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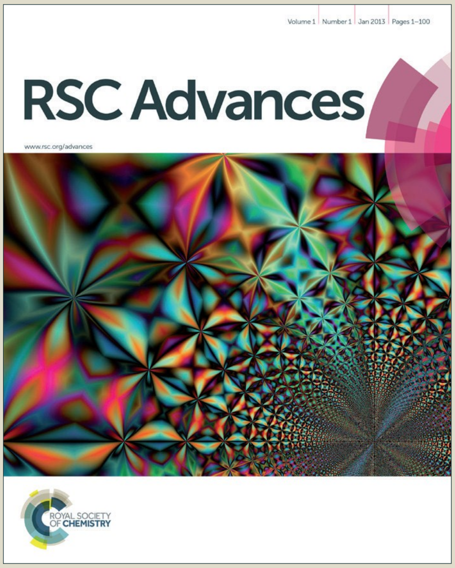

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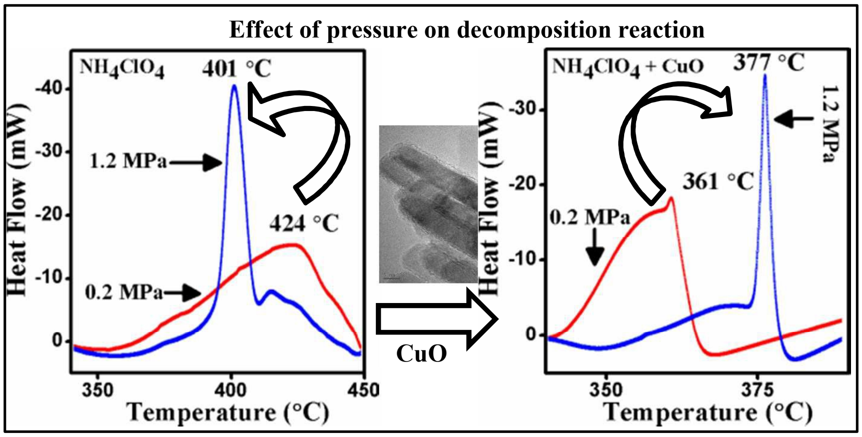
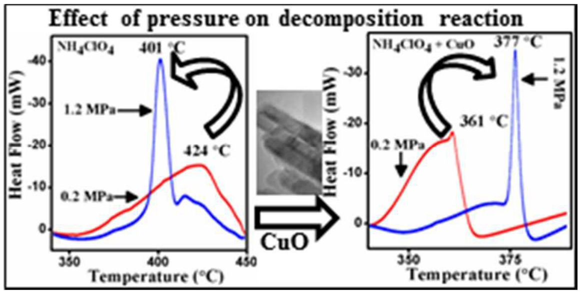
Graphical Abstract

Simultaneous effect of CuO nanocatalyst and pressure on the decomposition kinetics of ammonium perchlorate is analysed through high pressure decomposition studies.





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Pressure effects on the thermal decomposition reactions: A thermo-kinetic investigation

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The rate of chemical reactions is largely governed by three parameters namely, temperature, extent of reaction/reaction model and pressure. Usually, the pressure is assumed constant and experiments are carried out at 0.101 MPa (1 atm) pressure. Ammonium perchlorate (AP) is an extensively used solid propellant oxidizer and its decomposition kinetics has been attracting significant research interest for quite some time. In the present study, the influence of pressure on the decomposition reaction and kinetics of AP is investigated. As well, we have synthesized CuO nanorods, characterized with (scanning electron microscopy) SEM, (high-resolution transmission electron microscope) HRTEM, (selected area diffraction) SAED and (powder X-ray diffraction) PXRD and added to AP as catalyst and then the influence of pressure on the catalyzed decompositions are investigated. The decomposition behavior and kinetics was studied at three different pressures, 0.2, 0.6 and 1.2 MPa. The thermogravimetric analyzer and a high pressure differential scanning calorimeter was used for the studies. The studies reveal two different behaviors of catalyzed and non-catalyzed decomposition of AP under different pressure conditions. Promotion of secondary gas phase reactions by nitrogen and surface reactions on the nanocatalyst, promoting the oxidation reactions presumably lead to different decomposition behaviors of AP under different pressure conditions.

