



Recent advances in catalytic combustion of AP-based composite solid propellants

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ABSTRACT

Composite solid propellants (CSPs) have widely been used as main energy source for propelling the rockets in both space and military applications. Internal ballistic parameters of rockets like characteristic exhaust velocity, specific impulse, thrust, burning rate etc., are measured to assess and control the performance of rocket motors. The burn rate of solid propellants has been considered as most vital parameter for design of solid rocket motors to meet specific mission requirements. The burning rate of solid propellants can be tailored by using different constituents, extent of oxidizer loading and its particle size and more commonly by incorporating suitable combustion catalysts. Various metal oxides (MOs), complexes, metal powders and metal alloys have shown positive catalytic behaviour during the combustion of CSPs. These are usually solid-state catalysts that play multiple roles in combustion of CSPs such as reduction in activation energy, enhancement of rate of reaction, modification of sequences in reaction-phase, influence on condensed-phase combustion and participation in combustion process in gas-phase reactions. The application of nanoscale catalysts in CSPs has increased considerably in recent past due to their superior catalytic properties as compared to their bulk-sized counterparts. A large surface-to-volume ratio and quantum size effect of nanocatalysts are considered to be plausible reasons for improving the combustion characteristics of propellants. Several efforts have been made to produce nanoscale combustion catalysts for advanced propellant formulations to improve their energetics. The work done so far is largely scattered. In this review, an effort has been made to introduce various combustion catalysts having at least a metallic entity. Recent developments of nanoscale combustion catalysts with their specific merits are discussed. The combustion chemistry of a typical CSP is briefly discussed for providing a better understanding on role of combustion catalysts in burning rate enhancement. Available information on different types of combustion nanocatalysts is also presented with critical comments.

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1. Introduction

A typical composite solid propellant is a mixture of several chemical constituents which may include polymeric fuel, organic plasticizer/binder, crystalline inorganic oxidizer and additives. The final processed form of a solid propellant that is cast inside a solid rocket motor (SRM) is called propellant grain and it can be of various configurations and sizes depending on the mission requirement. Once the grain is ignited with the help of a suitably

designed igniter, it undergoes a self-sustained combustion reaction that releases huge mass of hot gaseous products. These gaseous products are made to eject through a convergent-divergent nozzle at very high exhaust velocity. The reaction force developed by the discharge of accelerated gases imparts the momentum to the rocket. CSP grains of few grams to several hundred tons have extensively been used in micro-thrusters, projectiles, rockets, launch vehicles and missiles [1–4].

The solid surface of CSP grain regresses by propagation of combustion waves in direction perpendicular to the burning surface. The propellant combustion is controlled by intricate heat transfer mechanism and cross flow velocity of combustion gases in the flame across the regressing propellant surface. The regression

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of the propellant web is usually expressed in terms of burn rate of the propellant. The ammonium perchlorate (AP) is a common oxidizer used in CSPs which can be dispersed homogeneously in the fuel-binder matrix in appropriate weight ratio. The major advantages of using AP in CSP is its ability to deliver high burning rate with inclusion of combustion catalysts besides improved mechanical properties and higher performance compared to other inorganic oxidizers. The catalysts exhibit potential to enhance the propellant burning characteristics even under those operating conditions where no other method is effectively implementable.

A large numbers of combustion catalysts have been investigated in the past and some of these are currently used in modern propellant formulations [1–3]. The catalysts containing transition metal oxides (TMOs) such as ferric oxide, cobalt oxide, manganese oxide, chromium oxide and copper chromite etc., have been found to enhance decomposition process of AP-based CSPs. The catalytic efficiency of these TMOs was largely influenced by their particle size, surface area and crystalline structure. Further, commercially available and synthesized metal-complexes, phthalocyanines, metallocenes and their derivatives have been selectively tested as burning rate catalysts and found to be effective. The fast burning CSPs are greatly in demand to meet challenging mission requirements in current scenario especially in military operations demanding quick response time. Some important combustion catalysts in nanoscale range have been found to be promising candidates for achieving extraordinary burning performances [5–7]. These materials in nanoscale range may have potential to reduce the activation energy, ensure rapid ignition and reduced reaction time and are advantageous over the bulk-sized catalysts. Keeping in view, the stringent selection criteria and safety aspects, properties like thermal stability and sensitivity to shock or impact, the metallic nano-catalysts like uni-centric metal oxides (UMOs), mixed metal oxides (MMOs), metal alloys, bi/tri-metallic composites, metallocene complexes and chelates have been evaluated to assess their influence on the ballistic performance of rocket propellants [8–12]. However, the size and surface effects of these nano-catalysts are greatly different from their bulk counterparts. Due to the importance of catalyst assisted combustion in propellant technology, the researchers have largely oriented their efforts towards comprehensive understanding of mechanism of catalysis under different operating conditions encountered in SRM.

Besides the novelty of structure, the catalytic properties of nanomaterials (NMs) are closely associated with their crystalline structure, size, surface area, dispersive quality and nature of agglomeration, which in turn largely depends on their preparation methodology [13,14]. The efforts have been made to synthesize NMs using approaches like sol-gel synthesis, co-precipitation, complexation, mechanical milling, hydrothermal, micro-emulsion and solution-combustion synthesis route, etc. [15–20]. The ideal methods for mass production of nanoscale combustion catalysts with desired merits are still the subject of continued investigations. It has been found that slight variation in crystal size, uniformity, structure and morphology of NMs from one batch to another may drastically influence the behaviour of catalyst in combustion reaction [21–23]. This review attempts to present the impact of different class of metallic nanocatalysts on decomposition, pyrolysis and combustion of CSPs and its ingredients. Efforts have also been made to compile the data related to particle size of NMs and its role towards influencing the decomposition temperature of propellants and its individual ingredients. The survey of available literature is made to illustrate the potential of different combustion nanocatalysts towards enhancement of combustion and decomposition behaviour mainly of AP-based CSPs. The chemistry of decomposition is discussed for understanding the complex physicochemical aspects of thermal decomposition of main components

of CSPs. Impact of nanoscale combustion catalysts on fuel-binder and oxidizer mass is also covered. Recent trends in nanocatalyst research related to their application in advanced propellants technology has been presented with emphasis on their special features such as large specific surface area, particle size in the propellants, explosives and pyrotechnics with better controls on ignition, combustion, safety and reliability. With introduction to the fundamental aspects of combustion of CSPs, efforts have been made to present various approaches used to improve their burn rate using solid state catalysts like TMOs, nanometals, nanotubes, metal complexes and alloys, graphenes and phthalocyanines besides different types of ferrocenes in liquid state, their efficacy in improving thermal decomposition behaviour of AP or fuel binder and overall energetics and combustion characteristics of CSPs in this paper.

1.1. Combustion chemistry of CSPs

The CSPs are highly energetic materials which have the capability to produce high temperature gaseous products on self-sustained combustion. Total energy produced by burning of propellant mass in controlled conditions is directly related to available thrust for propulsion. These propellants are safe to handle and deliver high performance in comparison to other types of solid propellants. A CSP is generally composed of a number of ingredients in composite solid mixture as presented in Table 1. Each component has specific roles in both propellant formulation and steady-state combustion.

A recent review on the combustion of AP/HTPB composite propellant has addressed physico-chemical processes occurring during propellant combustion, individual AP decomposition and binder melting/pyrolysis and accompanying primary and diffusion flames etc. and summarizes key aspects of our present understanding on the subject [6]. The experimental diagnostic techniques like Mass spectroscopy, Absorption spectroscopy, Fourier-transform infrared spectroscopy, planar laser induced fluorescence, spontaneous Raman scattering, Laser induced spectroscopy, Chemi-luminescence imaging and modern temperature sensors have been extensively used to investigate individual elements and their interaction during combustion process at different operating conditions. These inputs prove to be vital in modeling and simulation studies and their fine tuning to predict overall combustion behaviour of CSPs. For proper understanding of combustion reaction zones and associated flames, its sequence can be presented as shown in Fig. 1. The combustion zone comprises of two important domains, a condensed-phase reaction zone below the solid surface followed by gas-phase reaction regime with premixed and diffusion flame zones comprising of intermediate and final combustion products. The nature of these products depends on the fuel-oxidizer combination involved. In the condensed-phase, the pre-heating of the propellant also takes place due to heat transfer from propellant burning surface that leads to solid state reactions in fuel-oxidizer matrix beneath. The melting and vaporization of oxidizer and binder takes place subsequently on the surface which

Table 1
Main chemical ingredients of a typical CSP.

Primary ingredients	Secondary ingredients
Polymeric binder	Burning rate modifier
Inorganic oxidizer	Cross linking agent
Metallic fuel	Curing catalyst
Curative	Anti-oxidant

produces primary decomposition/pyrolysis products. The gas-phase combustion of the burning propellant mainly involves mixing of pyrolysis products of polymeric binder and decomposition products of oxidizer at molecular level that react in vapour phase [2,3]. The available heat as a result of highly exothermic reactions leads to very high temperature reactions leading to formation of the final combustion products.

It is well known that thermal decomposition of oxidizer mass of CSPs is greatly influenced by use of small concentration (≤ 3 wt%) of metal/metal oxide catalysts. In recent years, the nano-scale combustion catalysts containing transition metal oxides are preferred because of their large surface area that enhances the oxidizer-catalyst contact area leading to better catalytic activity. The crystal size, particle distribution and morphological texture of such nanocatalysts play an active role in modifying combustion characteristics of CSPs. The activation energy and kinetic mechanism of combustion reactions of CSPs especially in gas-phase and condensed state have also been found to improve significantly. Several researchers have concluded that the thermal degradation of CSPs and their major ingredients in conjunction with suitable

nanocatalyst generally produce 30–40% higher heat release as compared to their bulk sized catalysts. The thermal decomposition data of several CSPs with various metallic nanocatalysts are summarized in Table 2. The results are self-explanatory and the variation in phase transition, first LTD and first and second HTD and heat release is seen to be dependent on the type of catalyst used.

In general, it may be inferred that endothermic phase transition (orthorhombic to cubic) peak of AP remains largely unaffected, however, high temperature exothermic decomposition peaks exhibit sensitivity towards catalytic presence even as an admixture. Bimetallic catalysts are found to influence high temperature AP decomposition process significantly. The AP-HTPB composite solid propellants in presence of catalysts invariably reveal that high temperature decomposition peaks shift to a much lower value indicating that condensed phase combustion of catalysed propellants is greatly influenced in presence of nanocatalysts. A general scheme of decomposition of oxidizer, pyrolysis of fuel binder and subsequent combustion reactions is given below:

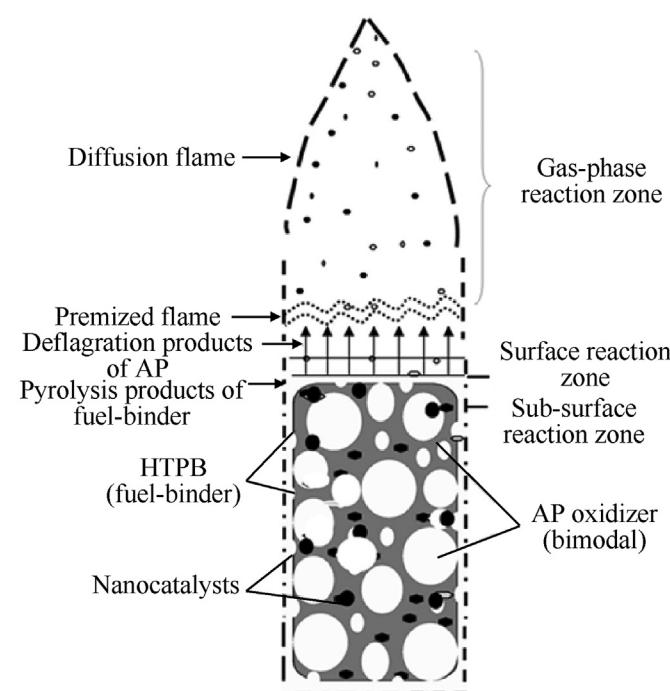
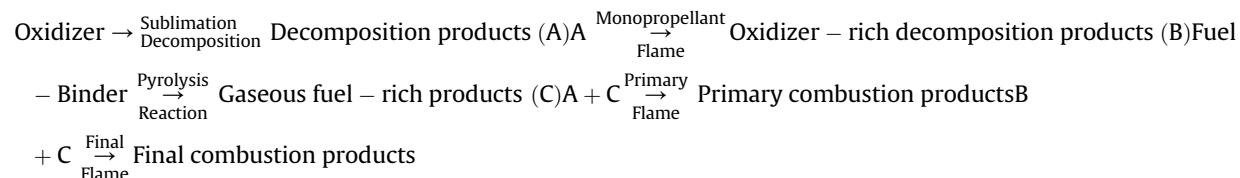


Fig. 1. Combustion regimes of a typical AP/HTPB based composite propellant strand containing nanocatalyst under ambient condition.

