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Thermal Decomposition of Mixtures of Ammonium per chlorate with Nd_2O_3 and Pr_2O_3

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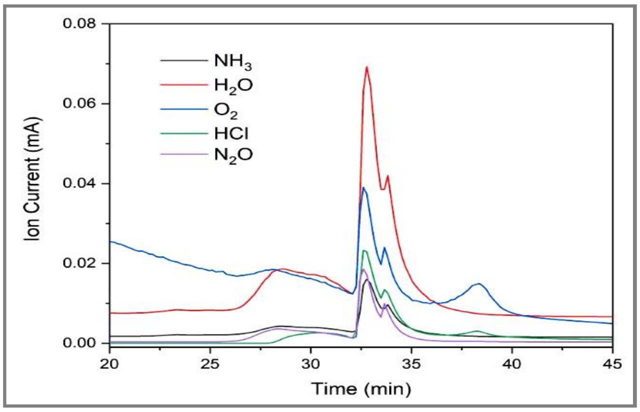
ABSTRACT

Thermal decomposition of ammonium per chlorate (AP) in the presence of lanthanide oxides L_2O_3, where L=Nd, and Pr, has been studied with TG–MS approach towards understanding the mechanistic aspects of thermal decomposition. Nd_2O_3 has no appreciable influence on the onset temperature of AP decomposition; and it brings down the end set temperature of AP decomposition. Pr_2O_3 influences both the LTD and HTD of pure AP. Addition of either Nd_2O_3 or Pr_2O_3 does not catalyze the evolution of HCl. Presence of Pr_2O_3 catalyzes both the LTD and HTD of AP. Both the catalysts contribute to the oxidation of ammonia to NO_2, rather than NO as in the case of pure AP. Release of O_2 is another favorable contribution by these oxides that have profound influence on the energetic of composite solid rocket propellants based on AP.

Graphical Abstract



MS Peaks corresponding to AP – Nd_2O_3 System.

Keywords: Ammonium per chlorate, Nd_2O_3, Pr_2O_3, TG-MS.

INTRODUCTION

Composite solid rocket propellant is an ad-mixture of polymeric–fuel binder such as hydroxyl-terminated polybutadiene (HTPB); energetic metallic–fuel; dioctyl esters as plasticizers; isocyanate curing agents; combustion rate modifiers, and other processing aids. In addition, it contains a major fraction of ammonium per chlorate (AP), a crystalline inorganic oxidizer, may be because of which, the thermal decomposition characteristics of AP has a bearing on the combustion characteristics of composite solid rocket propellants based on it. It is a well established fact that, those compounds that catalyze the thermal decomposition of AP will also have profound influence in modifying the combustion characteristics of composite solid rocket propellants based on AP [1-7].

For the past four and half decades, bulk-size transition metal oxides have been extensively used towards catalytic improvements in the thermal decomposition of AP [8-12]. The effect of ‘p’-type rare earth oxides with partially filled f - orbital’s, such as, La_2O_3, Pr_2O_3 and Nd_2O_3 on the thermal decomposition of AP has been studied by Survase *et al* [13]. Also, Survase *et al* [14] studied the effect of Nd_2O_3 on thermal and ballistic properties of AP based composite propellants employing DSC technique. The kinetics of thermal decomposition of AP in the presence of rare earth oxides of yttrium (Y_2O_3) and lanthanum (La_2O_3) was investigated by Raha *et al* [15]. Catalytic effect of nanoparticles of proviskite type oxides of $LaMO_3$ (M=Fe, Co, and Ni) on AP thermal decomposition of was reported by Wang *et al* [16].

Shalini *et al* [17] reviewed the catalytic effect of nanodimensional metal oxides (including various rare earth metal oxides) on AP thermal decomposition. Synthesis and characterization of nanoparticles of CeO_2, Pr_2O_3, and Nd_2O_3 through sol-gel technique and their influence on thermal decomposition of AP was reported by Supriya *et al* [18]. Yang *et al* [19] studied the catalytic effect of nanometer transition metal oxide and rare earth oxides on thermal decomposition of AP. Li *et al* [20] attributed the semiconducting properties of rare earth oxides of Pr_6O_{11}, Nd_2O_3, Sm_2O_3, Gd_2O_3, Er_2O_3, Yb_2O_3 synthesized through sol-gel technique, and their functional property of storing and releasing electron that resulted in the hysteresis of the first-exotherm of AP or advancing its second exothermic peak.

