

Iron Oxides' Influence on the Thermal Decomposition of Pure Ammonium Perchlorate: A Comprehensive Review

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Abstract

The combustion of ammonium perchlorate (AP) has long been a focal point in the development of solid rocket propellants, with particular attention paid to the catalytic effects of iron oxides. Beginning in the 1950s, researchers have diligently studied the kinetics and mechanisms underlying AP combustion, with a focus on both micron-sized and nano-sized iron oxide catalysts due to their widespread application in rocket formulations worldwide. This research effort specifically excludes investigations involving alternative iron oxide-based catalysts, such as doped or mixed oxides, or supported iron oxides, as they are not commonly utilized in major rocket propellant formulations. Despite variations in specific parameters like activation energy and heat of dissociation, the fundamental understanding of AP decomposition with iron oxides remains consistent with earlier findings. Notably, micron-sized catalysts have minimal impact on the low-temperature decomposition (LTD) of AP but can influence high-temperature decomposition (HTD) by altering decomposition temperatures and reducing activation energy. In contrast, nano-sized catalysts tend to accelerate the reaction to such an extent that the LTD phase is often bypassed altogether due to the rapid consumption of NH₃, a crucial component in the process. However, the transition to nano-sized particles presents a new challenge: the propensity for particle agglomeration. Current research endeavours are therefore dedicated to devising effective strategies to mitigate this issue and harness the full potential of nano-sized iron oxide catalysts in rocket propellant formulations.

Keywords: Solid Propellants, Ammonium Perchlorate, Iron Oxides, Thermal decomposition.

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I. INTRODUCTION

The rocket's velocity and acceleration are crucial factors in its design, dictating the materials selected for propulsion. Chemical propulsion, deriving energy from the chemical potential of a material, typically involves combustion. This process requires two essential components: the oxidizer (electron acceptor) and the fuel (electron donor). The propellant's specific energy and burn rate determine the amount of propellant mass needed for propulsion and its consumption rate, respectively. Common rocket propellant compositions worldwide often include HTPB (hydroxyl-terminated polybutadiene)/AP (ammonium perchlorate)/Aluminium, where HTPB and Aluminium serve as the fuel components, and AP as the oxidizer. The propellant's total specific energy depends on the relative ratios of these three components. Optimization of the

formula aims for optimal specific impulse, burn rate, and short- and long-term mechanical properties.

To accelerate the burn rate, burn rate modifiers or catalysts, typically comprising mixed oxides of transition metals are added. These modifiers facilitate AP decomposition through Lewis acid-base reactions. Interestingly, only two families of catalysts—iron oxide (double oxides of Fe⁺², Fe⁺³) and Copper Chromite (Cu⁺¹, Cu⁺²) (Cr⁺², Cr⁺⁶)—have been globally used for AP decomposition since the inception of composite solid propellants. While Titan and Ariane solid motors favour the ferric oxide family, Indian rockets prefer a copper and chromium oxide combination known as copper chromite [1-4].

Numerous studies worldwide have investigated the role of iron oxide, both micron and nano-sized, in modifying the burn rate of ammonium perchlorate.

However, this paper focuses solely on iron oxide's role and does not include research on alternative iron oxide-based catalysts such as doped or mixed oxides or supported iron oxides, as they are not commonly used in major rocket formulations.

II. Thermal Decomposition of AP

Ammonium perchlorate (AP) has become the predominant oxidizer in composite propellants due to its advantageous characteristics. These include a relatively high oxygen content, negative energy of decomposition, favourable ignition temperature, and pressures within the deflagration range, along with well-timed crystal transformations during heating for decomposition. As such, AP serves as the primary oxidizer in composite solid propellants. It typically presents as a white crystalline solid, often in powdery form, with orthorhombic crystal structure at room temperature transitioning to a cubic structure at 240°C without volumetric expansion. AP is notably oxidizer-rich and capable of sustaining self-deflagration above 20 bars. Its average particle size typically hovers around 300 μ , but when combined with 40 μ particles to form bimodal AP, it exhibits a higher burn rate compared to single-sized AP particles. Furthermore, AP's sublimation before decomposition eliminates uncertainties associated with liquid/melt phases, confining combustion to solid and gas phases. While ammonium nitrate was once considered an environmentally friendly alternative to AP due to its cost-effectiveness, low sensitivity, and absence of chlorine, its multiple crystal phase transitions at low temperatures and significant volume expansion during these transitions limited its suitability. Notably, at 32.1%, ammonium nitrate undergoes a phase change accompanied by a considerable volume shift [1-3].