Introduction

Being an important ingredient of rocket propellant compositions, the decomposition reaction of ammonium perchlorate (AP) has been exhaustively studied during the past few decades. Reasonably, the research interest is majorly motivated by the fact that the propellant combustion is largely governed by the AP decomposition process. AP belongs to onium salts, a class of compounds formed by proton transfer from the corresponding acid to the base. Such onium compounds during decomposition/dissociation return the proton from cation to anion with the formation of the initial molecules of acid and base. In AP, this equilibrium proton transfer lead to the dissociative sublimation and formation of ammonia and perchloric acid, and this may occur in both the condensed and gas phases. The thermal decomposition of AP involves low-temperature decomposition (LTD) includes sublimation, and high-temperature decomposition (HTD).[1-5] The LTD process is usually exothermic and oxidation of ammonia by the perchloric acid (HTD) is endothermic.[6] However, in closed sample holders LTD as well as HTD appears as exothermic events and this is attributed to the secondary gas phase reactions of the decomposition products rather than the solid-state decomposition.[7]

The kinetics of AP decomposition has been the subject of many studies and is well documented in the literature.[7-9] The fact that the dissociation products of AP, ammonia and perchloric acid, can either react together (LTD) or evaporate into the gas phase and diffuse away from the decomposing AP (sublimation) or undergo further reactions followed by oxidation of ammonia (HTD), and these possibilities makes it a complex phenomenon. The complex simultaneous occurrences of different reactions lead to a dependency of apparent activation energy (E_α) on the extent of reaction. When a catalyst is introduced into the AP decomposition process, the complexity increases even more. Another aspect which is often left out is the effect of pressure on the AP decomposition and kinetics. Decomposition reactions wherein the products are gases, the pressure plays a significant role in the reaction kinetics.[10,11] The products of AP decomposition are gases and hence the pressure has profound influence on its kinetics, and the relation can be mathematically represented as

$$k = f(T)f'(\alpha)f''(P).$$

Where k is the rate constant, T is the temperature, α is the extent of conversion and P is the pressure.

Apart from this, the propellant burn rate is directly related to the pressure inside the rocket motor.[12] Though the decomposition mechanism and burning characteristics of AP have been the subjects of a large number of investigations, very few reports are available on the effect of pressure on the decomposition reaction.[6,13] In addition, there are no reports

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Electronic Supplementary Information (ESI) available: [The theoretical background of kinetic analysis, differential thermogravimetric curves for AP and APC, DSC data used for kinetic calculations and CuO nanorod characterization data are supplied as ESI]. See DOI: 10.1039/x0xx00000x which investigate the effect of pressure and catalyst on the decomposition behaviour of AP. In the present investigation to understand the effect of pressure on the decomposition and kinetics of AP, DSC experiments were performed at three different pressures 0.2, 0.6 and 1.2 MPa.

The influence of compounds involving ions of metals of alternating valences was investigated by different groups and these ions are able to catalyze a great number of thermal transformations and oxidizing process, including those with participation of perchloric acid. Hence these metal/metal oxides essentially increase the rate of AP decomposition and frequently employed as promoters of combustion of AP-based mixtures.[14] Based on this knowledge[15,16] CuO nanorods were synthesized and mixed with AP and the simultaneous effect of catalyst and pressure was investigated. To get more insights into the complex decomposition mechanism and the simultaneous effect of the pressure and catalyst, the kinetics of decomposition process is investigated. A non-linear integral isoconversional method[17] was used for the kinetic analysis to understand the dependence of the E_α on the extent of conversion (α). The isoconversional methods of kinetic analysis permit to explore the multistep kinetics of the thermal decomposition reactions and helps in drawing mechanistic conclusions about the process.[18] As the method tracks the E_α changes throughout the entire decomposition process, it allows a more accurate kinetic assignment of the individual steps of complex decompositions, such as those typically observed for propellants.[19] Hence, the present work investigates the effect of pressure on the catalyzed and non-catalyzed thermal decomposition of AP and to understand the mechanism changes and subsequent kinetics changes of this process under different pressure conditions.

Experimental

Materials

The AP used in the present study was kindly provided by ammonium perchlorate experimental plant (APEP), Alwaye (Kerala, India). The AP was at least 99% pure, mean particle size was 300 µm and nearly spherical in morphology.

Preparation of nanocatalyst

CuO nanorod catalyst was prepared in the laboratory and the detailed synthesis procedure[24] and characterization is described in the Supplementary Information. Initially, CuO microspheres composed of nanorods[21,22] were formed and the microspheres were re-dispersed in ethanol, and ultrasonic agitated for 3 h in a 320 W bath ultrasonicator to get nanorods. The resultant colloidal solution was again dried under reduced pressure and used for further experiments.

Characterization of nanocatalyst

The synthesized CuO nanorods were characterized by powder X-ray diffraction (PXRD), High-resolution transmission electron microscopy (HRTEM), Selected area (electron) diffraction (SAED) and Scanning electron microscopy (SEM).

