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# Combustion Catalyst: Nano-Fe<sub>2</sub>O<sub>3</sub> and Nano-Thermite Al/Fe<sub>2</sub>O<sub>3</sub> with Different Shapes

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Additional information is available at the end of the chapter

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## Abstract

In order to enable the energetic materials to possess a more powerful performance, adding combustion catalysts is a quite effective method. Granular, oval, and polyhedral Fe<sub>2</sub>O<sub>3</sub> particles have been prepared by the hydrothermal method and used to fabricate Al/Fe<sub>2</sub>O<sub>3</sub> thermites. All the Fe<sub>2</sub>O<sub>3</sub> and Al/Fe<sub>2</sub>O<sub>3</sub> thermite samples were characterized using a combination of experimental techniques including scanning electron microscopy (SEM), energy dispersive spectrometer (EDS), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), transmission electron microscope (TEM), and high-resolution TEM (HRTEM). The non-isothermal decomposition kinetics of the composites and nitrocellulose (NC) can be modeled by the Avrami-Erofeev equation  $f(\alpha)=3(1-\alpha)[-ln(1-\alpha)]^{1/3}/2$  in differential form. Through the thermogravimetric analysis infrared (TG-IR) analysis of decomposition processes and products, it is speculated that Fe<sub>2</sub>O<sub>3</sub> and Al/Fe<sub>2</sub>O<sub>3</sub> can effectively accelerate the thermal decomposition reaction rate of NC by promoting the O-NO<sub>2</sub> bond cleavage. Adding oxides or thermites can distinctly increase the burning rate, decrease the burning rate pressure exponent, increase the flame temperature, and improve the combustion wave structures of the ammonium perchlorate/hydroxyl-terminated polybutadiene (AP/HTPB) propellants. Among the three studied, different shapes of Fe<sub>2</sub>O<sub>3</sub>, the granular Fe<sub>2</sub>O<sub>3</sub>, and its corresponding thermites (Al/Fe<sub>2</sub>O<sub>3</sub>(H)) exhibit the highest burning rate due to larger surface area associated with smaller particle size. Moreover, Al/Fe<sub>2</sub>O<sub>3</sub>(H) thermites have more effective combustion-supporting ability for AP/HTPB propellants than Fe<sub>2</sub>O<sub>3</sub> structures and the other two as-prepared Al/Fe<sub>2</sub>O<sub>3</sub> thermites.

**Keywords:** combustion catalyst, thermal decomposition mechanism, combustion wave structure

## 1. Introduction

Energetic materials (explosives, propellants, and pyrotechnics) are necessary material bases of high-performance weapons and ammunition, which are used extensively for both civil, military, and space applications. In order to enable the energetic materials to possess a more powerful performance, such as the high quantity of heat release, the high combustion temperature, the fast burning rate, and so on, adding combustion catalysts is a quite effective method.

In recent years, researchers pay much attention to the preparation and application of the combustion catalysis of nanoscale. Many studies reported that catalysts in nanoscale exhibit the absolute advantages both in accelerating the thermal decomposition process of the main energetic materials such as cyclotrimethylene trinitramine (RDX), nitrocellulose (NC), cyclotetramethylene tetranitramine (HMX), 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexanitro hexaazaisowurtzitane (CL-20), and 3-nitro-1,2,4-triazol-5-one (NTO), and in enhancing the ignition and combustion performances of the solid. For instance, the nano-sized  $\text{Cr}_2\text{O}_3$  particles decrease the ignition delay time by a factor 3.5 ( $16 \pm 2$  vs  $54 \pm 4$  ms) and accelerate the combustion rate ( $340 \pm 10$  mm s<sup>-1</sup>) of the Al/ $\text{Cr}_2\text{O}_3$  thermite, which is fabricated by  $\text{Cr}_2\text{O}_3$  micro- or NPs ( $\Phi \approx 20$  nm) and Al NPs ( $\Phi \approx 50$  nm) [1]. Pantoya [2] reported that nanocomposite thermites (Al/ $\text{MoO}_3$ ) can significantly reduce the ignition delay time compared with micron-composite thermites. Nitrocellulose nanofiber-based thermite textiles were studied and compared with the pure nitrocellulose and nano-aluminum incorporated nanofiber; the result indicates that the burning rates were enhanced by adding the Al/CuO thermite [3].

The abovementioned nanothermite contains two parts: metal fuel (Al, used due to its low cost, high density, and the efficient catalytic property [4]) and metal oxides ( $\text{Fe}_2\text{O}_3$ , CuO,  $\text{MnO}_2$ ,  $\text{MoO}_3$ , PbO [5],  $\text{Bi}_2\text{O}_3$ , etc.). The nanothermite system, as the metastable intermolecular composites (MICs) [6], can enhance the reactivity [7–9] through the oxidation-reduction reactions, which lead to high burning rate [10], high heat production [11], and negligible gas generation. The traditional thermite, Al/ $\text{Fe}_2\text{O}_3$ , is prepared in various nanoparticle size, shape, and composition [12] in order to be better applied in free-standing heat sources, air-bag ignition materials, hardware destruction devices, welding torches [13], and energetic material field. Both Al and  $\text{Fe}_2\text{O}_3$  particles have been used as catalysts not only in the thermal decomposition process of the main energetic components but also in composite solid propellants [14–17]. However, the effects of Al/ $\text{Fe}_2\text{O}_3$  nanoparticles on the thermal behavior and non-isothermal decomposition kinetics of NC are barely investigated. And, to the best of our knowledge, there has been no report about the dependence of catalytic properties of Al/ $\text{Fe}_2\text{O}_3$  thermites on the morphology of  $\text{Fe}_2\text{O}_3$  particles in combustion reactions to date.

Nitrocellulose (NC) is extensively applied as a main component in gun, blasting gelatin, dynamites, and rocket propellants [18–21] owing to its high flammability and explosiveness. In order to obtain more information about NC, the thermal decomposition mechanism of NC has been investigated. It is shown that the fission of oxygen-nitrogen bond is the first and rate-determining step during the decomposition process [22–25]. Quantities of

NO<sub>2</sub> gases, derived from the O-NO<sub>2</sub> bond cleavage, could stagnate in the polymer skeleton and lead to promote the secondary autocatalytic reactions (i.e., the heterogeneous reactions in condensed phase) [26]. Furthermore, Mahajan et al. [27] reported that copper oxide influences the combustion/thermal decomposition of NC in a way so as to retard the breaking of O-NO<sub>2</sub> bonds in solid phase. With the excellent characteristics of nanomaterials, we study the influence of Fe<sub>2</sub>O<sub>3</sub> particles and Al/Fe<sub>2</sub>O<sub>3</sub> thermites on thermal behavior and non-isothermal decomposition kinetics of NC in order to provide basic data for establishing the combustion model and studying the combustion process.

In this contribution, granular, oval, and polyhedral Fe<sub>2</sub>O<sub>3</sub> particles have been prepared by the hydrothermal method and used to fabricate Al/Fe<sub>2</sub>O<sub>3</sub> thermites by integrating Al nanopowders with Fe<sub>2</sub>O<sub>3</sub> at a stoichiometric ratio of Fe<sub>2</sub>O<sub>3</sub>:Al (71.1wt%:28.9wt%). All the Fe<sub>2</sub>O<sub>3</sub> and Al/Fe<sub>2</sub>O<sub>3</sub> thermite samples were characterized using a combination of experimental techniques including scanning electron microscopy (SEM), energy dispersive spectrometer (EDS), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), transmission electron microscope (TEM) and high-resolution TEM. The effects of Fe<sub>2</sub>O<sub>3</sub> nanoparticles and Al/Fe<sub>2</sub>O<sub>3</sub> on the thermal decomposition of NC have been investigated by the differential scanning calorimetry (DSC) method and the thermogravimetry with Fourier transform infrared analysis (TG-IR). The influences of Fe<sub>2</sub>O<sub>3</sub> and the corresponding thermite on the combustion properties of the ammonium perchlorate/hydroxyl-terminated polybutadiene (AP/HTPB) composite propellant were investigated and compared. Moreover, the combustion wave structures and the flame temperatures of AP/HTPB composite propellants containing thermites Al/Fe<sub>2</sub>O<sub>3</sub> are obtained at 4 MPa.

## 2. Experimental section

### 2.1. Synthesis of Fe<sub>2</sub>O<sub>3</sub> particles and Al/Fe<sub>2</sub>O<sub>3</sub> thermites

The granular, oval, and polyhedral Fe<sub>2</sub>O<sub>3</sub> particles were prepared following the procedures developed from our reports [28, 29], and denoted as Fe<sub>2</sub>O<sub>3</sub>(H), Fe<sub>2</sub>O<sub>3</sub>(o), and Fe<sub>2</sub>O<sub>3</sub>(p), respectively. Three corresponding thermites Al/Fe<sub>2</sub>O<sub>3</sub>(H), Al/Fe<sub>2</sub>O<sub>3</sub>(o), and Al/Fe<sub>2</sub>O<sub>3</sub>(p) were prepared [29] with a stoichiometric ratio of Fe<sub>2</sub>O<sub>3</sub>:Al (71.1wt%:28.9wt%) based on the calculation [30].

### 2.2. Preparation of Fe<sub>2</sub>O<sub>3</sub>-NC and Al/Fe<sub>2</sub>O<sub>3</sub>-NC

The Fe<sub>2</sub>O<sub>3</sub> particles or Al/Fe<sub>2</sub>O<sub>3</sub> thermite was evenly mixed with NC via grinding to obtain the composite materials, respectively. For the Fe<sub>2</sub>O<sub>3</sub>-NC composites, the Fe<sub>2</sub>O<sub>3</sub>:NC mass ratio was 1:1, while for the Al/Fe<sub>2</sub>O<sub>3</sub>-NC composites it was 1:1, too. The grinding process was maintained for 30 min to obtain light red or dark gray composite materials. The products were used for differential scanning calorimetry experiment, in order to assess the thermal behavior and the effects of Fe<sub>2</sub>O<sub>3</sub> particles or Al/Fe<sub>2</sub>O<sub>3</sub> on NC.



### 2.3. Preparation of AP/HTPB propellant formulations

The as-prepared  $\text{Fe}_2\text{O}_3(\text{H})$ ,  $\text{Fe}_2\text{O}_3(\text{o})$ ,  $\text{Fe}_2\text{O}_3(\text{p})$ , and their corresponding thermites are used as the burning rate modifiers in the preliminary AP/HTPB propellant formulation [29] as shown in Table 1.

