CHAPTER 2

2. LITERATURE REVIEW

2.1 Burn Rate Modifiers:

Burn rate modifiers are one of the important additives being added into the solid composite propellants (SCPs). The function of added additives such as plasticizer, bonding agents and catalyst are to modify the performance of SCPs except the specific impulse [Maycock *et al.* 1969]. **B**eing the low energy content material, these additives reduce the specific impulse of the SCPs. Burn rate modifiers are always of great interest in order to improve the ballistic properties of the solid rocket motor design [Jacobs *et al.* 1969 ; Boldyrev, 1968]. The best additives are those which are used in small quantity in order to improve the burn rate, and modify the sensitivity of burn rate on pressure as well as temperature in a controlled way. The burn rate modifiers enhance the catalysis in gaseous phase of the combustion. Burn rate of the propellant can be enhanced through burn rate modifiers, which are normally added to the basic composition of propellants without affecting its processing, mechanical and energetic properties. The most commonly used additives are p-type transition metal oxides such as Fe_2O_3, CuO, MnO_2, Nd_2O_3 and $CuCr_2O_4$.

2.2   The role of Additives on Thermal Decomposition of Ammonium Perchlorate:

Ammonium perchlorate (AP) decomposes in two steps namely low temperature decomposition (LTD) and high temperature decomposition (HTD). The specific feature of thermal decomposition of AP is extremely sensitive to the action of various additives. The actions of additives takes place in two way, one way is homo-phase in which the catalyst enters

into the AP lattice and second is hetero-phase in which catalysts retain their own phase independently [Boldyrev *et al.* 2006].

2.2.1 Homo-Phase Additives:

The homo-phase additives are introduced into the lattice of AP during the synthesis process and significantly affect its thermal decomposition pattern. These additives are grouped into three groups.

1. Additives responsible for a change in the conditions of proton, ion or electron transfer process

2. Additives that decomposes below the decomposition temperature of AP and acts as the precursors for catalytically active products

3. Additives that cause the above mentioned action in a combined way.

Foreign ion addition into the lattice of AP changes its physiochemical and thermal stability. Maycock *et al.* (1969) has introduced Ca^{2+}, SO_4^- and $C_2O_4^{2-}$ ions into the AP lattice, and observed that the divalent cation introduction increased the number of cation vacancies as per the electro-neutrality principal, and accordingly decreased the number of interstitial NH_4^+ ions. The electron theory of decomposition of AP states that NH_4^+ ions are responsible for accepting the released electron during the decomposition process. The decrease in the number of NH_4^+ ions is the reason for inhibition of thermal decomposition of AP. According to same electro-neutrality principle, the introduction of divalent anions into the lattice increases the anions vacancies. The interaction of anions with the cation decreases their concentration into the lattice. It prevents the recombination of interstitial NH_4^+ with cation vacancies, which causes the acceleration of thermal decomposition of AP. Jacobs *et al.* (1974) ; Boldyrev *et al.* (1968, 1970) ; Solymosi et

al. (1969) investigated the effect of doping of divalent cation of calcium, strontium, zinc and barium into the lattice of AP and concluded that decomposition process got accelerated in presence of these dopants. These results were in contrast to the observations of by Maycock *et al.* (1969).

2.2.2 Hetero-Phase Additives:

The high temperature decomposition (HTD) of AP is strategically important as it happens in the combustion zone of SCPs. Bircomshaw and Newman (1955) were among the first researchers who studied the action of various additives on the thermal decomposition of AP above 350°C . It was observed that the most effective additive that accelerated the thermal decomposition for AP was MnO_2 and Fe_2O_3 was the least. The Al_2O_3 had no effect on thermal decomposition rate of AP. Thermal decomposition of AP in the temperature range of 170-200°C was investigated by Hermony and Salmon (1962). The study concluded that cobalt and nickel oxides, exhibited the maximum catalytic activity, whereas, MnO_2 showed intermediate activity. However, oxides of chromium and magnesium affected the later stage of decomposition process. MnO_2 catalyst was been investigated in detailed by Galwey and Jacobs (1959). It was observed that thermal decomposition of AP reached 100% in presence of MnO_2 against the 30% for pure AP. It was also stated that the MnO_2 catalyzed only the HTD of AP. Thermal decomposition of AP in presence of copper (II) starts at 180°C against the temperature of 200°C. Jacobs and Kureishy (1962) observed that the Cu_2O decreased the deflagration delay time of AP due to its catalytic action and heat evolution during the oxidation to copper oxide. The doping of copper oxide with lithium increased its catalytic activity, whereas chromium doping with copper oxide reduced the catalytic activity.

2.3   Transition Metals and Metal Oxides:

Numerous studies have been carried out to observe the impact of transition metals and metal oxides on the thermal decomposition of AP. Liu *et al.* (2004) studied the effect of Ni, Cu, Al, NiCu of nanometer size on the thermal decomposition of AP. It was observed that in presence of nanometric Cu, Ni, Al, and NiCu powder, second exothermic peaks lowered by 130.2, 112.9, 51.8 and 140.4°C, respectively, with a small change in the first exothermic peak. Weifan *et al.* (2006) studied the effect of nano sized yittria on thermal decomposition of AP. The best composition of catalyst with AP was observed at 5%. Also, both LTD and HTD peaks merged together and appeared at 337.7°C, with the heat release of 1240 J/g. However, pure AP decomposed at 326.5 and 452.6°C, with the heat release of 515J/g. Chen *et al.* (2015) synthesized MnO_2 nanorods of different phases (α, β, γ and mixed phase) with the similar average diameter of 9.5nm and studied their effect they concluded that the catalytic activity of MnO_2 was size dependent not phase dependent. Moreover, mixed phase MnO_2 has exhibited the best catalytic activity and this phase lowered the HTD peak by 132.4°C. Chandru *et al.* (2012) studied the effect of β- MnO_2 on thermal decomposition behavior of AP. Addition of 2%w/w micron-sized β-MnO_2 to AP lowered the HTD peak temperature from 426.3 to 341.2°C (i.e by 85.1°C). However, the addition of merely 0.25% w/w mesoporous β-MnO_2 brought it down to 301.0°C. Comparatively, the mesoporous α-Fe_2O_3 at 2% w/w conc. reduced the HTD peak temperature to 317.3°C. The DSC analysis revealed an enhancement in the apparent heat released during the decomposition of AP in the presence of the prepared MnO_2 catalysts. Li *et al.* (2014) synthesized the hybrid material of Mn_3O_4 and carbonated bacterial cellulose (Mn_3O_4/CBC) by hydrothermal method and studied the effect of synthesized hybrid material on thermal decomposition of ammonium perchlorate. The author observed a remarkable decrease of