Preparation of AP–CuO mixture

AP–CuO mixture with 2% (by weight) CuO content (referred as APC) was prepared by blending on a mechanical stirrer for 12 h. The mixture was used for the thermal analysis and high pressure DSC studies.

Thermogravimetric (TG) analysis

Thermal or catalytic decomposition experiments of AP were carried out under nitrogen atmosphere in a TA instruments SDT Q600 TG/DSC instrument. In all experiments, 1-1.5 mg of sample was loaded in an open 90 µL alumina pan and heated. Nitrogen at a flow rate of 100 mL/min was used as the purge gas. The nonisothermal TG runs were conducted at heating rates (β) 7.5, 15 and 20 °C/min and the collected data was used for further analysis.

Pressure DSC analysis

The high pressure DSC analysis was carried out on a PerkinElmer DSC high pressure cell attached to a PerkinElmer DSC8000 instrument. Three different pressures 0.2, 0.6 and 1.2 MPa were used and under a given pressure condition DSC scans were performed at three different heating rates 20, 25 and 30 °C/min and used for further kinetic analysis. During the experiments 1.2-1.8 mg samples were loaded into open aluminium pans and the high pressure cell was pressurized with nitrogen before the start of the experiment and static nitrogen environment was maintained.

Kinetic analysis

A model free (isoconversional) non-linear integral method[17] was employed for the computation of kinetic parameters and further kinetic analysis. The third degree approximation proposed by Senum and Yang[23] has been used in the present study to evaluate the integral in the non-linear integral method. The mass data obtained from the nonisothermal TG runs were converted to α using the standard equation $\alpha = (m_0 - m_t)/(m_0 - m_f)$. Where m_0 is the initial mass m_f is the final mass and m_t is the mass at a given temperature. Further, the nonisothermal pressure DSC experiments were conducted at three different heating rates (β) and α was computed by striping the area under the DSC curve (ΔH) for a given process into smaller region and dividing each segment by the total area under the curve (ΔH). A MATLAB code based on trapezoidal numerical integration method was used to convert the area under the curve into α. An α interval of 0.05 was used to compute the apparent activation energy (E_α) from the isoconversional method. The theoretical background of kinetic analysis is given as Supplementary Information.

Results

Characterization of CuO nanocatalyst

The CuO nanorods were synthesized by hydrothermal method and characterized by SEM, HRTEM and PXRD. Fig. 1 shows the TEM images recorded after pro-longed exposure to ultrasonication and the nanorod morphology of the CuO nanoparticles is revealed in the image. The dimensions of the produced nanorods were ~50 nm in length and ~10 nm in breadth. The lattice fringe pattern seen in the image indicated the formation of very thin CuO nanorods. (The detailed characterization of nanocatalyst including SEM images are submitted as Supplementary Information).