No.	HTPB system/%	Al/%	Coarse AP/%	Superfine AP/%	Additives	Additives/%
N0	14.3	15.3	18.4	52.0	none	0.0
F1	14.3	15.3	18.4	52.0	$\text{Fe}_2\text{O}_3(\text{H})$	2.0
F2	14.3	15.3	18.4	52.0	$\text{Fe}_2\text{O}_3(\text{o})$	2.0
F3	14.3	15.3	18.4	52.0	$\text{Fe}_2\text{O}_3(\text{p})$	2.0
S1	14.3	14.5	18.4	52.0	Al/ $\text{Fe}_2\text{O}_3(\text{H})$	2.8
S2	14.3	14.5	18.4	52.0	Al/ $\text{Fe}_2\text{O}_3(\text{o})$	2.8
S3	14.3	14.5	18.4	52.0	Al/ $\text{Fe}_2\text{O}_3(\text{p})$	2.8

**Table 1.** The composition and content of composite propellant.

### 2.4. Samples characterization

The physical phase, composition, morphology, and structure of materials were characterized by SEM-EDS, TEM, XRD, and FT-IR. X-ray diffractograms were recorded on a D/MAX-3C (Japan) instrument using  $\text{Cu K}\alpha_1$  radiation ( $\lambda = 0.15406 \text{ nm}$ ) at 40-kV voltage and a 40-mA current ranging from  $10^\circ$  to  $80^\circ$ . SEM observations were carried out on a Quanta 400 FE-SEM (FEI Co., USA) at an acceleration voltage of 30 kV. EDS was measured using an INCAIE350 testing device from OXFORD Instruments INC (UK) with a discharge voltage of 4–10 kV and a distance of exactly 1 mm between the electrodes. The morphology and size of as-obtained products were investigated with a transmission electron microscope and high-resolution TEM on a Libra 200FE (Carl Zeiss SMT Pte Ltd., Germany). The sample structure and composition were characterized using Bruker Tensor 27 infrared spectrometer.

The specific surface area was determined with Brunauer-Emmett-Teller (BET) Procedure (Autosorb-1C-TCD, American Quantachrome Instruments).

The thermal behavior of the samples was investigated using DSC (Q2000, TA Co.) at a heating rate of  $10^\circ\text{C min}^{-1}$  from room temperature to  $300^\circ\text{C}$  in an  $\text{N}_2$  atmosphere at a flow rate of  $50 \text{ mL min}^{-1}$  under ambient atmospheric pressure. To explore the reaction mechanism of the intense exothermic decomposition processes of NC and  $\text{Fe}_2\text{O}_3\text{-NC}$  and to obtain the corresponding kinetic parameters (apparent activation energy ( $E_a/\text{kJ mol}^{-1}$ ), pre-exponential constant ( $A/\text{s}^{-1}$ )) and the most probable kinetic model function, the DSC curves at the heating rates of  $5.0$ ,  $10.0$ ,  $15.0$ ,  $20.0$ ,  $25.0$ , and  $30.0^\circ\text{C min}^{-1}$  were dealt by mathematic means.

The thermal decomposition studies of NC and  $\text{Fe}_2\text{O}_3\text{-NC}$  were also performed by the thermogravimetry (Netzsch STA409) with Fourier transform infrared (Bruker V70) analysis technique under nitrogen environment at the heating rate of  $10^\circ\text{C min}^{-1}$ .

The thermal behavior of the prepared thermites was carried out on a TA Instrument (Q600) device with a 10°C min<sup>-1</sup> heating rate, using N<sub>2</sub> with a flow rate of 100 mL min<sup>-1</sup>.

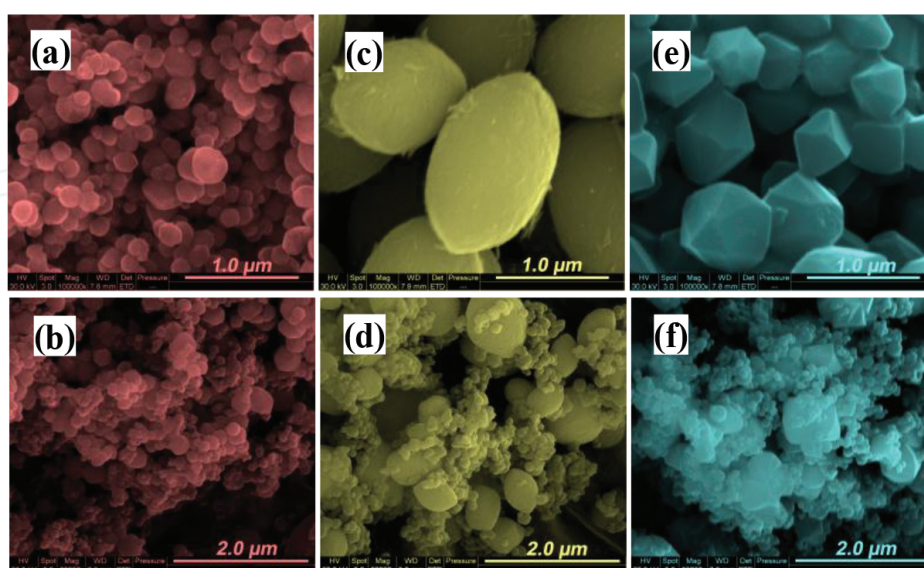
Burning parameters of AP/HTPB propellant including the rate and the pressure exponent were obtained by acoustic emission method by the AE/BX-2006 multifunction system [29].

### 3. Structure characterization

#### 3.1. Morphological characterization

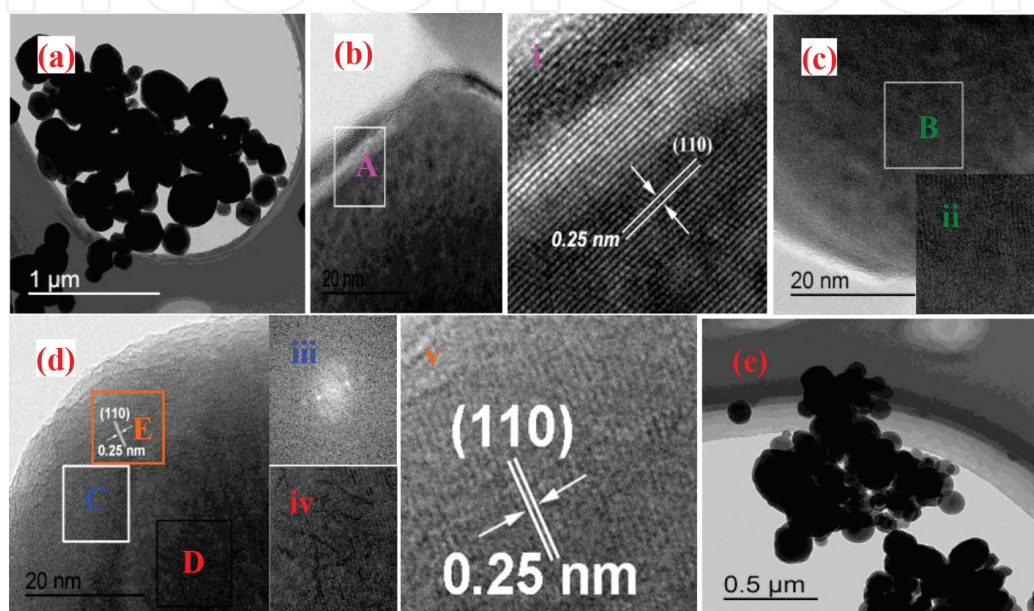
The microstructure characterizations of the Fe<sub>2</sub>O<sub>3</sub> particles and Al/Fe<sub>2</sub>O<sub>3</sub> thermites are determined by analytical SEM as well as TEM.

**Figure 1** shows the SEM images of the granular, oval, and polyhedral Fe<sub>2</sub>O<sub>3</sub> particles and the corresponding Al/Fe<sub>2</sub>O<sub>3</sub> thermite. From **Figure 1(a)**, it can be found that Fe<sub>2</sub>O<sub>3</sub>(H) particles are granular in shape with a relatively small size (average 200 nm) and seem somewhat aggregated. Fe<sub>2</sub>O<sub>3</sub>(o) particles (**Figure 1(c)**) have an oval shape and a rough surface morphology due to the adhesion of scrap irons. The shape of Fe<sub>2</sub>O<sub>3</sub>(p) (**Figure 1(e)**) particles is polyhedral, which is quite different from the other two samples. A closer examination of the SEM images indicates that Fe<sub>2</sub>O<sub>3</sub>(p) particles are not very uniform in size, agglomerated, and have larger surface-area-to-volume (S/V) ratio than that of Fe<sub>2</sub>O<sub>3</sub>(o) particles. **Figure 1(b)**, **(d)**, and **(f)** show the SEM images of Al/Fe<sub>2</sub>O<sub>3</sub>(H), Al/Fe<sub>2</sub>O<sub>3</sub>(o), and Al/Fe<sub>2</sub>O<sub>3</sub>(p), respectively. Some degree of aggregation can be found in the three thermite systems. Also, there seems to be favorable interfacial between Al and Fe<sub>2</sub>O<sub>3</sub> particles.



**Figure 1.** SEM images of Fe<sub>2</sub>O<sub>3</sub> (×100,000 magnification) and thermites Al/Fe<sub>2</sub>O<sub>3</sub> (×60,000 magnification). (a) Fe<sub>2</sub>O<sub>3</sub>(H), (b) Al/Fe<sub>2</sub>O<sub>3</sub>(H), (c) Fe<sub>2</sub>O<sub>3</sub>(o), (d) Al/Fe<sub>2</sub>O<sub>3</sub>(o), (e) Fe<sub>2</sub>O<sub>3</sub>(p), and (f) Al/Fe<sub>2</sub>O<sub>3</sub>(p).

Investigations of the low-magnification TEM image (**Figure 2(b)**) of  $\text{Fe}_2\text{O}_3(\text{H})$  nanoparticles indicate that most of the particles have an irregular sphere geometrical structure, and usually possess rough surfaces. Typical HRTEM images of the small part of  $\text{Fe}_2\text{O}_3(\text{H})$  nanoparticles were obtained and are shown in **Figure 2(b)**, (c), and (d). Just one set of clear lattice fringes with the interplanar distance of 0.25 nm could be seen in **Figure 2(b)**, (d), inset (i), and (v), which can be indexed to the (110) plane of rhombohedral  $\text{Fe}_2\text{O}_3(\text{H})$  structure. Excellent crystallinity is also confirmed by corresponding fast Fourier-transform (FFT) transformation (inset in **Figure 2(iii)**).

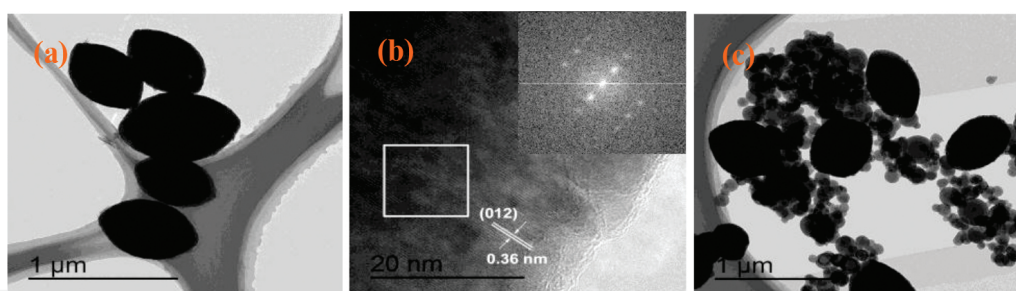


**Figure 2.** (a) and (e) show TEM images of  $\text{Fe}_2\text{O}_3(\text{H})$  and  $\text{Al}/\text{Fe}_2\text{O}_3(\text{H})$ , respectively; (b, c, d) HRTEM images of  $\text{Fe}_2\text{O}_3(\text{H})$  nanoparticles. Insets i and v are the high-resolution images of  $\text{Fe}_2\text{O}_3(\text{H})$  nanoparticles, insets ii and iv show a high-resolution image of  $\text{Fe}_2\text{O}_3(\text{H})$  nanoparticles containing stacking faults and dislocation tangles/networks on the surface, respectively, and inset iii shows the corresponding fast Fourier-transform (FFT) pattern of  $\text{Fe}_2\text{O}_3(\text{H})$  nanoparticles.