Extensive literature exists on the decomposition of pure AP from the 1950s to as recently as 2022, with

earlier studies focused on understanding how micron-sized additive catalysts influence combustion alongside micron-sized AP particles and their rate-limiting steps. Present interest, however, centers on the influence of nano-sized catalysts on micron-sized AP, spurred by the significant advancements in nanotechnology and quantum dots across various scientific and engineering disciplines. Nanoparticles offer distinct advantages, including a large superficial surface area and high surface energy, facilitating rapid kinetics without the need for mass transfer from pores.

Broadly, AP decomposition occurs across three temperature ranges: low temperature decomposition (LTD) below 300°C, high temperature decomposition above 350°C, and deflagration at 1100°C under adiabatic combustion conditions. Catalyst additions may affect all three ranges or predominantly target one temperature range, depending on catalyst type, surface structure, active site count, and reaction mechanism [4]. Additionally, nanoparticles present a unique challenge of agglomeration during propellant formulation and combustion processes.

a) Important properties of AP relevant to AP decomposition

AP undergoes reversible crystallographic transition from low temperature orthorhombic (9.202Å, 5.816Å, 7.449Å) to a cubic structure (cube edge 7.63Å) [5-7]. This phase transition is endothermic and associated with simultaneous sublimation and partial decomposition which is exothermic. Markowitz and Boryta [8] resolved this problem and estimated the heat of phase transition as 2.3±0.2 kcal/mole. Specific heat of AP is 0.309 cal.g⁻¹.°C⁻¹ between 150 and 240°C and 0.365 cal. g⁻¹.°C⁻¹ above the transition point [9]. Important properties of AP relevant to AP decomposition proposed by various researchers are tabulated below.

Table-1: Summary of important AP properties

Source of Data	Specific Heat of AP (cal. g ⁻¹ . K ⁻¹)			
	Ortho	Cubic	Melt	Gas
Guirao and Williams [10]	0.309	0.365	0.328	0.300
Hall and Pearson [19]	0.308	0.365	---	---
Beckstead, Derr and Price [11]	0.300	0.300	---	0.305
Manelis and strunin [12]	0.300	0.300	---	0.306
Price, Boggs and Derr [13]	0.332 (473K)	0.432 (673K)	---	---
Sohn [14]	---	---	---	0.312
Hertzberg [15]	0.370	0.370	---	---
Rosser, Inami and Wise [16]	0.333	---	---	---
Source of Data	Density (g. cm ⁻³)			
	Ortho	Cubic	Melt	
Guirao and Williams [10]	1.95	---	1.71	
Hall and Pearson [19]	1.95	1.71	---	
Beckstead, Derr and Price [11]	1.8	---	---	
Jacobs and Whitehead [20]	1.95	1.76	---	
Hertzberg [15]	1.95	---	---	
Sohn [14]	1.95	---	---	
Caveny and Pittman [17]	1.95	---	1.71	

Source of Data	Thermal Diffusivity (cm ² .s ⁻¹)		
	Solid	Melt	Gas
Hall and Pearson [19]	2.17 X 10 ⁻³	---	---
Kumar [18]	1.5 X 10 ⁻³	1.5 X 10 ⁻³	---
Rosser, Inami and Wise [16]	0.7 X 10 ⁻³ (673K)	---	---
Price, Boggs and Derr [13]	2.5 X 10 ⁻³	---	4.55 X 10 ⁻⁶ T

From the data, we infer that 1) the phase transition from orthorhombic to cubic occurs at 240^oC, with mild endotherm, 2) the volumetric expansion due to transition from orthorhombic to cubic is about 10% and 3) the corresponding increase in specific heat is about 16%.

b) Oxides of iron relevant to catalysis of AP decomposition

Iron Oxide, what various authors mentioned in the explosive and propellant research has a common

point, i.e., the structure is spinel or deviated spinel. It is observed that many authors did not specify the crystal structure when they quoted Fe₂O₃ or iron oxide. A few properties relevant to AP decomposition, as summarised in Table-2, are related to density, crystal form and melting point. Melting point is required, since as long as the material is solid, the decomposition of AP takes place as Gas-solid reaction and all the solid-gas kinetics were applicable. Melting point data suggests that all the phases upon heating ultimately result in haematite at near 500^oC except Fe₃O₄.