The CSP usually contains 70–86 wt% of oxidizer mass in comparison to total weight of propellant. So, the oxidizer is the major component in formulation of propellant and hence its decomposition plays vital role in overall combustion process of propellant. The interaction initially occurs at interface of AP and fuel-binder and as a result of this, the primary flame appears. This causes the liberation of heat by convective and conductive mechanism which facilitates the rise in temperature to assist fuel pyrolysis. The vapours of decomposed products appear in the form of oxidizer-rich diffusion flame. The rate of diffusion of vapours of fuel into oxidizer decomposition products determines the morphology of flames and its temperature. Combustion reactions take place within the gaseous mixture and are expected to occur very fast as compared to the rate of diffusion [3]. The explanation of involved chemistry for complete combustion of a propellant under the highly exothermic conditions and high operating chamber pressure in a rocket motor is a very complex issue. A quantitative mechanism of main combustion processes is now better understood following several systematic studies done in the past on individual propellant ingredients, their mixtures at different operating conditions that may vary from sub-atmospheric to high chamber pressure conditions of the solid rocket motor. Precision in analytical instrumentation and modern sensors have also contributed in a big way to acquire evidence about fast thermolysis reactions, high temperature response of major products and associated dissociation and recombination processes as discussed in subsequent section.

An exhaustive review [31] covers the thermal decomposition mechanism of work-horse oxidizer AP commonly used in CSPs. The AP molecule contains onium salts, a complex compound formed by

Table 2

Thermal decomposition data of AP and CSPs showing influence of metal nano-catalysts.

AP/CSPs/Nano-Catalysts	Phase Transition (T ₁)	1st HTD Peak (T ₂)	2nd HTD Peak (T ₃)	Heat Release /(k·Jg ⁻¹)	ΔT ₂ /°C	ΔT ₃ /°C	Refs.
	Endothermic/°C	Exothermic/°C			/°C	/°C	
AP	245	328	478	—	—	—	[24]
AP + 1% CNTs/CuO	245	323	363	—	5	115	
AP + 2% CNTs/CuO	245	343	—	—	135	—	
AP + 4% CNTs/CuO	245	333	—	—	145	—	
AP + 8% CNTs/CuO	245	320	—	—	158	—	
AP	246	295	414	—	—	—	[25]
AP + 1% n-Fe ₂ O ₃	245	287	365	—	8	49	
AP + 2% n-Fe ₂ O ₃	245	291	374	—	4	40	
AP + 3% n-Fe ₂ O ₃	245	293	378	—	2	36	
AP	246	285	420	—	—	—	[11]
AP + 1% Zn–Cu	245	278	335	—	7	85	
AP + 1% Zn–Ni	246	279	345	—	6	75	
AP + 1% Zn–Fe	247	280	374	—	5	46	
AP	244	322.7	477.2	0.436	—	—	[26]
AP/Cu (90 nm)	244	287.6	347	1.20	35.1	130.2	
AP/Ni (50 nm)	244	326.6	364.3	1.32	—	112.9	
AP/Al (30 nm)	244	328.6	425.4	0.903	—	51.8	
AP/NiCu (45 nm)	244	296.5	336.8	1.20	26.2	140.4	
AP/Cu (26 nm)	244	307.8	358.3	1.09	14.9	118.9	
AP/Ni (20 nm)	244	314.4	422.0	0.727	8.3	55.2	
AP/Ni (30 nm)	244	315.2	435.5	0.58	7.5	41.7	
AP/Al (25 nm)	244	318.9	469.5	0.302	3.8	7.7	
AP/HTPB	311.2	335.1	406.4	1.70	—	—	
AP/HTPB/Al (Base)	243.2	291	464	1.55	—	—	
Base + (0.25%) nMnO ₂	242.2	296	373	—	—	91	[6,27–29]
Base + (0.50%) nMnO ₂	243.1	290	358	—	6	15	
Base + (0.75%) nMnO ₂	242.8	285.1	349	—	4.9	9	
Base + (1.00%) nMnO ₂	242.9	285.3	346	—	—	3	
AP/HTPB/CNTs	266.9	328.5	380.9	—	—	25.3	
AP/HTPB/CNTs-Cu	271.2	353.4	—	—	—	52.4	
AP/HTPB	246	342	378	1.88	—	—	[30]
AP/HTPB/nCu-Co-O(I)	245	316	328	2.90	26	50	
AP/HTPB/nCu-Co-O(II)	245	304	339	2.62	38	39	
AP/HTPB/nCu-Co-O(III)	244	310	320	2.12	32	58	

Note: LTD = low temperature thermal decomposition, HTD = high temperature thermal decomposition, nMnO₂ = 45 nm, CNTs = 10–20 nm, nCu-Co-O = 125–200 nm.

proton transfer from the corresponding acid to the base. In-built proton of onium salts can be transferred from cation to anion on decomposition/dissociation which produces starting molecules of acid and base. The equilibrium proton transfer leads to the dissociative sublimation of AP and formation of ammonia and perchloric acid. It may occur in both the condensed and gas-phase reactions. The thermal decomposition of AP involves low temperature decomposition (LTD), sublimation, and gas-phase combustion reactions at high temperature. In LTD, the AP molecules decompose primarily into NH₃ and HClO₄ as given below:



The NH₃ and HClO₄ either react in the adsorbed layer on the surface of AP or desorbs and sublime leading to gas phase reactions. It is believed that adsorbed layer of HClO₄ is desorbed more rapidly than ammonia. This is because; the proton tends to combine with the ammonia molecule, a strong base rather than the ClO₄⁻ ion, only a moderately strong base. As the temperature rises, the polarization of NH₃ is readily increased, and its strong base character begins to soften at a much greater rate than that of the ClO₄⁻ ion. In contrast, the ClO₄⁻ ion will become stronger in nature than the ammonia molecule, and hence will extract the proton from it. The unbalanced HClO₄ decomposes according to the equations.



ClO₃ being highly unstable fragment dissociates further by either of the above-mentioned pathways. The OH radical takes hydrogen from ammonia until free nitrogen atoms are produced. Both the production of water and of nitrogen is highly exothermic reactions which supply the energy necessary to maintain the reaction process. This mechanism involves the recombination of sublimates. This is a slow reaction in comparison to dissociation reaction.



ClO* radical attacks NH₃ to produce NH₂ and ClOH. Repeated hydrogen abstraction from NH₂ gives NO and finally yields nitrogen and water molecules.

The thermal characterization (DSC/TGA) data of AP also suggests that sublimation is the major process which governs the AP decomposition. It has already been reported that the contribution of sublimation is insignificant under ambient pressure and it increases with the decrease of pressure. A different scenario is observed when the pressure is more than the ambient as is the case in rocket combustion process. An earlier study, where AP decomposition was conducted at ~5 MPa under nitrogen atmosphere concluded that the HTD peak shifts to lower temperatures with an increase in pressure. The reason for this observation was attributed

to the presence of N₂ that extensively promotes the gas phase reaction between NH₃ and HClO₄.

The complexity of heterogeneous combustion of CSPs is intimately linked to multiple ingredients used in the formulation besides large amount of oxidizer (>85 wt%) and fuel binder (nearly 13 wt%) and other specific additives that may or may not replace the oxidizer. Different types of solid propellants also find applications in gas generators, air bag industry, micro rockets and in several devices used for generating pressure or force in civil and mechanical domains. The CSPs are presently extensively used in very large boosters, assisted take off to small precision thrust generating devices on board of a satellite or space landers. Such applications need precise performance and control required for a particular mission and many a times require technical tweaking to some already designed and tested systems. Having said this, the motors and devices employing CSPs may also inherit or encounter combustion related problems like unsteady combustion [32], combustion instability, erosive burning, efficient metal combustion in metallized CSPs and issues related to smooth ignition and steady state combustion [33]. These vital aspects of solid propellant combustion are intimately linked to its chemical kinetics, aero-thermochemistry, composition and velocity of combustion gases and heat transfer related issues in the combustor. Many of these issues may be resolved or mitigated by addition of suitable additives or burn rate modifiers. Efforts are also being made to develop solid rocket motors that can be extinguished at command with precision termination of thrust and re-started using laser induced ignition or other suitable system. This technology when perfected may replace use of toxic and hazardous liquid propellant using rocket engines. Additives are also being explored to accomplish controlled and precise extinction of CSPs [34–36].

Future research direction on the subject may focus on developing a sound theory that merges the independent decomposition rates of oxidizer and binder that are often used now to predict burn rate. Some extensive investigations on AP related pathways of important decomposition reactions and products and their subsequent reactions under different experimental conditions have been reported and used for combustion modeling in the past. Nevertheless, the solid state reaction kinetics and prediction of condensed-phase heat release should be incorporated to develop a comprehensive theory of combustion of CSPs. The presence of partner ingredient drastically changes the independent thermal decomposition rates of oxidizer or fuel binder and as a result future modeling approaches must take this aspect into consideration. The quenching of CSPs at low pressure is yet to be investigated in depth to develop propellants that can be used in new generation solid rocket motors with start-stop-start capability. Such rocket motors may replace liquid rocket engines that are expensive, use toxic propellants and have small shelf life. Further, research of high-pressure combustion of energetic fuel binders is rarely reported in open literature. The detailed investigations and information on above mentioned aspects will facilitate development on comprehensive combustion model for CSPs that can precisely predict the burn rate of a given propellant under prescribed operating conditions. This endeavor is yet to be fulfilled after years of research and development work for want of clear understanding of complexities involved in combustion process of CSPs.

2. Approaches to improve burning rate with nanocatalyst

As mentioned earlier, the burn rate \dot{r} , largely controls the performance of a rocket system. Many chemical approaches have been developed to improve the burning rate of propellants. Some methods were found suitable for the purpose only in certain cases

[4]. The adopted approaches are mentioned below:

- Blending of particle size fractions of AP
- Size reduction of AP particles
- Incorporation of metal powder as fuel additive
- Selection of energetic polymers as fuel-binders
- Use of combustion catalysts as burn rate modifiers.

Execution of first three approaches [7,37] also poses few issues especially in processing of CSP. Addition of fine oxidizer particles beyond an optimum level to enhance burn rate may enhance viscosity of the slurry and reduce its pot life. The casting of such slurries in moulds becomes very difficult. Besides, the superfine particles of AP are prone to form agglomerates that are difficult to mix homogeneously in binder and under such circumstances a uniform burning rate is difficult to achieve from the processed propellant. The mechanical properties of the finished propellant may be adversely affected by use of nonconventional types of energetic binders. On the other hand, application of energetic fuel-binders such as Polybutadiene-acrylic acid (PBAA), Polybutadiene acrylic acid acrylonitrile (PBAN), Carboxyl terminated polybutadiene (CTPB), Glycidyl azide polymer (GAP) etc., are known to improve the performance of the solid propellants [38–41], however, these binders produce CSPs that are sensitive to shock and impact. It has also been reported that mechanical properties of such grains are inferior to HTPB-AP propellant and these are expensive to produce. The combustion catalysts in nanoscale have novel properties to achieve the higher performance w.r.t. conventional catalysts. This is attributed to its high surface area per unit volume which can speed-up the catalytic reactions. For this reason, novel approaches are being attempted to set a new paradigm for catalytic combustion of CSPs. Thus, use of efficient combustion catalysts for enhancement of performance is the best option that does not incur higher cost of development of advanced rocket motors. These catalysts can be utilized without difficulties in every type of propellant formulation. The combustion catalysts possess some unique features as listed below:

- Low-priced materials and commercially available
- A small quantity (few weight %) is only required
- No adverse effects on processing condition or strength
- Selectivity and simplicity in application
- Often non-toxic in nature
- Minimal risk on impact or shock
- Size and structure can be tailored by appropriate synthetic routes
- Ability to enhance performance of rocket motor
- Variable oxidation states suitable for multiphase reactions
- Ability to form stable compounds or complexes with ions, radicals and intermediates.