163°C in high temperature decomposition peak that appeared at 293.6 from 457.2°C. Zhang *et al.* (2014) studied the effect of ultra-long V_2O_5 nanowires on thermal decomposition of AP. It was observed that the decomposition temperature of AP decreased with the increasing catalyst loading, and the maximum decrease was found with 10% loading. It was stated that synthesized V_2O_5 nanowire had higher catalytic activity than the bulk V_2O_5. Various studies have been done on the effect of CuO, Co_2O_3 and $CuCo_2O_4$ on the thermal decomposition of AP. Lijuan *et al.* (2008) found that decomposition of AP in the presence of CuO nano-rods catalyst occurred at 349^OC, where the pure AP decomposed at $366^°$C. Thus, the decomposition of AP was improved significantly in the presence of CuO nanorods, having different surface area. Alizadeh-Gheshlaghi *et al.* (2012) observed that addition of nano size particles of CuO, Co_2O_3 and $CuCo_2O_4$ decreased the LTD to 325.72, 316, 308°C respectively as compared to 331.14°C for pure AP, whereas HTD was brought down to 353.14, 351.54 and 340.83°C respectively from 443.61°C. Moreover, $CuCo_2O_4$ showed better catalytic activity than others, which shifted the thermal decomposition temperature of AP down to about 103°C. Said *et al.* (1996) studied the role of cobaltite spinel, $CuCo_{3-x}O_4$, on the thermal decomposition of AP. It was observed that in presence of Co_3O_4 and CuO, AP decomposed in a single step at 96°C and 151°C lower temperatures w.r.t pure AP, respectively. The author lightened the effect of oxide composition on the thermal decomposition of ammonium perchlorate and emphasized that due to the addition of CuO into Co_3O_4 with x=0.1 and 0.3, increased the LTD. However, decomposition appeared more quickly at 264°C and became exothermic in just after the phase transition at 267°C. Further increase in CuO content up to x = 2.5, decreased the enhancement of decomposition to the maximum temperature range of 280-300°C. Wang *et al.* (2009) observed that addition of claw like CuO nanostructures in AP led to a significant reduction of the ending decomposition

temperature i.e. 350 and 353°C, respectively. Zhang *et al.* (2014) observed that the high temperature decomposition peak of AP decomposition decreased to 250°C from 450°C (i.e. by 200°C) in presence of synthesized nanoparticles of $Al(OH)_3.Cr(OH)_3$.

Effects of nanocomposites on AP thermal decomposition have also been widely studied. Eslami *et al.* (2016) studied the effect of AP/copper-chromium oxides core-shell nanocomposites on thermal decomposition of AP. This nanocomposite exhibited an excellent catalytic activity, and decreased the decomposition temperature by 74°C (from 420 to 346°C), with the heat release of 1510 J/g. Zhaoxia *et al.* (2012) studied the effect of MOX (M = Zn, Co, Fe)/AP shell-core nanocomposites for self-catalytically decomposition of AP. Owing to the existence of the shell of MOX nanocatalysts, ZnO/AP, Co_3O_4/AP and Fe_2O_3/AP nanocomposites showed excellent self-catalytic performances for the thermal decomposition of AP. These nanocatalysts have lowered the AP decomposition temperature to 272, 285, 337°C from 398°C, and increased the heat release to 1137, 1237, 1010 J g^{-1} from 584 J g^{-1}, respectively. Moreover, ZnO/AP nanocomposites with the mass ratio of ZnO:AP = 4:100 exhibited the best self-catalytic performance in decreasing the activation energy from 154.0 kJ/mol to 96.5 kJ/mol. Nickel oxides showed the same pattern of catalytic decomposition, as observed with copper oxide. The catalytic activity of NiO can be enhanced by thermal treatment. The catalytic activity of these additives decreases significantly above 500°C. Wang *et al.* (2005) studied the effect of nanoparticles of NiO and stated that the addition of 2% by wt NiO with AP decreased the decomposition temperature by 93°C and increased the heat of decomposition from 580 to 1490 J/g. Sharma *et al.*(2015) studied the effect of biosynthesized nickel oxide (NiO) and concluded that AP decomposition with 1% of NiO nano particles, the significant shift in LTD and HTD

which appeared at 35°C and 93°C prior to the pure AP decomposition temperature with no effect on crystallographic change temperature.

Iron (III) oxides are one of the prominent catalysts which are extensively studied for the use as burn rate modifier in rocketry. Joshi *et al.* (2008) synthesized ferric oxide in two different sizes of particles i.e. 30nm and 3.5nm by electrochemical method. The catalytic activity of the catalyst on the AP using DSC analysis showed that the overlapping of low and high temperature decomposition peaks appeared at 427 ^{O}C with the increasing concentration of catalyst. They concluded that α-Fe_2O_3 particles of 3.5 nm showed pronounced effect in lowering the HTD, and found the maximum shift of 77°C in presence of 5 % by wt. of as synthesized α-Fe_2O_3 compared to pure AP. Moreover, high heat release of 4.574 kJ/g at optimum 2 % by wt of Fe_2O_3 (3.5 nm) composition was also observed as compared to that of pure AP as 0.834 kJ/g. Song *et al.* (2010) studied the effect of as synthesized nanotubes of α-Fe_2O_3 on thermal decomposition of AP and observed the merging of both LTD and HTD together at 347°C. Xu *et al.* (2008) conducted the study of effect of Fe_2O_3 nanorods synthesized by hydrothermal method and observed no shift in low-temperature exothermic peak, where as shifts for high temperature exothermic peaks of AP appeared at 48.9, 16.8, 10 °C respectively. Zhang *et al.* (2011) studied the effect of carbon coating on the catalytic activity of nanoparticles of α-Fe_2O_3 of spherical and pod-like shape. It was observed that there was no significant effect on the shift of LTD in the presence of any kind of Fe_2O_3, whereas significant shift in HTD peak was observed that shifted to 380, 371 and 343°C from 452°C in presence of pod-like α-Fe_2O_3, sphere-like α-Fe_2O_3 and α-Fe_2O_3@C core–shell structure materials, respectively. It was concluded that α-Fe_2O_3@C exhibited higher catalytic activity towards the thermal decomposition of AP than α-Fe_2O_3. Singh *et al.* (2008) studied the effect of nanocrystalline transition metal oxides of Cr_2O_3 and Fe_2O_3 synthesized by

co-precipitation method & CuO synthesized by surfactant mediated method and Mn_2O_3 by reduction of metal complexes with hydrazine as the reducing agent with size of 54.3, 35.0, 46, 42 nm respectively. The catalytic effect on thermal decomposition of ammonium perchlorate was observed with shift of decomposition temperature downward by 150, 125, 100 and 75°C in the presence of Mn_2O_3, CuO, Fe_2O_3 and Cr_2O_3 respectively. Lu *et al.* (2014) studied the effect of ZnO/Ag nanocomposites on thermal decomposition of ammonium perchlorate and concluded that catalyst compositions containing of 4% by wt. of Ag reduced the final decomposition temperature of AP to 290°C from 453°C for pure AP (163°C).

