Nitrocellulose Catalyzed With Manganese Oxide Nanoparticles: Advanced Energetic Nanocomposite With Superior Decomposition Kinetics

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Catalyzed Nitrocellulose Nanocomposite: a Novel Energetic Composition with Superior Decomposition Kinetics for Advanced Microchips

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Abstract

Nanostructured energetic materials can fit with advanced energetic first-fire, and electric bridges (microchips). Manganese oxide, with active surface sites (negatively charged surface oxygen, and hydroxyl groups) can experience superior catalytic activity. Manganese oxide could boost decomposition enthalpy, ignitability, and propagation rate. Furthermore manganese oxide could induce vigorous thermite reaction with aluminium particles. Hot solid or liquid particles are desirable for first-fire compositions. This study reports on the facile fabrication of MnO₂ nanoparticles of 10 nm average particle size; aluminium nanoplates of 100 nm average particle size were employed. Nitrocellulose (NC) was adopted as energetic polymeric binder. MnO₂/Al particles were integrated into NC matrix via co-precipitation technique. Nanothermite particles offered an increase in NC decomposition enthalpy by 150 % using DSC; ignition temperature was decreased by 8 °C. Nanothermite particles offered enhanced propagation index by 261 %. Kinetic study demonstrated that nanothermite particles experienced drastic decrease in NC activation energy by - 42, and - 40 KJ mol⁻¹ using Kissinger and KAS models respectively. This study shaded the light on novel nanostructured energetic composition, with superior combustion enthalpy, propagation rate, and activation energy.

Keywords: Nanoparticles; Thermites; Hydrothermal synthesis; Energetic materials; Pyrotechnics; First-fire.
1. Introduction

Nanostructured energetic materials can offer interesting characteristics in terms of high heat output, high reaction rate, as well as controlled sensitivity [1-3]. Nanothermite (metal oxide/metal) can act as efficient high energy dense material, with high volumetric energy density compared with common explosives. Nanothermites can experience reaction rate 100 times compared with conventional counterparts [4-6]. Much research has been directed to the development of nanothermites for initiation means, propulsion, micro-actuator, and electric match compositions [4, 7-8]. Electric match includes a thin metal wire (bridge wire) coated with a dab of heat-sensitive pyrotechnic composition [9]. Hot solid or liquid particles are desirable for first-fire compositions. Reactive fuel particles such as aluminium can produce good heat output and hot solid particulates. Nanothermite particles (metal oxide/metal) are emerging class of high energy density materials. Nanothermites can enhance not only the heat output, but also the ignitability, thermal conductivity, and propagation rate [10]. Manganese oxide is one of the most effective oxidizers for nanothermite reactions. Furthermore MnO₂ has the potentials for catalytic decomposition of energetic materials. Low co-ordination surface oxygen atoms are negatively charged; they have the potential to act as electron donor to electron deficient explosive material [11]. Hydroxyl surface groups could be evolved at low temperature and could attack the NC cyclic ring with the release of active NO₂ [4, 12]. MnO₂ particles could induce condensed phase reaction of gaseous products with the increase in decomposition enthalpy (Figure 1) [13-15].
Fig. 1: Schematic for active surface sites of manganese oxide catalyst (i.e. negative surface oxygen, and hydroxyl groups).

On the other hand aluminium can experience decomposition enthalpy of 32000 J/g; it is of interest as high energy density material[16]. Aluminium can induce thermite reaction with MnO$_2$ nanoparticles; this binary mixture can secure solid particles at high reaction temperature [6]. Nitrocellulose (NC) is the most common energetic polymeric binder; NC can offer gaseous products of 871 l/kg and explosion heat of 4312 kJ/kg [17]. NC can be employed as energetic binder for advanced electric match compositions [18]. These features can offer enhanced propagation index (PI). PI is a simple method to assess mixture’s tendency to sustain burning upon initial ignition by an external stimulus (Equation 1) [9].