In spite of several attractive features of nanocatalysts used in recent times, the general focus has been to prepare nano-sized TMOs, their complexes, nanoalloys etc. using a cost effective process. The physical properties like surface morphology and surface area have been given importance to explain their efficacy. New direction in research should be oriented towards tailored nanocatalysts that may have molecular interaction with propellant ingredients and desired electron affinity. This will assist in positive change in solid-state and gas-phase reaction mechanisms between oxidizer and fuel to further improve reaction processes in flame zone to enhance combustion efficiency. New nanocatalyst may also have anti-agglomeration surface to ensure their homogeneous dispersion and possible solubility in liquid fuel binder. Efforts should also be made to produce nanocatalysts with optical

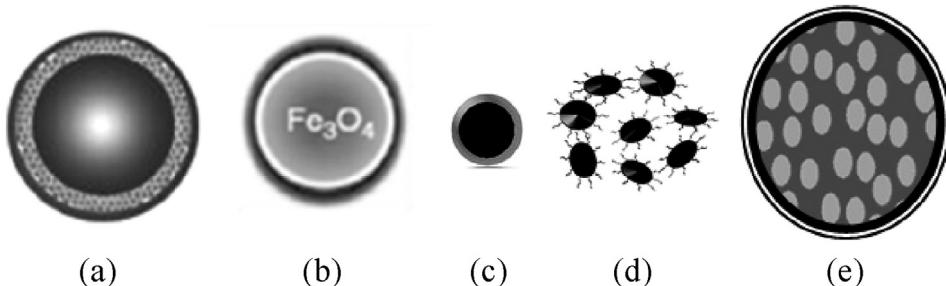


Fig. 2. Typical metallic core nanoparticles (a) SiO_2 coated nano TiO_2 (b) Nano Fe_3O_4 (c) Metal core Quantum dot (d) Functionalized quantum dots (e) Nano Fe_2O_3 decorated graphene quantum dots.

properties favourable to radiative heat transfer that could assist in combustion process.

3. Prospective nanoscale combustion catalysts

Investigation of nanoscale materials (NMs) as prospective catalysts has created promising avenues for their use in advanced propellant systems. The size of these NMs may lie between 1 and 100 nm, which is much smaller than bulk sized materials (over 20 μm). They can be produced by either the 'bottom-up' approach, i.e. building-up from individual atoms or molecules or the 'top-down' approach i.e. breaking-up bulk materials into nano-range through milling or nano cutting processes. Metallic cores of nanoparticles (NPs) obtained from precursors for catalytic processes are shown in Fig. 2.

The physical and chemical properties of NMs are found to be superior in many aspects as compared to their bulk counterparts. As a result, these materials have found great applications in catalysed combustion of CSPs, sensors, nonlinear optics, electronics, magnetism and many more [42]. Based on their size and structure, these NMs can be classified as following types:

- NMs of 0 dimensions: the length, breadth and height of such systems are limited into a single point, e.g. nanodots.
- NMs of 1 dimension: these NMs have only one parameter either length or breadth or height e.g. thin surface coatings
- NMs of 2 dimensions – the length and breadth are only considerable parameters for this class of NMs, e.g. nanowires and nanotubes.
- NMs of 3 dimensions-the length, breadth and height are the parameters which are considered, e.g. nanoparticles.

The size reduction of NMs does not affect the original nature of the substrates. However, their properties like electrical conductivity, elasticity, mechanical properties, color and reactivity exhibit a significant change. For example, the carbon in the form of graphite is soft and malleable but at nanoscale this becomes stronger than steel and also six times lighter in mass. The macro sized ZnO_2 is opaque and white that appears transparent at nanoscale. A nano-Cu is a highly elastic metal at room temperature that can be stretched 50 times higher than original length without breaking. Similarly, nano-Al particles combust efficiently when added as fuel additive.

Future high performance propulsion systems would require high energy density, high reaction rates, short ignition delay, very high burn rates and smooth flame spread across propellant surface. Addition of nanocatalysts in CSPs provide the most convenient and effective approach to achieve these objectives. These catalysts have a potential to provide improved thermal conductivity to CSPs that otherwise have poor conductivity and as a result hold promise to

influence sub-surface reactions, increase surface temperature to assist fuel pyrolysis and oxidizer decomposition rate besides allowing homogeneous dispersion of ultrafine catalyst throughout the gas phase reaction zone. These accelerated processes are expected to improve combustion phenomenon and lead to very high burn rates. Such catalysts may also be incorporated in liquid monopropellants and bipropellant systems to do away with structural catalytic system that is complex and relatively less reliable. The uniformly distributed or dissolved nanocatalyst in fuel will promise reduced ignition delay and higher combustion efficiency in LPR engines.

4. Recent trends in application of nanometals (NMs) as combustion catalysts

Application of combustion nanocatalysts has become the most reliable technique used for enhancement of combustion characteristics of rocket propellants [39,40]. A combustion nanocatalyst can have potential to improve the decomposition behaviour of both fuel and oxidizer individually or together. As mentioned earlier, the catalysts of nanoscale size show better performance than their bulk counterparts. Various nanometals in form of oxides, alloys, complexes, derivatives, etc., have been extensively studied as effective catalysts especially in AP based CSPs [43–45]. Studies have revealed that catalytic properties of one metal may be entirely different from others. An individual nanometal also exhibits change in catalytic behaviour as the particle size, crystal structures, agglomeration characteristics and environment etc., are varied. Due to uncertainty in the property of NMs from one batch to other, intensive research on all promising materials and their properties needs to be conducted [46,47] to select best option for an application.

Production of NMs with consistent particle size and surface properties is an important challenge for the researchers. Many metallic nanocatalysts which include pure metal nanoparticles (NPs), in form of compounds, complexes, composites and others have successfully been evaluated as potential catalysts. The enhancement of burning rate of CSPs with these catalysts has been the subject of many studies in the past and some important results are summarized in Table 3. The measurement of burning rate of CSPs both at ambient and high-pressure conditions are presented to show their efficacy in enhancement of burning rate at different concentration levels. In combustion studies conducted using metal nanocatalysts so far, interesting results on pressure dependence of burning rate have been obtained with varying solid propellant compositions. An effort has been made to classify metal catalysts separately on the basis of their individual structure for better understanding of their influence on burning rate and ballistic properties of CSPs. The details of each class of metallic nanocatalysts are discussed below.

Table 3

Burning rate data of CSPs showing influence of nano-scale metal catalysts.

Metal nano-catalysts	Weight % loading	Burn rate (\dot{r})/(mm/s), pressure regimes/MPa								Ref.
		Ambient	0.098	0.98	1.37	3.92	5.88	6.86	7.84	
AP/HTPB	—	—	—	1.63	—	—	—	—	—	[52]
do	NTO	0.5	—	1.92	—	—	—	—	—	—
do	Fe(NTO) ₂	0.5	—	2.04	—	—	—	—	—	—
do	CuO	0.5	—	2.02	—	—	—	—	—	—
do	Cu(NTO) ₂	0.5	—	2.51	—	—	—	—	—	—
do	Fe ₂ O ₃	0.5	—	1.94	—	—	—	—	—	—
AP/Al/HTPB	—	0.5	—	1.26	2.79	3.58	4.95	—	6.03	—
do	NTO	0.5	—	1.43	3.55	4.44	5.20	—	—	—
do	Cu(NTO) ₂	0.1	—	1.67	5.09	6.90	6.31	—	7.90	—
do	Cu(NTO) ₂	0.5	—	—	—	—	6.91	—	8.70	—
do	Cu(NTO) ₂	2.0	—	—	—	—	11.3	—	14.0	—
do	Fe(NTO) ₃	0.5	—	1.56	4.81	5.71	6.80	—	8.20	—
do	CuCr ₂ O ₄	0.5	—	—	—	—	8.00	—	10.5	—
do	CuCr ₂ O ₄	2.0	—	—	—	—	13.8	—	17.1	—
AP/Al/HTPB	#CuCr ₂ O ₄	2.0	—	—	—	—	—	—	9.4	—
do	#CuCr ₂ O ₄	2.0	—	—	—	—	—	—	10.4	—
do	#CuCr ₂ O ₄	2.0	—	—	—	—	—	—	15.5	—
do	n-Fe ₂ O ₃	2.0	—	—	—	—	—	—	12.7	—
AP/Al/HTPB	n-Fe ₂ O ₃	—	—	9.27	—	—	20.8	—	29.1	—
do	n-Fe ₂ O ₃	1.0	—	—	—	—	21.8	—	30.1	—
do	n-Fe ₂ O ₃	2.0	—	—	10.1	—	22.9	—	31.7	—
AP/HTPB	—	—	2.04	—	—	—	—	—	—	[55]
do	ZnO ₂	1.0	3.18	—	—	—	—	—	—	—
do	Cr ₂ O ₃	1.0	2.70	—	—	—	—	—	—	—
do	TiO ₂	1.0	3.03	—	—	—	—	—	—	—
AP/HTPB	MnC ₂ O ₄	1.0	2.50	—	—	—	—	—	—	[56]
AP/HTPB	—	—	—	—	—	—	6.00	6.11	6.55	—
do	n-Cr ₂ O ₃	0.25	—	—	—	—	7.16	7.55	8.00	—
do	n-Cr ₂ O ₃	0.50	—	—	—	—	7.19	7.59	8.11	—
do	n-Cr ₂ O ₃	0.75	—	—	—	—	7.20	7.72	8.30	—
do	n-Cr ₂ O ₃	1.00	—	—	—	—	7.22	7.88	8.40	—
AP/HTPB	—	—	1.22	—	—	—	—	—	—	[9]
do	Ni–Co	1.0	2.08	—	—	—	—	—	—	—
do	Ni–Cu	1.0	1.77	—	—	—	—	—	—	—
do	Ni–Zn	1.0	1.59	—	—	—	—	—	—	—
AP/Al/HTPB	n-MnO ₂	0.25	—	—	—	—	6.82	7.18	7.64	—
do	n-MnO ₂	0.50	—	—	—	—	6.89	7.36	7.76	—
do	n-MnO ₂	0.75	—	—	—	—	6.96	7.43	7.95	—
do	n-MnO ₂	1.00	—	—	—	—	7.10	7.54	8.02	—
AP/HTPB	#CuCr ₂ O ₄	2.00	—	—	—	6.40	—	—	—	[59]
do	#CuCr ₂ O ₄	2.00	—	—	—	7.91	—	—	—	—
AP/Al/HTPB	—	—	—	—	—	—	—	—	7.51	8.73
do	Bu*/HTPB	1/9	—	—	—	—	—	—	11.44	12.15
do	Bu*/HTPB	3/7	—	—	—	—	—	—	13.54	14.65
do	Bu*/HTPB	5/5	—	—	—	—	—	—	17.41	19.03
do	Bu*/HTPB	7/3	—	—	—	—	—	—	19.69	21.20
AP/Al/HTPB	Graphene	1.00	—	—	—	—	4.20	—	5.50	6.40
do	n-TiO ₂	1.00	—	—	—	—	5.25	—	6.80	7.90
do	**GTNC	1.00	—	—	—	—	6.80	—	8.40	9.10

Note: # prepared by different methods, *Bu = Butacene, **GTNC = Graphene decorated Titanium Dioxide.

4.1. Transition metals and their oxides

The effect of transition metals and their oxides on combustion of CSPs have been studied extensively by several investigators due to their interesting catalytic influence on decomposition and combustion of AP. Transition metals that have partially filled d-shell electrons make them ideal for participation in combustion reactions [2,3]. The reactivity of these metals can be understood by considering its important features as listed below:

- Ability to show variable oxidation state
- Capability of forming co-ordination compounds or complexes
- Multifunctional ability in combustion reaction
- Metal can burn exothermally in presence of air/oxidant.