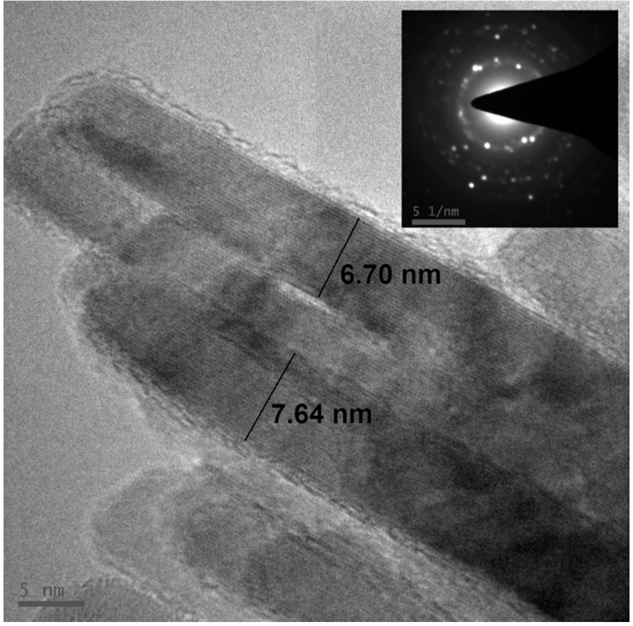

Figure 1. TEM image of CuO nanorods with electron diffraction pattern as inset

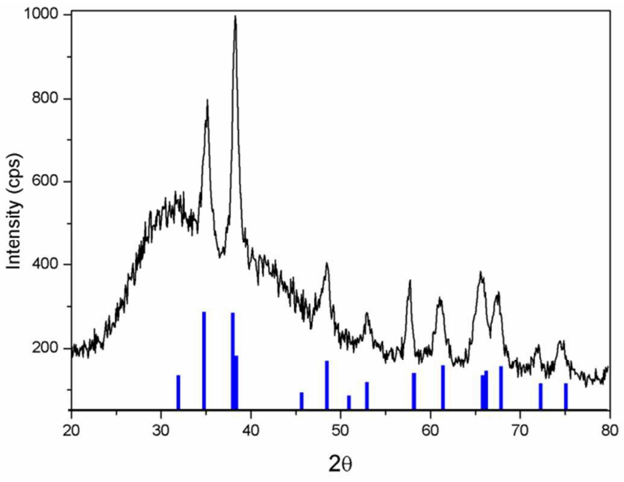

Figure 2. PXRD pattern of CuO nanorods

The PXRD reflections recorded for the sample is shown in the Fig. 2. The analysis revealed the formation of monoclinic CuO and the values were found to match with JCPDS card number 05-0661.

Thermogravimetric analysis

Initially, the thermogravimetric analyses of the AP samples were carried out, as explained in the experimental section. The thermal decomposition/mass loss curves of AP were recorded at three different heating rates 7.5, 15 and 20 °C/min. Indicating the LTD and HTD, the TGA (Fig. 3) has exhibited a two-stage weight loss. The two stage decomposition and catalytic effect was more clearly identified by the derivative weight loss curve (Fig. 1 of Supplementary Information).

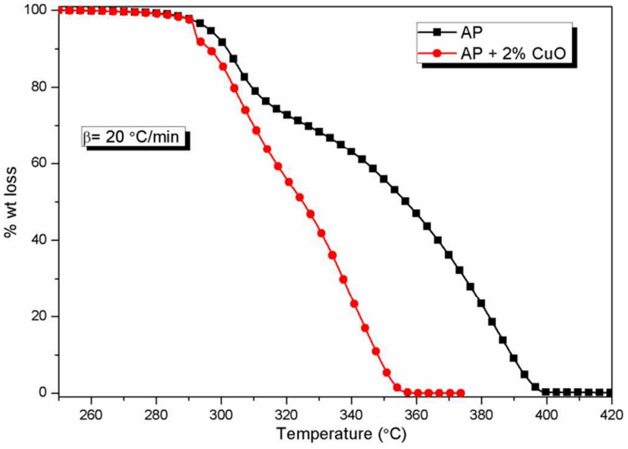

Figure 3. Nonisothermal thermogravimetric analysis curves for AP and APC samples

The thermogravimetric analysis of AP-nanorod mixtures (APC) was also carried out which indicated two-stage decomposition as in the case of AP. However, the HTD peak temperature was significantly lowered indicating the catalytic activity of CuO nanorod. The complete decomposition of AP (β=15 °C/min) was observed at 385 °C, while it was brought down to 348 °C in the presence of the nanocatalyst. Evidently, the LTD temperature showed a relatively insignificant change in peak temperature compared to the significant peak shift observed in the case of HTD.

High pressure DSC analysis

The samples AP and APC were then subjected to high pressure DSC (HPDSC) analysis. The heat flow curves (β=30 °C/min) obtained at 0.2 MPa for the samples AP and APC, are plotted together and shown in Fig. 4. Similar to the two stage decomposition behaviour exhibited by TG analysis was observed in the DSC analysis also. Addition of CuO has influenced the decomposition reaction in such way that the decomposition of AP in presence of nanocatalyst completed below 370 °C, which is otherwise completed at temperatures above 460 °C (Fig. 4). Further, HPDSC heat flow curves of AP and APC (β=30 °C/min) obtained at three different pressures are plotted and shown respectively in Fig. 5 and Fig. 6. Some interesting phenomena’s were observed in this analysis. When the pressure was increased from 0.2 to 1.2 MPa, the completion of AP decomposition reaction was shifted from 455 °C to 410 °C. On the other hand, though the decomposition reaction of APC was completed at significantly lower temperature than AP, at 0.2 MPa the APC decomposition reaction was completed at 368 °C and at 1.2 MPa it was raised to 382 °C. The shift in temperatures to higher values with respect to pressure was subsequently observed in the LTD peak, however, with a smaller change in peak temperature.

