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Review

Recent progress on ferrocene-based burning rate catalysts for propellant applications

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The Burning rate of a solid propellant predominantly influences its internal ballistic behavior and it has been well known that incorporation of small quantities of certain classes of organic and inorganic substance to a propellant can drastically alter its burning rate characteristics. The inclusion of energetic materials and burning rate catalysts (BRCs) from the metallocene family (e.g., ferrocene (Fc) and 2,2-bis (ethylferrocenyl) propane also known as catocene (Cat)) has been a promising avenue for efficiently increasing the burning rate of propellants. Fc-based materials are dominantly used as burning rate catalysts in solid propellants because of their low volatility, higher compatibility with organic binders, microscopic homogeneities in distribution, broad range of burning rate adjustments, better ignitability and distinct catalytic features. However, in solid composite propellants, Fc-based polymers and derivatives show undesired properties of high migration, that is travelling out from propellant grain to surrounding insulation material on prolong storage, evaporation or sublimation loss during processing and curing as well as phase separation by crystallization in low-temperature applications, limiting their application as BRCs. This article outlines the latest synthetic advancements in the field of Fc-based BRCs, as well as highlighting their catalytic and anti-migration mechanisms.

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Contents

1. Introduction

The development of rocket technology is perceived as a significant research aspect in aerospace industry. Most extensively used rockets in recent times for the shorter and middle ranges are equipped with propellants [1]. Propellants are widely used in chemical propulsion systems and they are the fundamental source

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for supplying chemical energy(driving force) in rockets et al. [2,3]. Most modern, highly energetic thrust producing solid propellants are "composite". These composite propellants are composed of energetic filler, as an oxidizer (65–70%) followed by metallic fuels (10–20%), binders (8–15%) and burning rate catalysts (BRCs) (2–5%). The oxidizer, most commonly the oxygen-rich crystalline inorganic perchlorates (such as ammonium perchlorate (AP)) and metallic fuel (aluminum (Al)) serves to produce the energy at the expense of their interaction while the BRCs are aimed to improve the propellants ballistic features [4–17].

Solid propellants should have a stable burning rate and a low pressure exponent while maintaining acceptable mechanical properties, aging characteristics, cost, processibility, and environmental aspects [16]. The use of efficient BRCs in solid propellant improves instantaneous combustion of the propellant, eliminates primary smoke and facilitates smooth burning rate [7,18], so a promising method for enhancing the composite solid propellant's performance is the use of BRCs in the solid propellant [19]. Currently, numerous BRCs have been reported such as Fc-based materials, oxides of transition metals, nano-particles, and metal chelates (organic metal chelates) [20–22]. The high surface energy of nano-particles makes them more effective and vigorous for thermal decomposition of AP [7,23]. Transition-metal oxides, though are cheaper and facile to produce but are unable to deliver any significant increase in burning rate, while organic metal chelates like organo copper chelates or iron lead double metal chelates etc. show good dispersion properties and are very effective in enhancing the burning rate of the composite solid propellants [24]. Amongst all, Fc-based BRCs in recent years have gained much attention. Due to their outstanding advantages like good compatibility (with organic binder), better fluidity and improved microscopic homogeneities in distribution, they are the most widely accepted BRCs for composite solid propellant. The efficient burning rate of different derivatives and polymers of Fc can be controlled by modifying its structure, molecular mobility and iron contents. They also give extraordinary effect in amplifying the burning rates of the butyl hydroxide propellants containing AP and aluminum powder, the most commonly used oxidizing agent and metallic fuel, respectively [25–31].

Simple polymers and derivatives based on Fc, can easily migrate from the propellant system both by diffusion as well as by surface migration mechanism. As a consequence, the migration further destroys the propellant homogeneity and permits higher burn rates only on the surface of the propellant than the rest of propellant. This undesirable situation causes the unpredictability of the burning rate which in turn renders unpredictable rocket performance, which may lead to explosions of the propellant in rocket flights [1,32]. Lately keen focus has been devoted towards the thermal decomposition of AP using novel Fc-based BRCs with good anti-migration properties [33].