Nanoscale transition metals are known to be superior catalytic materials in comparison to their micron size counterparts. Several

investigators have performed experiments to show their effectiveness on the combustion and decomposition mechanisms of CSPs. A comprehensive review of the prominent research work carried out in this domain is presented here. Liu et al. [26] have reported that the effect of nanoscale Ni, Cu, Al metals on the thermal decomposition of AP and found that it reduces the decomposition temperature of two exothermic peaks. The enthalpies of decomposition have also been enhanced in orders of Ni (1.32 kJ/g), Cu (1.20 kJ/g) and Al (0.90 kJ/g) respectively. These are much larger than that of pure AP (0.44 kJ/g) which indicates that the decomposition mechanism is improved. It has been reported [48] that crystal structure of NPs influences the combustion behaviour of CSPs. It was studied thoroughly in case of cobalt nanoparticles (Co-NPs). Three types of morphologies of Co-NPs have been prepared in-situ referred as ball, cauliflower and snowflake-like crystal patterns. Individual morphology of Co-NPs was used in the thermal decomposition of AP. Both exothermic

peaks corresponding to high thermal decomposition (HTD) were merged into a single sharp peak that shifted to a lower temperature effectively. The decreasing order of decomposition temperature are as follows; ball-like (316.3°C), cauliflower-like (311°C) and snowflake-like (284°C) respectively. The snowflake-like Co-NPs was found to the best morphology for improving decomposition performance of AP.

Zhou et al. [49] studied the effect of Co_3O_4 based nanocatalysts in the form of nanorods, nanosheets and nanocubes on thermal decomposition of AP and found that nanorods exhibit best catalytic activity. It is inferred that absorption of ammonia on AP surface inhibits its decomposition and catalyst absorbs ammonia on its surface with a typical binding energy, facilitating enhancement of AP decomposition. Different physical forms of catalyst show different binding energies of NH_3 and their effectiveness on AP decomposition depends on it. Green synthesis of MnCo_2O_4 nanoparticles has been reported by Juibari and Tarighi [50]. The catalyst has been found to exhibit excellent catalytic activity in thermal decomposition of AP. The detailed kinetic study using thermal analysis approach is conducted to propose plausible mechanism of catalytic action in the decomposition process of AP. Xiao et al. [51] investigated role of mesoporous ZnCo_2O_4 rods synthesized by oxalate co-precipitation method on thermal decomposition of AP. The catalyst showed excellent results and could reduce the HTD of AP by 162.2°C . The authors have proposed flow diagrams of decomposition process with and without catalyst to reveal its efficacy. It is shown that low annealing rate in preparation process of catalyst plays an important role in formation of the effective mesoporous catalyst with much larger specific area.

Duan et al. [62] have prepared Nickel nanoparticles (Ni-NPs) using hydrogen plasma technique. The average particle size of Ni-NPs was 36 nm approximately. It was evaluated in catalysis reaction with AP in embedded form and results were compared with micron-sized Ni. It was observed that Ni-NPs reduce the LTD from 330 to 328°C while HTD shifted from 440 to 410°C . The substantial reduction in HTD comprises of gas-phase reactions which are influenced by addition Ni-NPs. Song et al. [63] have studied effects of zinc (Zn) metal powder for both micron and nanoscale as combustion catalysts in CSPs and their components.

A marginal change in the peak temperature has been observed in both the sizes of Zn. However, the total heat releases in presence of Zn-NPs are much larger than Zn micron size powders. The work also evaluated the impact of magnesium nanoparticles (Mg-NPs) on the thermal decomposition of AP. The result showed that addition of a small amount of Mg-NPs effectively reduces the decomposition temperature and also increases the heat release value during decomposition process of CSPs. The metal oxides containing Fe in nanoscale range have been reported as excellent catalysts for AP-based propellant combustion. Among them, the nano- Fe_2O_3 attracted more interest mainly due to its surface and magnetic properties. A unique structural feature, i.e. more oxygen bound to Fe-surface, enables it to react vigorously with reacting elements. The scaling, crystal structure and particle size of n- Fe_2O_3 were found to have severe impact on catalytic property. Patil et al. [64] have reported that small size of n- Fe_2O_3 showed better results. This is attributed to availability of more active sites that contribute to further increase of rate of decomposition of deprotonised HClO_4 gas on the surface of catalyst [65,66]. Various shape of n- Fe_2O_3 including nanorods, irregular and octahedron showed different activity on the thermal decomposition of AP. The nano-rods of n- Fe_2O_3 exhibit better catalytic activity than other two types. The lowering in high thermal exothermic peaks of AP was found as 49°C , 16.8°C and 10°C when nanorods of n- Fe_2O_3 were incorporated. This has also demonstrated that size of 30 nm of n- Fe_2O_3 reduces HTD by 40°C (at 0.5 wt%) and 59°C (at 2 wt%). It is

revealed that percentage of nanoparticles lowered down the HTD considerably. Styborski et al. [67] carried out the burning rate measurements for AP/HTPB composite propellants with iron nanoparticles as additives. The addition of iron nanoparticles at a concentration level of 1 wt% has been found to increase the burn rate of AP-HTPB composite solid propellant by approximately one and half time. The various morphologies of CuO-NPs were prepared and added to examine the thermal decomposition of AP [37]. The results showed that two exothermic peaks combine together into an intense large peak. The enthalpy liberated during the reaction is much higher as compared to commercially available micron sized CuO. Wang et al. [23] compared the catalytic effect of bulk NiO and nanoNiO on the thermal decomposition of AP. The DTA curve revealed that HTD of AP is found at 300°C in the presence of NiO-NPs while bulk sized NiO showed it at 400°C . The Co_2O_3 nanoparticles (Co-NPs) also act as combustion catalyst during the thermal decomposition of AP. There was no significant change in endothermic peak but significant reduction in decomposition temperature of exothermic peaks was seen as compared to LTD and HTD of uncatalyzed oxidizer. The burning rate has also been enhanced 2–3 times using nanoscale $\text{CuO}, \text{NiO}, \text{Co}_2\text{O}_3$ and MnO_2 . The catalytic activity is further enhanced by increasing the percentage of these nanoparticles. The order of catalytic activity of NPs were found to be $\text{Co}_2\text{O}_3 > \text{CuO} > \text{NiO} > \text{MnO}_2$ [68]. Solymosi et al. [69] have studied the catalytic effect of N-doped ZnO nano particles (ZnO-NPs) on the thermal decomposition of AP. The result showed that ZnO with peculiar morphology helps in lowering the thermal decomposition temperature of AP. The activation energy is found to decrease from 178.22 to 93.51 kJ/mol with AP-ZnO NPs composition. The enhancement of catalytic activity could be explained on the basis of its oxygen valency and defects that are created by doping of nitrogen atom. Nanoscale CuCr_2O_4 has been found to be potential catalyst for the combustion of AP and respective CSPs. In this regard, it is demonstrated that the CuCr_2O_4 had better catalytic effect as compared to its bulk size catalyst [70]. The nanosized copper chromite lowers the HTD of AP and also decreases the activation energy significantly. It was also observed that nanoscale CuCr_2O_4 is better catalyst than nanoCuO. The decrease in the efficiency of nanoscale catalysts is observed due to the effect of agglomeration of superfine particles. It may be overcome by production of NMs with the help of composite processing technology. Such NMs as nanocatalysts greatly improve the catalytic behaviour. The nanoscale metal oxides like Fe_2O_3 , CuO and Co_2O_3 have been prepared by composite method and are found to be very useful in thermal decomposition as studied by Ma and his co-workers [71]. These composites were prepared by a novel solvent – nonsolvent method. In this method, the AP particles were coated by metal oxides nanocatalysts. The DTA curve indicated that there is no change in the transition temperature in presence of nanoscale metal oxides and composites of metal oxides/AP; however, the HTD is dramatically changed. The nanocore-shells of metal oxides with AP such as ZnO/AP, Co_3O_4 /AP and Fe_2O_3 /AP have been synthesized by facile liquid deposition technique at ambient conditions. These nanocatalysts have exhibited excellent self-catalytic behaviour. The self-catalytic activity mainly depends on the content of metal oxide nanoparticles that could be controlled by the concentration of metal salt in the precursor solution. In case of ZnO/AP nanocomposites, the ZnO:AP at mass ratio 4:100 is shown to exhibit the best self-catalytic performance and also lower activation energy that is reduced from 154.0 kJ/mol to 96.5 kJ/mol [72].

Vargeese et al. [73] have synthesized anatase and brookite phases of titanium dioxide (TiO_2) nanocatalyst from titanium alkoxide precursor. The average particle size was found in 10 nm range and anatase/brookite phase TiO_2 was confirmed by powder XRD and SAED. Catalytic effect of the TiO_2 nanocatalyst on thermal

decomposition reaction of AP was evaluated. The evaluation of effectiveness of nanoTiO₂ catalyst was computed by a non-linear integral isoconversional method and it was found that the activation energy is influenced as compared to non-catalysed AP decomposition reactions. The catalysed AP decomposition showed an unaffected LTD with extent of conversion between 0 and 0.30 is slowed down but later influences HTD in the range of 0.35 and 1. The possible reasons for the catalytic effect of TiO₂ nanoparticles on the HTD of AP are discussed based on the fact that the exposed cations and anions on the transition metal oxide nanoparticle surface act as acid-base site pairs and adsorb gaseous reactive molecules formed during the LTD of AP. It has been proposed by the authors that the efficacy of TiO₂ nanocatalyst may be attributed to the absorption of gaseous low temperature decomposition products of AP on cations and anions on the nanoparticle surface that act as acid-base site pairs and eventually influences the HTD of AP. Dave et al. [55] prepared TiO₂, ZnO₂, and Cr₂O₃ nanoparticles by quick precipitation method. Cui et al. [74] have studied catalytic performance of Cu/CNT on thermal decomposition of AP. It has been reported that HTD of AP decreases by 126.3 °C and LTD peak disappears. It may be concluded that catalytic performance of Cu in CSPs can be improved in presence of CNTs.

Generally, the properties of Nano Transition Metal Oxides (NTMOs) depend not only on their chemical composition but also on their structure, phase, shape, size, and size distribution. Moreover, control of the morphology is one of the primary requirements for improving their catalytic efficiency. It was also observed that the size distribution, phases, nanocrystalline textures were largely dependent on the synthesis methodology. In order to get uniform and repeatable combustion properties of CSPs, various researchers have made efforts for preparation of nanocatalysts with different techniques. Li and Cheng [75] have synthesized Cu–Cr–O nanocomposites via a citric acid complexing approach and demonstrated that these catalysts are useful in enhancing the catalytic-combustion of AP-HTPB based solid propellants. Dubey et al. [76] prepared nanocomposites of Mn with Co, Ni, and Zn by polyol method. These NPs showed the high reactivity toward total combustion of solid propellants. Kawamoto et al. [53] have prepared copper chromite from ceramic and co-precipitation methods, which were found to increase the burning rate of HTPB-based solid propellants. Rajeev et al. [77] synthesized Cu–Cr–O composites from thermal decomposition of copper ammonium chromate. They observed that the higher burning rates of solid propellants are the consequence of crystal structures, particle sizes and interspersed metallic phases of the precursors. The nanocomposites comprising of transition metals like copper and chromium have been prepared using different approaches like complexing and thermal decomposition of inorganic salts and used in propellant formulations to enhance combustion process of AP-HTPB propellants. The preparation method for nanosized copper chromite involving ceramic and co-precipitation approach that produced an effective catalyst has also been reported.