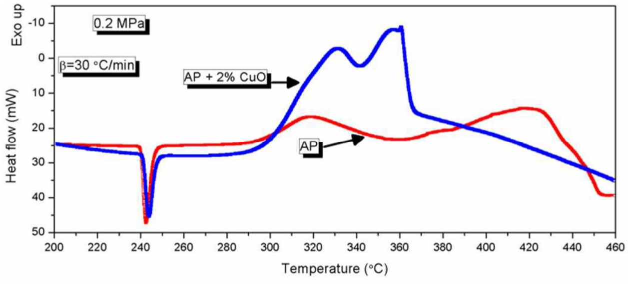

Figure 4. DSC heat flow curves obtained at 0.2 MPa for the samples AP and APC

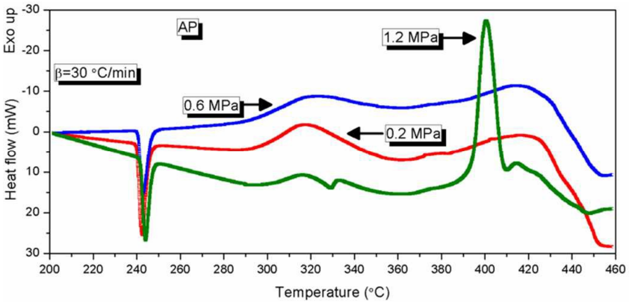

Figure 5. DSC heat flow curves obtained for AP at 0.2, 0.6 and 1.2 MPa

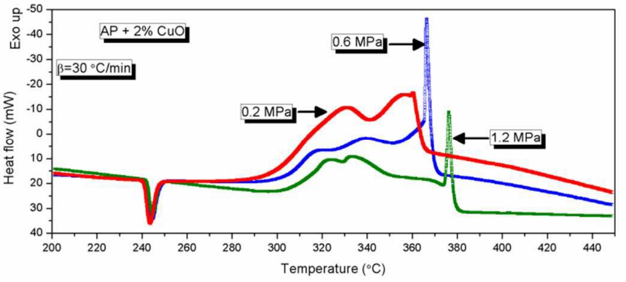

Figure 6. DSC heat flow curves obtained for APC at 0.2, 0.6 and 1.2 MPa

Kinetic analysis

From thermogravimetric analysis data

According to the isoconversional principle, the reaction rate at a constant conversion depends only on the temperature and based on this assumption calculations were performed to compute the E_α. The α values and there corresponding temperatures were calculated from the TG data obtained at three different heating rates and used to compute the E_α values for the decomposition reaction of AP and APC. To get more insights into the effect of CuO nanorods on the decomposition behaviour of AP, their kinetic curves, α against T, were plotted and shown in Fig. 7.

The comparison indicated a mechanism change in AP decomposition in the presence of CuO nanorod. The second stage decomposition of AP in the presence of CuO nanorod starts at significantly lower temperatures than that of AP. This temperature difference observed in α-T kinetic curves evidently point towards the catalytic activity of CuO nanorods on AP decomposition.

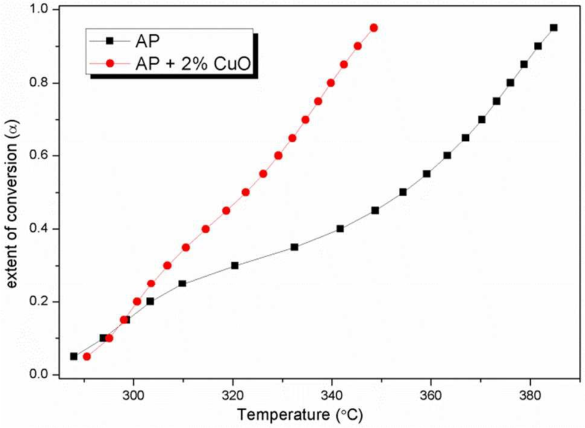

Figure 7. α against T kinetic curves obtained for AP and APC obtained at β = 15 °C/min

The comparison plots of E_α against α for AP and APC are shown in Fig. 8. For the AP, the E_α value decreases to 98 kJ mol^{-1} during initial ~30% decomposition, which accounts for the 0.1 to 0.3 region of α and then increases to 118 kJ mol^{-1}. The AP decomposition was described by an average activation energy of 108 kJ mol^{-1} while that of APC decomposition was described by 103 kJ mol^{-1}.

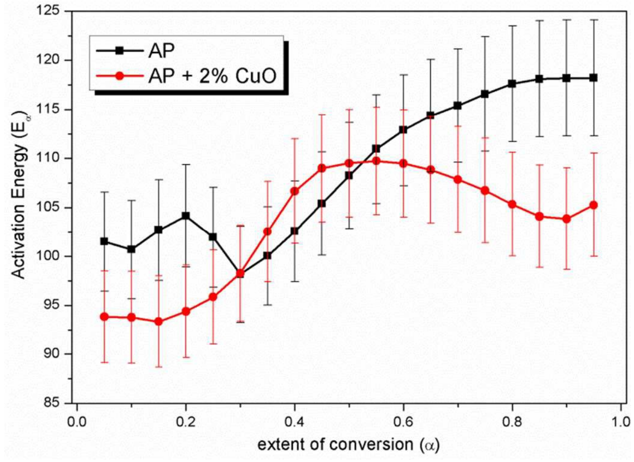

Figure 8. Variation of E_α with respect to reaction progress for AP and AP with nanocatalyst

From High pressure DSC data

The E_α for different AP samples at different pressures were computed using the heat of reaction/enthalpy values. To draw more realistic conclusions about the decomposition phenomena, the two processes, LTD and HTD, observed as two peaks in the DSC curves, were treated as two independent reactions.

