, quantum size, surface and macroscopic quantum tunnel [7–8]. Therefore, nanomaterials have been employed as catalysts to improve the thermal decomposition characteristics of energetic materials [9–11]. In recent years, nickel oxide (NiO) nanoparticles have received lots of attention for the electronic, magnetic and especially catalytic properties [7,12–14]. Wang et al. [15] have studied the catalytic behavior of NiO nanoparticles on the thermal decomposition of ammonium perchlorate (AP) which is the most common oxidizer in composite propellant.

The thermal decomposition can be investigated by many thermoanalytical methods such as thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). Compared to TG analysis alone which is only able to measure the total volatile as a single group, thermogravimetry–mass (TG–MS) coupling technique is highly preferred [16], because TG–MS spectrometry is suitable for studying the mass change during the thermal decomposition. Therefore, TG–MS technique has been used in a wide variety of qualitative and quantitative studies of the thermal decomposition of materials, the identification of gaseous products, and the thermal decomposition mechanisms [16–20].

In this work, we used TG–MS coupling technique to investigate the catalytic performance of NiO nanoparticles on the thermal decomposition process of double-base propellant composed of nitrocellulose (NC) and triethylene glycol dinitrate (TEGDN).

The nonisothermal decomposition reaction kinetics of double-base propellant containing the mixed ester of TEGDN and nitroglycerin (NG) has been reported [21–23]. It is hoped that this work will be helpful for further investigations on the properties of TEGDN/NC system propellants.

2. Experimental

2.1. Preparation of sample

All the reagents were of analytical grade. The catalyst used in TEGDN/NC propellant was prepared as reported in [15].

The sample used in the experiment is a TEGDN/NC propellant composed of 66.17% (mass fraction) NC which contained 12% of nitrogen and was from Xi'an modern chemistry research institute, 32.25% TEGDN ester and 0.91% other auxiliary additives. The proportion between TEGDN/NC propellant and the catalyst were 49:1 (wt%). The TEGDN/NC propellant without and with NiO nanoparticles was designed as sample 1 and sample 2, respectively.

2.2. Instrumentation

A simultaneous thermal analyzer (Mettler Toledo, model TGA/SDTA 851e) coupled on line with a quadrupole mass spectrometry (Pfeiffer Vacuum, model Thermostar GSD301T3) was applied for the TG–MS analysis on the thermal decomposition process

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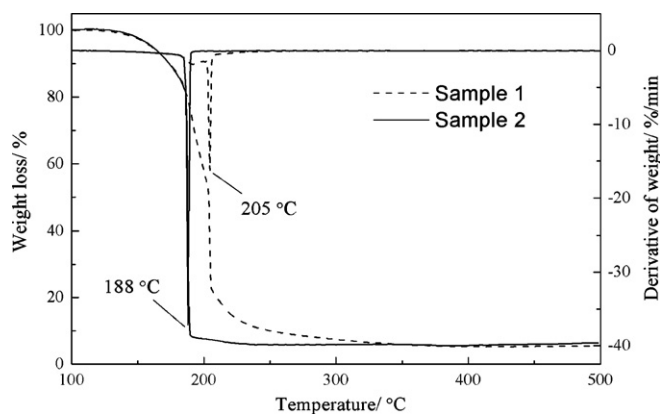


Fig. 1. TG-DTG curves of TEGDN/NC propellant without and with NiO nanoparticles.

of TEGDN/NC propellant. The mass spectrometer was operated with an electron impact ionizer with energy 70 eV, and the mass scan speed was 1 a.m.u s⁻¹. The connection between the TGA-SDTA apparatus and the mass spectrometer was done by means of a quartz capillary of 0.15 mm internal diameter, maintained at 150 °C. The capillary interface was placed near the sample pan as described in [17].

The thermal decomposition process was studied in the flowing argon gas atmosphere (purity, 99.99%; flowing rate, 30 ml min⁻¹; atmospheric pressure) at the heating rate of 20 °C min⁻¹ when the sample quantum was about 1.00 mg with Al₂O₃ crucible as reference, and the sample was placed in alumina crucible.

In order to ensure that there was no air in the instrument and calibrate the analyzer, the apparatus was operated in argon before the thermal decomposition process was performed.

3. Results and discussion

3.1. TG-DTG analysis on the thermal decomposition of the catalyzed TEGDN/NC propellant

The TG-DTG curves for TEGDN/NC propellant in presence of nano-NiO are shown in Fig. 1.