Rao et al. [30], have synthesized mixed metal oxides (MMO) containing Cu–Co–O by citric acid complexing method. Three types of MMO nanocatalysts, namely Cu₂Co₄O₃ (I), Cu₃Co₂O₄ (II) and Cu₄Co₂O₆ (III) were obtained that contained higher copper content i.e. 29.41, 48.31 and 56.13 wt% respectively. It was found that catalysts virtually had no effect on first endothermic decomposition temperature of AP that remained around 246 °C, however, second exothermic peak registered a significant change when catalysts were incorporated at a level of 2 wt%. It is further observed that all the catalysts prepared increase the heat of combustion of cured AP-HTPB propellants significantly with Cu₂Co₄O₃ (I) exhibiting its superiority over others due to high crystallinity and low agglomeration characteristics. These features also accounted for

the best burn rate of propellant observed among three different cases of nanocatalysts used in the study. Nanomaterials as ingredients and catalysts [10] are the focus of new research in the field of high energy materials and combustion. These are also being considered for micro thrusters and pyro MEMs etc. The main approaches for their synthesis involve physical, chemical and mechanical pathways. The selection of process is generally application based and can involve techniques like sputtering, spinning, RF plasma, pulsed laser ablation etc. The chemical methodology may use colloidal, sol-gel processing, micro emulsion, chemical vapour deposition, thermolysis and solution combustion besides high temperature pyrolysis. The melting, milling, physical vapour deposition and high voltage explosion of metallic wires are also used as mechanical techniques to obtain nanomaterials. The selection of a process for getting nanocatalysts and NTMOs in general, involves criteria such as high purity, homogeneity, uniform sizing of product particles besides low cost, eco-friendly and simpler process. The sol-gel processing technique addresses major concerns and desired product properties are obtained for use of NTMOs as combustion catalysts.

NTMOs with diverse morphological structure have attracted tremendous attention since past two decades. This is due to its remarkable catalytic, optical, magnetic, and electrical properties [78–80]. For example, the catalytic applications of some transition metals and their oxides such as CuO, Co₃O₄ [81], LaCo₃O₄ nanocrystals [82], MnO₂ [83], and oxides of lanthanides like La₂O₃, Pr₂O₃ and Nd₂O₃ [84], Nd₂O₃ [85] etc., in the thermal decomposition of AP have been studied. Many researchers have examined a variety of additives to examine their catalytic properties for AP decomposition. Among the NTMOs catalysts, spinel copper chromite (CuCr₂O₄) is found to be an effective catalyst for the CSPs used in rocket applications. It imparts a pressure-independent catalytic effect on the burning rate of AP moiety. Moreover, copper chromite has also been used as catalyst for various industrial processes such as dehydrogenation, oxidation and hydrogenation, and so similar reactions in combustion process of CSPs may be accelerated by it [86,87]. Also, the characteristics of copper chromite do vary according to the method of synthesis and can differently influence the efficacy of the catalyst. The burning behaviour of propellants is highly dependent on the thermal decomposition of AP. This has been extensively studied and improved by taking advantage of the catalytic activity of many NTMOs [88,89]. Since a lower decomposition temperature in the condensed phase leads to a higher burning rate, catalysts which decrease the thermal decomposition temperature of AP are always of interest in the field of solid propellant technology. The catalytic thermal decomposition of AP is remarkably sensitive to metal oxide additives and hence thermal decomposition characteristics of AP influence the combustion behaviour of the propellants. In addition, surface characteristics of catalysts influence the overall catalytic activity and condensed phase and gas phase combustion details of solid propellants [66].

NTMOs are expected to form an external oxide shell over core nanometal that plays an important role during catalytic activity in propellant burning. The shell/core composites of TMOs/AP are produced to avoid the agglomeration of TMOs nanocatalysts and improve their catalytic efficiency for the thermal decomposition of AP. Pure CuCr₂O₄ NPs were synthesized via a simple precipitation route without any surfactant combined with calcination at 600 °C. A series of Cu–Cr/AP nanocomposites have been prepared using solvent/non-solvent combination and found to exhibit an excellent catalytic activity by reducing the decomposition temperature of AP. The change in the calcination temperature and Cu/Cr molar ratio varies the size and shape of the Cu–Cr–O NPs that influences the catalytic thermal decomposition of AP [77,78].

In general, the activation energy, reaction rate, and thermal

decomposition temperature of AP have a significant influence on the combustion properties of solid propellants, especially on their combustion rate. The particle sizes chosen in propellant formulations are generally of two (bimodal) or occasionally more sizes (tri or multimodal) in order to achieve higher solid filler loading in the fuel binder matrix. The smaller size particles get into the interstitial spaces of bigger particles to provide improved compactness to CSPs. AP being in large concentration and the main provider of the oxidising species in the combustion process plays an import role. AP being a monopropellant produces ammonia and perchloric acid (Eq. (1)) to initiate the primary redox flame that subsequently transfers the heat back to the solid surface to pyrolyze fuel binder that eventually leads to generation of multiple flames on propellant surface. Involved chemical reactions in deflagration of AP are pressure and temperature dependent and are too many that can involve various dissociation and recombination reactions with different pathways. It is well known that AP particle size and its concentration influence the burn rate of CSP and provide a convenient approach to tailor it. Finer particle size of AP enhances the burn rate due to larger surface area it provides for deflagration reactions to take place. It may, thus, be inferred that very high burn rates can be achieved with superfine AP, however, the preparation of superfine AP is very dangerous and difficult, because the material is a strong oxidant and explosive in nature. Also, nanoscale particles tend to exhibit agglomeration phenomenon and AP as such is hygroscopic in nature. Superfine AP is technically too small in size to be mixed homogeneously with coarse AP and may result in lower catalytic activity [42,43].

CSP containing AP often give a violent response towards heating and machining or adding some active fuel ingredients. Necessary precautions are essential during extrusion of the propellant from mould if struck and sparks tools are used if trimming and cutting of the grain is required. Friction sensitivity of AP based propellants is also known to increase with higher concentrations of catalysts and can be correlated with the burning surface temperature that normally increases in catalysed propellant. Alone AP can burn and deflagrate as monopropellant nearly at 20 bar. Temperature sensitivity, impacts, or friction during the processing are the biggest concern of AP based CSPs. Procedural flaws or mishandling can cause uncontrolled deflagration, explosion or detonation. Combustion catalysts (micron/nano) are generally inert materials which are added to propellants for enhancing the properties of decomposition. It is reported that nanoscale metal catalysts can react with AP particles and release additional heat by catalytic decomposition reactions. Multiple active centres are also reported during the oxidation process of nanometal particles that have a high impact on the decomposition or combustion of AP. Thus, it is desirable to select the best catalyst with right particle size which does not alter the energetic and are safe for propellant formulation. For safe use of AP in solid propellants, critical decomposition energy has also been studied which revealed that it decreases with the reduction of AP particle size. When AP particle size is less than 3 μm , the critical decomposition energy is very small and so necessary caution in handling, sieving, mixing operations is essential [90,91].

4.2. Complexes of transition metals

A wide variety of complexes of transition metals were studied for modifying the ballistic properties of CSPs. The metal hexamine perchlorates [92], $[\text{Cu}(\text{NH}_3)_6](\text{ClO}_4)_2$, $[\text{CO}(\text{NH}_3)_6](\text{ClO}_4)_2$, $[\text{Ni}(\text{NH}_3)_6](\text{ClO}_4)_2$ and $[\text{Zn}(\text{NH}_3)_6](\text{ClO}_4)_2$ have been examined to evaluate the kinetics of thermal degradation and explosion delays for their potential use in the solid propellants and other energetic materials. Thermogravimetric (TG) measurements of these complexes revealed that deamination takes place at lower temperature

while intermediates formed during decomposition could be helpful in catalytic combustion of CSPs. The burning rate of AP-HTPB based CSPs has been found to increase considerably by adding 2% bis(ethylenediamine) metal perchlorates (BEMPs) complexes in forms of $[\text{M}(\text{en})_2](\text{ClO}_4)_2$ (where M = Mn, Fe, Co, Ni, Cu, Zn). Among all the synthesized BEMPs, $[\text{Fe}(\text{en})_2](\text{ClO}_4)_2$ has shown most effective catalytic property [93]. Thermal decomposition behaviour of BEMPs containing TMOs has shown effectiveness order of Fe>Cu>Co>Ni>Zn>Mn. The enhancement in the linear burning rate of CSPs with BEMPs at ambient condition was also investigated. The four types of bis(ethylenediamine) metal (II) nitrates (BEMNs) complexes $[\text{M}(\text{EDA})_2](\text{NO}_3)_2$ [94] were prepared and added at 2 wt % each in the AP-HTPB based propellant formulations. Thermolysis characteristics, activation energy, explosion delay and explosion temperature of CSPs containing these BEMNs were also studied. The values of activation energy and explosion temperature of CSP+ $[\text{Cu}(\text{EDA})_2](\text{NO}_3)_2$ were found much lowered than BEMNs of Co, Ni and Zn. Substantial increments in the steady burning rates were also observed. Kulkarni et al. [95] have prepared complexes of 3-nitro-1,2,4-triazol-5-one (NTO) and 2,4,6-trinitroanilino benzoic acid (TABA) with TMOs of Co/Cu/Ni/Fe and characterized with AP-HTPB based CSPs as burn rate modifiers. Thermal decomposition (DSC) data showed that inclusion of Fe-NTO in propellant formulation that led to an increase in $(-\Delta H)$ by -3000 J/g with decrease in exothermic peak decomposition temperature by nearly 30°C , whereas the Fe-TABA decreased exothermic peak temperature by $\sim 45^\circ\text{C}$ and showed increase in $(-\Delta H)$ by 2.7 times. The study also suggested that inclusion of Fe complexes of NTO/TABA into the CSPs improved the catalytic decomposition of AP-HTPB composition in condensed and near the gas phase. The linear burning rate of CSPs containing 2 wt% each of Cu, Co, Ni, Fe in NTO/TABA have also been found to increase significantly at ambient and high-pressure ranges. The best catalytic effect was obtained with Fe-NTO salt which increased the burning rate to the extent of ~80% as well as brought down the pressure index (n) to 0.18 (2–9 MPa). Cao et al. [96] have studied the influence of nano CuO and nano ZnO up to a pressure of 5 MPa on combustion behaviour of 5-aminotetrazole (5-AT)/Sr(NO₃)₂ based solid propellants. The results obtained using TG-FTIR were analyzed to propose the combustion mechanism of nanocatalysed propellants.

Trache et al. [97] have performed evaluation of the catalytic effects of oxamide (OXA) and azodicarbonamide (ADA) with AP-HTPB-Al based solid propellants. It was found that both OXA and ADA acted as effective burning rate suppressants. For proper understanding, thermal decomposition of ingredients and burning processes of CSPs with 0.5%–3.0 wt% OXA/ADA was carried out. It was observed that thermal decomposition of OXA exhibits only endothermic effects, whereas that of ADA presents both endothermic and exothermic effects in the sample propellants. The study has also revealed that OXA and ADA reacted both in the condensed and gas phases and influenced the burning rate pressure index effectively. Gang et al. [98] synthesized 3 new Co(II) complexes: $[\text{Co}(3,3'\text{-Hbpt})_2(\text{H}_2\text{pm})(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$ (I), $[\text{Co}(4,4'\text{-Hbpt})(\text{pm})0.5(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ (II) and $[\text{Co}(3,4'\text{-Hbpt})(\text{pm})0.5(\text{H}_2\text{O})_3]\cdot 2\text{H}_2\text{O}$ (III) for promoting the thermal decomposition of AP in the CSPs. Where, 3,3'-Hbpt referred to 3,5-bis(3-pyridyl)-1H-1,2,4-triazole; 4,4'-bpt indicated 3,5-bis(4-pyridyl)-1H-1,2,4-triazole, 3,4'-Hbpt referred 3-(3-pyridyl)-5-(4'-pyridyl)-1H-1,2,4-triazole and H₄pm = pyromellitic acid. The TGA, DTA and DSC thermal methods were used to characterize the decomposition properties of AP with all 3 Co (II) complexes. The data obtained during the characterization suggested that complexes I and II have superior quality of catalytic decomposition of AP and may prove to be promising combustion catalysts in CSPs for advanced purposes.

A promising energetic green combustion catalyst, 1,8-

dihydroxy-4,5-dinitroanthraquinone barium salt (DHDNEBa) has been synthesized for modifying the decomposition of CSPs by metathesis reaction [99]. The apparent activation energy of DHDNEBa using Kissinger's method was found to be 177.3 kJ/mol. The entropy, enthalpy and free energy of activation of the first thermal decomposition were found as 8.16 J/mol·K, 168.0 kJ/mol and 163.4 kJ/mol, respectively. The self-accelerating decomposition temperature (SADT) and critical temperature of thermal explosion were observed to be 282 °C and 297 °C, respectively.