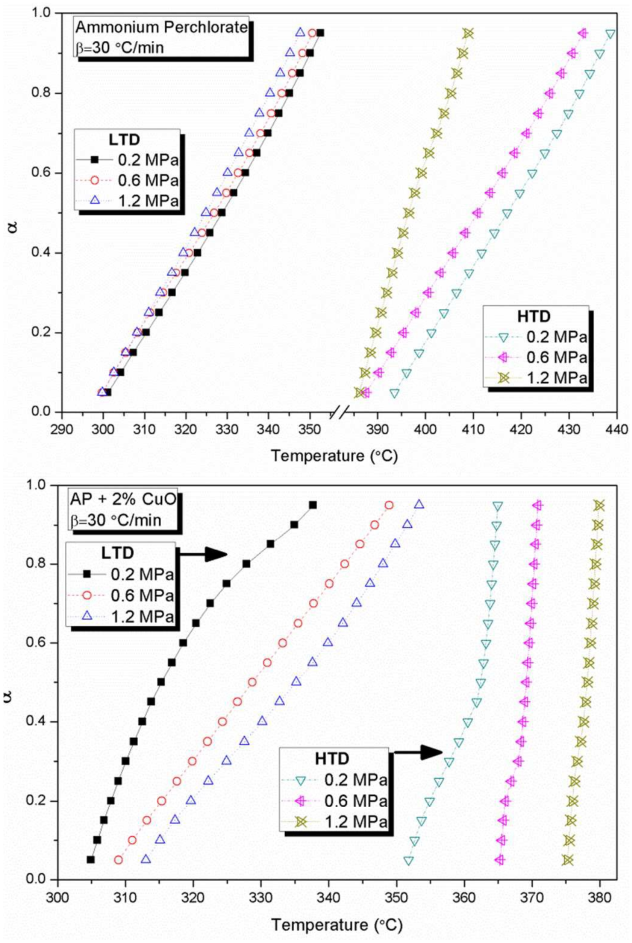

Figure 9. α against T kinetic curves corresponding to LTD and HTD for the samples AP and APC under different pressure

The kinetic curves (β=30 °C/min) of AP and APC plotted (Fig. 9) for three different pressures were compared. As mentioned earlier, in case of AP the increase in pressure lowered the decomposition temperature while in the case APC the decomposition temperature increased with pressure. Analysis of the kinetic curves revealed that the LTD is not significantly affected by the addition of the catalyst and this behaviour was observed in one of the earlier studies[21] and is reported in literature. On the other hand, the HTD was largely influenced and the 95% of decomposition of APC was completed at distinctly low temperatures at 365 °C, compared to that of AP at 438 °C (for P = 0.2 MPa). But for the APC, the plots indicate an increase in the temperature of completion of decomposition for HTD with respect to increase in pressure. However, the difference in peak temperature of HTD was nominal and was in the range of 10 °C and the difference in LTD peak temperature was negligible with respect to pressure.

Calculated E_α values were plotted against α to evaluate their dependency and subsequently to draw mechanistic conclusions about the process under investigation. The E_α values calculated for LTD reaction of AP and APC at three different pressures are plotted and shown in Fig. 10. As observed in the case of α-T kinetic curves, both showed different behaviour with an increase in pressure. The average activation energy required for the LTD of AP at pressures 0.2, 0.6 and 1.2 MPa was found to be 120, 117 and 108 kJ mol^{-1} respectively, while that of APC was found to be 67, 75 and 92 kJ mol^{-1}. Analogous to this observation, the E_α calculated for HTD of AP and APC illustrated a decrease or increase in peak temperature with respect to the increase in pressure. The average activation energy for the HTD of AP at pressures 0.2, 0.6 and 1.2 MPa was found to be 118, 112 and 99 kJ mol^{-1} respectively, while that of APC was found to be 58, 64 and 74 kJ mol^{-1}. These observations are not rather unusual because the α-T kinetic curves permitted to envisage these results.