2.4   Ferrites:

Ferrites are the chemical compounds having the general formula AFe_2O_4, where A is another metal Due to their advance electric and magnetic properties. Cobalt ferrites have been widely studied using various methods of synthesis in different applications in modern electronic technologies, microwave absorbers, catalysis and in biomedical applications. Cobalt ferrite is a cubic spinel structured ferrite, which has been synthesized through different methods in the past. Singh *et al.* (2008) studied the effect of mixed ternary metal ferrite on thermal decomposition of ammonium perchlorate and found that the catalytic activity increased with the increase of catalyst amount and cobalt zinc ferrite exhibited the highest catalytic activity over their metal ferrites. Zhao *et al.* (2010) studied the effect of synthesized $CoFe_2O_4$ nanoparticles on the thermal decomposition of ammonium perchlorate. Differential scanning calorimetry (DSC) analysis was carried out in the presence of varying concentrations (from 1, 2, and 5 by wt %) of this catalyst. It was observed that irrespective of the catalyst concentration, the second event of thermal decomposition which occurred at 326.2°C disappeared in the presence of $CoFe_2O_4$

nanoparticles. HTD of AP declined from 433.2 to 307.5°C with 5 wt% of the catalyst, with a concomitant change in the heating rate (when reduced from 20°C.min^{-1} to 5°C.min^{-1}). Liu *et al.* (2010) stated that thermal decomposition of AP in presence of nano-$CuFe_2O_4$ particles comprise of two processes: endothermic and exothermic, which occured at 250 and 445°C, respectively. Nanometer copper ferrite showed high catalytic activity in thermal decomposition of AP. However, maximum catalytic activity i.e. reduction of decomposition temperature of 105°C was observed with 5% of $CuFe_2O_4$ content.

2.5   Chromites:

Chromites are mixed-metal oxides, having the spinel formula of AB_2O_4, where A and B are transition metals of A^{2+} and B^{3+}. The spinel structure has attracted the attention of researchers due to their high mechanical resistance and high thermal and chemical stability. There are two types of spinel structures. (1) normal spinel, characterized by cation A^{2+} and B^{3+} occupying tetrahedral and octahedral sites respectively and (2) inverse spinel, in which cation A^{2+} fill one half of the octahedral sites and cation B^{3+} take up the other half of the octahedral positions and all tetrahedral coordination sites . Li *et al.* (2007) studied the effect of Cu-Cr-O nanocomposites on solid composite propellant and concluded the study with the outcome of higher burn rate and lower pressure exponent. The authors found that the molar ratio of Cu/Cr of 0.7 has exhibited the most stable combustion at all operating pressure. Patil *et al.* (2008) observed that the nano-copper chromite ($CuCr_2O_4$) showed best catalytic effects as compared to nano-cupric oxide (CuO) in lowering the high temperature decomposition of AP by 118°C at 2 wt.%. with high heat releases of 5.430 and 3.921 kJg^{-1}in presence of nano-CuO and $CuCr_2O_4$, respectively. Snoop *et al.* (2015) studied the effect of rod shaped copper chromite nanoparticles, having diameter of

20-30 nm and 200-300 nm length, on thermal decomposition of AP. It was observed that decomposition of AP got reduced by 60°C in presence of three phases of oxides, viz., CuO, $CuCr_2O_4$ and $CuCrO_2$. Grossman *et al.* (2016) observed that amine modified boron nitride accelerated the thermal decomposition, which occurred at 325°C against the 430°C for pure AP. The effect of the catalyst was also observed on the burn rate of SCPs, which revealed a 30% increase against the baseline of propellant burn rate.

2.6   Graphene Based Transition Metal Oxides:

Graphene, an isolated planar sheet of carbon hexagons consisting of sp^2 hybridized C–C bond with a π-electroncloud, has attracted the attention of scientists, technologist and engineers from different backgrounds. Thin flakes consisting of few layers of carbonatoms, including monolayer graphene, could be very important because of their interesting physical and structural characteristics. Also, its promising potential application in technological fields have been reported, such as components in microelectronic devices, transparent conductive films, gas sensors, gasstorage, heat dissipation, energy storage, solar cells, reinforcement for polymer and support for catalyst nanoparticles.

Graphene is chemically inert, however, graphite oxide (GO, the starting material utilized to prepare graphene) is active and readily exfoliated into GO in solutions due to the présence of oxygen containing functional groups (such as hydroxyl, epoxy, carboxyl and carbonyl groups). Due to the ease of its manipulation in solutions, large surface area and numerous nucleation centres created by the oxygen containing functional groups, GO could be an excellent supporting material to load nanoparticles. The combination of rGO and nanoparticles could exhibit extraordinary properties that can not provided with their individual components [Zhao et

al. 2014]. One significant advantage of graphene supported metal oxides burn rate modifier is that, it provides the high catalytic activity due to the large no of active site on the surface as well as enhances the uniform distribution of the burn rate modifier throughout the propellant mixture Ping *et al.* (2006) conducted the experimental study to investigate the effect of as synthesized Cu/CNT composite on thermal decomposition of ammonium perchlorate. They concluded the study that the AP decomposition appeared in a single stage and single peak of decomposition decreased by 126.3°C in presence of Cu/CNT**.** Zhang *et al.* (2014) studied the effect of nitrated graphene oxide on thermal decomposition of AP. It was observed that monolayer of NGO with 1.45 wt. % nitrogen content displayed a better catalytic property on AP decomposition in contrast to GO. It was attributed to more active sites in NGO, which increase the rate of heterogeneous decomposition of deprotonized $HClO_4$ gas on the surface of particles. Li *et al.* (2012) stated that the addition of Ni/graphene nano-composites (1%) could slightly decrease the lower temperature of decomposition of AP from 315.1^{o}C for pure AP to 300.1^{o}C and decrease the higher decomposition temperature from 427.8 to 330.5^{o}C. It suggests that nano-Ni particles reduce the activation energy of decomposition of AP and graphene facilitated better flow of electrons which further increased the rate of decomposition of deprotonization of $HClO_4$ gas on the surfaces of catalyst particles. Li *et al.* (2013) synthesized ultrafine Mn_3O_4 nano-particles loaded on graphene sheets and studied its effect on thermal decomposition of AP. Only graphene oxide exhibited no significant effect on thermal decomposition of AP and decomposition of AP occurred at 362.7°C in presence of 5% of nano MnO_4 particles. However, a tremendous effect of synthesized and dispersed particles of Mn_3O_4 with graphene sheet was observed on thermal decomposition of AP. It was observed that 5% of Mn_3O_4 with graphene sheet reduced the AP decomposition temperature by 141.9°C and it occurred at 291.8°C in a single stage. Li *et al.*