Particles containing a certain extent of lattice defects such as dislocation and stacking fault caused by the high pressure, temperature, and concentration through the hydrothermal treatment have also been found. **Figure 2(c)** gives an example of a series of diagonal and straight-stacking faults within a particle throughout most of the surface. It can be seen more clearly in an enlargement of a local region (inset ii). **Figure 2(d)**, the area “D” marked black pane and the corresponding inset (iv), shows a high-resolution image of the  $\text{Fe}_2\text{O}_3(\text{H})$  nanoparticles containing dislocation tangles/networks on the surface. These linear and plane defects mentioned above have profound effects on the growth and property of the  $\text{Fe}_2\text{O}_3(\text{H})$  nanoparticles [31, 32].

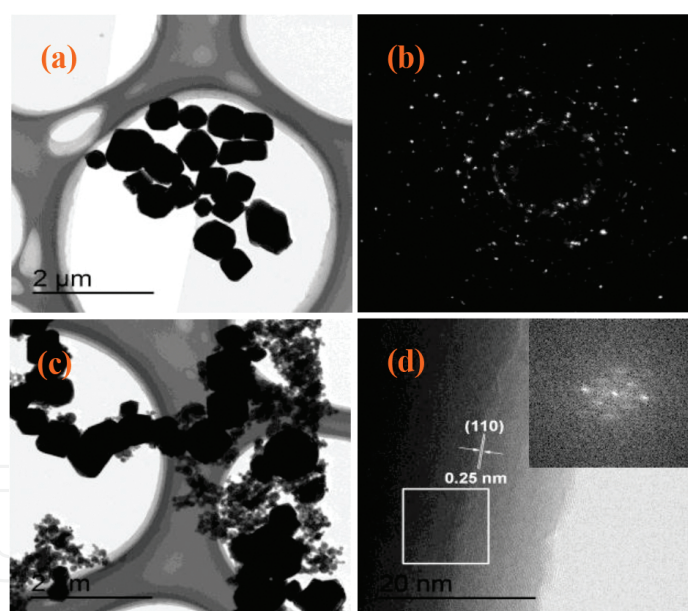
**Figure 3** shows the oval  $\text{Fe}_2\text{O}_3(\text{o})$  particles with the length-to-diameter ratio (L/D ratio) of 1.47–1.59. From **Figure 4(b)**, it is really easy to find out the rough surface of  $\text{Fe}_2\text{O}_3(\text{o})$  particle, which is consistent with the SEM measurement. In the TEM image of  $\text{Al}/\text{Fe}_2\text{O}_3(\text{o})$  thermites, the small spherical Al nanoparticles stick together, and also with the  $\text{Fe}_2\text{O}_3(\text{o})$  particles.





**Figure 3.** (a) and (c) show TEM images of Fe<sub>2</sub>O<sub>3</sub>(o) and Al/Fe<sub>2</sub>O<sub>3</sub>(o), respectively; (b) HRTEM image of Fe<sub>2</sub>O<sub>3</sub>(o) and the corresponding fast FFT pattern (inset).

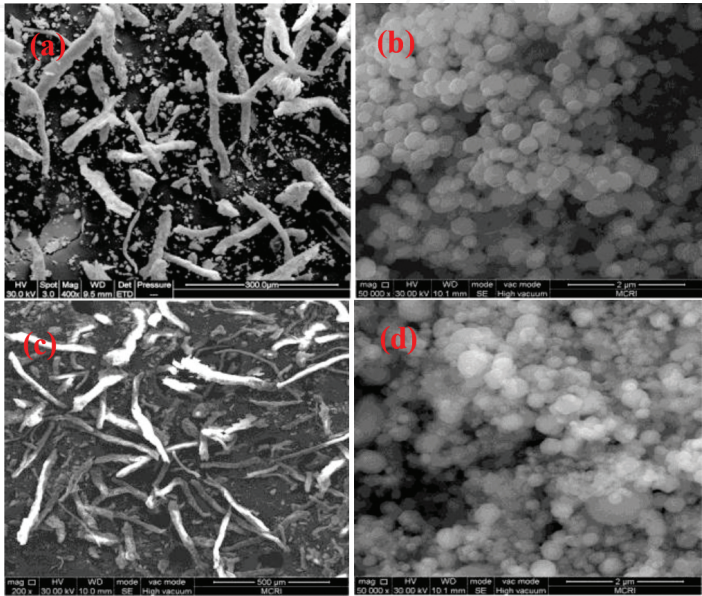
**Figure 4(a)** and **(c)** show the TEM images of the Fe<sub>2</sub>O<sub>3</sub>(p) and Al/Fe<sub>2</sub>O<sub>3</sub>(p), respectively. It is obvious to see that almost all of the Fe<sub>2</sub>O<sub>3</sub>(p) particles are polyhedral in shape, which adhere to the Al particles as seen in **Figure 4(c)**. The corresponding selected area electron diffraction (SAED) pattern shown in **Figure 4(b)** indicates that the Fe<sub>2</sub>O<sub>3</sub>(p) particles are single crystals. **Figure 4(d)** shows the fringes with the interplanar distance of 0.25 nm in a typical HRTEM image of a Fe<sub>2</sub>O<sub>3</sub>(p) particle, which agree well with the (110) lattice spacing of the rhombohedral hematite.



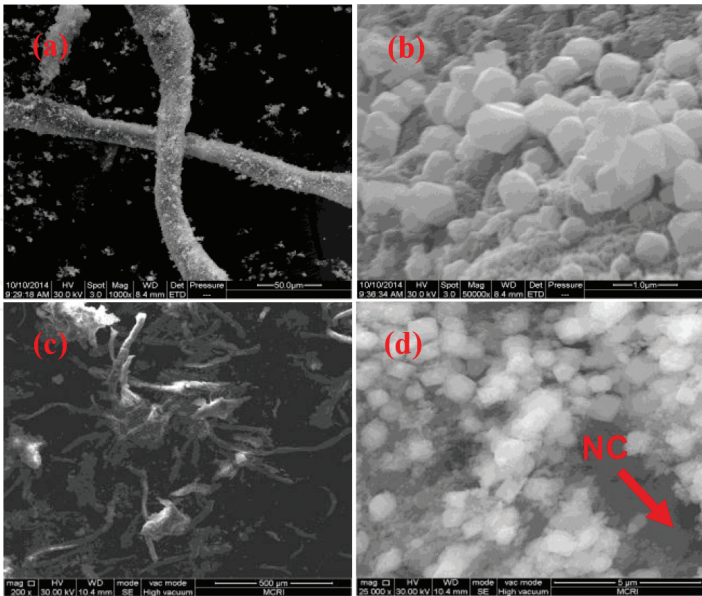
**Figure 4.** (a) and (c) show TEM images of Fe<sub>2</sub>O<sub>3</sub>(p) and Al/Fe<sub>2</sub>O<sub>3</sub>(p), respectively, (b) Selected area electron diffraction (SAED) pattern of Fe<sub>2</sub>O<sub>3</sub>(p) and (d) HRTEM image of Fe<sub>2</sub>O<sub>3</sub>(p) and the corresponding fast FFT pattern (inset).

**Figures 5–7** show the SEM images of Fe<sub>2</sub>O<sub>3</sub>(H), Fe<sub>2</sub>O<sub>3</sub>(p), Fe<sub>2</sub>O<sub>3</sub>(o), and the corresponding Al/Fe<sub>2</sub>O<sub>3</sub>, respectively. Take **Figure 5**, for instance. The SEM observation of Fe<sub>2</sub>O<sub>3</sub>(H)-NC and Al/Fe<sub>2</sub>O<sub>3</sub>(H)-NC in **Figure 5** shows that the two composites have rough, irregular surface morphology under low magnification, probably due to the agglomeration of Fe<sub>2</sub>O<sub>3</sub>(H) nanoparticles or Al/Fe<sub>2</sub>O<sub>3</sub>(H). From **Figure 5(a)** and **(c)**, it can be found that the vast majority

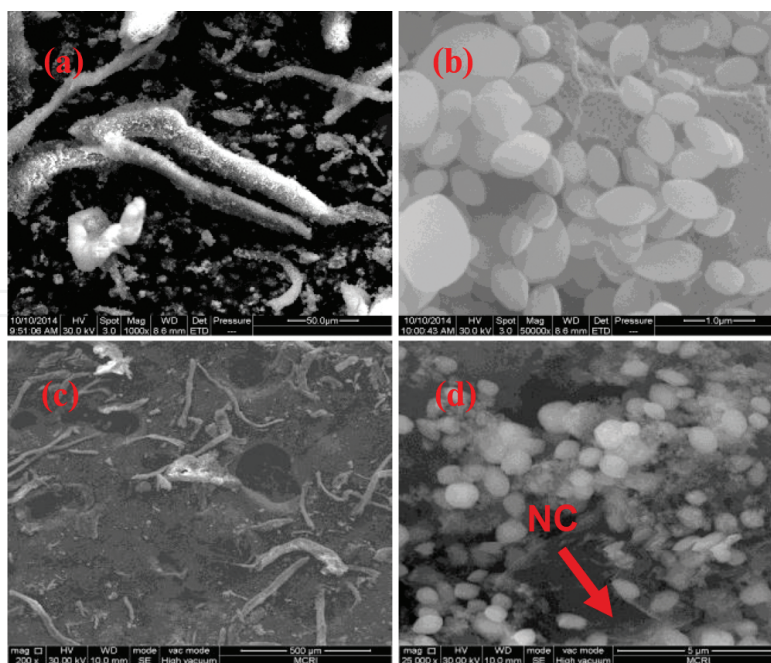
of  $\text{Fe}_2\text{O}_3(\text{H})$  particles or  $\text{Al}/\text{Fe}_2\text{O}_3(\text{H})$  adhered on the surfaces of NC short fibers. Also, some small  $\text{Fe}_2\text{O}_3(\text{H})$  (or  $\text{Al}/\text{Fe}_2\text{O}_3(\text{H})$ ) agglomeration and NC fragments can be observed. The enlargement of a local region on the surface of  $\text{Fe}_2\text{O}_3\text{-NC}$  and  $\text{Al}/\text{Fe}_2\text{O}_3(\text{H})\text{-NC}$  in **Figure 2(b)** and **(d)** indicates that the mechanical-grinding treatment has not changed the basic shape and particle size of  $\text{Fe}_2\text{O}_3$  and Al.



**Figure 5.** SEM images of  $\text{Fe}_2\text{O}_3(\text{H})\text{-NC}$  and  $\text{Al}/\text{Fe}_2\text{O}_3(\text{H})\text{-NC}$ . (a)  $\text{Fe}_2\text{O}_3(\text{H})\text{-NC}$  ( $\times 400$  magnification), (b)  $\text{Fe}_2\text{O}_3(\text{H})\text{-NC}$  ( $\times 50,000$  magnification), (c)  $\text{Al}/\text{Fe}_2\text{O}_3(\text{H})\text{-NC}$  ( $\times 200$  magnification), and (d)  $\text{Al}/\text{Fe}_2\text{O}_3(\text{H})\text{-NC}$  ( $\times 50,000$  magnification).