Table-2: Summary of Iron Oxide properties [21]

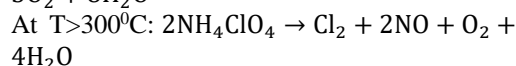
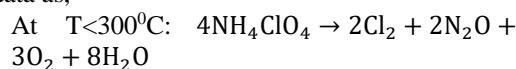
Iron Oxide	Molar mass, g/mol	Density, (g/cm ³)	Melting temperature, ^o C	Structure
α-Fe ₂ O ₃ (haematite)	159.69	5.26	1565	Hexagonal close-packing (Alternative: cubic close-packed)
β- Fe ₂ O ₃	159.69	5.11	Converts to α-Fe ₂ O ₃ when heated above 500 ^o C	Cubic, bixbyite-like structure
ε-Fe ₂ O ₃	159.69	5.08		Orthorhombic
γ-Fe ₂ O ₃ (maghemite)	159.69	4.87	Converts to α-Fe ₂ O ₃ when heated above 400 ^o C	Inverse spinel
ζ-Fe ₂ O ₃	159.69	4.99	Not available	Monoclinic
Fe ₃ O ₄ (magnetite)	231.54	5.18	1590	Inverse spinel
FeO (wustite)	71.84	5.72-5.61	1377	Two interpenetrating FCC structures

III. Effect of micron-sized oxides of iron on the thermal decomposition of AP

Jacobs and Whitehead [20] in their paper in 1968 reviewed the works of various researchers on combustion of AP, their reaction products, temperature, activation energy, heat of combustion etc. They concluded that

1. AP starts decomposing at temperature >150^oC. AP undergoes this low temperature decomposition which is autocatalytic below 300^oC and net decomposition is nearly 30%.
2. The next decomposition step was below 300^oC which was called LTD zone. It involves phase transition of AP from orthorhombic to cubic around 240^oC, followed by sublimation, sublimation associated decomposition. Various researchers proposed the reaction mechanism based on the experimental analysis of the reaction intermediates and reaction products, estimated the activation energy and reaction energy.
3. The third and important step was high temperature decomposition (HTD) above 350^oC. Here the decomposition goes to completion and was not autocatalytic. Concurrently, AP sublimates and dissociates, i.e., it undergoes dissociative sublimation. Bircumshaw and Newman [42-44]

summarized these results along with their own data as,



The principle decomposition products published by Dode [10, 22] were O₂, N₂, N₂O, Cl₂+ClO₃, H⁺ for LTD and in HTD in addition to these products they reported the presence of HNO₃, HCl, NO and absence of H⁺. Drops of liquid condensate from AP contained HNO₃, HClO₄, and HCl [11]. The most detailed investigations using mass spectrometry were those of Pellett and Saunders [12] who have established product yields (relative to Cl₂) for H₂O, O₂, N₂O, NO₂, and HCl, from which they deduce the equation

$$12\text{NH}_4\text{ClO}_4 \rightarrow 4\text{Cl}_2 + 4\text{N}_2\text{O} + 4\text{HCl} + 4\text{NO}_2 + 7\text{O}_2 + 22\text{H}_2\text{O}$$

The products of decomposition of AP in LTD and HTD regimes have been identified by several research groups [23-32], and were a mixture of various species, i.e. H₂O, O₂, N₂, NO, NO₂, N₂O, Cl₂, HCl, ClO₂, ClO, HOCl, HClO₂, ClO₃, HClO₃, HClO₄ etc. The later research went into the direction of understanding the

reaction mechanism by establishing electron transfer or proton transfer as the principle way AP decomposition occurs. These studies of course, account for the reaction products indirectly.