Unver and co-worker's reported that burning rate and anti-migration properties can be controlled by using linkage of Fc-based polymers [32]. Therefore, researchers are still finding some cheap and productive ways to avoid problems related with burning rate and migration [31].

On the other side, Fc-based hydroxyl terminated polybutadiene (HTPB) was expected to have good aging and burning rate properties due to its better anti migration abilities [24]. Similarly, Fc-based hyperbranched polymers have dragged much attention because of their higher molecular masses, low viscosities and more importantly due their outstanding catalytic properties [34–36]. Mostly, dinuclear Fc derivatives show good performance, when an active group (hydroxide, amidocyanogen, etc.) is introduced. The introduction of active groups increases the polarity of Fc derivative, which decreases the migration in the propellant system [37].

2. Burning rate and BRCs

The propellant burns layer by layer and the linear rate of regression of propellant grain is generally expressed in mm/s, inch/s or cm/s [38,39]. Burning rate is defined as the linear rate of regression of the propellant or the distance travelled by the flame front per unit time perpendicular to the free surface of the propellant grain, at a known pressure and temperature [39,40]. The burning rate of composite solid propellant is dependent on surface area, catalyst concentration, fuel to oxidizer ratio, particle size, and state of aggregation [39,41–43]. Burning rate can be tuned by applying different techniques such as inclusion of high burning rate energetics, operating motor at high or low chamber pressure, chemical catalysis, modification of the propellant grain (for increasing thermal diffusivity) and smaller constituent particle size [43–45]. In the case of reduced particle size the flame zone lies closer to the propellant surface where it provides more subsurface heating which results in augmentation of burning rate [46,47].

The high burning rates are associated to the generation of high thrust levels, therefore thrust can be enhanced with better burning rate properties [14]. Certain significant aspects affecting burning rate are pressure in combustion chamber, propellant grain's initial temperature, motor acceleration, spin and velocity of the combustion gases [6,42,44,48].

It has been well defined that the introduction of either organic or inorganic substances to a solid rocket propellant in small quantity could bring about drastic changes in its burning rate. Generally these additive materials are added up to 3% (of mass level) and found to be the most effective way for regulating the burning rate of propellant [56]. The burning rate modifiers (also known as ballistic modifiers), are used to tailor ballistic properties of propellants. These burning rate modifiers which enhances the of the propellant are named as the burning rate enhancers or BRCs [1].

BRCs provide key role in acceleration of propellant's burning rate with adequate driving force to the rocket [32]. The addition of BRCs in the composite solid propellant changes the pressure index of the solid propellant, eliminates primary smoke and reduces sensitivity to temperature and pressure. These BRCs improves ignition performance and combustion stability to achieve desired engine design thrust [49,50]. BRCs accelerate gaseous phase decomposition of fuel and oxidizer in the combustion chamber, which results in the escalation of burning rate [40].

3. Synthesis of Fc-containing BRCs

The thermal decomposition temperatures for AP can be enhanced by using Fc-containing polymers and derivatives. The shift in decomposition temperatures of AP affects the combustion process of a composite propellant. Fc-based BRCs are classified into different major categories as: Fc-based compounds and derivatives, Fc-based dendrimers and hyperbranched polymers and Fc-based polymers [1].

3.1. Synthesis of Fc-based compounds and derivatives

Numerous Fc containing compounds and derivatives are well recognized as BRCs due to their excellent burning rate catalytic properties.

Xuelin Liu and co-workers synthesized *N, N*-bis[(ferrocenylmethyl) dimethyl] alkylene-diammonium dinitrates and dipicrates as Fc-based BRCs [51], and also synthesized ionic compounds, 1-(ferrocenylmethyl)- imidazolium paired with polycyano anions. The results of these polycyano-based compounds showed elevated catalytic action on the thermal decomposition of AP [52]. Molecular structures of these compounds are shown in

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