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Thermal Decomposition of Ammonium Perchlorate in the Presence of Nanosized Ferric Oxide

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ABSTRACT

The catalytic effect of two different sizes of α-Fe_2O_3 nanoparticles synthesised using an electrochemical method was investigated on the thermal decomposition of ammonium perchlorate (AP) using differential scanning calorimetry as a function of catalyst concentration. The nanosized ferric oxide particles exhibited more of a catalytic effect on the thermal decomposition of AP than commercial Fe_2O_3 particles. A lowering of the high-temperature decomposition of AP by 59 °C was observed after mixing with 2 Wt per cent of α-Fe_2O_3 particles with the very fine size of 3.5 nm. The mixture produced a high heat release of 4.574 kJ/g compared to 0.834 kJ/g of pure AP. The kinetic parameters were evaluated using Kissinger method. The decrease in the activation energy and increase in rate constant confirmed the catalytic activity of these nanoparticles.

Keywords: α-Fe_2O_3 nanoparticles, ammonium perchlorate, thermal decomposition, DSC, catalysis, differential scanning calorimetry

1. INTRODUCTION

Composite solid propellants are the major source of chemical energy in space vehicles and missiles. Ammonium perchlorate (AP) is widely used as an oxidiser in compsite solid propellants[1-2]. The ballistics of a composite propellant can be improved by adding a catalyst such as ferric oxide (Fe_2O_3), copper oxide (CuO), copper chromite ($CuO.Cr_2O_3$), nickel oxide (NiO), etc, which accelerates the rate of decomposition of AP[3-6]. Recent investigations have shown that nanoparticles of transition metal oxides, without any agglomeration can increase the burning rate[7]. The efficiency of catalytic action increases sharply in nanosize oxide particles than micro scale oxide particles[8]. The size distribution, morphology and nanostructure of particles are very important characteristics and do affect the kinetics of decomposition of ammonium perchlorate.

The nanomaterials show novel properties mainly due to their reduced dimensions, which result in domination of the surface over bulk[9-11]. The size of nanoparticles especially in the range of 1–10 nm, strongly influences the catalytic properties, which is the reason why research efforts are directed towards the development of reliable methods for the size selective preparation of these materials. Many properties of nanosized α-Fe_2O_3 such as high surface area, large number of surface atoms, oxygen vacancies on its surface enable it as an excellent catalyst[12]. Above all, it is structurally simple, highly stable, easy to synthesise and inert to side reactions. With reduced particle size of Fe_2O_3, the surface-to-volume ratio increases. Hence, nano ferric oxide becomes more efficient and active in thermal decomposition of AP. In their earlier paper, the authors studied the thermal decomposition of AP/hydroxyl-terminated polybutadiene (HTPB)-based composite propellant both in the presence and absence of nano ferric oxide and achieved high heat release, up to 40 per cent with retention of well-separated necklace like structure of α-Fe_2O_3 in HTPB[13]. Therefore, the present study necessitates a detailed investigation on the effect of variation of concentration of catalyst on the thermal decomposition of ammonium perchlorate using varied particle sizes of nano Fe_2O_3.

In this study, synthesised nano Fe_2O_3 of two different sizes were mixed with AP and their effect on thermal decomposition of AP evaluated systematically using differential scanning calorimetry (DSC). Also, the influence of nano Fe_2O_3 at different concentrations has been studied. The activation energy and heat release were determined by DSC. The kinetic parameters were computed using Kissinger method.