Yu *et al.*, [21] presented the synthesis through micro-emulsion technique, and characterization of nanocrystals (60nm) of NdCrO; its effect on thermal decomposition of AP. The mechanism of catalytic action attributed to the presence of superoxide ion of O_2^- on the surface of NdCrO causing different extent of oxidation of ammonia resulting from the decomposition of AP. The influence of nanometer sized and micrometer sized Nd_2O_3 on ammonium per chlorate thermal decomposition was evaluated by Zou, Min *et al* [22], and these authors proposed that, the newly formed chloride of neodymium oxide (NdOCl) species are responsible for the overall thermal decomposition of AP over Nd_2O_3.

Chrysin complexes having formula Ln $(C_{15}H_9O_4)_3.H_2O$, where Ln = Tb (III), Ho (III), Er (III) and Yb (III) were synthesized and characterized by Janusz Pusz *et al* [23]. Phytoconstituents assisted green synthesis of cerium oxide nanoparticles for thermal decomposition and dye remediation was reported by Sharma *et al* [24], wherein the role of nano-cerium oxide particles in the thermal decomposition of AP was discussed. Zhang *et al* [25] described the preparation and catalytic activity of M_2O_3 / CNTs (M = Y, Nd, Sm) nano-composites by solvo-thermal process.

In the present work, attempt has been made to understand catalytic thermal decomposition of AP in the presence of oxides of rare earth metals (M) where M = Nd and Pr, employing TG-MS and DSC techniques.

MATERIALS AND METHODS

The ammonium per chlorate (AP) employed in this work was obtained from Ammonium per chlorate Experimental Plant (APEP) of Vikram Sarabhai Space Centre, Indian space research organization

(ISRO), Department of Space, Government of India. The catalysts Nd_2O_3 and Pr_2O_3 were procured from SD Fine Chemicals Limited. The thermal decomposition studies were carried out employing a sample mass of 5 mg; inert gas (N_2) flow -rate of 50mL.min^{-1}, and a sample heating rate of 10°C min^{-1} were maintained. Experiments were carried out in a TA Instruments, Model SDT Q600 TD System.

RESULTS AND DISCUSSION

The thermo gravimetric (TG) and derivative thermo gravimetric (DTG) curves for pure AP are shown in figure 1, it can be seen that, the thermal decomposition of AP takes place in two distinct stages. During the first –stage decomposition 28.2 percent of the material is lost, and in the second step the remaining material is lost. The cessation of decomposition of AP after about 28.2 percent decomposition in the initial stage is in tune with the earlier observations [3, 26-31]. The temperature of onset of decomposition is ~253°C, and the temperature of end set of decomposition is at ~ 430°C.

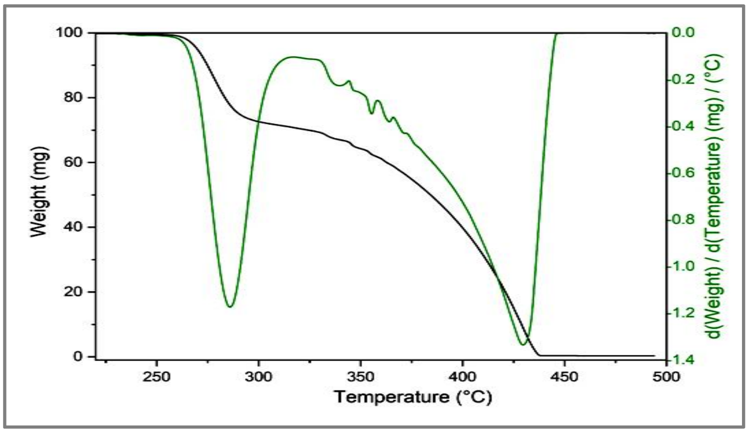


Figure 1. TG – DTG Curves of pure Ammonium per chlorate.