Copper β -resorcylate (cupric 2,4-dihydroxy-benzoate, β -Cu) nanoparticles have been prepared and characterized as combustion catalyst [100]. The results showed that the nano-sized β -Cu was of semi-spherical shape and of homogeneous distribution with a uniform size of 100 nm. The formation mechanism of β -Cu nanoparticles in the whole process was discussed in detail. Furthermore, the catalytic properties of β -Cu were investigated. The TG/DSC study showed that nanosized β -Cu could be a promising additive for accelerating the thermal decomposition of ammonium perchlorate (AP).

Nanoscale triaminoguanidine nitrate (TAGN) having average particle size of 218.7 nm was synthesized by Wang et al. [101] for accelerating the decomposition of AP based composition of CSPs. A mix of 10 wt% nano TAGN with 90% AP was used for thermal characterization studies. The results obtained by DSC analysis were found interesting in regard to higher activation energy (152.34 kJ/mol) than pure AP (117.21 kJ/mol) and exothermic peak temperature of pure AP 478.5 °C shifted to extremely lower level(287.2 °C). The activation free energy of samples was also calculated and found positive indicating appropriate stability of the energetic compositions. The authors have also proposed decomposition mechanism explaining that nano TAGN initially decomposes into hydrazine and later it consumes HClO_4 and other gaseous products of AP. They have also highlighted about the limitations of TAGN especially in large scale propellants formulation.

4.3. Binary nanometallic composites and nanoalloys

The range of properties of metallic systems can be enlarged by use of binary mixtures of intermetallic elements or metallic alloys. The surface structure, binary composition and properties of nanoalloys are vital as these plays important role in influencing their chemical reactivity especially in catalyzing reactions. Nanoalloys are also of interest as these may display structures and properties which are distinct from those of the pure elemental cluster and bulk alloys. Certain methods such as co-decomposition, direct/inverse deposition, co-reduction methods etc., are adopted in production of nanoalloys with known and controlled surface properties. These materials were utilized practically for improving the burning characteristics of CSPs and decomposition of their ingredients. The binary nanoparticles of Ni, Cu, and Al as nanoalloys were optimized as attractive catalyst for the thermal decomposition of AP [102]. Chaturvedi et al. [103] have studied metal nanoalloys Co–Cu, Co–Fe, and Co–Zn for thermal decomposition of AP and found them very effective. Singh et al. have investigated the

effect of bimetallic nanocrystals such as Cu–Co, Cu–Fe, Cu–Zn, Ni–Cu,Ni–Co, and Ni–Zn on thermal decomposition of AP [104]. The effect of ternary alloy nanoparticles on thermal decomposition of AP was also studied and it was found that all nano alloy particles are effective in thermal decomposition of AP. They also evaluated bimetallic nanocomposites of Mn with Co, Ni and Zn in AP-HTPB composite solid propellants and observed enhancement in burning rate.

Singh et al. [105] have prepared bimetallic nanoalloys of Ni–Cu, Ni–Co and Ni–Zn by hydrazine reduction of respective metal chloride in ethylene glycol obtaining particle sizes of the orders of 34, 43 and 30 nm respectively. These nanoalloys were found to be interactive in the thermolysis of AP and AP-HTPB composite solid propellants and caused enhancement of the overall burn rate. TG studies revealed that the HTD peak of AP in thermogram is seen to shift enormously. Among the bimetallic nanoalloys, Ni–Co nanoalloy is reported as the best catalyst [106]. Dave et al. [107] have also synthesized Ti nanoalloys such as Ti–Co; Ti–Zn; Ti–Cu by hydrazine reduction method. Average particle sizes of these nanoalloys were measured using data obtained by XRD and SEM analysis. The data as presented in Table 4 was then fitted to standard Scherrer's equation. Ti-nanoalloys in all compositions were found to be good nanocatalysts for the thermal decomposition of AP as supported by TGA/DTA analyses. Ti–Zn nanoalloy yields the lowest activation energy whereas Ti–Co combination in CSP gives the highest burn rate.

Kumar et al. [108] have performed experiments on decomposition mechanism of oxidizers containing AN, and AN/KDN binary composites with Cu–Co-oxides as combustion nanocatalyst. The attempt was made to trace out the major combustion products based on thermal analytical data and their activation energies were calculated using Ozawa-Flynn-Wall (OFW) isoconversional method. It was suggested that addition of 2 wt% Cu–Co-oxide nanocatalyst leads to reduction of the activation energy of AN and AN + KDN compositions. The evaluation of detailed kinetics of thermal decomposition of AN and KDN in varying proportion was also made. These values were compared with CuO- kinetic data and it was revealed that nanocatalysts are effective in improving the combustion characteristics of AN-based propellants [109].

4.4. Ferrocene and their derivatives

So far, a wide variety of metallic nanocatalysts have been discussed and these are solid-state nanomaterials. In solid forms, these catalysts may pose some issues in propellant processing if used in high concentrations. The inclusions of solid-state NPs in the propellant slurry may produce specific degree of inhomogeneity and thus may induce variation in the burning rate of CSPs at different grain locations. The viscosity of propellant slurry also increases drastically as the solid-state NPs are added to the propellant composition. The casting of propellant mix in the confined moulds and mandrels under vacuum is not an easy task. Wang et al. [23] have noticed that an erratic burning may results if such propellants are not homogenized properly. To eliminate these shortcomings,

Table 4
Ti-nanoalloys and their key characteristics as combustion catalysts [107].

Sample	Particle size/nm	Activation energy/(kJ·mol ⁻¹)	Burning rate/(cm·s ⁻¹)	r^*/r
CSP	—	245	2.041	1.00
CSP + Ti–Co	28.2	190	3.472	1.70
CSP + Ti–Ni	16.1	118	2.882	1.41
CSP + Ti–Zn	24.6	81	2.700	1.32

Note: r^* and r is burn rate of CSP with and without Ti-nanoalloys respectively at ambient condition.

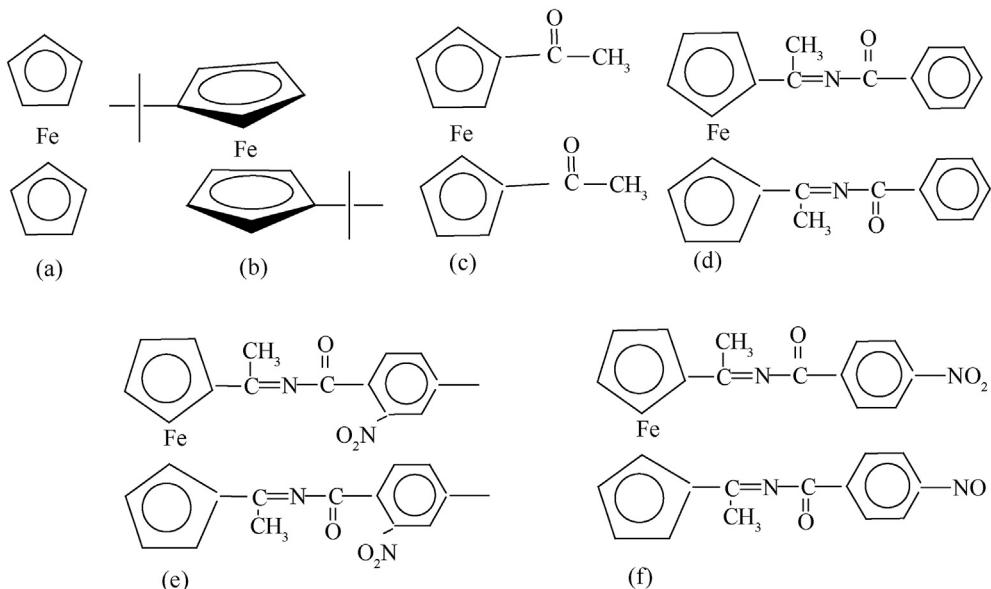


Fig. 3. Chemical structures of ferrocene and its derivatives used as combustion catalysts; (a) Ferrocene (b) di-tert-butyl ferrocene (c) di-acetyl ferrocene (d) 1,1'-diacetylferrocene benzoyl hydrazone (e) 1,1'-dimethyl o-dinitrop -dinitrobenzoylhydrazoneacetylferrocene (f) 1,1'-diacetylferrocene-p-nitrobenzoylhydrazone [3].

some efforts have been made by considering iron containing metallocene instead of NPs [3,60]. In this regard, the ferrocene and its derivatives have been identified as attractive candidates. These catalysts usually impart high burn rates and bring down the pressure index which is almost equal to AP-HTPB based CSPs.

Sometimes ferrocene derivative also acts as cross-linking agents and plasticizers in special conditions [110–114]. These are chemically compatible with other ingredients of the propellant compositions. In addition, these additives do not adversely affect the mechanical properties, have better microscopic homogeneities in distribution and superior ignitability of the propellant. Besides, they have minor influence on sensitivity to impact, friction and the ageing even at high concentrations of around 2–5 wt%.

Kishore et al. [3] have reported several ferrocene derivatives with special property for use in rocket propellants as shown in Fig. 3. During combustion of CSPs, ferrocenes break down into hydrocarbons and Fe gets oxidized into Fe_2O_3 , liberating significant quantity of energy. In-situ FeO is formed which is expected to be in finer molecular state, even smaller than what is obtained by milling

process. The derivatives of ferrocene are assumed to be involved in multiple roles as compared to the ferrocene alone in combustion process. A clear understanding of mechanism involved in various stages of catalytic combustion is still required.

Ferrocene derivatives containing silicon compounds have been reported in both solid as well in liquid native states. These serve as curing agents, burning catalysts and bonding agents. The 2, 2-bis (ethyl ferrocenyl propane), commonly known as catocene, butyl ferrocene and 1, 3-diferrocenyl-1-butene are in liquid state and can have potential application in solid propellants. One representative ferrocene derivative is presented in Fig. 4. The catalytic efficiency of these compounds is many times higher than typical n- FeO . Since, their native state is liquid, this causes migration from solid matrix and that remains a challenge for scientists working on propellant formulation. Several attempts have been made to protect migration tendency of ferrocene derivatives from solid surfaces of CSP. A prominent method is to insert ferrocenyl groups into the backbone

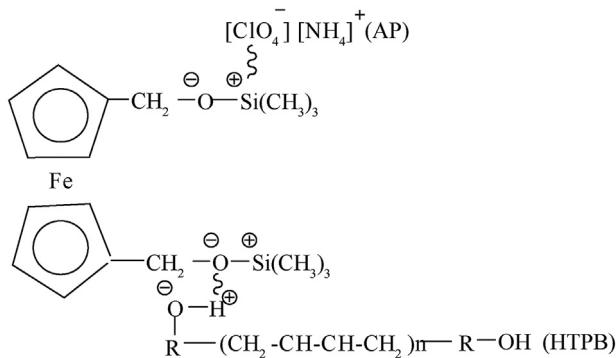


Fig. 4. Possible catalytic sites of 1,1' - bis (trimethylsiloxyethylferrocene with AP-HTPB [3].