(2012) studied the effect of mixed metal oxides of NiAl-layered double hydroxide/carbon (LDH/C) nano-composites on thermal decomposition of AP. The peak temperature of AP decomposition decreased significantly from 460 to 301°C whereas activation energy of AP decomposition with mixed metal additives was observed to be 74.6 and 80.4 KJ mol^{-1} by two different methods Kissinger correlation and Ozawa-Flynn-Wall, respectively [Vyazovkin and Wight, 1999]. Ling *et al.* (2017) observed that rice-shaped nano-structured MnO_2 (5~10 nm in width and 10~30 nm in the length) on carbon nano-tube (CNT) exhibited superior catalytic performance during AP thermal decomposition at 120°C. With an addition of 3 wt% of composite to AP, the second exothermic peak temperature decreased by 160.2°C, with a heat release, four times that of pure AP. Dey *et al.* (2015) observed that 5 % weight Fe_2O_3 concentration was considerably more effective as compared to other compositions. Moreover, the burn rate of propellant was observed to increase from micron-sized Fe_2O_3 (30% increases) to nano-sized Fe_2O_3 (37% increase). However, the burn rate increased to about 50% as compared to nano- and micron-sized Fe_2O_3 in presence of nano-composite of graphene and iron oxide.

2.7   Methods of Catalyst Preparation:

2.7.1   Co-Precipitation Method:

The co-precipitation is one of the simplest and most widely used methods for the preparation of hopcalite catalyst. The synthesis of hopcalite by co-precipitation of soluble salts of the constituent metals in a suitable solvent and then co-precipitated by adding an acid/base or another reagent to cause the precipitation [Jones *et al.* 2009]. The precipitation of the catalyst has three stages: super saturation, nucleation, and growth. After ageing, filtration, thorough washing with deionized water, a precipitate is obtained in an amorphous phase or crystalline phase. This is followed by drying, calcinations, and activation [Makwana *et al.* 2013]. These precursors can

be readily converted into the catalyst by thermal treatment. The various characterization techniques confirm that the co-precipitation method produces lower crystalline and higher surface area than other methods [Njagi *et al.* 2011].

The chemical phases dispersed surface area, porous structure and particle size and shape are created in a single step in co-precipitation method. It can be reached by very high metal loading up to 80% and low solubility in hydroxides, alkaline media [Severino *et al.* 1998]. The pH, temperature, stirring, precursor's recovery and thermal treatment are the key features in the final material morphology, structure, and performance [Feaviour *et al.* 2007]. In the co-precipitation method, the phase association contains two elements, if one of them contained in an anion and the second one are cation, the precipitate would have a fixed or at least very inflexible composition [Li *et al.* 2007].

2.7.2 Sol-Gel Method:

The hopcalite catalysts are prepared by the sol-gel method. The reagents (nitrate, acetate salts of desired oxides) are first dissolved in distilled water in stochiometric amounts. A given amount of complexing agents dissolved in deionized water is added to this solution as a ligand. The solution is adjusted to pH (7.5-8.0) with propionic acid or ammonia or acetic acid, stirred and heated to a temperature of 60-80$^{\text{o}}$C for 4h. Syrup thus obtained is heated to 100$^{\text{o}}$C for 24h in air, followed by calcination at 450$^{\text{o}}$C for 2h or at 600$^{\text{o}}$C for 2h. After calcination, the catalyst with high surface area is obtained [Jones *et al.* 2008].

2.7.3   Impregnation Method:

The impregnation is related to an ion exchange or adsorption process. It consists of contacting a solid with liquid components to be deposited on the surface. During impregnation, many different processes take places at different rates. The type of product depends upon the nature of reactants (liquid and solid surfaces) and the reaction conditions. The main parameters affecting the liquid are pH, nature of solvent and concentrations of dissolved substances. The impregnation is one of the simplest methods of preparing the supported catalysts.

The water solution containing the metal precursor is contacted with a porous support [Raub *et al.* 2000]. The electrostatic forces monitor the adsorption mechanism and process conditions of different profile of active phases [Wojciechowska *et al.* 2007]. The calculated amount of Cu-nitrate is added into the distilled water, and then MnO_2 support is added under stirring conditions. The solution is dried overnight at 80^oC, and then calcined at 400^oC for 2h. A series of CuO/MnO_2 catalyst with different CuO loading are synthesized by the incipient wetness impregnation method [Prockop *et al.* 2007].

2.7.4   Reactive Grinding Method:

The reactive grinding is an essential preliminary operation and is sometimes use for producing particular catalysts. The crushing and grinding operation is aimed at producing particles of desired size [Clarke *et al.* 2015]. The crushing and grinding process is used with the material of natural origin or with products of action category. The grinding may take place in the absence (dry) or presence (wet) of a liquid, usually water. This is a unique and valuable process to make CuMnOx catalyst. The fused mass is crushed into the irregular lumps and sieved to the proper size [Chhatwal *et al.* 1975].

The powder, obtained after reactive grinding, has a broad particle size distribution. A typical example of CuMnOx catalysts prepared by the reactive grinding method is given by Clarke *et al.* (2015). In this preparation method, 10 cm zirconia grinding vessel with six 15 mm zirconia grinding balls was used. All grinding is performed at $25^{o}C$ temperature in the presence of $Cu_2(OH)_2CO_3$ and $MnCO_3$, mixed in 1:2 copper to manganese molar ratio. A mixture of precursor is ground for varying periods of time (0.5-72h) at 400 rpm. The resulting dry solid powders is recovered and calcined in static air $415^{o}C$ for 2h, with a ramp rate of $2^{o}C/min$ from ambient temperatures [Fang *et al.* 2013].