From the profile of the thermogravimetry curves, it can be found that the catalyst has little influence on the initial decomposition process. However, the thermal decomposition process of TEGDN/NC propellant in presence of the catalyst becomes acute at about 188 °C and attains 100% mass loss below 250 °C, while the final decomposition temperature of the TEGDN/NC propellant is about 350 °C. According to the thermal behavior of NC and TEGDN [5,6] and as reported in [21–23], it is believed that the initial decomposition is mainly induced from the volatile and decomposition of TEGDN. Therefore, it can be indicated that NiO nanoparticles have greater influence on the thermal decomposition of NC than that process of TEGDN.

As it is shown on the TG-DTG curves, NiO nanoparticles have a positive effect on the thermal decomposition of TEGDN/NC propellant. Therefore, the mass spectrometer was applied to monitor the evolved gases in order to investigate the detailed changes of gaseous products during the thermal decomposition process.

3.2. MS analysis on the thermal decomposition of the catalyzed TEGDN/NC propellant

The evolution of gases could provide information on the chemical reactions occurring during thermal decomposition, and the thermal decomposition process was monitored by MS on-line. The evolution curves of the gaseous products released in argon

are shown as ion current versus temperature curves in Fig. 2 (a–g).

According to the characteristic ion fragments of $m/z=26$, MS curves for $m/z=27$ can be ascribed to the evolution of HCN⁺ (Fig. 3). Considering the isotope effects and according to the MS curves for $m/z=28$, $m/z=29$ and $m/z=30$, the ion currents of $m/z=29$ could be mainly ascribed to the evolution of HCO⁺ rather than ¹³CO.

As it is shown, there are two peaks on the MS curves for $m/z=46$. It is known that NO is the most intense fragment of NO₂ according to the reference mass spectra in NIST database [24]. Therefore, from the profile of MS curves for $m/z=30$, it is believed that the first peak (peak 1) on the MS curves for $m/z=46$ is attributed to the evolution of NO₂ while the second (peak 2) is caused by the evolution of HCOOH gas.

According to the profile of MS curves, it can be easily found that after adding 2% NiO nanoparticles to TEGDN/NC propellant, the ion currents of the evolved products during thermal decomposition attain the peak values at lower temperatures, which is corresponding to the TG-DTG analysis. And as shown in Fig. 2, it can be seen that when temperature is below 188 °C the initial volatile species are mainly CO (&N₂), HCHO, NO and CO₂ as well as some of H₂O, HCN and NO₂.

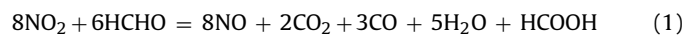
In order to avoid complexity and conveniently compare relative quantities of volatiles, the relative intensity values (peak area) of individual ions of TEGDN/NC propellant are designed as 100%, while the relative intensity values of individual ions in presence of NiO particles are based on those of corresponding 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 [18].

Table 1 compiles the intensity values (peak areas) of individual ions for the samples. The proportion between HCO⁺ ($m/z=29$) and HCHO⁺ ($m/z=30$) is almost 1 [24], so the intensity of HCO⁺ can be taken as the intensity of HCHO⁺. Therefore, in Table 1, the intensity of HCHO⁺ is obtained by the analysis of MS curves for $m/z=29$. And after the deduction of the intensity of HCHO⁺, the intensity of $m/z=30$ is regarded as that of NO⁺.

As shown in Table 1, it can be concluded that adding 2% NiO nanoparticles can result in the increase of $m/z=27$ (HCN⁺), 28 (CO⁺, N₂⁺) and 30 (HCHO⁺) MS signals. However, the intensities of $m/z=18$ (H₂O⁺), 30 (NO⁺), 44 (mainly CO₂⁺) and $m/z=46$ (HCOOH⁺) are decreased with the catalysis of NiO on the thermal decomposition of TEGDN/NC propellant.

Although the ion current of $m/z=28$ can be ascribed to the evolution of CO and N₂, according to the element conservation law, it is believed that the intensity increase of the ion current of $m/z=28$ is mainly induced by the increase of the CO evolution.