The TG–DTG curves for AP-Nd_2O_3 mixture are presented in figure 2. The onset temperature (253°C) observed in the case of pure AP is shifted by about 33.82 ° C towards higher temperature region in the presence of Nd_2O_3 (286.82°C). Similarly, the end set temperature of decomposition for pure AP (430°C) is shift by 27.44°C towards lower temperature region (402.56°C), indicating the catalytic action by Nd_2O_3. The TG-DTG curves for AP-Pr_2O_3 mixture are shown in figure 3. The onset temperature (253°C) observed in the case of pure AP is shifted by about 5.86° C in the presence of Pr_2O_3 (258.86 °C), which is a marginal shift towards high temperature zone. Similarly, the end set

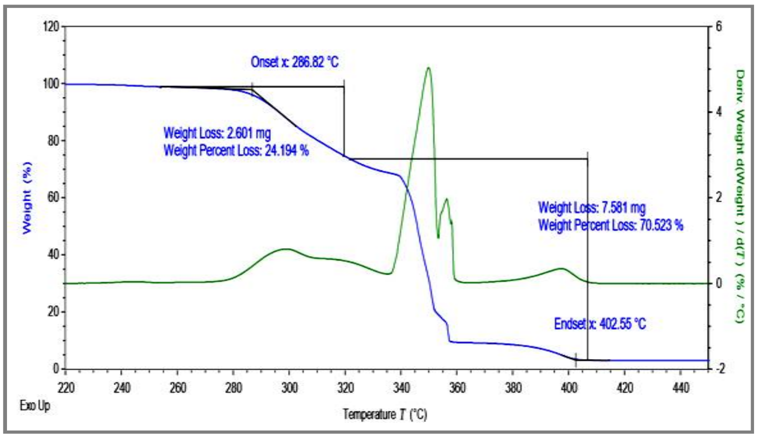


Figure 2. TG–DTG Curves of AP–Nd_2O_3 Mixture.

temperature of decomposition for pure AP (430°C) is shift by 27.79°C towards lower temperature region (402.21°C) indicating the catalytic action by Pr_2O_3. In other words, Pr_2O_3's presence has least effect on the onset temperature of decomposition while catalyzing the high temperature decomposition.

Differential Scanning Calorimetric (DSC) curves for pure AP; AP-Nd_2O_3; and AP- Pr_2O_3 mixtures are presented in figure 4. It can be seen from figure 4 that, the presence of these catalysts (Nd_2O_3 and Pr_2O_3) does not influence much of the crystallographic phase-transition of AP from orthorhombic to cubic phase. The presence of Pr_2O_3 lowered the low-temperature decomposition (LTD) peak by about 21°C; and the high-temperature decomposition (HTD) peak is lowered by 24°C (from 393°C), indicating catalysis.

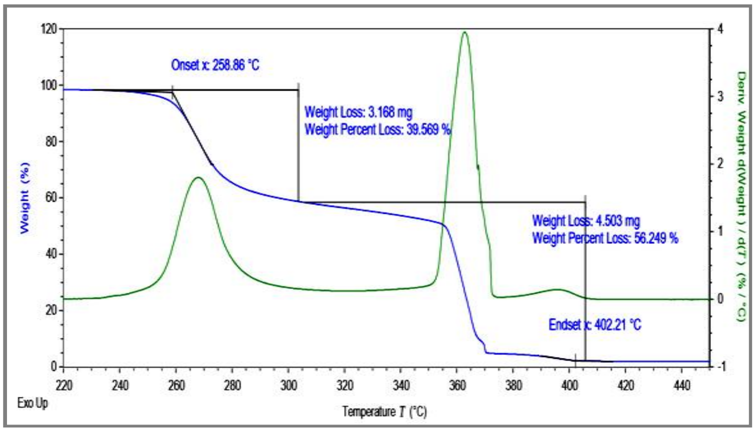


Figure 3. TG – DTG Curves of AP – Pr_2O_3 Mixture.