$$PI = \frac{\Delta H_{reaction}}{T_{ignition}}$$

Compositions with high reaction enthalpy and low ignition temperature can secure self sustained propagation at high rate. NC has recently been employed to modify some energetic
material; NC was employed as energetic coating for Al/CuO nanoparticles for underwater ignition [19-21]. Nanothermite particles can offer vigorous exothermic reaction, with high gravimetric heat output compared with conventional explosives [22-24]. These novel characteristics inspire us to utilize NC as energetic binder for colloidal nanothermite particles. MnO$_2$ nanoparticles of 10 nm were developed using hydrothermal synthesis. Aluminum nanoparticles of 100 nm particle size were developed by wet milling. MnO$_2$/Al nanoparticles were re-dispersed in acetone; NC was dissolved in acetone colloid. MnO$_2$/Al/NC nanocomposite was developed via co-precipitation. Uniform distribution of nanothermite particles into NC was verified via SEM and elemental mapping. The impact of nanothermite particles on NC thermal behaviour was evaluated using DSC and TGA. Nanothermite particles offered an increase in total heat release by 150 %, with decrease in ignition temperature by 8 $^\circ$C. Propagation index was enhanced by 261 %. Main decomposition kinetic parameters were investigated using Kissinger and KAS models. Nanothermite particles experienced drastic decrease in NC activation energy by 10 % using Kissinger and KAS models.

2. Experimental

2.1 Synthesis of MnO$_2$ nanoparticles

MnO$_2$ particles were manufactured using hydrothermal processing. Nanoparticles were fabricated in continuous manner via direct mixing of metal salt with supercritical fluid. Schematic for continuous hydrothermal synthesis is provided (Figure S1). Further details about hydrothermal synthesis can be found in the following references [5, 22, 24]. Nano-oxide particles were flocculated from their synthesis medium and re-dispersed in organic solvent with aluminium nanoparticles.
2.2 Development of NC nanocomposite

Nanoparticles have natural tendency to aggregate with decrease in their surface area [25]. Enhanced dispersion characteristics could be accomplished via integration of dispersed particles into energetic matrix [5, 25]. Stoichiometric binary mixture of MnO$_2$/Al nanoparticles was re-dispersed into acetone; consequently NC was dissolved in acetone colloid. The hybrid nanocomposite material was developed via co-precipitation technique (Figure 2).

![Fig. 2: Schematic for integration of colloidal nanothermite particles into NC via co-precipitation technique.](image)

2.3 Characterization of NC nanocomposite

Size and shape of synthesized nanothermite particles were investigated using TEM (JEM-2100F by Joel Corporation). Morphology of dry particles was investigated with SEM, ZEISS SEM EVO 10 MA. Morphology of developed NC nanocomposite was investigated with SEM; elemental distribution of nanothermite particles into energetic matrix was investigated with EDAX detector.
2.4 Thermal behaviour of NC nanocomposite

Nanothermite particles can act as efficient high energy density material. Thermal behaviour of MnO$_2$/Al/NC nanocomposite was investigated using DSC Q200 by TA. The tested sample was heated up to 500 °C, at 5 °C min$^{-1}$. MnO$_2$/Al/NC weight loss was with temperature was further assessed using TGA 55 by TA.

2.5 Kinetics analysis

Kinetic analysis is vital to assess the main decomposition parameters including: pre-exponential factor (A), kinetic model (f(α)), and activation energy (Ea) [26-27]. The impact of nanothermite particles on NC decomposition kinetic was assessed using TGA. The weight loss of tested sample was recorded at different heating rates 2, 4, 6, 8 and 10°C·min$^{-1}$. Kissinger and Kissinger–Akahira–Sunose (KAS) were adopted for kinetic analysis.