2.7.5   Hydrothermal Method:

The hydrothermal method is considered for the modification of precipitates gels induced by temperature under ageing in the presence of water. These transformations are usually carried out at low temperatures $(100\text{-}300^{°}C)$. This method involves textural or structural modifications of solid as summarized below:

I.   The small crystals converted into large crystals.

II.   The small amorphous particles turned into large amorphous particles.

III.   The amorphous solids into crystalline solids.

IV.   The high porous gel into a lower porous gel.

The hydrothermal transformations usually occur within liquid phases. The variables of these types of operations for a given solid are pH, temperature, pressure, time and concentration. In other instance, the hydrothermal transformations are carried out during the operations, such as precipitation, washing, drying and extrusion. The manganese doped $CuO\text{-}CeO_2$ catalyst with Mn/Cu molar ratio of 1:5 at variable calcination temperature are prepared by hydrothermal method [Fuzhen *et al.* 2015]. The optimum calcination temperature of CuMnOx catalyst is

300^oC for 2h. The appropriate calcination temperatures can promote the formation of the Cu-Mn-Ce-O ternary oxide solid solution, adjust the degree of crystallinity of CeO_2 and enhance the formation of oxygen vacancies [Fortunato *et al.* 2000].

2.7.6 Pyrolysis Method:

The pyrolysis is a thermo chemical decomposition of organic materials at elevated temperature in the absence of oxygen. Pyrolysis is a type of thermolysis, most commonly observed in organic materials exposed to high temperatures. The flame spray pyrolysis is used to produce a broad range of high purity nanopowders ranging from single metal oxides to more complex mixed oxides [Liu *et al.* 2012]. The flame spray pyrolysis is a one-step process, in which a liquid feed – a metal precursor dissolved in a solvent – is sprayed with an oxidizing gas into a flame zone. The spray is combusted, and the precursors are converted into nanosized metal or metal oxide particles. The flame spray pyrolysis techniques allows for the preparation of a vast range of materials, including meta-stable phases due to the rapid quenching process [Benjamin *et al.* 2016].

The mixture of different precursors like Mn-nitrate and Cu-nitrate are added into the de-ionized water, and fed through a commercial nozzle with liquid feed rates ranging from 2.5 to 5 mL/min. It is ignited by a surrounding supporting flame to prevent the main flame from self-extinguishing. The supporting flame gas flow consisted of 1.5 L/min CH_4 and 3L/min O_2 [Liu *et al.* (2012)]. Thermal mass flow controller regulates all gas flows. The synthesized black voluminous powders are collected by a binder less glass fiber filter, with the help of a rotary vane pump. The synthesized hopcalite catalyst gave mixtures of $Cu_{1.5}Mn_{1.5}O_4$ and Mn_3O_4 with different mass fractions depending on the initial Cu : Mn ratio [Hu *et al.* (2000)].

2.8   Burn Rate Modifier and Their Role:

Solid composite propellants are the vital fuel systems used in modern rocketry. Solid rocket motors (SRMs) and space vehicles (SVs) derive energy through solid composite propellants [Shutton *et al.* 2000]. The key ingredients of these solid propellants are hydroxyl terminated polybutadiene (HTPB), aluminium (aluminum) powder (Al) and ammonium per-chlorate (AP). The role of HTPB is to provide the structural integrity to the propellant, Al acts as the metallic fuel and AP is the most popular oxidizer used worldwide in the propellant formulation [Huang *et al.* (2015), Chandru *et al.* 2012, Reid *et al.* 2014, Grossman *et al.* 2016, Reid *et al.* 2007, Stephens *et al.* 2010 and Li *et al.* 2012]. The burn rate of a conventional propellant is governed by the combustion behavior of the solid composite propellant and is a function of the thermal decomposition of AP [Davenas, 1992 ; Jacob *et al.* 1969 ; Boldyrev, 2006 ; Huang *et al.* 2015 ; Grossman *et al.* 2016]. Transition metals and metal oxides are used as catalysts to enhance the rate of thermal decomposition of AP, eventually modifying the burn rate. The oxides of iron, manganese, copper, nickel and chromium copper chromites are widely used as the burn rate modifiers in the solid composite propellant [Reid *et al.* 2007]. Activated copper chromite (ACR), with chemical formula $CuCr_2O_4$ (Cu–Cr–O), is the industrial catalyst used extensively in solid composite propellants. Solid composite propellants with high burn rate and thereby reduced ignition delay and operational time are needed for modern space vehicles. Thermal decomposition of AP is greatly dependent on the composition (presence of any catalyst), particle size and shape of AP which ultimately determine the burn rate of SCP. Higher the burn rate with the lower pressure exponent is the desirable requirement. Thus, thermal decomposition of AP is the most deciding key factor to get desired burn rate of SCP. It provides a control to play with burn rate of solid composite propellant for achievement of remarkable burn

rate of SCP. Thermal decomposition of AP is highly affected by the additives of transition metals, transition metal oxides and their mixtures. The decomposition mechanism has been understood by the concept of electron and proton exchange at the elevated temperatures as reported by Boldrev *et al.* (2006). They studied the governed mechanism of thermal decomposition of AP and proposed electron and proton transfer process. AP is decomposed in two stages; low temperature decomposition governed by the electron transfer process and high temperature decomposition initiated by proton transfer process. The transition metals, transition metal oxides, and composites of ternary materials such as MnO_2, CuO, NiO, $CoFe_2O_4$, Fe_2O_4, $CuCr_2O_4$ etc. are common catalysts being used to enhance the thermal decomposition of AP [Boldyrev, 2006 ; Dedgaonkar *et al.* 1990 ; Kishore *et al.* 1979 ; Liu *et al.* 2004 ; Song *et al.* 2010 ; Gheshlaghi *et al.* 2012; Zhang *et al.* 2011 ; Xu *et al.* 2008 ; Chandru *et al.* 2012 ; Liu *et al.* 2008 ; Zhao *et al.* 2010 ; Chen *et al.* 2008]. In previous researches copper chromite (CuO, $CuCr_2O_4$) [Said *et al.* 1996; Dubey *et al.* 2012], ACR and titanium oxide (TiO_2) [Fitzgeral *et al.* 2004; Song *et al.* 2010] have been used as the metal oxide catalysts which have considerably decreased the onset temperature of AP decomposition when used individually as additives. Recent developments in the area of carbon based materials such as carbon nanotubes (CNT), graphene oxide (GO) and reduced graphene oxide (rGO) promised better catalysts and catalyst support due to their high specific surface area, high thermal and electrical conductivity. Dispersion difficulty of CNT leads to its restricted applications whereas due to hydrophilic nature of GO/rGO and ease of synthesis provides the potential precursor material for synthesis of graphene. Graphene is a two dimensional sheet of carbon owing the honeycomb structure which provides the high specific surface area with superior electrical and thermal conductivity [Hummers *et al.* 1958 ; Pei *et al.* 2012]. The rGO has tremendous electron transfer properties.