2. EXPERIMENTAL

Ammonium perchlorate (monomodal 4 μm) obtained from High Energy Materials Research Laboratory (HEMRL), Pune, was recrystallised and used further. The recrystallised AP was mixed with electrochemically synthesised α-Fe_2O_3 nanoparticles of two different sizes, 30 nm and 3.5 nm in the ratio 0.5 per cent, 1 per cent, 2 per cent, and 5 per cent by weight[14]. The iron oxide catalyst was prepared using tetra butyl ammonium bromide (TBAB) for controlling the particle size and as a supporting electrolyte. The Fourier transform infrared (FTIR) studies of the catalyst were done

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to understand the role of TBAB in the formation of iron oxide and the decomposition of AP. After thorough mixing of AP with the catalyst, the resultant mixture was subjected to DSC analysis. The thermal decomposition of AP, i.e., the heat release and exothermic nature of the oxidiser decomposition was analysed on Perkin Elmer TAC 7/DX. Samples (1-2 mg) were taken over a temperature range 50 °C to 500 °C at different heating rates, viz., 5 °C/min, 10 °C/min, 15 °C/min, 20 °C/min and 25 °C/min. An ultra-pure nitrogen atmosphere was maintained throughout the DSC run. The DSC was also carried out for the mixture of AP and commercial Fe_2O_3 (30 μm) at 10 °C/min. The phenomenological and kinetic data of all the samples were calculated from the DSC data. The FTIR spectra were recorded using *KBr* pellet in the range 400 cm^{-1} to 4000 cm^{-1} on Schimadzu FTIR 8400 spectrophotometer.

3. RESULTS

Figure 1 shows the infrared spectra of electrochemically synthesised as prepared and annealed samples of Fe_2O_3 nanoparticles. In the as prepared sample, the *N-H* stretching was observed at 3203.5 cm^{-1} while *C-H* vibrations were seen at 2858.3–2923.9 cm^{-1}. These υ_{C-H} and υ_{N-H} frequencies confirmed the strong adsorption of TBAB species on the surface of Fe_2O_3 particles[15]. Also υ/cm^{-1} 2057.9 corresponds to binding of ammonium ion with metal clusters. All the υ_{C-H}, υ_{N-H} and $\upsilon_{NH_3^+ \text{- metal}}$ vibrations disappear with successive annealing at 500 °C and 800 °C. This confirms the removal of adsorbed TBAB ligand. The formation of Fe_2O_3 nanoparticles was confirmed from 434–478 cm^{-1} *Fe-O* stretching vibration[16]. The broad IR bands at 565 cm^{-1} attributed to the formation of α-Fe_2O_3 (Hematite) with no phase transformation[17].

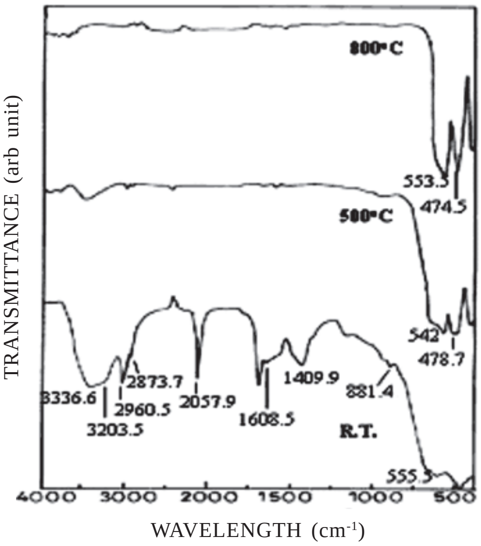


Figure 1. FTIR spectra of as prepared Fe_2O_3 and after annealing at 500 °C and 800 °C.

The decomposition of AP strongly depends on the prevailing experimental conditions of pressure, temperature, and whether it occurs in an open or closed system. The chemical reactivity is influenced by active volume, surface of the sample container, and temperature distribution prevailing in it. Decomposition of AP often depends on the degree of purity. The experimental DSC curves obtained for pure AP and for the mixture of commercial Fe_2O_3 and AP are shown in Fig. 2. The endothermic peak at 243 °C in pure AP represents the phase transition from orthorhombic-to-cubic form due to the rotation of perchlorate ion[1].