**Figure 6.** SEM images of  $\text{Fe}_2\text{O}_3(\text{p})\text{-NC}$  and  $\text{Al}/\text{Fe}_2\text{O}_3(\text{p})\text{-NC}$ . (a)  $\text{Fe}_2\text{O}_3(\text{p})\text{-NC}$  ( $\times 1000$  magnification), (b)  $\text{Fe}_2\text{O}_3(\text{p})\text{-NC}$  ( $\times 50,000$  magnification), (c)  $\text{Al}/\text{Fe}_2\text{O}_3(\text{p})\text{-NC}$  ( $\times 200$  magnification), and (d)  $\text{Al}/\text{Fe}_2\text{O}_3(\text{p})\text{-NC}$  ( $\times 25,000$  magnification).



**Figure 7.** SEM images of  $\text{Fe}_2\text{O}_3(\text{o})\text{-NC}$  and  $\text{Al}/\text{Fe}_2\text{O}_3(\text{o})\text{-NC}$ . (a)  $\text{Fe}_2\text{O}_3(\text{o})\text{-NC}$  ( $\times 1000$  magnification), (b)  $\text{Fe}_2\text{O}_3(\text{o})\text{-NC}$  ( $\times 50,000$  magnification), (c)  $\text{Al}/\text{Fe}_2\text{O}_3(\text{o})\text{-NC}$  ( $\times 200$  magnification), and (d)  $\text{Al}/\text{Fe}_2\text{O}_3(\text{o})\text{-NC}$  ( $\times 25,000$  magnification).

### 3.2. Structure and composition

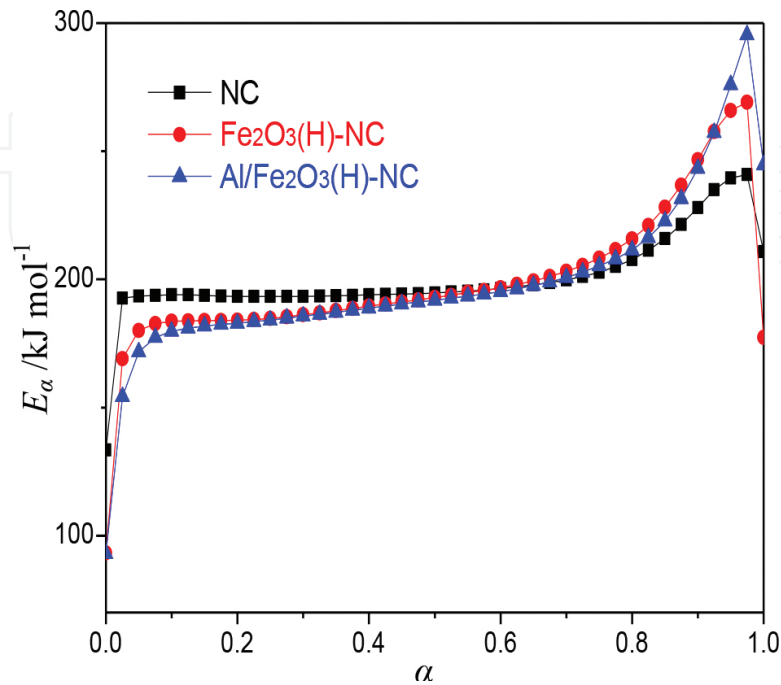
Structure and composition of  $\text{Fe}_2\text{O}_3$  and thermite were characterized using EDS, XRD, and FTIR techniques. The results [29] show that the three prepared iron oxides are  $\text{Fe}_2\text{O}_3$  with a stoichiometric ratio of O:Fe (3:2), because their typical XRD patterns coincided with JCPDS: 33-0664, and the hematite lattice vibration is identified at 480 and 571  $\text{cm}^{-1}$  [33]. The EDS data show that the thermite samples contain Al element. XRD patterns of thermites reveal no reaction between Al (JCPDS: 65-2869) and  $\text{Fe}_2\text{O}_3$ . It can be found that the presence of water peaks in FTIR spectra of thermites, which is a common phenomenon in the nanomaterials [34–38] especially with the presence of Al particles.

### 4. Thermal analysis

To explore the reaction mechanism of the intense exothermic decomposition process of NC,  $\text{Fe}_2\text{O}_3(\text{H})\text{-NC}$ , and  $\text{Al}/\text{Fe}_2\text{O}_3(\text{H})\text{-NC}$  and to obtain the corresponding kinetic parameters (apparent activation energy ( $E_a/\text{kJ mol}^{-1}$ ), pre-exponential constant ( $A/\text{s}^{-1}$ )) and the most probable kinetic model functions, the DSC curves at six heating rates of 5.0, 10.0, 15.0, 20.0, 25.0, and 30.0  $^{\circ}\text{C min}^{-1}$  were dealt by mathematic means, and the temperature data corresponding to the conversion degrees ( $\alpha$ ) were found. The values of  $E_a$  were obtained by Ozawa's method from the iso-conversional DSC curves at the heating rates of 5.0, 10.0, 15.0, 20.0, 25.0, and 30.0  $^{\circ}\text{C min}^{-1}$ , and the  $E_a\text{-}\alpha$  relation is shown in **Figure 8**. From **Figure 8**, one can see that



the activation energy slightly changes in the section of 0.10–0.80 ( $\alpha$ ), and the ranges were selected to calculate the non-isothermal reaction kinetics parameters.



**Figure 8.**  $E_a$  versus  $\alpha$  curve of NC,  $\text{Fe}_2\text{O}_3(\text{H})\text{-NC}$ , and  $\text{Al/Fe}_2\text{O}_3(\text{H})\text{-NC}$  by Flynn-Wall-Ozawa's method.

Six integral methods (MacCallum-Tanner, Šatava-Šesták, Agrawal, general integral, universal integral, and Flynn-Wall-Ozawa) and one differential method (Kissinger) were employed [39–43]. Forty-one types of kinetic model functions and the basic data were put into the integral and differential equations for calculation. The kinetic parameters and the probable kinetic model function were selected by the logical choice method and satisfying the ordinary range of the thermal decomposition kinetic parameters for energetic materials ( $E_a = 80\text{--}250 \text{ kJ mol}^{-1}$ ,  $\log A = 7\text{--}30 \text{ s}^{-1}$ ). These data together with their appropriate values of linear correlation coefficient ( $r$ ), standard mean square deviation ( $Q$ ), and believable factor ( $d$ , where  $d = (1-r)Q$ ) are presented in **Tables 2–4**. The values of  $E_a$  and  $\log A$  obtained from each single non-isothermal DSC curve are in good agreement with the calculated values obtained by Kissinger's method and Ozawa's method. We consider the  $\text{Fe}_2\text{O}_3\text{-NC}$  composites as an example, and conclude that the reaction mechanism of the intense exothermic decomposition process of  $\text{Fe}_2\text{O}_3\text{-NC}$  is classified as Avrami-Erofeev equation  $G(\alpha) = [-\ln(1-\alpha)]^{2/3}$ . Substituting  $f(\alpha)$  with  $3(1-\alpha)[- \ln(1-\alpha)]^{1/3}/2$ ,  $E_a$  with  $192.11 \text{ kJ mol}^{-1}$ , and  $A$  with  $10^{18.54} \text{ s}^{-1}$  in Eq. (1),

$$\frac{d\alpha}{dT} = \frac{A}{\beta} f(\alpha) e^{-E/RT} \quad (1)$$

where  $f(\alpha)$  and  $d\alpha/dT$  are the differential model function and the rate of conversion, respectively.

Method	$\beta/^{\circ}\text{C min}^{-1}$	$E_a/\text{kJ mol}^{-1}$	$\log (A/\text{s}^{-1})$	$r$	$S$	$d$
MacCallum-Tanner	5	207.98	20.55	0.9983	$4.45 \times 10^{-4}$	$7.50 \times 10^{-7}$
	10	205.40	20.25	0.9984	$4.11 \times 10^{-4}$	$6.38 \times 10^{-7}$
	15	209.33	20.68	0.9988	$3.25 \times 10^{-4}$	$3.98 \times 10^{-7}$
	20	209.34	20.67	0.9987	$3.49 \times 10^{-4}$	$4.61 \times 10^{-7}$
	25	211.75	20.91	0.9990	$2.56 \times 10^{-4}$	$2.48 \times 10^{-7}$
	30	210.10	20.76	0.9982	$4.69 \times 10^{-4}$	$8.30 \times 10^{-7}$
Šatava-Šesták	5	204.55	20.23	0.9983	$4.45 \times 10^{-4}$	$7.50 \times 10^{-7}$
	10	202.12	19.94	0.9984	$4.11 \times 10^{-4}$	$6.38 \times 10^{-7}$
	15	205.83	20.35	0.9988	$3.25 \times 10^{-4}$	$3.98 \times 10^{-7}$
	20	205.83	20.33	0.9987	$3.49 \times 10^{-4}$	$4.61 \times 10^{-7}$
	25	208.11	20.56	0.9990	$2.56 \times 10^{-4}$	$2.48 \times 10^{-7}$
	30	206.56	20.42	0.9982	$4.69 \times 10^{-4}$	$8.30 \times 10^{-7}$
Agrawal	5	207.20	20.49	0.9982	$2.37 \times 10^{-3}$	$4.30 \times 10^{-6}$
	10	204.54	20.18	0.9983	$2.19 \times 10^{-3}$	$3.67 \times 10^{-6}$
	15	208.37	20.60	0.9987	$1.73 \times 10^{-3}$	$2.29 \times 10^{-6}$
	20	208.33	20.58	0.9986	$1.86 \times 10^{-3}$	$2.65 \times 10^{-6}$
	25	210.68	20.81	0.9990	$1.36 \times 10^{-3}$	$4.43 \times 10^{-6}$
	30	209.03	20.66	0.9981	$2.49 \times 10^{-3}$	$4.77 \times 10^{-6}$
General integral	5	205.81	18.98	0.9985	$2.36 \times 10^{-3}$	$4.33 \times 10^{-6}$
	10	203.30	18.69	0.9983	$2.18 \times 10^{-3}$	$3.69 \times 10^{-6}$
	15	207.22	19.10	0.9987	$1.72 \times 10^{-3}$	$2.30 \times 10^{-6}$
	20	207.24	19.09	0.9986	$1.85 \times 10^{-3}$	$2.66 \times 10^{-6}$
	25	209.64	19.33	0.9989	$1.36 \times 10^{-3}$	$4.43 \times 10^{-6}$
	30	208.02	19.18	0.9981	$2.48 \times 10^{-3}$	$4.79 \times 10^{-6}$
Universal integral	5	207.20	20.49	0.9982	$2.37 \times 10^{-3}$	$4.30 \times 10^{-6}$
	10	204.54	20.19	0.9983	$2.19 \times 10^{-3}$	$3.67 \times 10^{-6}$
	15	208.37	20.60	0.9987	$1.73 \times 10^{-3}$	$2.29 \times 10^{-6}$
	20	208.33	20.58	0.9986	$1.86 \times 10^{-3}$	$2.65 \times 10^{-6}$
	25	210.68	20.82	0.9990	$1.36 \times 10^{-3}$	$4.43 \times 10^{-6}$
	30	209.03	20.66	0.9981	$2.49 \times 10^{-3}$	$4.77 \times 10^{-6}$
Mean		207.48	20.22			
Flynn-Wall-Ozawa		185.68 ( $E_{eo}$ )		0.9998		
		197.56 ( $E_{po}$ )		0.9979		
Kissinger		199.68 ( $E_K$ )	19.82	0.9977		
Mean ( $E_{eo}$ , $E_{po}$ , $E_K$ )		194.31				

Note:  $E$  with the subscript of eo and po is the apparent activation energy obtained from the onset temperature ( $T_e$ ) and the peak temperature ( $T_p$ ) by Ozawa's method,  $E$  with the subscript of  $K$  is the apparent activation energy obtained from the peak temperature ( $T_p$ ) by Kissinger's method.