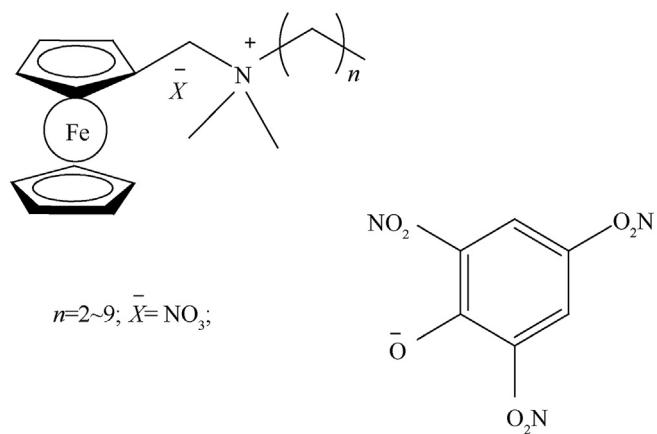
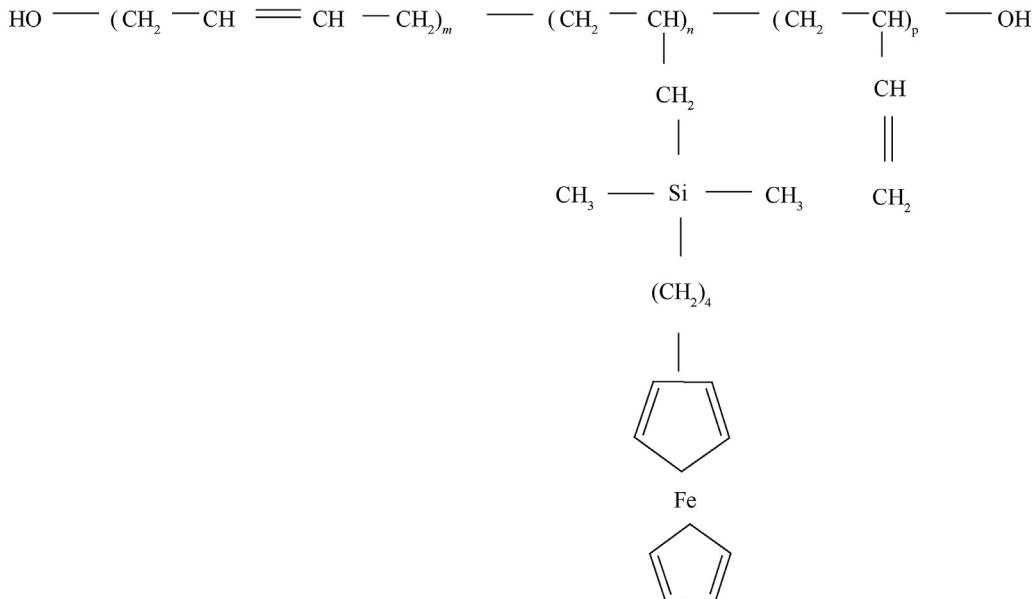


Fig. 5. A representation of ferrocenylmethyl-alkyldimethylammonium nitrates and picrate [118].

**Fig. 6.** Molecular structure of Butacene having multiple reactive centres.

of polymeric binders by ferrocene precursors. However, these compounds have shown some undesirable properties that result into uneven burning and aging characteristics are also affected [115–117]. Some compounds showed properties of low volatility, good thermal stability, and higher catalytic effects on the CSPs with respect to mononuclear ferrocene derivatives. In the similar context, Gore et al. [115] have synthesized and characterized the total four numbers of ferrocene derivatives, namely 2,4-dinitrophenylhydrazine, 1-pyrrolidinylmethyl ferrocene, di-tert-butyl ferrocene and 1,3-diferrocenyl-1-butene (DFB). They have also conducted experiments with AP-HTPB based CSPs and observed that these derivatives show better catalytic property, tensile strength and high percentage of elongation than Fe_2O_3 and n-butyl derivatives. The DFB has been found as best catalysts among all prepared derivatives. By adopting the modular synthetic strategy, Gu et al. [118] have prepared total 16 ionic ferrocene derivatives for retarding the solvent migration from propellants surfaces. The nitrate and picrate groups are specially added to the structures as counter ions which exhibit low migration tendency and high catalytic effect on CSPs as depicted in Fig. 5.

The synthesis of ferrocene-based porphyrins incorporating transition metals like zinc, cobalt, nickel and copper is reported. It was observed that catalytic effect of free porphyrin and Zn (II) and Ni (II) porphyrins were similar to that of catocene, however, Cu(II) and Co (II) containing porphyrins showed higher catalytic activity in terms of burn rate of CSP and improved thermal decomposition of AP. Further, migration of catalysts was found to be significantly arrested. No work has been reported on combustion of CSPs containing NMs in conjunction with ferrocene derivatives. Varghese et al. [119] have observed that the liquid ferrocene derivatives exhibited limiting effect during burning as concentration of catalysts is increased. The burning characteristics of such systems cannot be explained based on available combustion model. The Societe Nationale des Poudres et Explosifs (SNPE), France, has developed a binder by grafting ferrocenyl groups on to the pendant $\text{C}=\text{C}$ double bonds in the vinyl component of hydroxyl terminated polybutadiene (HTPB). This prepolymer is named Butacene [60], its structure is given in Fig. 6.

Gore et al. [120] have made efforts to study the burning rate of

aluminized AP-propellants by partial replacement of HTPB by butacene. At the level of 25% butacene replacement with HTPB 60% higher burning rate were achieved. However, 10–20% higher burning rate has been observed on 50% butacene replacement while negligible changes have been found on total replacement of HTPB binder in same propellants. Due to catalytic effects, the butacene based solid propellants show lower pressure exponent (n) of the burning rate which is a desirable property. The functionalized ferrocenes like ferrocene polyglycol oligomer (FPGO) have been evaluated as viable liquid ballistic modifier for AP-HTPB based propellants. It improved the burning rate of solid propellants and also free it from migrating problems. The data investigated during the combustion reactions suggested that burning mechanism were comparable to n-butyl ferrocenes and di-ferrocenyl-1-butene [121].

The ferrocene-grafted hydroxyl-terminated polybutadiene (Fc-HTPB) containing 0.20, 0.52, 0.90, and 1.50 wt% iron have been synthesized by FC alkylation method. By incorporation into Fc-grafted binder, there was no adverse effect found on the mechanical property of the cured propellants. However, burning rate has been found as 8.66 mm/s, much higher than AP-HTPB propellants [119]. In a recent review of chemical modification of HTPB for tailoring the certain properties of propellants is available [122]. For improving the combustion property and burning rate, the prepolymers such as Butacene®, FPDS-g-HTPB, Fc-HTPB, BiFc-g-HTPB, HTPB-[Fe(CO)₃]x, PPA-HTPB-PPA and PNBE-HTPB-PNBE may be considered, however, HTPBs have shown promising results. In order to develop a low migrating combustion catalyst, seven different transition-metal complexes of 5-ferrocenyl-1*H*-tetrazole(HFcTz) termed [Cu₂(bpy)₂-(FcTz)₄]·2C₂H₅OH,

Table 5
Comparative properties of graphene with CNTs [131].

Properties	Graphene	CNTs
Fracture strength/GPa	124	45
Density/(g·cm ⁻³)	>1	1.33
Thermal conductivity/(W·Mk ⁻¹)	5000	3000
Electrical conductivity/(S·cm ⁻¹)	10 ⁶	5000
Charge mobility/(cm ² V ⁻¹ s ⁻¹)	200,000	100,000
Specific surface area/(m ⁻² ·g ⁻¹)	2630	400

$[\text{Pb}(\text{phen})_2(\text{H}_2\text{O})_3](\text{FcTz})_2 \cdot \text{H}_2\text{O}$, $[\text{Mn}(\text{phen})_2(\text{H}_2\text{O})_2](\text{FcTz})_2$, $[\text{Ni}(\text{phen})_3](\text{FcTz})_2 \cdot 9\text{H}_2\text{O}$, and $[\text{Co}(\text{phen})_3](\text{FcTz})_2 \cdot 9\text{H}_2\text{O}$ have been synthesized and characterized with different energetic materials [123] where, bpy = 2,2-bipyridine and phen = 1,10-phenanthroline. Prepared complexes have enough thermal stability and exhibited quasi reversible redox systems. The catalytic effects of these complexes in extents of 2–5% on AP, 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), and 1,2,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) have shown excellent decomposition effects as well as high burning rates in the propellants formulations. Among the complexes, Ni/Co based catalysts have been found superior for burning rate enhancement.

4.5. Graphene nanomaterials

Graphene has attracted attention due to its unique properties like high carrier mobility, room temperature quantum effect and ambipolar electric field effect [124]. This has a distinct property to combine its graphinic units together that leads to formation of 3D functional materials. The graphite is a simple example of 3D materials that is composed of multilayer structure [125]. Graphene in the form of carbon nanotubes (CNTs) contains fewer graphene layers in nanoscale, displays amazing properties in comparison to the bulk form [126,127]. These special properties make graphene one of the most appealing material for various applications [61,128,129]. Physical properties of graphene and a comparison with CNTs are presented in Table 5. Graphenes have an exclusive potential to increase the catalytic property by modifying its surface with suitable metal oxides or nanoparticles. The research in this direction has been undertaken with preparation Cu/CNT nanocomposites to observe the catalytic effect on AP [130,131].

The Ni/CNT and Co/CNT nanocatalysts prepared by microwave irradiation process were evaluated for their catalytic effect on the thermal decomposition of AP. From the DTA curve, decrease of HTD of AP by 100.5 °C and 174 °C and increase in the heat release by 1.21 and 0.8 kJ/g in case of Ni/CNT and Co/CNT catalysts was noted. The HTD reduction was observed by 126.3 °C and peak of LTD disappeared in case of Cu/CNT nanocomposites. Nano diamond (ND) supported metal catalysts have been found to exhibit excellent catalytic activity. Sui et al. [130] have reported ND/Cu nanocomposites as an excellent catalyst for thermal decomposition of AP. Results showed that by adding ND/Cu nanoparticles and pure Cu nanoparticle (2 wt%), two exothermic peaks of AP merged to one and thermal decomposition temperatures of AP decreased by 115 °C and 107 °C respectively. From the results, it may be inferred that ND/Cu and Cu NCs were strong catalyst for AP decomposition; however, ND/Cu is seen to be more effective.

Dey et al. [61] have done extensive work towards using graphene as functional catalytic materials in increasing the performance of rocket propellants. Initially, the potential of graphene and nanoparticles together in catalytic combustion of CSP was investigated. This led to the synthesis of graphene-titanium dioxide nanocomposite (GTNC) by microwave irradiation process. They have reported a scheme for synthesis GTNC as depicted in Fig. 7. Thermal characterization of AP with GTNC (up to 5 wt%) has been carried out which showed decrease in decomposition temperature from 412.87 °C to 372.50 °C. Simultaneously, the value of ΔH was found to increase from 2053 J/g to 3903 J/g. The burn rate of CSP in the presence of GTNC is also enhanced by two times approximately.

Graphene-Iron Oxide Nano Composite (GINC) has also been studied as an efficient catalyst for AP decomposition and found to increase the burn rate of CSPs [131]. In synthetic process, n-FeO (20–30 nm) was decorated on graphene and subsequently employed as burn rate modifier. In a set of experiments, 1–5 wt % GINC were utilized and it was observed that the burn rate could be increased by 52% approximately which is more than bulk FeO (30 wt%) and n-FeO (37 wt%). Significant change in decomposition temperature of AP has also been observed in presence of GINC. Isert et al. [132] have also synthesized decorated graphene with nanoscale iron oxide catalyst using different techniques. This functional material was found to disperse well in the medium and this also tends to reduce the agglomeration. Changes in burning rate of CSP with catalysed and uncatalyzed propellants have been investigated. The effect on burning rate on encapsulating the catalyst inside the fine AP crystals compared to control propellant where it is added to the binder is also investigated. It was found that the highest burning rates occur in propellants where the graphene is decorated with nanoscale iron oxide catalyst and encapsulated in the fine AP. The next highest burning rates were observed in propellants with decorated graphene that is physically mixed into the propellant. The lowest burning rates were found in propellants where the graphene is undecorated (no catalyst impregnated). There is little difference in burn rates between compositions with encapsulated or physically mixed graphene when compared to base propellant.