The DSC curve exhibits two prominent exothermic stages. In pure AP, the first exothermic peak at low-temperature (LTD) 331 °C is attributed to the partial decomposition of AP. The second and the main high-temperature (HTD) exothermic peak at 467 °C corresponds to complete decomposition of intermediate products into volatile product (Fig. 2). The representative decomposition of AP in the presence of 0.5 Wt per cent of α-Fe_2O_3 (3.5 nm) is shown in Fig. 3 at different heating rates, viz., 5 °C/min, 10 °C/min, 15 °C/min, 20 °C/min and 25 °C/min. The shift in the low temperature decomposition was observed in the range 270 °C–320 °C while the high-temperature decomposition shows changes in its position. Depending upon the concentration changes of nano α-Fe_2O_3 particles (2 Wt per cent and 5 Wt per cent), the overlap in two stages, i.e. low and high temperature decomposition and the shift in only high temperature decomposition was observed. In AP+0.5 Wt per cent ferric oxide composition, the high temperature decomposition shifts from 427 °C to 465 °C, with increasing heating rate from 5 °C/min to 25 °C/min (Fig. 3). Similar types of shifts with increasing heating rate were observed in 1 Wt per cent, 2 Wt per cent and 5 Wt per cent concentration of catalyst, such as 410 °C to 458 °C, 392 °C to 437 °C, and 381 °C to 429 °C, respectively. As the heating rate increased

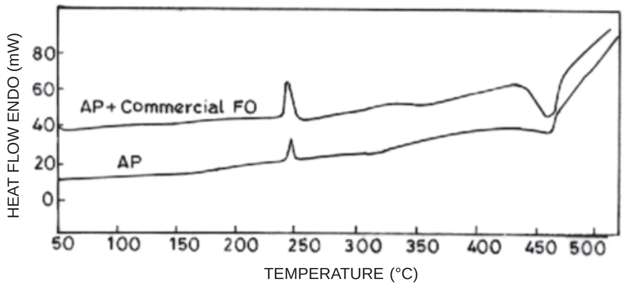


Figure 2. DSC of pure AP and AP + 2 % commercial Fe_2O_3 (FO) at 10 °C/min.

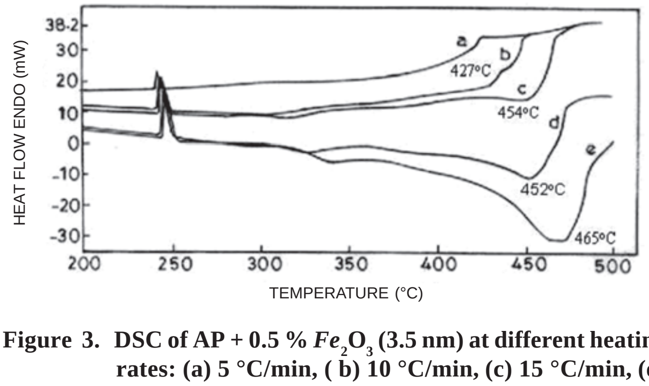


Figure 3. DSC of AP + 0.5 % Fe_2O_3 (3.5 nm) at different heating rates: (a) 5 °C/min, (b) 10 °C/min, (c) 15 °C/min, (d) 20 °C/min, and (e) 25 °C/min.

from 5 °C/min to 25 °C/min, greater input of energy per unit time was applied across the sample and reference cells. This results in an increase in overall sensitivity of DSC instrument and shift in high temperature decomposition peak towards higher temperatureside. Slower heating rate improves the peak resolution and hence detects the peak at earlier temperature. Such shifts were also observed in 30 nm sized α-Fe_2O_3 compositions of AP.