In 1972, Yazdi *et al.*, [33] studied AP combustion under deflagration conditions. Deflagration varies with pressure hence two limits will come into picture the lower pressure limit (LPL) and upper pressure limit (UPL). By nature, AP burning will not continue below certain pressure and goes to self-quenching. He estimated the LPL as 300 psi (~ 20 atm) and compared to various studies, 45 atm (Friedman, 1957 [34]); 22 atm (Levy, 1962 [35]). There was a dispute whether UPL exists for AP whereas Friedman estimated UPL as 300-500 atm, Levy suggested UPL doesn't exist. Yazdi was in line with Levy's view. He found that catalyst changes the LPL by changing surface structure. He concluded from his experiments that Fe₂O₃ increases LPL at small concentrations and decreases LPL at high concentrations. Maximum increase in LPL was observed at 0.1 mole% of Fe₂O₃. He further concluded that catalyst concentration, the way they were distributed and its particle size matters in altering the LPL.

In 1988, Boggs *et al.*, [36] studied decomposition/deflagration of AP with Fe₂O₃ ranging from 2 to 8 %. At 2% of Fe₂O₃ the deflagration and temperature sensitivity significantly increase as compared to pure AP, however at 8% the burn rate was lower than pure AP but deflagration rate and the slope of the burn rate curve were still higher.

In 1999, Vyazovkin *et al.*, [37] studied the kinetics of thermal decomposition of cubic AP and proposed a kinetic scheme using TGA-DSC. He pointed out that there was a significant period for reaction to start which he called it as induction period/nucleation period. We were going to see some more discussion later regarding the importance of this induction period especially when we deal with Nanomaterials. A few researchers called induction period as ignition delay period. Processes that occur after 30% decomposition were controlled by competition between mass transfer, controlled decomposition and sublimation. In open systems, sublimation which was endothermic becomes dominant making the AP porous.

Another summary review paper came in 2006 by Boldyrev [38] pointed out that reaction nuclei takes place at some locations on the surface like edge dislocations and cross over points in crystal. They also form at sub-surface, i.e., up to 20 to 30 microns below the surface. He compared the two opposite mechanisms of decomposition; one electron transfer mechanism proposed by Bircumshaw *et al.*, and the other proton transfer mechanism by Jacobs [39] and gave his own conclusion. $\text{ClO}_4^- + \text{NH}_4^+ \rightarrow \text{ClO}_4^0 + \text{NH}_4^0$; Electron transfers from ClO_4^- and neutralises NH_4^+ , electron transfer occurs on surface only. Similarly, in the reaction,

$\text{NH}_4^0 \rightarrow \text{NH}_3 + \text{H}^0$; H^0 migrates over the lattice. ClO_4^0 further reacts with hydrogen leading to H₂O and ClO₃, where ClO₃ acts as a trap for e⁻ giving rise to ClO₃⁻. ClO₃⁻ and ClO₄⁻ react with ammonia and form secondary products. He mentioned that Raevsky and others [40] explained the electrons transition was from valence band to conduction band whereas Galwey and Jacobs [41] suggested formation of molecular complex [NH₄.ClO₄] due to local transfer of electrons from anion to cation. This complex directly leads to reaction products and formation of the complex was a rate controlling step. On the other hand, Jacobs *et al.*, [39] presented the proton transfer from cation to anion like $\text{NH}_4^+\text{ClO}_4^- \rightarrow \text{NH}_3 \cdot \text{H} - \text{ClO}_4 \rightarrow \text{NH}_3 - \text{HClO}_4 \rightarrow \text{NH}_3 + \text{HClO}_4 \rightarrow \text{NH}_{3(\text{g})} + \text{HClO}_{4(\text{g})} \rightarrow$ Secondary Products via sublimation dissociation reactions. This mechanism was substantiated in the studies of decomposition product analysis [47], product analysis sublimation/dissociation [48], acceleration in vapour decomposition of perchloric acid [45, 46] and influence of dopants [49]. The author suggests that the proton transfer was more likely strictly at the surface and explains the LTD; however at HTD electron transfer mechanism was predominant. The decomposition of ammonia and perchloric acid was in gas phase. This was in line with the prediction using molecular dynamics [50]. Addition of Fe₂O₃ has little effect on LTD. Fe₂O₃ acts at 320-380°C corresponding to HTD. He suggests that the catalytic action was due to formation of iron perchlorate.