Apparently, from the area under the HTD peak, the enthalpy released is relatively high compared to pure AP. In the case of AP – Nd_2O_3 system, the LTD peak is broadened and shifted to high-temperature region by about 14°C; while the HTD peak is lowered by about 36°C from that of pure AP. Also, the area under the HTD peak is more significant indicating catalytic activity.

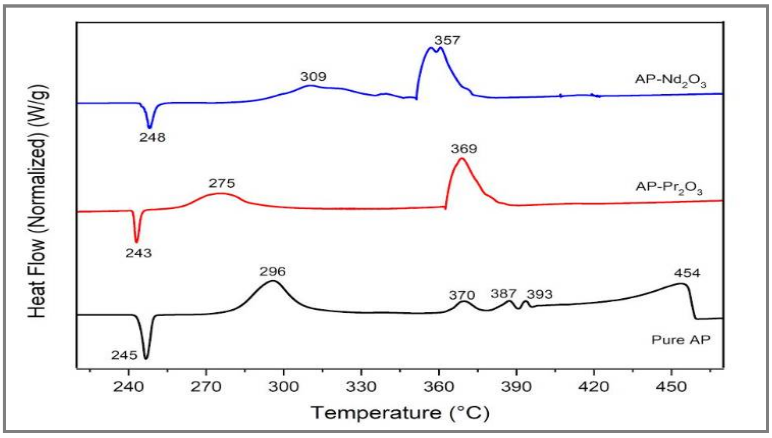


Figure 4. DSC Curves of pure AP; AP–Nd_2O_3 and AP–Pr_2O_3 Mixtures.

From figure 4, it can be seen that, in the case of AP–Nd_2O_3 system, the low-temperature decomposition (LTD) peak of pure AP occurring at 296°C, is shifted to a marginally high-temperature region to309°C, indicating the inhibitory effect of Nd_2O_3on the LTD of AP; while the high–temperature decomposition (HTD) peak of pure AP is lowered from 454°C to 357°C, a catalytic effect on the HTD of AP.

In the case of AP – Pr_2O_3 mixture, the LTD of pure AP is lowered to 275°C from 296°C indicating the catalytic effect on the LTD of AP; while the HTD of pure AP occurs at 367°C in the presence of Pr_2O_3, down from 454°C for pure AP. Thus, we notice that, Nd_2O_3 catalyzes HTD of pure AP, while Pr_2O_3 has a positive catalytic effect on both LTD and HTD peaks of pure AP. Thus, we observe that, while Pr_2O_3 catalyzes both LTD and HTD of AP; Nd_2O_3 catalyzes only the HTD of AP. Figure 5 corresponds to that of pure AP, and the decomposition products being NH_3, H_2O, NO, and HCl of which H_2O is more predominant.

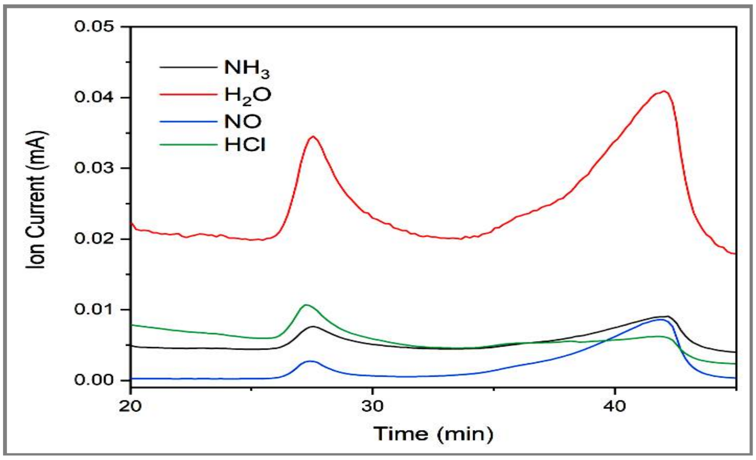


Figure 5. MS Peaks corresponding to pure AP.