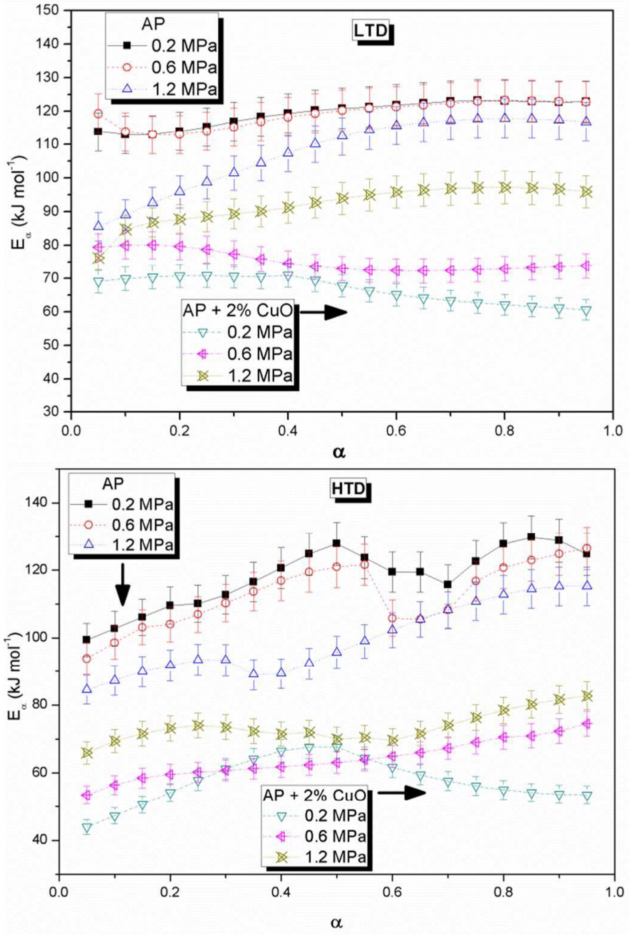

Figure 10. Variation of E_α with respect to reaction progress for LTD and HTD of AP and APC under different pressures

Discussions

The SAED pattern obtained for the nanorods were containing well defined spots with some shallow rings present (Fig. 11 and Fig. 12 of Supplementary Information). The change in the appearance of SAED, from mostly rings to mostly spots, pattern point towards few number of particles present in the selected area. This suggests that the nanoparticles are not single crystals and it is composed of a large number of small crystallites. Also, the SAED pattern was obtained for the CuO are found to match with the PXRD reflections.

As suggested by many earlier researchers, the decomposition of onium salt, ammonium perchlorate, involves the dissociative sublimation through a proton transfer reaction which in turn yields ammonia and perchloric acid.[1-4,7-9]

$$NH_4ClO_4^- \longrightarrow NH_{3\,(g)} + HClO_{4\,(g)} \quad \text{(R1)}$$

The dissociative sublimation process is endothermic in nature while the oxidation of ammonia by the corresponding acid is exothermic in nature. Usually, the particular pathway of onium salt decomposition depends on the nature of the anion.[5] In AP the decomposition pathways, especially HTD, is not only influenced by the thermal stability of anion ClO_4^-, but also by catalyst additives and / or experimental conditions. Hence, the heat of reaction of HTD is largely dependent on the type of sample enclosure (open pans, closed pan, closed pan with pinhole, etc.), employed for the thermal investigation and flow rate or pressure of the purge gas as well as the addition of decomposition catalysts.[6] Irrespective of these influencing parameters, and changes in HTD, the LTD always appears as an exothermic event. By and large the pressure conditions are known to govern AP decomposition reaction in pure form as well as in the mixture. Under the conditions which promote the secondary reactions, such as, under the high pressure conditions with no purge gas, the HTD appears as an exothermic event. In the present study, HPDSC analysis (high pressure conditions with no purge gas) provided enough platform for secondary reactions and both LTD and HTD appeared as exothermic peaks.

The dissociation products of AP, ammonia and perchloric acid, either react in the adsorbed layer on the surface of AP or desorb and sublime interacting in the gas phase. During the reactions occurring in the adsorbed layer the perchloric acid is desorbed more rapidly than ammonia, which causes incomplete oxidation of ammonia, creating a saturated atmosphere of ammonia.[4] In TG analysis, the LTD occurring around 300 °C accounts for the initial ~30% decomposition and the HTD occurring above 350 °C accounts for the complete decomposition of AP and the different stages correspond to change in the decomposition mechanism of AP.