Therefore, according to the MS analysis and on the principle of element conservation, the trend can be understood based on the fact that when 2% NiO nanoparticles are present in TEGDN/NC propellant, more of the carbon, hydrogen and nitrogen will be converted to CO, HCHO, and HCN rather than other compounds. As seen in Table 1, it can be found that among the gaseous products, the amount of HCHO gas increases most evidently. As reported in [6], HCHO is an important product during the thermal decomposition which will participate in the production of other gaseous products. Therefore, it is considered that with the catalysis of NiO, HCHO is suppressed to take part in reaction (1).



Based on the fact that the amount of HCN and CO increases while the amount of H₂O, CO₂ and NO decreases, our supposition is that

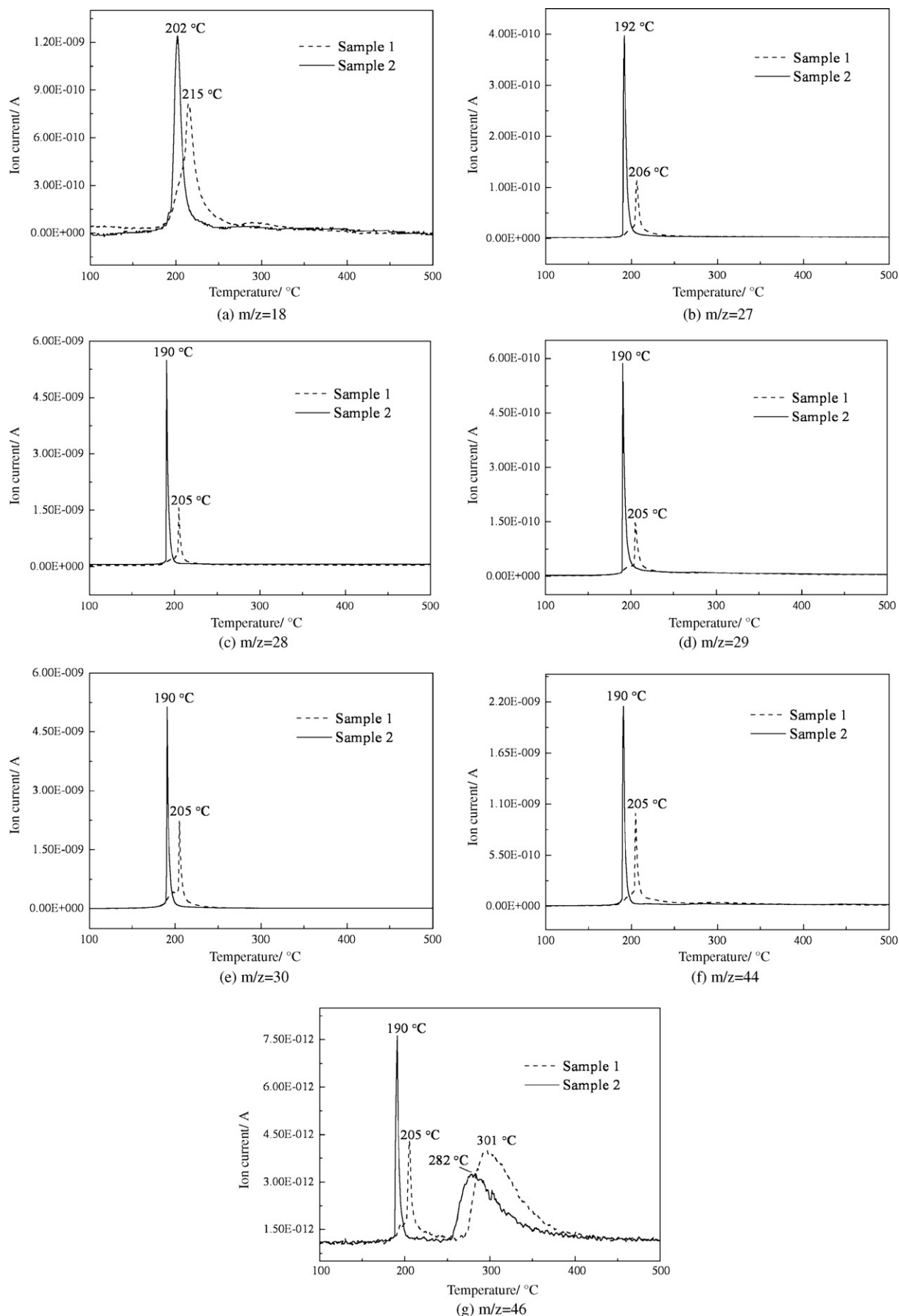


Fig. 2. MS curves of the evolved gases during the thermal decomposition of TEGDN/NC propellant without and with NiO nanoparticles.

