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Modified iron oxide nanoparticles as burn rate enhancer in composite solid propellants

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ABSTRACT

The composite solid propellants (CSPs) are the main chemical propulsive force behind missiles and rockets. These propellants consist of pre-polymer (binder), aluminium as fuel and oxidizer with Ammonium perchlorate (AP) as a major oxidant. The burn rate modifier (BRM) is elementary requirement of the AP based composite solid propellants to achieve higher burning rates. The metal oxide nanoparticles are known to act as catalyst in the propellant composition and are the key to enhance the burn rate. Herein, the iron oxide nanoparticles (γ-Fe_2O_3) were synthesized without and with capping agent (coconut oil) before thoroughly characterized for their phase purity. The results clearly show significant change in burn rate for modified γ-Fe_2O_3 nanoparticles when compared to the standard bulk material for similar propellant composition.

1. Introduction

Nano-catalysis is a vast and fast-growing field involving the effective use of nanomaterials for a variety of homogenous as well as heterogeneous propellants for energetic applications. These class of catalysts play a major role in the reaction process either slowing or accelerating it without actually becoming a part of the reaction. The rate of a reaction is altered by employing a catalyst offering a different pathway irrespective of the thermodynamics of the process without disturbing the final product and thus affecting the transition state and activation path. The catalytic activity is a surface phenomenon onto which oxidation as well as reduction takes place and by the virtue of which the reaction proceeds further [1–4]. The catalytic activity of the materials is very common with much more enhanced activity observed in the nano-regime as large surface area is available for the reaction to proceed. Nowadays, the nanomaterials are of much interest due to their large surface area to proceed in a particular application [3–5]. The control or enhancement in the catalytic activity can be achieved by introducing some oxidizing agents or reducing agents along with the nanomaterials. The stability of energetic materials is vital which affects thrie storage. A part of the propellants where metal oxides provide better stability and hence they become suitable candidates for such energy applications [6,7].

A solid propellant is a mixture of fuel and oxidizer producing a large amount of gas with deflagration [8]. The propellants can be classified as: Nitrate ester based (SB, DB and TB) and Composite Propellants [9–11]. The composite propellants used in modern rockets, spacecrafts consists of binder (polybutadiene-acrylonitrileacrylic acid (PBAN), polysulfides, hydroxyl terminated polybutadiene (HTPB), polybutadiene-acrylic acid (PBAA), polyurethane (PU) and carboxyl). The composite propellants widely use polybutiene units such as HTPB that help in binding fuel and oxidizer. The other major components are oxidizer AP (~67%) and Al fuel around (~18%). Their major application lies in rocket propulsions. The devices using propellants find their uses in moving heavy load pistons, driving the big turbines, to start engines in rockets as well as aircrafts, pumping fluids out of deep wells, operating rocket valves along with the source of heat for other machinery. Apart from the major ingrediants, solid propellants also have minor ingrediants such as plascticizers, burn rate modifiers and opacifiers etc [12–17].

The thrust for the propulsion of the rocket depends on the mass flow rate of the fuel consumed per second. The desired thrust is the result of the fast combustion occurring on the surface of the fuel and oxidizer mixture causing the change in the size and shape [18]. The rapid propulsion of the rocket can be achieved with faster burning rate. The efficiency of the propellant is given by determinating the burn rate, which is directly interrelated to pressure within the chamber whether it is lowered or raised accordingly [19a]. The pressure index of a

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propellant plays a vital role in the determination of burn rate and during the rocket propulsion. The relation between the pressure index and burn rate is given by Vielle's Law [19b]: r= $a\ P^n$; where r is the burn which is dependent on pressure inside the chamber and initial propellant temperature, P -pressure within chamber, a - coefficient by means of propellant initial temperature (~ 0.04–0.0015), n - pressure index/exponent i.e. of propellant composition. The enhancement in the burn rate can be achieved by employing some additives/catalyst which posses low pressure index value suitable for highly efficient solid rocket propellent [20,21].

The basic requirement for a positive catalyst as a Burn rate modifier (BRM) is small and fine particles with crystal lattice defects along with better adsorption ability possessing large surface area. The burn rate modifier (BRM) is known to enhance or reduce the burn rate and also the exponent (n), ensuring better safety [22–24]. Ferric oxide (Fe_2O_3) possessing a particle size of about 0.25–0.65 microns is known to be used widely as a catalyst over other metal oxide materials such as ZnO, CuO, Al_2O_3, SiO_2 etc. for composite propellants owing to its established ability to decompose Ammonium perchlorate (AP) at higher temperature ranging between 320˚ - 380 ˚C [25a,b,c,d]. It has been documented that the efficiency of ferric oxide intensifies suddenly with the transition from micro size regime to nano sized regime with higher surface area, excess oxygen vacancies along with surface atoms making it as an excellent catalyst [26].

Thus, in this article, the authors have successfully employed modified iron oxide nanoparticles (uncapped as well as coconut oil capped) *via* a simple co-precipitation technique for its application as a burn rate modifier with enhanced burn rate as well. The synthesized nanoparticles were thoroughly characterized confirming the formation of iron oxide nanoparticles. The theoretical studies were conducted for both the modified Fe_2O_3 nanoparticles and the standard bulk Fe_2O_3 particles at three pressure values to find the effectiveness in enhancing burn rate. The results obtained from theoretical studies formed a basis for carrying out experimental studies using the as-synthesized synthesized Fe_2O_3 nanoparticles.