**Table 2.** Calculated values of kinetic parameters of decomposition reaction for NC.

Method	$\beta/^{\circ}\text{C min}^{-1}$	$E_a/\text{kJ mol}^{-1}$	$\log(A/\text{s}^{-1})$	$r$	$Q$	$d$
MacCallum-Tanner	5.0	182.76	17.71	0.9888	$4.32 \times 10^{-2}$	$4.82 \times 10^{-4}$
	10.0	190.67	18.63	0.9913	$3.36 \times 10^{-2}$	$2.92 \times 10^{-4}$
	15.0	178.17	17.25	0.9949	$1.97 \times 10^{-2}$	$1.00 \times 10^{-4}$
	20.0	196.93	19.31	0.9934	$2.58 \times 10^{-2}$	$1.72 \times 10^{-4}$
	25.0	203.11	19.97	0.9940	$2.32 \times 10^{-2}$	$1.38 \times 10^{-4}$
	30.0	208.59	20.60	0.9946	$2.08 \times 10^{-2}$	$1.11 \times 10^{-4}$
Šatava-Šesták	5.0	180.74	17.53	0.9888	$4.32 \times 10^{-2}$	$4.82 \times 10^{-4}$
	10.0	188.21	18.40	0.9913	$3.36 \times 10^{-2}$	$2.92 \times 10^{-4}$
	15.0	176.41	17.10	0.9949	$1.97 \times 10^{-2}$	$1.00 \times 10^{-4}$
	20.0	194.12	19.04	0.9934	$2.58 \times 10^{-2}$	$1.72 \times 10^{-4}$
	25.0	199.95	19.67	0.9940	$2.32 \times 10^{-2}$	$1.38 \times 10^{-4}$
	30.0	205.38	20.27	0.9946	$2.08 \times 10^{-2}$	$1.11 \times 10^{-4}$
Agrawal	5.0	182.16	17.69	0.9878	$2.30 \times 10^{-1}$	$2.80 \times 10^{-3}$
	10.0	189.92	18.58	0.9906	$1.79 \times 10^{-1}$	$1.69 \times 10^{-3}$
	15.0	177.45	17.22	0.9944	$1.05 \times 10^{-2}$	$5.88 \times 10^{-4}$
	20.0	196.02	19.24	0.9928	$1.37 \times 10^{-1}$	$9.95 \times 10^{-4}$
	25.0	202.11	19.89	0.9935	$1.23 \times 10^{-1}$	$7.90 \times 10^{-4}$
	30.0	206.79	20.51	0.9942	$1.11 \times 10^{-1}$	$6.44 \times 10^{-4}$
General integral	5.0	180.77	16.22	0.9877	$2.29 \times 10^{-1}$	$2.81 \times 10^{-3}$
	10.0	188.67	17.11	0.9905	$1.78 \times 10^{-1}$	$1.70 \times 10^{-3}$
	15.0	176.27	15.79	0.9944	$1.05 \times 10^{-1}$	$5.87 \times 10^{-4}$
	20.0	194.91	17.78	0.9927	$1.37 \times 10^{-1}$	$9.95 \times 10^{-4}$
	25.0	201.06	18.42	0.9935	$1.23 \times 10^{-1}$	$7.98 \times 10^{-4}$
	30	206.78	19.03	0.9942	$1.10 \times 10^{-1}$	$6.43 \times 10^{-4}$
Universal integral	5.0	182.16	17.69	0.9878	$2.30 \times 10^{-1}$	$2.80 \times 10^{-3}$
	10.0	189.92	18.58	0.9906	$1.79 \times 10^{-1}$	$1.69 \times 10^{-3}$
	15.0	177.45	17.22	0.9944	$1.53 \times 10^{-1}$	$4.88 \times 10^{-4}$
	20.0	196.02	19.24	0.9928	$1.37 \times 10^{-1}$	$9.95 \times 10^{-4}$
	25.0	202.11	19.89	0.9935	$1.23 \times 10^{-1}$	$7.99 \times 10^{-4}$
	30.0	207.79	20.51	0.9942	$1.11 \times 10^{-1}$	$6.44 \times 10^{-4}$
Mean		192.11	18.54			
Flynn-Wall-Ozawa		188.33 ( $E_{\text{po}}$ )		0.9993		
Kissinger		189.98 ( $E_K$ )	18.76	0.9992		
Mean ( $E_{\text{eo}}, E_{\text{po}}, E_K$ )		189.16				

Note:  $E$  with the subscript of eo and po is the apparent activation energy obtained from the onset temperature ( $T_e$ ) and the peak temperature ( $T_p$ ) by Ozawa's method,  $E$  with the subscript of  $K$  is the apparent activation energy obtained from the peak temperature ( $T_p$ ) by Kissinger's method.

**Table 3.** Calculated values of kinetic parameters of decomposition reaction for  $\text{Fe}_2\text{O}_3(\text{H})\text{-NC}$ .

Method	$\beta/^\circ\text{C min}^{-1}$	$E_a/\text{kJ mol}^{-1}$	$\log(A/\text{s}^{-1})$	$r$	$S$	$d$
MacCallum-Tanner	5	174.56	16.81	0.9958	$2.84 \times 10^{-3}$	$1.21 \times 10^{-5}$
	10	178.30	17.27	0.9967	$2.22 \times 10^{-3}$	$7.36 \times 10^{-6}$
	15	185.26	18.04	0.9971	$1.94 \times 10^{-3}$	$5.61 \times 10^{-6}$
	20	183.79	17.87	0.9969	$2.10 \times 10^{-3}$	$6.59 \times 10^{-6}$
	25	207.72	20.50	0.9965	$2.33 \times 10^{-3}$	$8.11 \times 10^{-6}$
	30	195.50	19.15	0.9962	$2.53 \times 10^{-3}$	$9.56 \times 10^{-6}$
Šatava-Šesták	5	173.00	16.67	0.9958	$2.84 \times 10^{-3}$	$1.21 \times 10^{-5}$
	10	176.53	17.11	0.9967	$2.22 \times 10^{-3}$	$7.36 \times 10^{-6}$
	15	183.10	17.84	0.9971	$1.94 \times 10^{-3}$	$5.61 \times 10^{-6}$
	20	181.71	17.68	0.9969	$2.10 \times 10^{-3}$	$6.59 \times 10^{-6}$
	25	204.31	20.18	0.9965	$2.33 \times 10^{-3}$	$8.11 \times 10^{-6}$
	30	192.76	18.89	0.9962	$2.53 \times 10^{-3}$	$9.56 \times 10^{-6}$
Agrawal	5	174.00	16.79	0.9953	$1.51 \times 10^{-2}$	$7.04 \times 10^{-5}$
	10	177.61	17.24	0.9964	$1.18 \times 10^{-2}$	$4.29 \times 10^{-5}$
	15	184.45	17.99	0.9968	$1.03 \times 10^{-2}$	$3.26 \times 10^{-5}$
	20	182.94	17.82	0.9966	$1.12 \times 10^{-2}$	$3.84 \times 10^{-5}$
	25	206.67	20.42	0.9962	$1.24 \times 10^{-2}$	$4.67 \times 10^{-5}$
	30	194.49	19.07	0.9959	$1.34 \times 10^{-2}$	$5.53 \times 10^{-5}$
General integral	5	174.00	16.79	0.9953	$1.51 \times 10^{-2}$	$7.04 \times 10^{-5}$
	10	177.61	17.24	0.9964	$1.18 \times 10^{-2}$	$4.29 \times 10^{-5}$
	15	184.45	17.99	0.9968	$1.03 \times 10^{-2}$	$3.26 \times 10^{-5}$
	20	182.94	17.82	0.9966	$1.12 \times 10^{-2}$	$3.84 \times 10^{-5}$
	25	206.67	20.42	0.9962	$1.24 \times 10^{-2}$	$4.67 \times 10^{-5}$
	30	194.49	19.07	0.9959	$1.34 \times 10^{-2}$	$5.53 \times 10^{-5}$
Universal integral	5	172.64	15.35	0.9953	$1.51 \times 10^{-2}$	$7.09 \times 10^{-5}$
	10	176.39	15.80	0.9963	$1.17 \times 10^{-2}$	$4.31 \times 10^{-5}$
	15	183.32	16.55	0.9968	$1.03 \times 10^{-2}$	$3.27 \times 10^{-5}$
	20	181.88	16.39	0.9965	$1.11 \times 10^{-2}$	$3.85 \times 10^{-5}$
	25	205.65	18.94	0.9962	$1.23 \times 10^{-2}$	$4.68 \times 10^{-5}$
	30	193.52	17.63	0.9959	$1.34 \times 10^{-2}$	$5.53 \times 10^{-5}$
Mean		186.34	17.91			
Flynn-Wall-Ozawa		172.66( $E_{eo}$ )		0.9941	$4.87 \times 10^{-3}$	
		194.23( $E_{po}$ )		0.9990	$8.60 \times 10^{-4}$	
Kissinger		196.18( $E_K$ )	19.44	0.9989	$4.56 \times 10^{-3}$	
Mean( $E_{eo}$ , $E_{po}$ , $E_K$ )		187.69				

Note:  $E$  with the subscript of  $eo$  and  $po$  is the apparent activation energy obtained from the onset temperature ( $T_e$ ) and the peak temperature ( $T_p$ ) by Ozawa's method,  $E$  with the subscript of  $K$  is the apparent activation energy obtained from the peak temperature ( $T_p$ ) by Kissinger's method.