The DSC curves of AP in the presence of different particle sizes of nano Fe_2O_3 show noticeable changes in the decomposition pattern as shown in the Figs 4-7 at 10 ^{o}C/min. In all the compositions, nano α-Fe_2O_3 additives have no effect on crystallographic transition temperature, i.e., the endotherm, while large differences were observed in high-temperature exothermic peak. The position of exotherm strongly depends upon the size of Fe_2O_3 particles. For 0.5 Wt per cent and 1 Wt per cent addition of 30 nm and 3.5 nm sized α-Fe_2O_3 nanoparticles, the high-temperature decomposition of AP decreased from 467 °C (pure AP) to 445 °C, 427 °C (AP+0.5 Wt per cent Fe_2O_3) and 441°C, 432 °C (AP+1 Wt per cent Fe_2O_3) respectively (Figs 4-5).

Similar type of lowering in temperature such as 410 °C, 408 °C (AP+2 Wt per cent Fe_2O_3), 373 °C, 390 °C (AP+5 Wt per cent Fe_2O_3), has been observed in Figs 6-7 at higher catalyst concentrations. This decrease in temperature indicates that nano α-Fe_2O_3 in very fine size regime shows an efficient catalytic effect on the thermal decomposition of AP.

Among two different sizes used in compositions, the 3.5 nm α-Fe_2O_3 particles showed pronounced effect in lowering the high temperature decomposition as 40 °C (0.5 Wt per cent), 35 °C (1 Wt per cent), 59 °C (2 Wt per cent), 77 °C (5 Wt per cent) compared to pure AP. Such a marked reduction in high temperature exotherm is attributed to the presence of large number of active sites, higher surface area, and smaller particle size of synthesised α-Fe_2O_3. As mentioned earlier, the lowering in decomposition temperature was observed wrt decrease in particle size from 30 nm to 3.5 nm at 0.5, 1, and 2 Wt per cent compositions. Only at AP + 5 Wt per cent Fe_2O_3 composition, with decrease in particle size, the reverse effect in temperature from 373 °C (30 nm Fe_2O_3) to 390 °C (3.5 nm Fe_2O_3) was observed due to higher concentration of nano Fe_2O_3. In addition, an interesting observation of high heat release (ΔH) was observed as 4.574 kJ/g at optimum 2 Wt per cent Fe_2O_3 (3.5 nm) composition compared to pure AP as 0.834 kJ/g, which is the highest value achieved so far using nanometal oxide catalyst (Table 2 and 4).

Liu, *et al*. reported a heat release of 1.32 kJ/g for 30 nm sized *Ni* particles, which is only 30 per cent as compared to the results obtained[9]. Also in both the 5 Wt per cent and 2 Wt per cent of catalyst mixing, the heat release was as large as 70–80 per cent more than the pure AP, indicating enhancement in decomposition of AP due to very fine size of Fe_2O_3. Due to higher surface to volume ratio of nano

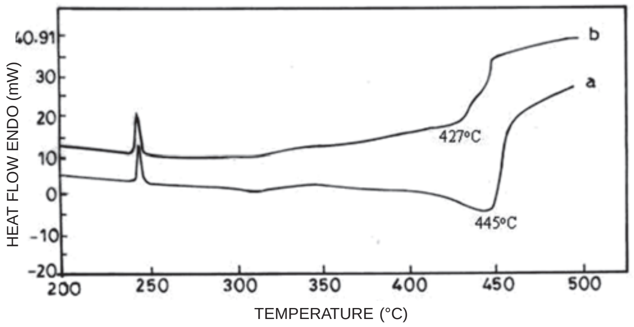


Figure 4. DSC of AP+ 0.5 Wt % Fe_2O_3 at different particle sizes: (a) 30 nm and (b) 3.5 nm at 10 °C/min.

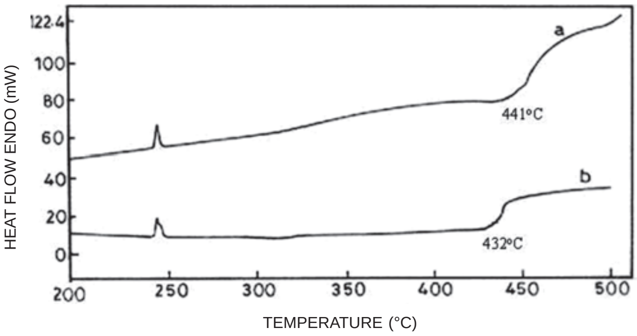


Figure 5. DSC of AP+ 1 Wt % Fe_2O_3 at different particle sizes: (a) 30 nm and (b) 3.5 nm at 10 °C/min.