2. Materials and methods

2.1. Materials

Ferric Nitrate ($Fe(NO_3)_3$), Ferrous Sulphate ($FeSO_4$), Ammonium hydroxide (NH_4OH), absolute ethanol, acetone and toluene were purchased from Sigma Aldrich India Ltd and were used as received. The coconut oil used as a capping agent was obtained from the local market. The deionized water was used during the process of synthesis and washing as well as cleaning purpose (18.2 M Ω). The absorption spectroscopy was carried on UV/Vis spectrophotometer Specord 210 with the initial range of 200–1100 nm. The X-ray diffraction (XRD) analysis was completed with the help of Bruker D8 advance XRD at of 40 kV, 120 mA with Cu Kα radiation (λ = 0.1546 nm) at 2θ ranging in 10–90˚.The size and shape of synthesized nanoparticles was analysed with the help of ZEISS Gemini Scanning electron microscope (SEM) instrument operated at 30 kV and Technai G2 Transmission electron microscope (TEM) instrument operated at 300 kV.The functional groups identification was achieved with the help of Fourier transform infrared (FTIR) spectra on a Perkin Elmer Spectrum-Two infrared spectrometer with the initial range of 4000 to 400 cm-1. Thermogravimetric Analyser (TGA) & Differential Scanning Calorimeter (DSC) analysis was performed on TA Instruments SDT Q600 between 30 °C and 490 °C with heating rate of 10 °C/min. The specific surface area was estimated using F-Sorb 2400CE BET surface area analyser. The theoretical studies were carried out using Chemical Equilibrium with Applications (CEA 400). The actual burn rate experiments were performed in solid strand burn rate measurement system working on acoustic emission principle.

2.2. Synthesis of uncapped iron oxide (IO) nanoparticles

The synthesis of size-controlled iron oxide nanoparticles was accomplished using a simple technique i.e. chemical co-precipitation without using any surfactant. In a typical synthesis method, 0.033 M (5.01 gm) ferrous sulphate ($FeSO_4$) and 0.029 M (7.01 gm) ferric nitrate ($Fe(NO_3)_3$) were taken in a round bottom flask filled with deionized water. The dropwise addition of ammonium hydroxide (NH_4OH) was done till the pH (10–14) was achieved. The reaction process involved stirring at temperature 90 ˚C under nitrogen atmosphere for 4–5 h. The reaction mixture was then collected with the help of a bar magnet along with discarding of the supernatant solution. The removal of any unreacted materials was achieved using centrifugation method with solvent used as ethanol and acetone. The black precipitate collected after centrifugation was dried at 50 ˚C in an air oven for 6–8 h. The dried black precipitate was then crushed into fine powder and was used for further analysis and testing without any further purification [27,28].

2.3. Synthesis of capped iron oxide (IOO) nanoparticles

The typical synthesis was carried out using the same process as mentioned above with addition of coconut oil as a capping agent for controlling the size of the nanoparticles. The introduction of the coconut oil was done simultaneously with the addition of ammonium hydroxide (NH_4OH) dropwise. Toluene was used for washing any oil residue left in the reaction mixture along with the use of ethanol and acetone for the removal of any unreacted material. The product was separated by centrifugation method. The black precipitate collected after centrifugation was dried in an air oven for 6–8 h at 50˚C and crushed to fine powder for further analysis and testing as obtained.

2.4. Burn rate analysis

2.4.1. Theoretical/simulation process

The theoretical calculations were run on a software namely 'Chemical Equilibrium with Applications' (CEA 400), which is generally used for energetic material applications. The software was utilized in order to compare the effect of bulk iron oxide and nano iron oxide on ballistic parameters in terms of wt. % variation to the standard composition. The increase in iron oxide (wt. %) accompanied by decrease in percentage of AP.

The study was conducted by employing three variations of bulk iron oxide and nano iron oxide (0.5%, 1% and 2 wt.%). The thermodynamic data as well as thermal transport property has to be the input for the system to perform calculations whereas the thermodynamic data for the nano regime iron oxide particles was absent in the program which was obtained from open source and used (Table 1).

2.4.2. Experimental process

The burn rate measurements were carried out in a solid strand burn rate measurement system at 70 ksc (kgf/cm^2) in the absence of burn rate additives with varying wt. % of micron sized, uncapped and coconut oil capped iron oxide nanoparticles.

Table 1
The standard composition of CSPs used for computational studies.

S. no	Component	~ Wt. %
1	HTPB-binder	9.5–9.8
2	***Iron-oxide (bulk)***	**0.5**
3	Butanediol (n-BD)	0.06–0.09
4	Tri-Methylol Propane (TMP)	0.02–0.05
5	Toluene Diisocyanate (TDI)	0.65–0.72
6	***Ammonium perchlorate (AP)***	***67***
7	Aluminium powder	16–19
8	Dioctyl-adipate (DOA)	2–4