**Table 4.** Calculated values of kinetic parameters of decomposition reaction for Al/Fe<sub>2</sub>O<sub>3</sub>(H)-NC.

The kinetic equation of the exothermic decomposition reaction may be described as

$$\frac{d\alpha}{dT} = \frac{10^{18.71}}{\beta} (1-\alpha) [-\ln(1-\alpha)]^{1/3} \exp\left(-2.31 \times 10^4 / T\right) \quad (2)$$

The values ( $T_{e0}$  and  $T_{p0}$ ) of the onset temperature ( $T_e$ ) and peak temperature ( $T_p$ ) corresponding to  $\beta \rightarrow 0$  were obtained by Eq. (3), and the self-accelerating decomposition temperature ( $T_{\text{SADT}}$ ) was obtained by Eq. (5) [39–43]. The values ( $T_{\text{SADT}}$  and  $T_{p0}$ ) are 182.03 and 194.10°C, respectively.

$$T_{e(\text{or } p)} = T_{e0(\text{or } p)} + a\beta_i + b\beta_i^2 + c\beta_i^3 \quad i=1-4 \quad (3)$$

where  $a$ ,  $b$ , and  $c$  are coefficients.

$$T_{\text{SADT}} = T_{e0} \quad (4)$$

The thermal ignition temperature ( $T_{\text{be0}}$  or  $T_{\text{TIT}}$ ) was obtained by substituting  $E_{e0}$  and  $T_{e0}$  into the equation of Zhang et al. (Eq. (5)) [44], and the critical temperatures of thermal explosion ( $T_{\text{bp0}}$  or  $T_b$ ) were obtained by substituting  $E_{p0}$  and  $T_{p0}$  in Eq. (5). The values ( $T_{\text{TIT}}$  and  $T_b$ ) are 191.44 and 204.16°C, respectively,

$$T_{\text{be0}(\text{or } \text{bp0})} = \frac{E_0 - \sqrt{E_0^2 - 4E_0RT_{e0(\text{or } p0)}}}{2R} \quad (5)$$

The thermal behaviors of NC are also analyzed with the same method using the data in **Figure 8**. The results show that the reaction mechanism of the intense exothermic decomposition process of them is classified as reaction order  $f(\alpha) = 3(1-\alpha)[- \ln(1-\alpha)]^{1/3}/2$ ,  $G(a) = [- \ln(1-\alpha)]^{2/3}$ . The DSC curves of  $\text{Fe}_2\text{O}_3(\text{p})$ -NC,  $\text{Al}/\text{Fe}_2\text{O}_3(\text{p})$ -NC,  $\text{Fe}_2\text{O}_3(\text{o})$ -NC, and  $\text{Al}/\text{Fe}_2\text{O}_3(\text{o})$ -NC at a heating rate of  $10^\circ\text{C min}^{-1}$  are listed in Figures S1 and S3 (Supplementary data), respectively. The  $E_a$ - $\alpha$  relations of  $\text{Fe}_2\text{O}_3(\text{p})$ -NC,  $\text{Al}/\text{Fe}_2\text{O}_3(\text{p})$ -NC,  $\text{Fe}_2\text{O}_3(\text{o})$ -NC, and  $\text{Al}/\text{Fe}_2\text{O}_3(\text{o})$ -NC are shown in Figures S2 and S4 (Supplementary data). **Table 5** and the supplementary data (Tables S1–S4) show the calculated values of kinetic parameters of decomposition reaction for NC,  $\text{Fe}_2\text{O}_3(\text{H})$ -NC,  $\text{Al}/\text{Fe}_2\text{O}_3(\text{H})$ -NC,  $\text{Fe}_2\text{O}_3(\text{p})$ -NC,  $\text{Al}/\text{Fe}_2\text{O}_3(\text{p})$ -NC,  $\text{Fe}_2\text{O}_3(\text{o})$ -NC, and  $\text{Al}/\text{Fe}_2\text{O}_3(\text{o})$ -NC. From **Table 5**, it can be found that (1) the  $E_a$  values of NC-based composites containing  $\text{Fe}_2\text{O}_3$  and  $\text{Al}/\text{Fe}_2\text{O}_3$  are less than that of NC; (2) the  $E_a$  value of NC-based composites containing  $\text{Al}/\text{Fe}_2\text{O}_3$  is less than that of NC-based composites containing the corresponding  $\text{Fe}_2\text{O}_3$ ; (3) among the three  $\text{Fe}_2\text{O}_3$  particles,  $\text{Fe}_2\text{O}_3(\text{H})$  is the best catalyst because  $E_a$  of  $\text{Fe}_2\text{O}_3(\text{H})$ -NC is the lowest; (4) the  $E_a$  value of  $\text{Al}/\text{Fe}_2\text{O}_3(\text{o})$ -NC is 0.16 and 5.57  $\text{kJ mol}^{-1}$  lower than that of  $\text{Al}/\text{Fe}_2\text{O}_3(\text{H})$ -NC and  $\text{Al}/\text{Fe}_2\text{O}_3(\text{p})$ -NC, respectively, but the thermal ignition temperature and the critical temperature of thermal explosion of  $\text{Al}/\text{Fe}_2\text{O}_3(\text{o})$ -NC are so high. Therefore, the

prepared Fe<sub>2</sub>O<sub>3</sub>(H) and Al/Fe<sub>2</sub>O<sub>3</sub>(H) are the two kinds of promising catalysts developed in accelerating the decomposition rate or the process of NC.

Sample	$E_a/\text{kJ mol}^{-1}$	$\log(A/\text{s}^{-1})$	$T_{e0}/^\circ\text{C}$	$T_{p0}/^\circ\text{C}$	$T_{be0}/^\circ\text{C}$	$T_{bp0}/^\circ\text{C}$	$\Delta S^\circ/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta G^\circ/\text{kJ}\cdot\text{mol}^{-1}$
NC	207.48	20.22	181.76	197.00	191.42	206.69	138.40	199.68	134.61
Fe <sub>2</sub> O <sub>3</sub> (H)-NC	192.11	18.54	182.03	194.10	191.44	204.16	106.21	189.98	140.35
Al/Fe <sub>2</sub> O <sub>3</sub> (H)-NC	186.34	17.91	175.57	190.02	185.71	199.59	94.31	196.18	152.46
Fe <sub>2</sub> O <sub>3</sub> (p)-NC	200.67	19.45	176.38	196.42	185.53	206.82	123.72	185.65	127.56
Al/Fe <sub>2</sub> O <sub>3</sub> (p)-NC	191.75	18.51	180.29	195.55	190.25	205.52	106.31	185.39	135.56
Fe <sub>2</sub> O <sub>3</sub> (o)-NC	202.69	19.68	178.87	187.64	187.93	197.14	128.29	195.50	136.39
Al/Fe <sub>2</sub> O <sub>3</sub> (o)-NC	186.18	17.87	179.82	191.87	189.39	201.97	93.50	187.43	143.95

**Table 5.** Calculated values of kinetic parameters of decomposition reaction for NC, Fe<sub>2</sub>O<sub>3</sub>(H)-NC, Al/Fe<sub>2</sub>O<sub>3</sub>(H)-NC, Fe<sub>2</sub>O<sub>3</sub>(p)-NC, Al/Fe<sub>2</sub>O<sub>3</sub>(p)-NC, Fe<sub>2</sub>O<sub>3</sub>(o)-NC, and Al/Fe<sub>2</sub>O<sub>3</sub>(o)-NC.

By thermal analysis, the addition of Fe<sub>2</sub>O<sub>3</sub>(H) and Al/Fe<sub>2</sub>O<sub>3</sub>(H) did not change the kinetic model function of NC, reduced the value of  $E_a$ , and the critical temperature of thermal explosion, thus Fe<sub>2</sub>O<sub>3</sub>(H) nanoparticles and Al/Fe<sub>2</sub>O<sub>3</sub>(H) thermites could accelerate the decomposition rate or process of NC. Furthermore, the effects of Fe<sub>2</sub>O<sub>3</sub>(H) nanoparticles and Al/Fe<sub>2</sub>O<sub>3</sub>(H) on the thermal decomposition of NC have been investigated by the thermogravimetry with Fourier transform infrared analysis (TG-IR).

The TG-IR-hyphenated technique is a highly preferred approach for investigating the thermal degradation of energetic materials. The TG-thermogravimetric derivative (TG-DTG) curves of NC, Fe<sub>2</sub>O<sub>3</sub>(H)-NC, and Al/Fe<sub>2</sub>O<sub>3</sub>(H)-NC at a heating rate of 10°C/min are presented in **Figure 9**. Just one stage of the total mass loss can be found from the decomposition processes of NC, Fe<sub>2</sub>O<sub>3</sub>(H)-NC, and Al/Fe<sub>2</sub>O<sub>3</sub>(H)-NC. The total weight loss of NC is 68.41%, while that of Fe<sub>2</sub>O<sub>3</sub>(H)-NC and Al/Fe<sub>2</sub>O<sub>3</sub>(H)-NC are about 34.77 and 31.12%, respectively, which is lower than that of NC due to the remaining Fe<sub>2</sub>O<sub>3</sub> and some residues.

A series of temperature values of typical points including the initial decomposition temperature ( $T_i$ ), the extrapolated onset temperature ( $T_e$ ), the peak temperature ( $T_L$ ), the extrapolated end temperature ( $T_c$ ), and the final temperature ( $T_f$ ) deserve special attention. Compared with the degradation process of NC, these typical temperature values of Fe<sub>2</sub>O<sub>3</sub>(H)-NC and Al/Fe<sub>2</sub>O<sub>3</sub>(H)-NC obviously are reduced under the influence of Fe<sub>2</sub>O<sub>3</sub>(H) nanoparticles and Al/Fe<sub>2</sub>O<sub>3</sub>(H) as seen in **Figure 9(b)** and **(c)**. The peak temperatures of NC, Fe<sub>2</sub>O<sub>3</sub>(H)-NC, and Al/Fe<sub>2</sub>O<sub>3</sub>(H)-NC are 209.43, 208.59, and 210.24°C, respectively.

The apparent variation of IR characteristic absorption peaks of the gaseous decomposition products of NC, Fe<sub>2</sub>O<sub>3</sub>(H)-NC, and Al/Fe<sub>2</sub>O<sub>3</sub>(H)-NC corresponding to the thermal decomposition process at the typical temperature points ( $T_i$ ,  $T_e$ ,  $T_L$ ,  $T_c$ , and  $T_f$ ) is shown in **Figure 10** and **Table 6**. It can be found that the gaseous products detected include CO, NO<sub>2</sub>, NO, N<sub>2</sub>O, HCHO,



and HCOOH during the decomposition process of NC with and without the Fe<sub>2</sub>O<sub>3</sub>(H) nanoparticles or Al/Fe<sub>2</sub>O<sub>3</sub>(H).

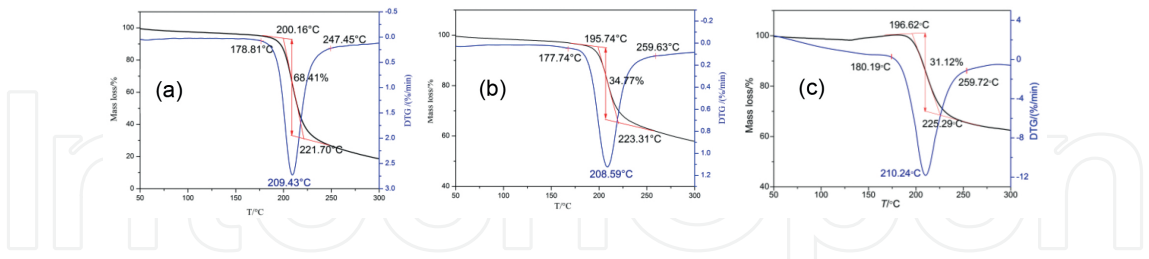


Figure 9. TG-DTG curves of NC (a), Fe<sub>2</sub>O<sub>3</sub>(H)-NC (b), and Al/Fe<sub>2</sub>O<sub>3</sub>(H)-NC (c).