These inheriting properties of graphene have created the tremendous scope of its potential application in catalytic era especially in the field of thermal decomposition of AP promoted with the effect of electron and proton transfer process.

It is interesting to exploit the catalytic properties of transition metal oxide based materials and graphene based materials both in single system. Recently, graphene based transition metal oxides composites (Fe_2O_3, TiO_2, Co_3O_4 and MnO_2 etc.) have been prepared and their effect on thermal decomposition of AP has been studied [Yuan *et al.* 2014 ; Li *et al.* 2013 ; Lei *et al.* 2012 ; Wang *et al.* 2011 ; Zhang *et al.* 2014 ; Guan *et al.* 2011]. Li *et al.* (2012) has synthesized the Ni/Graphene based nanocomposites using the simple one-spot method and observed the single step decomposition of AP. However in 2013, the same group observed the negligible effect of pure graphene on modification in thermal decomposition of AP, whereas, nano particles of Mn_3O_4 dispersed on GO have shown tremendous effect [Li *et al.* 2013]. Yuan *et al.* (2014) studied the thermal decomposition of AP in presence of Fe_2O_3/GO and observed a single step decomposition of AP at much lower temperature with high energy release against the individual effects of Fe_2O_3 and GO [Yuan *et al.* 2014].

According to the previous literature, copper chromites ($CuO.CuCr_2O_4$) [Liu *et al.* 2008, Zhao *et al.* 2010 and Chen *et al.* 2008] and titanium oxide (TiO_2) [Hummers *et al.* 1958 ; Pei *et al.* 2012 ; Park *et al.* 2009] are the most efficient metal oxide catalysts which considerably decreased the onset temperature of AP decomposition when they used individually as additives in the AP. Despite the extensive and individual utilization of copper chromites and titanium oxide to affect the burn rate of AP, the physics and chemistry of their catalytic roles are not fully known. The lack of adequate information on the use of copper chromites and TiO_2 indicates a tremendous gap requiring further study.

Table 2.1 gives a summary of the available experimental work on the development, characterization and application of burn rate modifiers.

Table 2.1: Summary of Reported Work on Burn Rate Modifiers.

S/N	Burn rate modifier	Material & Methods	Characterization techniques	Results & Comments	References
Transition Metals and Transition Metal Oxides:					
	Single crystalline Ni nanoparticales	Nickle rod; DC hydrogen plasma method	XRD, TEM, BET, selected area electron diffraction (SAED), TG-DTA	Addition of Ni nanoparticles of metal oxide by 2-5wt% in AP decreases its thermal decomposition temperature by 92-105ºC and increases its apparent decomposition heat by 787.1 – 796.1 J/g.	Duan *et al.* (2008)
	Cu nanoparticles	$CuSO_4.5H_2O$, ethylene glycol NaOH, $N_2H_4.H_2O$; Reduction of CuSO4 with hydrazine in ethylene glycol under microwave irridation	XRD, FE-SEM, HR-TEM TG, DSC	Decrease in the activation energy of thermal decomposition of AP as well as composite	Dubey *et al.* (2012)

			propellant & Reduction with final decomposition temperature of AP along with the enhanced burning rate of composite propellant	
Ni, Cu, Al and NiCu nanometric size of powders	H_2O, $N_2H_4.H_2O$, HCHO $NiSO_4. 6H_2O$, $CuSO_4.4H_2O$ ethanol nanometer Al powder, micrometer Al, Ni, Cu powders and AP(30 µm) ; Precipitation method	TEM & SEM- for measuring the average particles size, XRD , Energy dispersive spectroscopy (EDS)	Decrease in the activation energy of AP for both LTD & HTD	Liu *et al.* (2004)
Bimetallic nanocrystals Cu-Co, Cu-Fe, Cu-Zn	Metal chloride, ethylene glycol, hydrazine , NaOH; Reduction of hydrazine in ethylene glycol	XRD, EDX, HR-TEM, SAED	Nano-particles of size of 10-38nm.In presence of Cu-Co, LTD decreased to 278 from 310ºC and HTD to 318	Srivastava *et al.* (2010)

			from 414°C. Cu-Fe LTD came down to 285°C and HTD to 325°C. Cu-Zn HTD decreased to 300°C with disappearance of LTD peak.	
Nano size Yitteria				Weifan *et al.* (2006)
Different phases of MnO_2	$(NH_4)_2S_2O_8$, $MnSO_4.H_2O$; Hydrothermal Method	XRD, TEM, HRTEM		Chen *et al.* (2015)
Mesoporous β-MnO_2	$Mn(NO_3)_2$ and mesoporous silica ; Impregnation method	XRD, DSC	HTD peak of AP changed into sharp exothermic peak & pure Co_3O_4 lowered the TD of AP by 96°C, pure CuO reduced it by 151°C.Composite of CuO and Co_3O_4 increased the	R.ArunChandru *et al.* (2012)

			LTD with quick sharp exothermic peak	
Mn_3O_4 / Carbonated Bacterial Cellulose	Glconacetobacter & Xylinum, Hestrin-Schramm: for bacterial cellulose, $Mn(CH_3COO)_2.4H_2O$ and anhydrous alcohol; Hydrothermal Method	XRD, HRTEM, Raman spectroscopy, XPS	Decomposition temperature of AP reduced to 293.6 from 457.2°C with the appearance of single exothermic peak.	Li. *et al.* (2014)
Ultra long V_2O_5 nanowires	V_2O_5 & H_2O_2; Hydrothermal method	XRD, SEM, TEM	Thermal decomposition temperatures of AP in the presence of 1,3,5 and 10wt% of V_2O_5 nanowires decreased by 42, 66,73 and 88.1°C , respectively.	Zhang *et al.* (2014)
CuO nanorods	$Cu(NO_3)_2.3H_2O$ (99.5%) and NaOH (96%); Conventional wet	XRD, TG-DTA, TEM, BET, FT-IR	Decrease in HTD of AP by 126.3°C (478.1	Chen *et al.* (2008)

			to 351.8°C). LTD peak of AP disappeared.	
Nano sized CuO, Co_3O_4 and $CuCo_2O_4$ powders	Metal nitrates, NaOH, H_2O_2, deionized water, ethanol, oxalic acid, cetyltriethylammnonium bromide (CTAB); Co-precipitation, oxalate decomposition method, Sol – gel method	TG-DSC, DSC, FT-IR, XRD, SEM, TEM, and BET	HTD of AP shifted downward by 103°C	Gheshlaghi *et al.* (2012)
Copper cobaltite spinel $Cu_xCo_{3-x}O_4$	Pure cobalt and copper oxides, NH_4ClO_4; Basic metal carbonates decomposition	TG-DTA,	AC increased the burn rate to 25mm/s at 70bar. combination of AC &IO burn rate was further increased to 50mm/s at 70 bar with Pressure Index (n) of 0.65	said *et al.* (1996)
Claw-like CuO	$Cu(NO_3)_2$ .3H_2O and hexamethylenetetramine($C_6H_{12}N_4$);	XRD, SEM and TEM	Nano-tetrapods of CuO nanostructures	Wang *et al.* (2009)