At this juncture, researchers began shifting their focus towards harnessing nanotechnology for solid propellants. This transition primarily directed attention towards catalyst additives, possibly due to their application in smaller quantities yet yielding significant effects.

IV. Effect of nano-sized oxides of iron on the thermal decomposition of AP

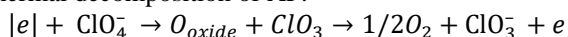
Zhenye Ma *et al.*, [51] in 2004 studied the effect of nano-Fe₂O₃ prepared by custom solvent-nonsolvent method using DTA-TG studies. Since Fe₂O₃ was agglomerating at nano scale they studied the effect with different methods of addition, one direct addition and other co-precipitation with AP. They compared these results with micron sized Fe₂O₃. Their experiments revealed that the Fe₂O₃ shifts the decomposition at 331°C to 322°C whereas this stage disappeared in co-precipitated samples. There was remarkable shift in HTD temperature from 453°C to 389°C. The activation energy also significantly shifted from 165.5 to 109.1 kJ/mol.

Xu *et al.*, [52] in 2008 studied the role of α-Fe₂O₃ on AP decomposition by preparing α-Fe₂O₃ in the form of nanorods and compared with micron sized, usual octahedron α-Fe₂O₃. Micron octahedron α-Fe₂O₃ did not alter the LTD but nanorods eliminated LTD peak. They pointed out that nanorods could significantly shift the HTD temperature, promotes heterogeneous

decomposition at lower temperatures by deprotonation of HClO_4 gas on the solid surface.

Satyavati *et al.*, [53] indicated the works of Nakamura *et al.*, [54] who suggested the formation of iron perchlorate, Halawy [55] who suggested the formation of nitryl perchlorate as intermediates. They also confirmed that nano Fe_2O_3 works on HTD only at both sub-surface and gas phase reactions by lowering activation energy and temperature of decomposition. They proposed that HClO_4 desorbs faster than NH_3 . Hence, HClO_4 was consumed faster and ammonia rich environment forms thereby reducing the temperature of decomposition. Fe_2O_3 adsorbs gaseous products formed below 350°C and allows the reaction to go to near completion. Hence, the size of Fe_2O_3 matters.

The effect of various nanocrystalline catalysts including Fe_2O_3 were also studied by Kapoor *et al.*, [56]. They prepared Fe_2O_3 using precipitation method. They found that nano- Fe_2O_3 affects through electron transfer process. They suggested that the rate controlling step in catalysed AP decomposition was transfer of electron from ClO_4^- ion to a positive hole in p-type semiconducting catalysts. Annihilation of positive hole in the valence band of metal oxides (active sites for accepting electrons released from ClO_4^- ion) increases the thermal decomposition of AP.

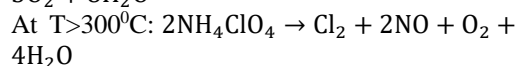
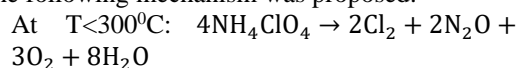


A study by Mahinroosta [57] revealed that the presence and the percentage of nano- Fe_2O_3 significantly reduced the HTD temperature of AP like the previous studies. At $>3\%$ nano- Fe_2O_3 , they recorded the vanishing of LTD signature when nanoparticles were used and the decomposition signature was seen at 347.9°C which corresponds to HTD temperature which otherwise was 455°C . However, no specific reason was attributed for the vanishing of LTD peak when the particle size was reduced to nanosized.

Limin Song *et al.*, [58] compared the effect of conventional $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles on the thermal decomposition of AP with $\alpha\text{-Fe}_2\text{O}_3$ nanotubes. The usual hydrothermal method was used with different process steps for the preparation of nanoparticles and nanotubes. They also confirmed the disappearance of LTD peak in the presence of both the nano catalysts but there was a little or no difference between nanoparticles and nanotubes with respect to reduction in HTD temperature (454°C to 347°C – nanoparticles; 454°C to 343°C – nanotubes).