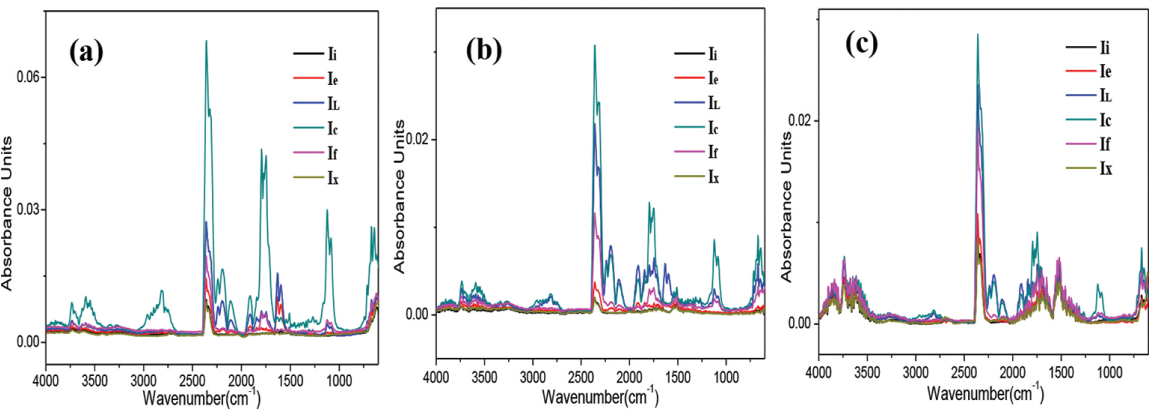


Figure 10. IR spectra of the gases evolved from the degradation of NC (a), Fe<sub>2</sub>O<sub>3</sub>(H)-NC (b), and Al/Fe<sub>2</sub>O<sub>3</sub>(H)-NC (c).

NC		Fe <sub>2</sub> O <sub>3</sub> (H)-NC		Al/Fe <sub>2</sub> O <sub>3</sub> (H)-NC	
T/°C	Gaseous products	T/°C	Gaseous products	T/°C	Gaseous products
164.92 (T <sub>x</sub> )	H <sub>2</sub> O, CO <sub>2</sub>	160.47 (T <sub>x1</sub> )	H <sub>2</sub> O, CO <sub>2</sub> , NO <sub>2</sub>	164.40 (T <sub>x2</sub> )	H <sub>2</sub> O, CO <sub>2</sub> , NO <sub>2</sub> , NO
178.81 (T <sub>i</sub> )	H <sub>2</sub> O, CO <sub>2</sub> , NO <sub>2</sub>	177.74 (T <sub>i1</sub> )	H <sub>2</sub> O, CO <sub>2</sub> , NO <sub>2</sub>	180.19 (T <sub>i2</sub> )	H <sub>2</sub> O, CO <sub>2</sub> , NO <sub>2</sub> , NO
200.16 (T <sub>e</sub> )	H <sub>2</sub> O, CO <sub>2</sub> , NO <sub>2</sub> , NO	195.74 (T <sub>e</sub> )	H <sub>2</sub> O, CO <sub>2</sub> , NO <sub>2</sub> , NO	196.76 (T <sub>e</sub> )	H <sub>2</sub> O, CO <sub>2</sub> , NO <sub>2</sub> , NO
209.43 (T <sub>i</sub> )	H <sub>2</sub> O, CO <sub>2</sub> , NO <sub>2</sub> , NO, N <sub>2</sub> O, HCHO, HCOOH	208.59 (T <sub>i</sub> )	H <sub>2</sub> O, CO <sub>2</sub> , CO, NO <sub>2</sub> , NO, N <sub>2</sub> O, HCHO, HCOOH	210.24 (T <sub>i</sub> )	H <sub>2</sub> O, CO <sub>2</sub> , CO, NO <sub>2</sub> , NO, N <sub>2</sub> O, HCHO, HCOOH
221.70 (T <sub>c</sub> )	H <sub>2</sub> O, CO <sub>2</sub> , CO, NO <sub>2</sub> , NO, HCHO, HCOOH	223.31 (T <sub>c</sub> )	H <sub>2</sub> O, CO <sub>2</sub> , CO, NO <sub>2</sub> , NO, N <sub>2</sub> O, HCHO, HCOOH	225.47 (T <sub>c</sub> )	H <sub>2</sub> O, CO <sub>2</sub> , CO, NO <sub>2</sub> , NO, N <sub>2</sub> O, HCOOH
247.45 (T <sub>f</sub> )	H <sub>2</sub> O, CO <sub>2</sub> , NO	259.63 (T <sub>f</sub> )	H <sub>2</sub> O, CO <sub>2</sub> , CO, NO, HCOOH	259.72 (T <sub>f</sub> )	H <sub>2</sub> O, CO <sub>2</sub> , NO <sub>2</sub> , NO

Note: T<sub>x</sub>, some temperature below the initial decomposition temperature; T<sub>x1</sub>(T<sub>x2</sub>), some temperature below T<sub>i1</sub>(T<sub>i2</sub>); T<sub>i</sub>, the initial decomposition temperature; T<sub>i1</sub>, the initial decomposition temperature of the obvious exothermic peak of Fe<sub>2</sub>O<sub>3</sub>(H)-NC; T<sub>i2</sub>, the initial decomposition temperature of the obvious exothermic peak of Al/Fe<sub>2</sub>O<sub>3</sub>(H)-NC; T<sub>e</sub>, the extrapolated onset temperature; T<sub>c</sub>, the peak temperature; T<sub>f</sub>, the extrapolated end temperature; T<sub>f</sub>, the final temperature.

Table 6. Gaseous products generated during the decomposition processes of NC, Fe<sub>2</sub>O<sub>3</sub>(H)-NC, and Al/Fe<sub>2</sub>O<sub>3</sub>(H)-NC at different temperatures.

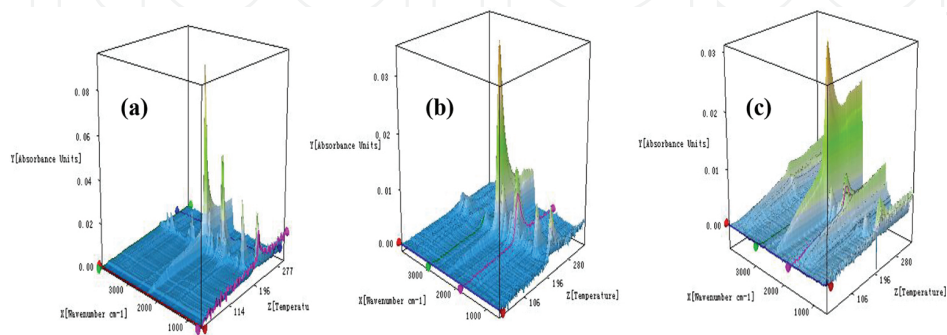
**Table 6** lists the gaseous products generated during the decomposition processes of NC, Fe<sub>2</sub>O<sub>3</sub>(H)-NC, and Al/Fe<sub>2</sub>O<sub>3</sub>(H)-NC at the typical temperature points. At the initial decomposition temperature ( $T_i$ ), the IR absorption peaks of H<sub>2</sub>O (3600–3740 cm<sup>-1</sup>), CO<sub>2</sub> (2360, 670 cm<sup>-1</sup>), and NO<sub>2</sub> (1593–1635 cm<sup>-1</sup>) [45, 46] are easily identifiable (**Figure 10(a, I<sub>i</sub>)** and (b, I<sub>i</sub>)). During the whole testing process, the existence of H<sub>2</sub>O and CO<sub>2</sub> from the ambience is the outside disruptive factor, which cannot be ignored. In order to prove that H<sub>2</sub>O and CO<sub>2</sub> gas detected at 178.81°C are not the products of NC decomposition, the variation of IR absorption peaks at 164.92°C is obtained, which is shown in **Figure 10(a, I<sub>x</sub>)**. The TG-DTG curves of NC in **Figure 9(a)** show that the decomposition of NC has not occurred at 164.92°C and begins from 178.81°C. By comparing the curves  $I_x$  (164.92°C) and  $I_i$  (178.81°C) in **Figure 10(a)**, the bands at 3600–3740 cm<sup>-1</sup> are assigned to O-H-bonding-stretching vibrational modes for water as an impurity because of the extremely similar absorptive intensities. Apart from the impurity peaks of H<sub>2</sub>O, it can be concluded that CO<sub>2</sub> gas is not the initial degradation product because the intensities of the detected CO<sub>2</sub> gas are basically unchanged at both 164.92 and 178.81°C shown in **Figure 10(a, I<sub>x</sub> and I<sub>i</sub>)**. Furthermore, the noticeable IR bands of NO<sub>2</sub> are found in the region of 1593–1635 cm<sup>-1</sup> at the beginning of the decomposition of NC shown in the curve  $I_i$  (**Figure 10(a)**) [46], which means that the NO<sub>2</sub> gas is an initial degradation product. The above results concur with those of several previous studies [22, 23, 47, 48] in which the O-NO<sub>2</sub> bond is deemed to be the first step leading to the release of NO<sub>2</sub>



The NO<sub>2</sub> stagnates in the polymer skeleton and then reacts with the RO• radical or its degradation products. It is particularly necessary to point out that the signal of NO<sub>2</sub> was present as shown in the IR spectrum in **Figure 10(b, I<sub>x</sub>)** at 160.47°C ( $T_{x1}$ ). The intensities of NO<sub>2</sub> peaks increase with temperature, which is very different from the decomposition of NC. It is a fact that NC could be slowly decomposed as the temperature increases further, which has been enhanced by Fe<sub>2</sub>O<sub>3</sub>(H) nanoparticles due to their catalysis. That is, the Fe<sub>2</sub>O<sub>3</sub>(H) nanoparticles could accelerate the O-NO<sub>2</sub> bond cleavage and the release of NO<sub>2</sub>. For this reason, the absorption peaks of H<sub>2</sub>O and CO<sub>2</sub> exist not only from the environment but also from the degradation of Fe<sub>2</sub>O<sub>3</sub>(H)-NC at 160.47°C ( $T_{x1}$ ). Moreover, both NO<sub>2</sub> and NO are detected besides the H<sub>2</sub>O and CO<sub>2</sub> gases, which indicates that Al/Fe<sub>2</sub>O<sub>3</sub>(H) can make NC decompose faster than Fe<sub>2</sub>O<sub>3</sub>(H) does.