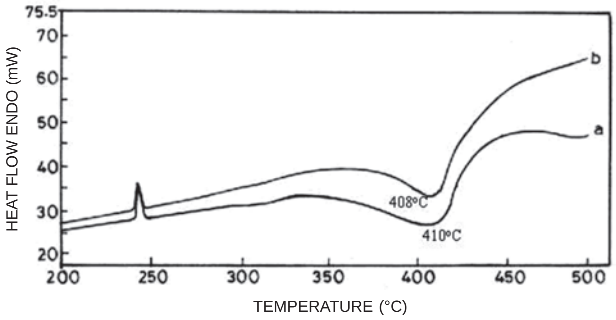


Figure 6. DSC of AP+ 2 Wt % Fe_2O_3 at different particle sizes: (a) 30 nm and (b) 3.5 nm at 10 °C/min.

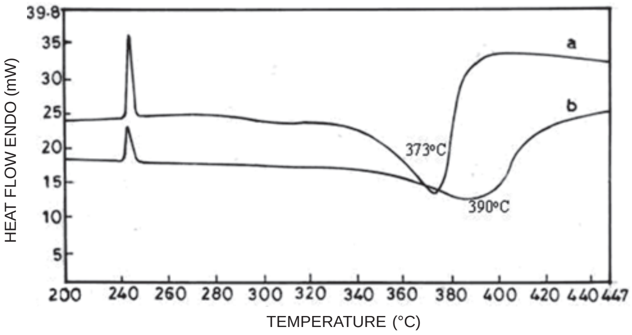


Figure 7. DSC of AP+ 5 Wt % Fe_2O_3 at different particle sizes: (a) 30 nm and (b) 3.5 nm at 10 °C/min.

Table 1. Kinetic parameters for 30 nm sized nano Fe_2O_3 at various percentages

AP + 30 nm Fe_2O_3	HTD (°C)	E_a (kJ/mol)	A (min^{-1})	k (s^{-1})	ΔH (kJ/g)
0.5 Wt %	445	108.08	2.27×10^{7}	1.37×10^{-3}	1.105
1.0 Wt %	441	80.47	1.58×10^{5}	2.58×10^{-3}	3.814
2.0 Wt %	410	144.04	5.55×10^{10}	5.49×10^{-3}	2.987
5.0 Wt %	373	121.50	2.13×10^{9}	4.97×10^{-3}	1.447

Table 2. Kinetic parameters for 3.5 nm sized nano Fe_2O_3 at various percentages

AP + 3.5 nm Fe_2O_3	HTD (°C)	E_a (kJ/mol)	A (min^{-1})	k (s^{-1})	ΔH (kJ/g)
0.5 Wt. %	425	122.04	1.54×10^{6}	4.95×10^{-3}	1.115
1.0 Wt. %	432	105.30	1.00×10^{9}	3.69×10^{-3}	3.494
2.0 Wt. %	408	102.53	1.84×10^{7}	4.98×10^{-3}	4.574
5.0 Wt.%	390	104.75	4.35×10^{7}	4.02×10^{-3}	1.244

Table 3. Kinetic parameters for pure AP and for mixture of AP + 2 Wt % commercial Fe_2O_3

Compositions	HTD (°C)	E_a (kJ/mol)	ΔH (kJ/g)	A (min^{-1})	k (s^{-1})
Pure AP	467	324.24	0.834	4.31×10^{27}	5.61×10^{-4}
AP + 2 % Commercial Fe_2O_3	460	174.59	1.782	1.99×10^{12}	2.13×10^{-3}

Fe_2O_3, there is less sputtering of particles during decomposition. This causes less mechanical loss and more efficient heat transfer within the composite causing high heat release[13]. The higher heat release may also be due to efficient combustion of NH_3 with chlorine oxides in presence of finer Fe_2O_3 particles.