Nano- Fe_2O_3 prepared by urea hydrolysis of ferric nitrate was used for studying the thermal decomposition of AP by Deepthi *et al.*, [59]. In order to resolve the agglomeration issue, they added nano alumina and nano ZnO as additives. They concluded that 1) Nano- Fe_2O_3 accelerates the thermal decomposition of AP 2) the dispersion of the catalysts in the additives

showed a further improvement 3) The LTD signature still exists but there was no change 4) The HTD temperature reduced from 375°C to 370°C for 0.3% micro Fe_2O_3 and 375°C to 365°C for 0.3% nano- Fe_2O_3 5) With the addition of nano alumina, HTD temperature further reduced to 346°C and to 314°C with the addition of nano ZnO. The following mechanism was proposed:



Although spinel structures were favourable for electron transfer mechanisms, the whole literature was talking about the use of alpha phase of ferric oxide. We were not sure whether Fe exists as Fe^{2+} in addition to Fe^{3+} or not. In general, the so-called iron oxide was a chemical mixture of Fe^{2+} and Fe^{3+} and was termed as magnetite phase. Wang *et al.*, [60] was the first people who specifically mentioned that they used magnetite. They studied the effect of magnetite in the form of nanosheets, nanoparticles and nanorods on the thermal decomposition of AP. Their study revealed that 1) magnetite also was a good burn rate catalyst 2) magnetite (nanosheets, particles, rods) didn't alter the phase transition of AP 3) Similar to nano $\alpha\text{-Fe}_2\text{O}_3$, it vanished the LTD peak. 4) The shape of the catalyst affected the activity considerably. Nanosheets reduced the HTD temperature significantly followed by nanoparticles and nanorods. They concluded from their experiments that decomposition of AP was influenced by the exposed surface area but not by the specific surface area. Coming to the reaction mechanism, they proposed oxidation of ammonia by perchlorate ion in gas phase as the rate controlling step in AP decomposition.

Campos *et al.*, [61] studied the effect of ferric oxide nanoparticles especially in γ -phase (maghemite) on the thermal decomposition of AP and compared with $\alpha\text{-Fe}_2\text{O}_3$ results. Amorphous silica was used as a dispersion/encapsulating agent. They found that amorphous silica didn't significantly affect the HTD temperature for both $\alpha\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3$. Hence, silica may be a good dispersion agent for future formulations that use nanoparticles. They made two different $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles, which differ in separation technique and drying process leading to change in surface area ($388, 290 \text{ m}^2/\text{g}$) and diameter ($D_{50} = 16, 54 \mu\text{m}$). The lower diameter particles significantly affected the HTD temperature (from 418°C (pure AP) to $353, 380^\circ\text{C}$).

Another way of making nanoparticles was by mechanical means such as grinding using high energy ball-mills. Hosseini *et al.*, [62] tried this method and prepared $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles and studied their catalytic activity on thermal decomposition of AP. The grinding time was kept as variable, at 40h and 60h. Although, there was no much change in the average particle size (23nm, 20nm), there was a large difference in decomposition temperature (from 422°C (pure AP) to

392.1, 380.5°C). In addition, the particles with 60h grinding showed vanishing of LTD. It means that after 60h of grinding the particles behave in comparison with the nanoparticles prepared by chemical means. Of course, they evaluated the corresponding heat release (from 880 J/g (pure AP) to 1050.1, 1338.2 J/g) probably for the sake of completion.

Three different structural samples of α -Fe₂O₃ i.e., pod-like, sphere-like, core-shell nano composite (coated with amorphous carbon for avoiding agglomeration) were prepared by hydrothermal method and its effect on thermal decomposition of AP was investigated by Zhang *et al.*, [63]. LTD peak disappeared for all the three samples but the maximum reduction in HTD temperature was noticed for core-shell nanocomposites (452°C (pure AP) to 380, 371, 343°C respectively). Unlike earlier silica as dispersive agent, here amorphous carbon was participating in the decomposition. From their experiments they inferred that 1) Catalytic activity was predominantly in gas phase 2) Presence of partially filled 3d orbit in Fe³⁺ helps in e⁻ transfer process 3) Better activity by sphere-like α -Fe₂O₃ was attributed to smaller size and higher active sites 4) α -Fe₂O₃ coated with carbon has remains of C_{1/4}C and C_{1/4}O which increase e⁻ transfer and heat conduction.