				Solution process method			in AP decomposition temperature changed to 350°C from 412°C	
Al(OH)$_3$.Cr(OH)$_3$ nanoparticles	Al$_2$(SO$_4$)$_3$, Cr(NO$_3$)$_3$, Na$_2$SO$_4$, urea, PVP, deionized water; Precipitation method	XRD, TG-DSC, XPS, TG-MS, TEM, SAED, FT-IR	Final decomposition temperature of AP decreased to the 245°C from 450°C	Zhang *et al.* (2014)
NiO nanoparticles	Bulk NiO, NiO nanoparticle size, nickle acetate and sodium hydroxide; Solid state reaction	XRD, TEM, FTIR	2% of NiO nanoparticles to AP decreased the decomposition temperature by 93°C with the increase heat of decomposition from 590 to 1490 J g−1.	Wang *et al.* (2005)
Biosynthesized NiO nanoparticles	Gigantea leaves, nickel nitrate; biosynthetic method	SEM, EDAX, TEM, XRD, FTIR	The sift of 93°C in HTD & 35°C in LTD was observed	Sharma *et al.* (2015)

α-Fe_2O_3 - 30 & 3.5 nm	Electrochemical method	DSC, FT-IR, DSC	Decreased HTD of AP to 460°C from 467°C with heat release of 4.574 kJ/g w.r.t. 0.834 kJ/g of pure AP	Joshi *et al.* (2008)
α-Fe_2O_3 nanotubes	$K_4[Fe(CN)_6].3H_2O$, distilled water, H_2O_2; Hydrothermal method	XRD FT-IR, TEM, DSC	Decreased the HTD of AP to 347°C from 454°C. Disappeared LTD in presence of 2% by wt.	Song *et al.* (2010)
Nanorods and micro-octahedrons of Fe_2O_3	$FeCl_3.6H_2O$ aqueous formamide; One step hydrothermal treatment of iron (III) chloride	XRD, FE-SEM, TEM, and FT-IR	nanorods were of 10-25 nm in diameter and 50-100nm in length & Decreased HTD of AP to 387.5°C form 436.4°C. Octahedron were 100-400 nm in size & HTD of AP	Xu *et al.* (2008)

			occurred at 426.4°C.	
α-Fe$_2$O$_3$ coated with amorphous carbon	FeCl$_3$, H$_2$C$_2$O$_4$.2H$_2$O, distilled water, (CTAB), NH$_3$.H$_2$O , HNO$_3$; Solution method	XRD, Raman spectroscopy, SEM, EDX, TEM, FT-IR, TG-DTA	Thermal decomposition temperature of AP in presence of pod-like α-Fe$_2$O$_3$, sphere like α-Fe$_2$O$_3$ and α-Fe$_2$O$_3$ @C are reduced by 72, 81, and 109°C respectively.	Zhang *et al.* (2011)
Nanocrystalline transition metal oxides Cr$_2$O$_3$, Fe$_2$O$_3$	Metal acetates of Cr, Fe, glacial acetic acid, KMnO$_4$, CuCl$_2$,cetyltriethylam mnonium bromide (CTAB), NaOH ; Precipitation method	XRD, TG-DTA-DSC	Mn$_2$O$_3$, CuO, Fe$_2$O$_3$, Cr$_2$O$_3$ synthesized with size of 54.3, 35.0, 46, 42nm.Final decomposition temperature of AP shifted downward by 150, 125, 100, 75°C by the addition of Mn$_2$O$_3$, CuO, Fe$_2$O$_3$, Cr$_2$O$_3$	Kapoor *et al.* (2008) .

				respectively.	
	N-doped ZnO/Ag nanocomposites	$Zn(CH_3COO)_2 \cdot 2H_2O$, $AgNO_3$, urea, citric acid; Deflagration method	XRD, XPS, HR-TEM	Catalyst samples containing 4% by wt Ag offered the best catalytic performance and reduced the final decomposition temperature of AP to 290°C from 453°C of pure AP	Lu et. al., (2014)
Ferrites:					
	Mixed Ternary Transition Metal Ferrites nanocrystallites	AP, Nitrates of Cu, Ni, Zn, Fe(III) and Co NaOH ; Co-Precipitation Method	XRD, BET, FT-IR	Catalytic activity increases with the increase of catalyst amount where as cobalt zinc ferrite has exhibited the highest catalytic activity	Singh *et al.* (2008)
	$CoFe_2O_4$ Nanocrystallites	$FeCl_3 \cdot 6H_2O$ $CoCl_2 \cdot 6H_2O$, sodium acetate, ethylene	XRD, TEM, SAED, TG-	Catalytic performance of $CoFe_2O_4$	Zhao *et al.* (2010)

		glycol polyethylene glycol abs. ethanol ; Solvothermal Process	DSC	nanocrystallites is significant and the decrease in the activation energy and the increased in the rate constant for AP	
	Nanometer $CuFe_2O_4$	Cupric nitrate, ferric nitrate and malic acid ; Auto-combustion	XRD, TEM, DTA	Average particle size of $CuFe_2O_4$ is 26nm. Thermal decomposition temperature of AP in presence of 5% w/w of $CuFe_2O_4$ decreased by 105°C.	Tian Liu et. al., (2008)
Chromites:					
1.	Cu-Cr-O nanocomposites	$Cu(NO_3)_2, Cr(NO_3)_3$, deionized water, citric acid ; Citric acid complexing approach	TG-DTA, XRD, TEM, SEM	Cu/Cr molar ratio of 0.7 high burning rate with the lowest pressure exponent (n) 0.43	Li *et al.* (2007)