Table 1
Relative peak areas of individual ions of the samples measured by TG–MS analysis.

| Ion (<i>m/z</i>) | 18 | 27 | 28 | 30 | 30 | 44 | 46 (peak 1) | 46 (peak 2) |
|------------------------------------|------------------|-------|-------|-------|------|-----------------|-----------------|-------------|
| Assignments | H ₂ O | HCN | CO | HCHO | NO | CO ₂ | NO ₂ | HCOOH |
| TEGDN/NC propellant (%) | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| TEGDN/NC propellant with 2%NiO (%) | 93.7 | 132.8 | 133.2 | 139.1 | 93.9 | 63.3 | 105.8 | 68.0 |

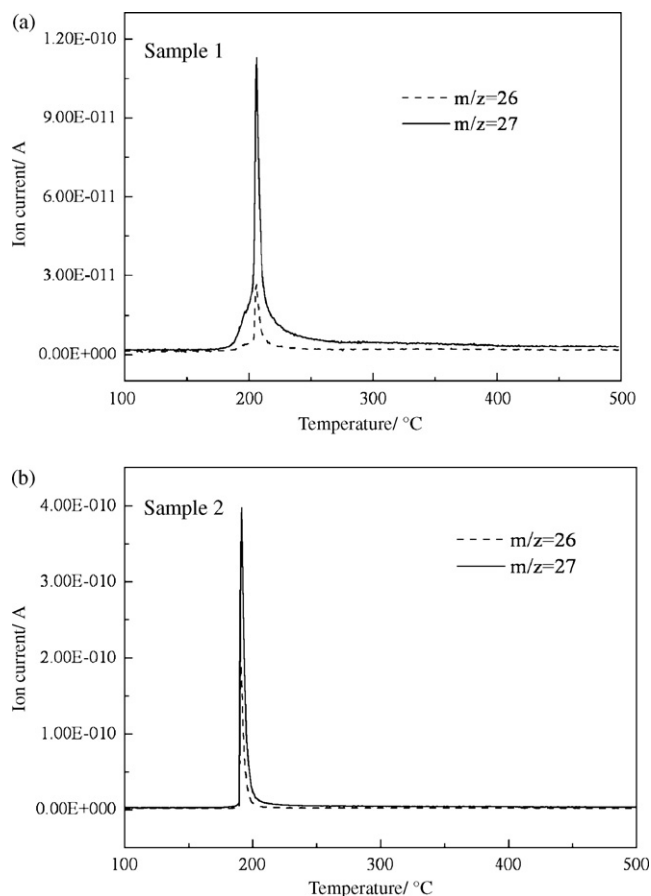


Fig. 3. MS curves of *m/z*=26 and *m/z*=27 during the thermal decomposition of sample 1 and sample 2.

with the catalysis of NiO, the reaction below is promoted.



4. Conclusions

NiO nanoparticles have a positive effect on the thermal decomposition of TEGDN/NC propellant. Adding 2% NiO nanoparticles to the TEGDN/NC propellant can accelerate the weight loss rate of the thermal decomposition after around 188 °C but has little influence on the decomposition process before 188 °C. It is indicated that NiO nanoparticles have greater influence on the thermal decomposition of NC than that process of TEGDN.

MS analysis shows that the catalyst results in the increase in intensity of *m/z* = 27, 28 and 29 MS signals, but the decrease of the intensity of *m/z* = 18, 30, 44 and 46 (peak 2) MS signals. It is considered that with the catalysis of NiO, more of the nitrogen, carbon and hydrogen will be converted to HCN, CO and HCHO rather than NO, CO₂ and H₂O.

It is helpful to study the catalytic effects on compositions change of the gaseous products because the formation enthalpy of gaseous products is correlative with the decomposition reaction heat and

the composition of gaseous products can be related to the pressure during the thermal decomposition. So the study on the composition changes of gaseous products of TEGDN/NC propellant will be helpful for us to understand the hazards and risks of the propellant, and this work will be useful for further investigations on the properties of TEGDN/NC system propellants.

Acknowledgement

We gratefully acknowledge the National Natural Science Foundation of China (No.10776014) for the financial support.

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