2.5.1 Activation energy calculation

Activation energy (Ea) can be evaluated from Kissinger’s model (Equation 2)

\[
\frac{-E_a}{R} = \frac{d \ln(\beta/T_p^2)}{d(1/T_p)}
\]  

(2)

Where β, and Tp are the heating rate, and peak temperature at that heating rate respectively [28-29]. Furthermore, precise evaluation of activation energy (Ea) can be accomplished by Kissinger–Akahira–Sunose (KAS) (Equation 3) [30].

\[
\ln \left( \frac{\beta_i}{T_{a,i}^{1.5}} \right) = \text{Const} - 1.0008 \frac{E_a}{RT_a}
\]  

(3)

3. Results and discussions

3.1 Characterization of nanothermite particles

TEM micrographs revealed mono-dispersed MnO$_2$ particles of 10 nm average particle size (Figure 3-a); lattice diffraction pattern confirmed mono-crystalline structure (Figure 3-b).
Fig. 3: TEM micrograph of fabricated MnO$_2$ nanocatalyst (a), lattice crystalline structure (b).

Morphology of MnO$_2$ particles was investigated with SEM; SEM micrographs emphasis the high tendency of MnO$_2$ particles to decrease their number over drying process (Figure 4) [31-34].

Fig. 4: SEM micrographs of dry MnO$_2$ nanocatalyst.

Elemental mapping confirmed stochiometrically balanced MnO$_2$ composition with uniform elemental distribution of Mn, and O (Figure 5).
Fig. 5: Elemental mapping of synthesized MnO₂ nanocatalyst.

TEM micrographs of aluminum particles demonstrated nanoplates of 100 nm average particle size (Figure 6-a). Incident beam diffraction demonstrated highly crystalline structure (Figure 6-b).

Fig. 6: TEM micrographs of aluminum nanoparticles.

3.2 Characterization of NC nanocomposites

Incorporation of colloidal particles into energetic matrix can secure enhanced levels of particle dispersion [35-37]. Enhanced particle (metal oxide/metal) dispersion is mandatory for high reaction rate, and heat release rate. Morphology of dry NC nanocomposite was investigated with SEM. SEM
micrographs demonstrated NC fibres with 20 µm diameter (Figure 7-a), with uniform dispersion of nanothermite particles into energetic matrix (Figure 7-b).

**Fig. 7:** SEM micrographs of NC (a), MnO$_2$/Al/NC nanocomposite (b).

Elemental mapping (using EDX detector) confirmed uniform dispersion of nanothermite particles into NC matrix (Figure 8).

**Fig. 8:** Elemental mapping for of NC (a), MnO$_2$/Al/NC nanocomposite (b).

Integration of colloidal nanothermite particles into NC matrix demonstrated uniform particle dispersion.

### 3.3 Thermal behaviour of NC nanocomposite

Nanothermite particles offered an increase in NC total heat release by 150 %, with decrease in ignition temperature by 8 °C using DSC (Figure 9). The surge increase in total heat release can offer enhanced ignitability and self-sustained reaction at high propagation rate.
Fig. 9: DSC thermogram for NC and MnO$_2$/Al/NC nanocomposite.

MnO$_2$/Al/NC demonstrated enhanced propagation index by 261 % (Equation 1); enhanced propagation was ascribed to enhanced nanothermite particle into the energetic matrix. Nanothermite particles can secure vigorous exothermic reaction with the release of solid oxide as high temperature. These characteristics can inherit novel characteristics for electric match and ignition compositions. TGA analysis (Figure 10) confirmed DSC outcomes; MnO$_2$/Al/NC demonstrated decrease in main decomposition temperature by 8 °C compared with NC.
3.4 Decomposition kinetics of NC nanocomposite

3.4.1 Kinetic parameters via Kissinger model

The impact of nanothermite particles on NC kinetic decomposition was investigated using nonisothermal technique. MnO₂/Al/NC nancomposite was investigated using TGA; weight loss was investigated at four different heating rates of 2, 4, 6, 8 and 10 °C·min⁻¹ (Figure 11).
Fig. 11: TGA thermograms of NC (a), MnO$_2$/Al/NC nanocomposite (b)

The activation energy of MnO$_2$/Al/NC nanocomposite was evaluated to NC; activation energy was obtained from the slope of the straight line by plotting $\ln(\beta/T^2)$ versus $(1/T)$ at the five heating rates (Figure 12).
Fig. 12: Kissinger method to determine the activation energy of NC (a), MnO$_2$/Al/NC (b).