Nanoparticles shaped as wires were another attractive material which can be used in propellants. Zhiliang *et al.*, [64] synthesised magnetite nanowires by hydrothermal method and studied its catalytic activity on the thermal decomposition of AP. Whereas Wang *et al.*, reported the vanishing of LTD peak with magnetite nanoparticles this paper reported that LTD phase still exists but there was no change in LTD temperature with increase in % magnetite. As usual the HTD temperature significantly reduced from (434°C (pure AP) to 405, 393, 391, 387, 385°C with 1, 2, 3, 4, 5% magnetite respectively). They concluded that addition of magnetite nanowires catalysed HTD region only and proposed a mechanism that magnetite provides a bridge for transfer of electrons from perchlorate ions to ammonium ions via the partially filled 3d orbitals of iron atoms thus decreasing the activation energy of HTD zone.

Another interesting iron compound for AP decomposition was the intermediate phase of iron hydroxides which upon calcination leads to γ -Fe₂O₃. This phase was water included and termed 2L-ferrihydrite/goethite/lepidocrocite etc. depending on the process methods. Zhen Ge *et al.*, [65] studied the effect of such intermediate on the AP decomposition. His analysis showed that the intermediate was near to 2L-ferrihydrite. They prepared nanocomposites with AP and studied the decomposition. Their argument was that AP contains the pores in the nanometer size due to their gel-skeleton structure and AP was up to 80%, co-precipitation of nano ferric oxide must be better than physical addition. They inferred 1) γ -Fe₂O₃ was a n-type semi-conductor, so defects in lattice, unoccupied 3d

orbitals facilitate electron transfer process of both LTD, HTD temperatures of AP decomposition 2) Lone pair electrons of N exited in HNO and NH₃ could interact with unsaturated sites on the surface of Fe₂O₃. This leads to lack of electronic states on N and weakens H-O bond, thereby activation energy of NH₃, O, HNO, HClO was reduced.3) In the heating process of decomposition, it was likely that 2L-ferrihydrite loses water and forms a stable ferric oxide crystal. It means that active sites become more active at the instance of dehydration.4) They reported LTD temperature reduction from 300.1°C to 256.6°C and HTD temperature reduction from 435.1°C to 348.9°C with a corresponding increase in enthalpy from 438.1 to 972.8 J/g.

Another study where α -Fe₂O₃ was prepared in a rotary packed bed reactor using high-gravity reactive precipitation method was used for studying the effect on AP decomposition by Cao *et al.*, [66]. They reported that LTD peak exists but there was no much variation in LTD temperature with decrease in particle size (127nm to 84nm). However, HTD peak reduced (437.4°C to 384°C). Correspondingly, activation energy reduced from 218 kJ/mol to 163.3 kJ/mol and heat of decomposition increased from 860 J/g to 1235 J/g.

One method of controlling agglomeration in nanoparticles was dispersing in a liquid medium. Since the particle size was small it becomes a colloid. Sherif *et al.*, [67] prepared ferric oxide by hydrothermal process using water at 350°C and 240 bars and 0.05M ferric nitrate at 25°C drop wise at 240 bars. The resultant liquid phase was colloidal with zeta potential of 38.5mV implying that the colloidal state was stable. Using this colloid, they prepared AP ferric oxide composite by co-precipitation using solvent-nonsolvent method after bringing the colloid pH to 9. These experiments resulted in the following observations and conclusions 1) the endothermic peak of pure AP at 240°C associated with H of 102.5 J/g, which we generally associate to phase transition from orthorhombic to cubic was decreased to 62.1 J/g at 240°C. They reasoned that this was because of the action of catalyst on the endothermic decomposition. Perhaps this explanation needs a further study.2) vanishing of LTD peak as expected for nanoparticles. The HTD peak shifted from 452.8°C to 390.4°C with a corresponding increase in heat release from 489.8 J/g to 1230.4 J/g. 3) they suggested that their catalyst promotes the oxygen formation, i.e., the decomposition of HClO₄ and by adsorbing the gaseous HClO₄ onto its surface 4) the encapsulation of ferric oxide onto AP, they found was very effective promotes intimate mixing.