Figure 6 corresponds to AP – Nd_2O_3 system and the decomposition products include - NH_3, H_2O, O_2, HCl, and N_2O of which H_2O and O_2 are predominant. This indicates that the presence of Nd_2O_3, while facilitating the release of pure oxygen from AP, oxidizes the primary product of NH_3 to NO_2 rather than NO as in the case of pure AP. Figure 7 corresponds to the system AP–Pr_2O_3 wherein the products of decomposition include –NH_3, H_2O, HCl, N_2O and O_2. It is observed that, the primary product of NH_3 being oxidized to NO_2 in addition to release of pure oxygen as in the case of AP–Nd_2O_3 system.

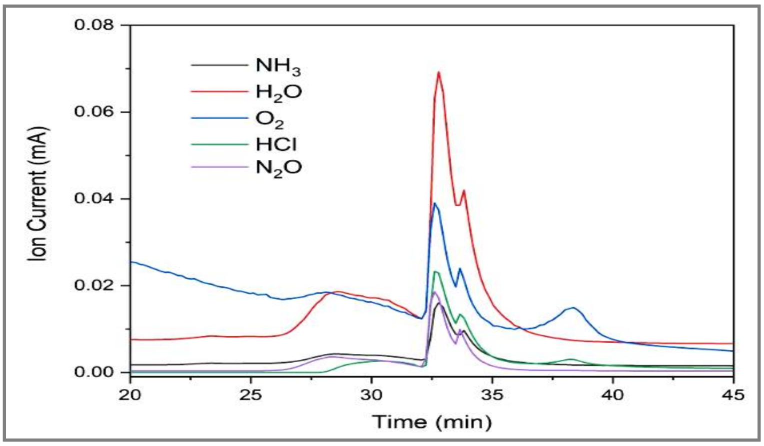


Figure 6. MS Peaks corresponding to AP – Nd_2O_3 System.

Here again, it is evident that, H_2O and O_2 are the predominant products of decomposition. Another important observation is that, the presence of the oxides does not catalyze HCl (a corrosive gas) evolution, thereby indicating better performance probability of composite solid rocket propellants performance employing AP as the oxidizer.

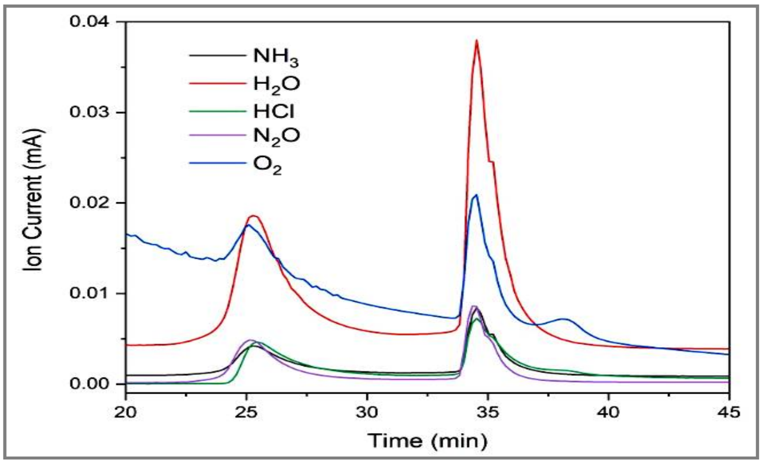


Figure 7. MS Peaks corresponding to AP – Pr_2O_3 System.

APPLICATION

These results are useful to solid rocket propulsion technologists in modifying solid rocket propellant formulations to suit their requirements of combustion rates of these propellants for specific mission requirements.

CONCLUSION

- Nd_2O_3 has no appreciable influence on the onset temperature of AP decomposition; and it brings down the end set temperature of AP decomposition.
- Pr_2O_3 influences both the LTD and HTD of pure AP.
- Addition of either Nd_2O_3 or Pr_2O_3 does not catalyze the evolution of HCl.
- Both the catalysts contribute to the oxidation of ammonia to NO_2, rather than NO as in the case of pure AP.
- Release of O_2 is another favorable contribution by these oxides that have profound influence on the energetic of composite solid rocket propellants based on AP.

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