3.1 Kinetics of Thermal Decomposition

Kinetic analysis was carried out for high temperature decomposition of AP for all the compositions. The Arrhenius activation parameters, viz., energy of activation (E_a), frequency factor (A), rate constant (k) were evaluated from DSC results using ASTM standard method based on Kissinger's correlation[13, 18-19]. The values of E_a, A, and k at high temperature decomposition for all the compositions are shown in Tables 1 and 2. From Table 1 and 2, it can be seen that in both the compositions, E_a has been lowered by 60–75 per cent than the pure AP and commercial Fe_2O_3. This lowering in E_a is in agreement with the earlier reports[20-21]. A is also found to vary with the E_a values (Table 1 and 2). This may be due to the increase in reactant concentration at the catalyst surface, which accelerates the reaction through a relatively high frequency factor. This has been further confirmed by k values, which show increasing trend with the increase in catalyst concentration in all the compositions, as expected (Table 1 and 2). The increase in the rate constant clearly indicates enhanced catalytic activity in all the synthesised compositions of α-Fe_2O_3. However, the commercial Fe_2O_3 sample does not show any significant effect on the rate constant for the thermal decomposition of AP (Table 3) due to micro size of the particles. The kinetic data reported for AP decomposition in the presence of different nano/bulk transition metal oxides are summarised in Table 4. Table 4 provides further justification of high heat release and low E_a in the samples so far achieved.

Table 4. Reported data from the literature on the AP decomposition in the presence of different nano/bulk transition metal oxides

Catalyst	ƛH (kJ/g)	E (kJ/mol)	References
Cu (90 nm)	1.20	155	[9]
Ni (50 nm)	1.32	167	[9]
$NiCu$ (45 nm)	1.2	154	[9]
Cu (26 μm)	1.09	--	[9]
Ni (30 μm)	0.58	--	[9]
NiO (2 % 10 nm)	1.49	--	[11]
Fe_2O_3 (1 % bulk)	--	120	[30]
Fe_2O_3 (2.5 % bulk)	--	132	[31]
Fe_2O_3 (4.8 % bulk)	--	143	[32]
Cr_2O_3(4.8 % bulk)	--	117	[32]
Fe_2O_3 (Nano)	1.08	--	[33]
CuO (Nano)	1.42	--	[33]

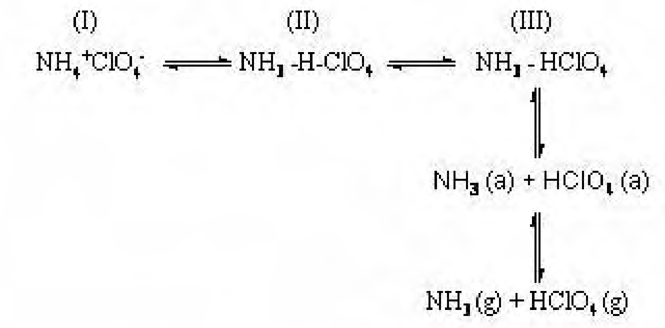
4. DISCUSSION

The catalytic effect of Fe_2O_3 is observed mainly on high-temperature decomposition process and not on the initial stages of decomposition. The nano Fe_2O_3 affects not only the solid ammonium perchlorate but also the reactions proceeding in the gas phase. The lowering in activation energy and high temperature decomposition supports this observation and further confirms that the subsurface reactions and the reactions occurring in the gas phase are closely connected with each other. Different opinions on the mechanism of catalytic action of Fe_2O_3 exist.