Most recently an extraordinary work has been done by Melo et al. [133], towards synthesizing different types of graphene-based functional materials for catalytic applications. The graphene oxide quantum dot (GOQD) and reduced GOQD (rGOQD) were synthesized using a simple oxidative treatment and sonication process. GOQD and rGOQD were used as supporting agents for in situ generation of gold nanoparticles, avoiding the use of additional stabilizers. GOQD resulted as a better support than rGOQD because of the presence of higher functional groups that can interact with gold. Theoretical studies through density functional theory revealed the important role of the epoxy groups of GOQD on the

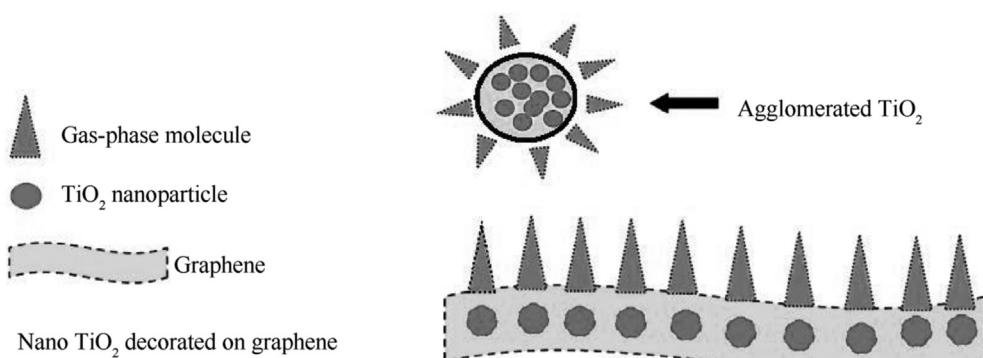


Fig. 7. Functionality of graphene-titanium dioxide nanocatalysts (GTNC) [61].

stabilization of gold. GOQD and GOQD-Au were tested for the first time as catalysts in the decomposition of CSPs. The presence of GOQD not only lowered the thermal decomposition temperature of ammonium perchlorate (AP) but also enhanced the exothermic heat release of AP in comparison to graphene and GOQD-Au increased the total energy release. The effect on the decrease of the decomposition temperature of AP was found to be not as significant as compared to other previously reported catalysts.

4.6. Metal phthalocyanines

Over the past four decades, investigators have made constant efforts for the discovery of ideal combustion catalyst with repeatable properties and outstanding performance of CSPs [134–136]. Many researchers have undertaken their studies for these purposes. Metal Phthalocyanines (MPc) have also been identified as prospective catalytic materials in propellant technology. These metallic systems possess some novel properties which can also be useful in the fields of molecular electronics, liquid crystal displays, gas sensors and organic laser materials. The MPcs have been considered as excellent catalysts because of their peculiar structure as shown in Fig. 8, and ability to transfer electron for the reactions. The central cavity of a typical MPc-core is known to be capable of accommodating 63 different ions. The functionality of these groups depends upon the conjugated 18 π electrons which invariably are present in the molecular structures [137]. These are extremely stable in responses to thermal, light and humid environments. Studies have revealed that the MPcs cores are good radiation absorbers and have potential to oxidize the chemical reactions. Bill et al. [138] reported that copper phthalocyanine (CuPc) reduces the pressure exponent and enhances the combustion characteristics. It has also been reported that CuPc is an effective catalyst even in low pressure regimes [139].

Fong et al. [140] have studied the effect of CuPc on DDI-cured AP-HTPB based CSP and found that it enhances the burning characteristics and reduces the pressure exponent considerably. Bain and Rudy [141] have inferred that addition of CuPc can reduce the combustion instability of CSPs. Several other studies have also been performed to prove their efficiency and utility in CSPs. It has been concluded that the di-oxygen binding feature in all the characterized MPcs is responsible for enhancing the combustion characteristics of CSPs. Transition metal phthalocyanine complexes have shown better catalytic efficiency due to its solubility in the binder molecules of rocket propellant. This results in more consistent and reproducible burn rate. The transition metal phthalocyanine complexes are well characterized compounds and thermally stable up to 500–600 °C. So, these may prove to be quite suitable catalysts in

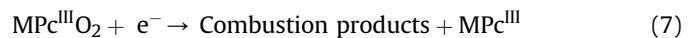
Table 6
Catalytic nature of metal phthalocyanines.

Metal phthalocyanines	Fuel-catalyst	Oxidizer-catalyst
Fe-Pc	Yes	—
Cr-Pc	Yes	—
Cu-Pc	Yes	Yes
V-Pc	Yes	Yes
Co-Pc	—	Yes
Mn-Pc	—	Yes
Ni-Pc	—	Yes
Zn-Pc	—	Yes

solid composite propellants.

The catalytic role of the metal phthalocyanine complexes in augmenting reactions related to fuel-binder and/or HTPB/AP propellant is presented in Table 6. The order of reactivity can be described as: Fe-Pc > Cr-Pc > Cu-Pc > V-Pc > Co-Pc > Mn-Pc > Ni-Pc > Zn-Pc [136]. Singh [135] has investigated the effect of metal phthalocyanine (MPc) on catalytic combustion of both HTPB fuel binder and AP-HTPB based CSPs. Analytical methods for characterization of MPc moieties have been used and correlation between the physical properties of catalysts and combustion characteristics of fuel binder and CSPs has been attempted. It is concluded that inclusion of 3 wt% MPc has led to an appreciable increase in the burn rate of the propellants which is observed to be nearly three times in case of cobalt phthalocyanine. Kakumanu et al. [123] have studied thoroughly the catalytic effect of three phthalocyanines such as Cu-Pc, Co-Pc and Fe-Pc on combustion of AP-HTPB based CSPs. The TGA data revealed that after incorporation MPcs in CSP formulations, a major weight loss in the temperature range of 200–400 °C is observed which is much larger than uncatalyzed CSP. Based on DTA results as presented in Table 7, there is no remarkable change noticed in LTD peaks.

However, the HTD peak was reduced significantly. As per the nature of DTA curves, it has been suggested that catalytic reaction gets initiated nearly at 250 °C. After this, an exothermic peak is observed and this observation is in close agreement to the reported results by Rajic and Suceska [134]. Thermal decomposition mechanism and plausible reactions are presented below:



In presence of MPc, the extracting rate of oxygen molecule from HClO_4 may enhance and induce redox coupling for conventional reactions as described above in the chemical equations. Thus, the rate of overall reaction increases which is desirable for improvement of the combustion characteristics of CSPs [136].

Future research directions on use of a variety of available nanocatalysts in particular application shall depend on our detailed understanding of their type, size, shape, compatibility and ease of propellant processing to begin with. Subsequently, their qualitative

Table 7
Differential thermal analysis (DTA) data [136].

Sample	LTD (Endo) peak/C	HTD (Exo) peak/C
AP-HTPB	246	428
AP-HTPB + Cu-Pc	245	336
AP-HTPB + Co-Pc	245	346
AP-HTPB + Fe-Pc	244	334

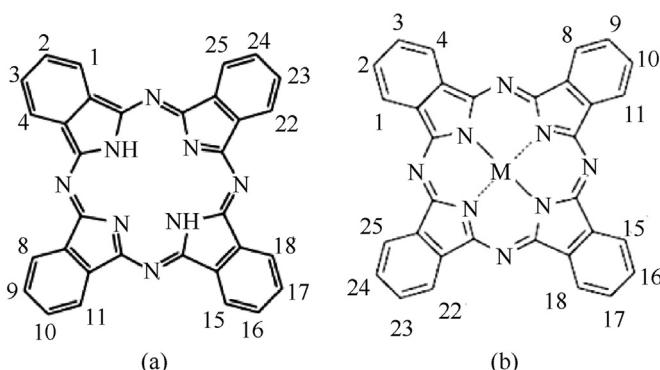


Fig. 8. Typical structures of (a) phthalocyanine ring and (b) metal phthalocyanine.

and quantitative effect on propellant ingredients alone and in conjunction need to be experimentally investigated. The unacceptable problem areas like adverse effect on mechanical properties, ballistic characteristics and safe storage life, if any, need to be resolved. For example, graphene decorated with nanocatalyst may inhibit agglomeration of nanoparticles, nanocatalyst coated AP can assist their combustion, proper selection of their shape and size may address propellant processing issues. Research on hybrid nanocatalysts that may structurally inherit advantages of two different entities is in initial stages and need to be carried out intensively in near future. The mechanism of action of nanocatalysts on overall combustion of CSPs need to be investigated to optimize various aspects of their usage with energetic materials. One important area that has not been investigated, is the influence of such catalysts on combustion products of CSPs and whether smoke generation may be curtailed or mitigated in rocket motor operations by using it. Nanocatalysts may conveniently replace fine component of AP in CSP formulations and ease their processing when higher solid filler loadings are required without changing its burn rate. The efficacy of such catalysts on rocket performance at high operating pressure range (3–15 MPa) is to be investigated in detail at different equivalence ratios. This research work may prove important in development of fuel rich propellants for specific applications.

5. Conclusions and future scope of work

Combustion catalysts have great role in propellant technology. Several characteristics of such catalysts have been included for their suitability and applications in the CSPs. Use of catalytic materials in the propellant formulation is a convenient approach which has ample potential to improve the propulsive performance as compared to other techniques. These catalysts in nanoscale size have been confirmed to be more attractive for advanced solid rocket missions. Catalytic properties of nanocatalysts play crucial role in influencing combustion characteristics, burning mechanism, spatial distribution of released energy and overall steady state combustion dynamics of the CSPs. A detailed understanding of burning properties and combustion characteristics of nanocatalysed CSPs is essential before these are employed in actual rocket motors.

To date, numerous researches on nanocatalysts have been undertaken with an aim to identify the best catalyst for possible performance advantages. The detailed literature survey revealed that the TMOs are the most widely studied catalysts which were used in numerous applications in solid rocket motors and pyrotechnic applications. Recent interest has shifted towards synthesis, characterization, augmentation of oxidizer decomposition and efficacy in propellant combustion of several nanocatalysts and new researches have been conducted in this advanced area. However, the findings and results available from these studies are often fragmentary in nature and intensive work is required to develop a deeper understanding about most attractive preparation approaches and mechanism of catalytic activity on propellants and their ingredients. In this paper, an attempt has been made to summarize information about all available nanocatalysts. It is divided into different groups depending upon the physical properties, catalytic ability, chemical reactivity etc. The advantages, attainable merits and their limitations are described individually in different sections. The nanocatalysts containing transition metals and its oxides, complexes, binary nanocomposites and nanoalloys have been given due mention. Metal phthalocyanines, ferrocenes and graphenes have also been included in the text as these also exhibit promising properties as catalyst in combustion of solid rocket propellants.

Recent work on synthesis of graphene decorated functional materials with metal nanoparticles has exhibited amazing catalytic behaviour when incorporated in solid rocket propellants. It has also been observed that such graphenes can improve burning rate 2–3 times higher than other nanocatalysts. The graphene-titanium dioxide (GTNC), Iron Oxide Nano Composite (GINC) and graphene oxide quantum dot (GOQD) have emerged recently as novel candidates that may eventually prove to be superior combustion catalysts. Performance aspects of CSPs in association with graphene functional materials as catalyst have also been highlighted and described. The prospects in this area are enormous and further research work shall open new avenues in the designing and synthesis of energetic nanocatalysts with multifunctional combustion efficacy.

Current state of knowledge has indicated the process of preparation of nanocatalyst significantly influences their catalytic efficacy. Research and development work to identify the best process including operating conditions is required to produce nanocatalysts suitable for propellant combustion that can ensure repeatability of burn rate characteristics. The scaling up of the process should be possible to produce high quality nanocatalysts at industrial scale to reduce cost and improve availability. Further, standards for characterization of such materials need to be finalized in order to compare their physio-chemical properties, surface morphology, particle shape and size etc.

Some advancement has been made to understand the thermal decomposition behaviour of oxidizers like AP and AN and related chemical kinetics in presence of nanocatalysts of different types, however, investigations on mechanism of deflagration explaining pathways of catalytic action and rate controlling steps is yet to be understood clearly. Burning rate results on various nanocatalysed CSPs are available in literature and significant influence of catalysts has been demonstrated. There is lot of work needed to be carried out to elucidate the important parameters that influence the combustion efficiency of catalysed CSPs and their relative role in condensed phase, surface and gas phase combustion of propellants. No work appears in open literature on the ignition behaviour of nanocatalysed CSPs and evidence of any departure from standard propellant system needs to be acquired, due to incorporation of nanocatalysts. Efforts should also be made to identify suitable nanocatalysts that can influence the pyrolysis rate of fuel binder as well. A success in this effort would greatly facilitate the requirement of ultra-fast burning CSPs for tactical missiles. Lastly, very little progress has been made to test nanocatalysed CSPs in proof motors to assess their impact on performance parameters and combustion efficiency.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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