While NC experienced mean activation energy of 430 KJ·mol$^{-1}$; MnO$_2$/Al/NC nanocomposite demonstrated mean activation of 388 KJ·mol$^{-1}$. MnO$_2$ particles with negative oxygen surface and hydrous surface can act as efficient catalyst with decrease in activation energy [7-8, 13].

3.4.2 Kinetic parameters via KAS model

The activation energy at the different fractional conversion was determined by using modified Kissinger–Akahira–Sunose (KAS) method. The kinetics parameters of NC and MnO$_2$/Al/NC are tabulated in Table 1.

**Table 1: Kinetic parameters of MnO$_2$/Al/NC nanocomposite using (KAS) model to pure NC.**

<table>
<thead>
<tr>
<th>$\alpha$ reacted</th>
<th>NC</th>
<th>MnO$_2$/Al/NC nanocomposite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_a$ (kJ mol$^{-1}$)</td>
<td>Log A (s$^{-1}$)</td>
</tr>
<tr>
<td>0.05</td>
<td>420</td>
<td>50</td>
</tr>
<tr>
<td>0.1</td>
<td>418</td>
<td>51</td>
</tr>
<tr>
<td>0.15</td>
<td>417</td>
<td>52</td>
</tr>
<tr>
<td>0.2</td>
<td>420</td>
<td>53</td>
</tr>
<tr>
<td>0.25</td>
<td>421</td>
<td>50</td>
</tr>
<tr>
<td>0.3</td>
<td>418</td>
<td>51</td>
</tr>
</tbody>
</table>
The mean value of the activation energies of NC and MnO\textsubscript{2}/Al/NC nanocomposite was 420 kJ·mol\textsuperscript{-1} and 380 kJ·mol\textsuperscript{-1} respectively. These findings confirmed results from Kissinger’s model.

4. Conclusion and future work

MnO\textsubscript{2}/Al can secure one of the most vigorous nanothermite reactions in terms of heat output, gaseous products. Mono-dispersed MnO\textsubscript{2} particles of 10 nm particle size were developed by hydrothermal synthesis. Aluminium nanoplates of 100 nm were adopted. Integration of colloidal nanothermite particles into nitrocellulose offered enhanced dispersion characteristics. Consequently high interfacial surface area, high heat release rate can be achieved. Nanothermite particles offer an increase in NC heat output by 150 %; additionally the ignition temperature was decreased by 8 °C. Nanothermite particles offered an enhanced propagation index of NC by 261. Additionally, nanothermite particles offered decrease in NC activation energy by 10 %. It can be concluded that nanothermite particles can act as catalyst and high energy density material due to synergism between aluminium and MnO\textsubscript{2} nanoparticles.
Reference


Figures

Figure 1

Schematic for active surface sites of manganese oxide catalyst (i.e. negative surface oxygen, and hydroxyl groups).
Figure 2

Schematic for integration of colloidal nanothermite particles into NC via co-precipitation technique.

Figure 3

TEM micrograph of fabricated MnO2 nanocatalyst (a), lattice crystalline structure (b).

Figure 4

SEM micrographs of dry MnO2 nanocatalyst.
Figure 5

Elemental mapping of synthesized MnO2 nanocatalyst.

Figure 6

TEM micrographs of aluminum nanoparticles.
Figure 7

SEM micrographs of NC (a), MnO2/Al/NC nanocomposite (b).

Figure 8

Elemental mapping for of NC (a), MnO2/Al/NC nanocomposite (b).
Figure 9

DSC thermogram for NC and MnO2/Al/NC nanocomposite.

Figure 10

TGA thermogram of NC (a), and MnO2/Al/NC nanocomposite (b).
Figure 11

TGA thermograms of NC (a), MnO2/Al/NC nanocomposite (b)
Figure 12
Kissinger method to determine the activation energy of NC (a), MnO2/Al/NC (b).