According to Nakamura[22], *et al.*, the catalytic action of Fe_2O_3 is due to the formation of iron perchlorate as an intermediate compound. Halawy[23], *et al.* think that the mechanism of the action of Fe_2O_3 is connected with the formation of nitryl perchlorate as an intermediate compound.

These authors also established a correlation between specific surface of the catalyst and its activity. Burcat[24], *et al.* showed that during decomposition of solid fuels Fe_2O_3 catalyses decomposition not only of AP but also of the binder. Several studies were carried out to understand the mechanism of decomposition of AP[25-26]. Reviews by Hall and Pearson[27], Jacobs and Whitehead[1] and Kishore[28] *et al*. give good accounts of the mechanism of thermal decomposition of AP, but still it remains a matter of debate. The AP is a typical dielectric; hence at low temperature of thermal decomposition, the process cannot be sustained by electron-transfer because of its low probability. This rules out the possibility of electron transfer mechanism. The primary products detected in the experiments by different researchers were ammonia and perchloric acid. This allowed assuming that the primary stage of process of thermal decomposition of AP is proton transfer.

According to the mechanism reported by earlier research groups[2], Step I involves pair of ions in perchlorate ammonium lattice. Step II involves the decomposition step that starts with proton transfer from the cation NH_4^+ to the anion ClO_4^- via molecular complex and which then in Step III decomposes into ammonia and perchloric acid. The molecules of NH_3 and $HClO_4$ either react in the adsorbed layer on the surface of perchlorate or desorb and sublime interacting in the gas phase.



Many reactions occur rapidly in the gas phase between NH_3 and $HClO_4$, forming the side products such as O_2, N_2O, Cl_2, NO, and H_2O at low temperature (<350 °C). During a process occurring in the adsorbed layer it was assumed and reported in earlier reports that perchloric acid is desorbed more rapidly than ammonia, which causes incomplete oxidation of ammonia, creating a saturated atmosphere[29] of NH_3. As a result, high- temperature decomposition decelerates and undergoes incomplete transformation. During the second exothermic decomposition NO, O_2, Cl_2, and H_2O products were formed in the gas phase reactions. Due to huge surface area of nano Fe_2O_3 there are many active sites on the surface. The surface atoms in nanosized particles are more active than the bulk atoms since they have fewer adjacent coordinate atoms and unsaturated sites. Therefore, these surface active sites adsorb above gaseous reactive molecules, which were formed below 350 °C and during second decomposition step in gas phase causing complete decomposition of AP. This exhibits high- temperature decomposition at lower- temperature with increase in catalytic efficiency. This is also supported by FTIR studies as mentioned earlier describing the removal of TBAB with heating at 400 °C and above. The hydrocarbon part $(C_4H_9)_4\ N^+Br^-$ of the ligand attached to Fe_2O_3 particles must be assisting as a fuel in the decomposition of AP at a lower temperature than required. This is also reflected in lowering of activation energy. As compared to nano metal oxide catalyst, commercial micro scale catalyst covers much less surface around the perchlorate and therefore do not produce much more catalytic effect. Hence with the same content of metal oxide powder, commercial micro scale Fe_2O_3 (2 Wt per cent) slightly lowers the high temperature decomposition peak of AP (Table 6, Fig. 1) while the nano α-Fe_2O_3 (2 Wt per cent) shows enhanced catalytic activity.

CONCLUSIONS

The DSC study reveals that the nanosized Fe_2O_3 particles synthesised by electrochemical method have best catalytic effect on the high- temperature decomposition of AP. The pronounced effect in lowering the high temperature decomposition was found at 2 Wt per cent with high heat release as 4.574 kJ/g compared to 0.834 kJ/g of pure AP. Commercial micro scale Fe_2O_3 can decrease the high-temperature decomposition of AP; however their effects are less pronounced than nanoparticles. The kinetic parameters such as activation energy, rate constant further confirmed the enhancement in catalytic activity of AP.

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