Another technique of encapsulation was fractional crystallisation. Spencer *et al.*, [68] studied the effect of nano and micron sized ferric oxide encapsulated within AP of two different sizes (106, 20 μ). They found that 1) Behaviour of AP-encapsulated micron Fe₂O₃ was approximately equal to AP-encapsulated nano Fe₂O₃ 2)

Fe₂O₃ works both in physical mixture as well as encapsulated methods for both micro and nano scale but nano mixture was better 3) Fine AP in all cases was better than coarse AP in combination 4) Nano encapsulated Fe₂O₃ was equivalent to physically mixed nano Fe₂O₃ 5) Activity of nano encapsulated Fe₂O₃ was better than micro encapsulated Fe₂O₃. All the observations were in line with the earlier studies.

In addition to the above methods of preventing agglomeration of nano ferric oxide both as a raw material and as a part of the combustion lot of research was there with carbon-supported transition metal oxides (TMOs). The advent of graphene nanocomposites made a revolution in the catalysis per se and solid propellant research was not an exception. Chen *et al.*, [69] in 2020 presented the summary of the work carried out in this line in their review paper. In addition to Fe, they also mentioned the work carried out using Co, Ni, Zn, and Cu. In their own words they attributed the enhancing of thermal decomposition of AP to synergetic effect of graphene and transition metal oxides, surface area, and higher exposed active sites and accelerated electron transportation. The graphene, m-g-C₃N₄ which was classified as a Lewis base absorbs HClO₄ onto its surface. This makes the activation energy for decomposition of AP to decrease and favours the decomposition. As a semiconductor also m-g-C₃N₄ was beneficial as its band gap was about 2.70 eV. Once graphene was excited the valence band holes and conduction band electrons can be formed on the surface of graphene. For improved adsorption of HClO₄ and NH₃ this property was beneficial. The gaseous HClO₄ reacts with electron to form superoxide which further reacts with valence band holes and ammonia to generate N₂O, H₂O and NO₂. In simple terms, graphene acts as a catalyst itself in addition to the TMOs.

V. CONCLUSIONS

This is an attempt to consolidate and evaluate the kinetics and mechanisms involved in the combustion of AP, with and without iron oxide catalysts. Given its critical role in rocketry, our focus is specifically on examining the catalytic effects of iron oxide, both in micron and nano sizes, despite the abundance of data on other variants of iron oxide-based catalysts. Through this survey, several key insights have surfaced:

1. AP decomposition exhibits two distinct and well-defined combustion zones: LTD occurring at 300°C and HTD at 370°C. The separation of these zones may lead to quenching of decomposition in the absence of adequate pressure.
2. During LTD, AP decomposes into NH₃ and HClO₄, which adsorb onto the AP surface. While HClO₄ undergoes further decomposition in the gas phase, NH₃ continues to adhere to AP, resulting in porosity.
3. The addition of micron-sized Fe₂O₃ does not alter this mechanism during LTD.
4. Upon further heating or under increased pressure beyond the lower pressure limit, combustion

progresses, leading to NH₃ desorption and decomposition, known as HTD.

5. Micron-sized Fe₂O₃ catalyst influences combustion at HTD through a series of contributions, including adsorption on the catalyst surface, electron transfer to HClO₄, decomposition, and desorption with electron transfer as the rate-controlling step.
6. Nano-sized Fe₂O₃ eliminates the step of NH₃ adsorption and does not fundamentally alter the catalytic mechanism, focusing instead on electron transfer. The high availability of Fe ions accelerates the electron transfer mechanism, promoting AP decomposition during HTD.
7. The presence of nano-sized Fe₂O₃ introduces a new challenge for propellant designers: particle agglomeration within the formulation and during combustion, posing distinct combustion-related issues.

In summary, while nano-sized Fe₂O₃ offers a significantly larger specific surface area, it cannot serve as an immediate replacement for micron-sized particles due to the complexities associated with particle agglomeration and combustion.

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