**Figure 11** shows the 3D-IR spectra of gas products of NC, Fe<sub>2</sub>O<sub>3</sub>(H)-NC, and Al/Fe<sub>2</sub>O<sub>3</sub>(H)-NC at a heating rate of 10°C min<sup>-1</sup>. At the initial decomposition temperature, the IR absorption peaks of H<sub>2</sub>O (3600–3740 cm<sup>-1</sup>), CO<sub>2</sub> (2360, 670 cm<sup>-1</sup>), and NO<sub>2</sub> (1593–1635 cm<sup>-1</sup>) [46, 47] are easily identifiable (**Figure 11**). With the progress of the thermal decomposition process, the gas productions such as NO (1762–1965 cm<sup>-1</sup>), CO (2194 cm<sup>-1</sup>), N<sub>2</sub>O (2241 cm<sup>-1</sup>), HCHO (2814 and 1746 cm<sup>-1</sup>), and HCOOH (1080–1128 cm<sup>-1</sup>) are detected [26, 47]. By comparing the gaseous products generated during the decomposition processes of NC, Fe<sub>2</sub>O<sub>3</sub>(H)-NC, and Al/Fe<sub>2</sub>O<sub>3</sub>(H)-NC at different temperatures, it can be concluded that Fe<sub>2</sub>O<sub>3</sub>(H) and Al/Fe<sub>2</sub>O<sub>3</sub>(H) can accelerate the O-NO<sub>2</sub> bond cleavage and the release of NO<sub>2</sub> gas. The evolution of HCOOH

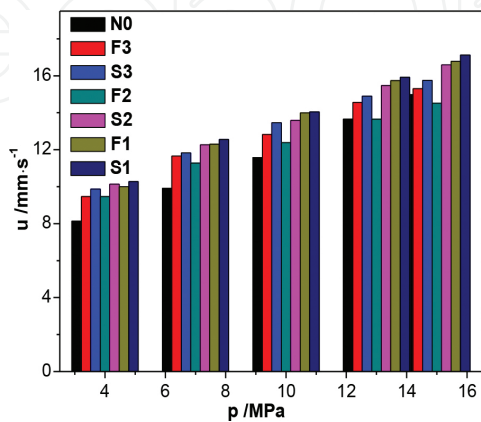
gases is the products of the secondary autocatalytic reactions of NC [24, 26]. From **Figure 11**, the intensities of all these gas products are very strong, which can be taken as an important signal of identifying the faster decomposition rate of  $\text{Fe}_2\text{O}_3(\text{H})\text{-NC}$  and  $\text{Al/Fe}_2\text{O}_3(\text{H})\text{-NC}$  composites than that of NC. One of the reasons for generating quantities of gases is that the condensed phases break down fast with the presence of  $\text{Fe}_2\text{O}_3(\text{H})$  nanoparticles and  $\text{Al/Fe}_2\text{O}_3(\text{H})$ . It has to be pointed out that  $\text{Al/Fe}_2\text{O}_3(\text{H})$  thermite is a better catalyst than  $\text{Fe}_2\text{O}_3(\text{H})$  nanoparticles for reducing the activation energy and accelerating to break the  $\text{O-NO}_2$  bond during the thermal decomposition process of NC.



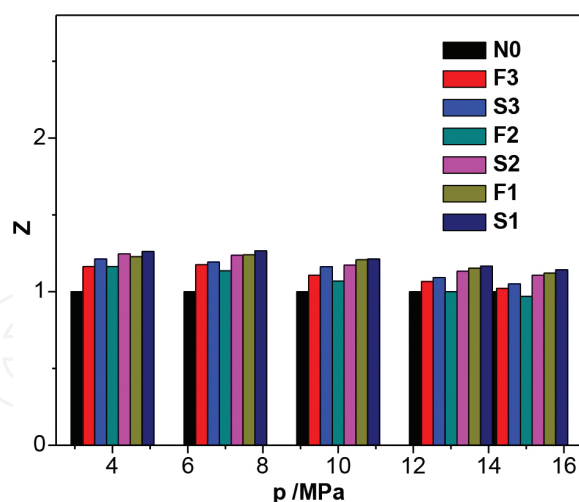
**Figure 11.** 3D-IR spectra of gas products of NC (a),  $\text{Fe}_2\text{O}_3(\text{H})\text{-NC}$  (b), and  $\text{Al/Fe}_2\text{O}_3(\text{H})\text{-NC}$  (c) at a heating rate of  $10^\circ\text{C min}^{-1}$ .

### 5. Combustion catalysts used in AP/HTPB propellants

**Figure 12** shows the burning rate ( $u$ ) versus pressure ( $p$ ) curves of AP/HTPB propellants. Based on the experimental data, the pressure exponent ( $n$ ) can be calculated [29, 49]. The catalytic efficiency is another evaluation index of the combustion catalyst [29], which is shown in **Figure 13**.



**Figure 12.** Burning rate ( $u$ ) versus pressure ( $p$ ) curves of AP/HTPB composite propellants.



**Figure 13.** Efficiency of AP/HTPB composite propellants.

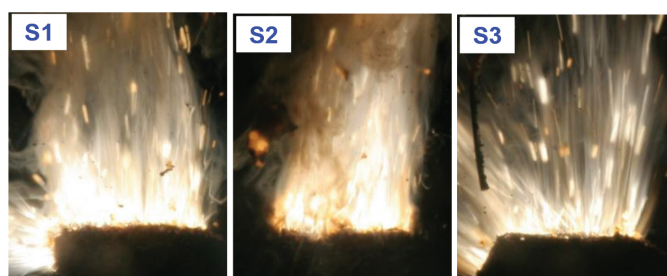
The burning rate of all the formulations increases as the pressure rises within 4–15 MPa. For the formulations containing Fe<sub>2</sub>O<sub>3</sub>, the burning rate is in the order: F2<F3<F1. For the formulations with thermite, that order is S1>S2>S3. The BET-specific surface areas of Fe<sub>2</sub>O<sub>3</sub>(H), Fe<sub>2</sub>O<sub>3</sub>(o), and Fe<sub>2</sub>O<sub>3</sub>(p) are 5.3, 3.1, and 6.9 m<sup>2</sup>/g, respectively. Possibly due to the aggregation of Fe<sub>2</sub>O<sub>3</sub>(H), its specific surface area is smaller than that of Fe<sub>2</sub>O<sub>3</sub>(p), which is opposite to what we expected simply based on the particle size. However, when the particles are dispersed to the formulations, Fe<sub>2</sub>O<sub>3</sub>(H) particles are believed to have a larger surface area than Fe<sub>2</sub>O<sub>3</sub>(p) based on the particle size. Therefore, the superior combustion performance can be ascribed to the dominant role of the surface area of the Fe<sub>2</sub>O<sub>3</sub> particles. From **Figures 12 and 13**, the formulations containing thermites all have better burning rate and combustion-supporting ability than the formulations containing the corresponding Fe<sub>2</sub>O<sub>3</sub>. And thermite with a smaller size of Fe<sub>2</sub>O<sub>3</sub> (H) particles has a higher burning rate.

A good formulation is considered to have a high burning rate with a low pressure exponent. From **Table 7**, it can be found that Fe<sub>2</sub>O<sub>3</sub> can take effect on decreasing the pressure exponent of the propellant. Considering the role of Al nanopowders and the thermite reaction in enhancing the burning rate, thermites Al/Fe<sub>2</sub>O<sub>3</sub> are the better burning rate modifiers in improving the combustion performances of AP/HTPB composite propellants. Overall, the Al/Fe<sub>2</sub>O<sub>3</sub>(H) is the best combustion catalyst.

<i>p</i> /MPa	<i>n</i> <sub>N0</sub>	<i>n</i> <sub>F1</sub>	<i>n</i> <sub>F2</sub>	<i>n</i> <sub>F3</sub>	<i>n</i> <sub>S1</sub>	<i>n</i> <sub>S2</sub>	<i>n</i> <sub>S3</sub>
4–7	0.35	0.37	0.31	0.37	0.36	0.34	0.32
7–10	0.42	0.36	0.26	0.27	0.31	0.29	0.36
10–13	0.63	0.45	0.37	0.48	0.48	0.50	0.39
13–15	0.65	0.45	0.43	0.35	0.51	0.49	0.39

**Table 7.** The burning rate pressure exponent of formulations under different pressure.

Moreover, the combustion wave structures of AP/HTPB composite propellants containing Al/Fe<sub>2</sub>O<sub>3</sub> thermite obtained at 4 MPa are shown in **Figure 14**. The flames of the three compositions (**Figure 14**) are entirely yellowish that is caused by the fuel-rich diffusion flame generated by the decomposed gases of the binder and the AP particles [50]. There is no obvious dark zone, which is different from the double-base propellants. Above the burning surface, both the AP flame and the diffusion flame produced by the decomposed gases exist simultaneously, leading to major heat release of the combustion process. High flame temperature up to 2700 K was generated at the center of the luminous flame as in the case of Al/Fe<sub>2</sub>O<sub>3</sub>(H) catalyst. Thick gray smoke was formed surrounding the yellowish flame of the formulation S2, due to the incomplete burning. When adding Al/Fe<sub>2</sub>O<sub>3</sub>(p) thermite to the AP/HTPB propellants, the front luminous flame of formulation S3 was blown down to the downstream and numerous Fe<sub>2</sub>O<sub>3</sub> and Al particles were ejected from the burning surface. The results of the combustion wave structures and flame temperature characteristics indicate that the Al/Fe<sub>2</sub>O<sub>3</sub>(H)-containing propellant formulation is the best formulation among the tested samples.



**Figure 14.** Combustion wave structures of AP/HTPB composite propellants contain thermites Al/Fe<sub>2</sub>O<sub>3</sub>: (S1) Al/Fe<sub>2</sub>O<sub>3</sub>(H), (S2) Al/Fe<sub>2</sub>O<sub>3</sub>(o), and (S3) Al/Fe<sub>2</sub>O<sub>3</sub>(p).

## 6. Conclusion

In summary, the structural effect of different sizes and shaped Fe<sub>2</sub>O<sub>3</sub> particles on the performance as enhancers, with or without Al, in the thermal decomposition process of NC and the combustion of AP/HTPB has been studied and compared. The as-prepared Fe<sub>2</sub>O<sub>3</sub> particles and Al/Fe<sub>2</sub>O<sub>3</sub> have good compatibility with NC from DSC thermal analysis, suggesting the safely use of Fe<sub>2</sub>O<sub>3</sub>-NC and Al/Fe<sub>2</sub>O<sub>3</sub>-NC composites. The non-isothermal decomposition kinetics of the composites and NC can be modeled by the Avrami-Erofeev equation  $f(\alpha)=3(1-\alpha)[- \ln(1-\alpha)]^{1/3}/2$  in differential form. Through the TG-IR analysis of decomposition processes and products of the composites and NC, it is speculated that the as-prepared Fe<sub>2</sub>O<sub>3</sub> particles and Al/Fe<sub>2</sub>O<sub>3</sub> can effectively accelerate the thermal decomposition reaction rate of NC by promoting the O-NO<sub>2</sub> bond cleavage. Among the three studied different shapes of Fe<sub>2</sub>O<sub>3</sub>, the granular Fe<sub>2</sub>O<sub>3</sub> and its corresponding thermite (Al/Fe<sub>2</sub>O<sub>3</sub>(H)) exhibit the highest burning rate due to the larger surface area associated with a smaller particle size. Moreover, the Al/Fe<sub>2</sub>O<sub>3</sub>(H) thermites have more effective combustion-supporting ability for AP/HTPB composite propellants than Fe<sub>2</sub>O<sub>3</sub> and the other two as-prepared Al/Fe<sub>2</sub>O<sub>3</sub> thermites. Moreover, adding the thermites to



the composite propellants could contribute to increasing the flame temperature and improving the combustion wave structures of the formulations. In all, the addition of the prepared oxides or thermites can distinctly increase the burning rate, enhance the flame temperature, and decrease the burning rate pressure exponent of the AP/HTPB composite propellants.

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