	Copper Chromite	$Cu(NO_3)_2.3H_2O$, citric acid anhydrous, glycine $Cr(NO_3)_3.9H_2O$, distilled water ; Solution combustion method	XRD, X-ray photoelectron spectroscopy (XPS), BET, SEM, TG-DTA	Synthesized nanosize, pure phase of the spinel compound. The comparison between BET surface area and the burn rate depicted that surface area difference caused the variation in burn rate between the samples	Sathis kumar *et al.* (2012)
	Copper Chromite	Copper nitrate trihydrate, ammonium dichromate, ethylamine ammonia solution chromium trioxide trihydrate and ammonium perchlorate ;Thermal decomposition	TG-DSC, TG-MS, SEM, XRD, FT-IR	The downward shift of 60°C of decomposition temperature was observed.	Snoop *et al.* (2015)

	Amine Modified Boron Nitride	Melamine ($C_3N_6H_6$), Boric acid (H_3BO_3) and HNO_3 ; Hydrothermal Method	DSC, TGA, SEM, XPS, high pressure strand burner	Burning rates of propellants containing 0.5% of the micron- and nano-sized BN materials increased by about 30% where as Propellants containing the synthesized BN material decreased the burning rate by as much 25%.	Grossman *et al.* (2016)
Graphene Based Transition Metal Oxide Composites:					
9.	Cu/CNT	Copper nano tubes, cupric sulfate, sodium hydroxide EDTA, PVP, AP ; Chemical Reduction Method	SEM, TEM, FT-IR, XRD, XPS, AAS, DTA and EDS	Decreased HTD of AP to 265°C from 426.3°C in the presence of 5% w/w at the heating rate of 5°C/min & LTD peak disappeared	Ping *et al.* (2006)
	Ni/Graphene nanocomposites	Graphite oxide prepared by expanded graphite, $NaNO_3$,	XRD, Raman spectroscop	With 1%w/w of Ni/graphene HTD of AP	Li *et al.* (2012)

	H_2SO_4, $KMnO_4$, H_2O_2, $NiCl_2.6H_2O$; Modified Hummers Method	y, FT-IR, XPS, TEM, BET, FE-SEM	decreased to 330.5°C from 427.8°C & Low temperature peak disappeared	
NiAl- layered double hydroxide/Carbon	$Ni(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, NaOH, Na_2CO_3 and $C_6H_{12}O_6$; Hydrothermal Process	XRD, SEM, TEM, TG-DTA	Decomposition temperature reduced by 159°C and activation energy were observed 74.6 and 80.4 KJmol^{-1}	Li *et al.* (2012)
Mn_3O_4 nanoparticles on graphene	Expanded graphite, $NaNO_3$, H_2SO_4, $KMnO_4$, H_2O_2, $Mn(COOH)_2.4H_2O$; Modified Hummers Method	XRD, Raman spectroscopy, FT-IR, XPS, TEM, BET	The decomposition temperature was decreased by 141.9°C (from 433.7 to 291.8°C). graphene oxide independently not found good burn rate modifier but transition metal or transition metal oxide's hybrid with the	Li *et al.* (2013)

				graphene oxide became the most promising burn rate modifier.	
	Nitrated Graphene oxide	Graphite powder, $KMnO_4$, $NaNO_3$, 30% H_2O_2, H_2SO_4, HNO_3 HCl , absolute ethyl alcohol and AP ; Modified Hummer Method.	FTIR, Raman spectroscopy, CP/MAS CNMR, XPS, AFM, EA	10% of NGO decreased decomposition temperature of AP by 106°C and increases the apparent decomposition heat from 875 to 3236 J/g.	Zang *et al.* (2014)
12.	Activated Charcoal, Iron oxide		SEM, TGA, DSC, strand burner	Decreased HTD of AP by 126.3°C (478.1 to 351.8°C). LTD peak of AP disappeared.	Verma *et al.* (2010)
14.	Nitrated Graphene oxide	Graphite powder, $KMnO_4$, $NaNO_3$, H_2O_2, H_2SO_4, HNO_3, HCl, absolute ethyl alcohol ammonium perchlorate ; Modified Hummers Method	Raman spectroscopy, FT-IR, XPS, Atomic force microscopy (AFM) for thickness and	Decreased the decomposition temperature of AP with 10% Nitrated graphene decreased the TD by 106°C (from 456 to	Zhang *et al.* (2014)

			composition of graphene oxide and nitrated graphene oxide, TG, DSC	350°C) with Apparent decomposition heat of 3236 J/g from 875 J/g	
26.	$MgAl_2O_4$ nanoparticles:	$Mg(NO_3)_2.6H_2O$ $Al(NO_3)_3.9H_2O$ and citric acid $(C_6H_8O_7.H_2O)$ and deionized water Sol-gel Method	XRD, BET, SEM , EDS, TEM	HTD of AP decreased by 78.3 °C	Guan *et al.* (2011)

From Table 2.1 it is evident that a wide range of burn rate modifier has been tested by earlier workers. These have ranged from single to binary metal powders (e.g. Al, Cu, Ni, Cu-Co, Cu-Fe, Cu-Zn), metal oxides (e.g. NiO, V_2O_5, Fe_2O_3, Cr_2O_3, MnO_2, CuO, Co_3O_4, YO_2), hydroxide $Al(OH)_3.Cr(OH)_3$, mixed oxides $CuCo_2O_4$, $CuCr_2O_4$, $CuFe_2O_4$ and mixed hydroxide $(Ni.Al(OH)_4$, Ni.Al layered double hydroxide to amine modified boron nitride The best result have been shown by NiAl- layered double hydroxide/carbon by reduction in the decomposition temperature of AP by 159°C with the observed activation energy of 74.6 and 80.4 $KJmol^{-1}$.

Recently carbon nano tube and graphene based burn rate modifiers like Cu/CNT, Ni/graphene nanocomposites, NiAl layered double hydroxide /carbon, Mn_3O_4 nanoparticles on graphene,

nitrated graphene oxide, activated charcoal, nitrated graphene oxide have also been used by few workers. The results, however, are inconclusive.

2.9   Objective:

In view of the above limitations of the available information on burn rate modifiers following goals have been set for this work.

➢ To synthesize and characterize of mixed oxides of Cu, Cr and Ti using sol-gel technique and optimize the concentration of TiO_2 for maximizing the catalytic action.

➢ To study the catalytic behavior of synthesized catalysts on thermal decomposition of ammonium perchlorate.

➢ To prepare reduced graphene oxide (rGO) using graphite oxide (GO) obtained through the modified Hummer method.

➢ To synthesize and characterize the rGO based mixed oxides of Cu, Cr with optimized concentration of TiO_2 using sol-gel technique.

➢ To study the effect of rGO based mixed metal oxides on thermal decomposition of ammonium perchlorate and burn rate of a solid composite propellant.