The average activation energy values obtained for AP in the present investigation using thermogravimetric data is 108 kJ mol^{-1}. Further, the LTD was characterized by (α between 0.1 to 0.3) an average activation of 101 kJ mol^{-1} while that of HTD was characterized by 112 kJ mol^{-1} this phenomenon is commonly observed near ambient pressure conditions. Considering the fact that the confidence interval for this data set was calculated to be 105-112 kJ mol^{-1} and earlier reports suggesting activation energy of 121 kJ mol^{-1}, the calculated values are comparable with literature reports.[4] Moreover these activation energy values correspond to E_α required for the sublimation. Overall, at $\alpha > 0.3$, the estimates are similar to the activation energy of sublimation 125 kJ mol^{-1}determined by earlier researchers.[22] The value of E_α corresponding to the maximum temperature represents the greatest because of the contribution from sublimation to the overall rate of decomposition.[7]

The E_α calculated for LTD of AP from HPDSC data was varying in the 80-120 kJ mol^{-1} region at different pressures. While that of APC showed lower values ranging from 65-90 kJ mol^{-1}. Conversely, the E_α values for HTD found to vary significantly for both AP and APC. As described, the sublimation is the major process which governs the AP decomposition. It has already been reported that the contribution of sublimation is insignificant under ambient pressures and it increases with the decrease of pressure.[7] We have a different scenario here where the pressure is more than the ambient pressure. Also, the present observation is matching with an earlier study, where AP decomposition was conducted at ~5 MPa under nitrogen atmosphere and concluded that the HTD peak shifts to lower temperatures with an increase in pressure. The reason for this observation is assumed to be the N_2 extensively promoting the gas phase reaction between ammonia and perchloric acid.[13] However, no attempt was made to provide any insight into this observation. Also, keeping the point that, after the addition of CuO into AP, the HTD peak shifts to higher temperatures as we increase pressure. The reason for this may be, the observed E_α is that of the sublimation process, but not only confined to perchloric acid/ammonia sublimation.

$$4HClO_4 \longrightarrow Cl_2 + 5O_2 + 2ClO_2 + 2H_2O \quad \text{(R2)}$$

$$2Cl_2 + 2H_2O \longrightarrow 4HCl + O_2 \quad \text{(R3)}$$

$$2NH_3 + 2ClO_2 \longrightarrow N_2O + Cl_2 + 3H_2O \quad \text{(R4)}$$

$$N_2O + O_2 \longrightarrow NO + NO_2 \quad \text{(R5)}$$

Looking at the decomposition mechanism of AP (R2-R5),[26] the formed perchloric acid decompose (R2) and produce a variety of chlorine oxide including Cl_2O, a potential oxidizing agent with strong catalytic capacity, which is most likely to interact with ammonia as per the (R4). The main product of (R4) is N_2O, and as the reaction proceeds the adsorbed perchloric acid in the solid AP reaches the maximum and consequently outflow amount of perchloric acid reaches the minimum. This occurs about 350 °C (β=20 °C/min and P = 0.2MPa) and above this temperature the relative adsorption of perchloric acid amount decreases and reverse changes occurs in the case ammonia. After the first stage, for the region α> 0.3, the E_α is governed by the mass controlled decomposition process and sublimation.

Since the decomposition of perchloric acid and the oxidation of ammonia proceed with heat generation and the sublimation proceeds with heat absorption, the E_α will be governed by the ratio of the amounts of AP that decompose to the amount that sublimate. In the general case, E_α will depend on the fraction of the dispersed substance[14] and the heat supply from the gas phase reactions. Also considering the fact that, a particular critical pressure of the products exists, and after this pressure is attained, the rate of decomposition decreases independently of the degree of conversion achieved at a given time.[27] In AP, it is known that the complete reaction halts due to the condensation of water vapour on the crystal defects of the crystal lattice. As the pressure increases and the sublimation process becomes restricted and the surface reactions become prominent at higher pressures, which lead to the decrease in the E_α values. As a result, the exothermic decomposition is likely to become controlled by mass-transfer along the solid surface and desorption, which are usually characterized by relatively low activation energies.[7]

In the case of APC, the autocatalytic reaction between the products of $HClO_4$ and NH_3, is already present, and in addition to that catalyst has further lowered the required E_α. The reason may be well proposed from the interaction between N_2O and metal oxides.[28,29] The formation of nitrogen molecule and an adsorbed oxygen atom is expected to be the first step of the interaction, which is represented by the following equation,

$$N_2O + e^- \longrightarrow N_2 + O^-_{ads} \quad \text{(R6)}$$

Owing to the fact that this adsorption reaction readily occurs at room temperature in CuO, it is reasonable to infer that the reaction is very rapid at AP decomposition temperatures.[25] Considering (R4) where the N_2O is produced and assuming that it is decomposed by the CuO at a faster rate, the reaction equilibrium will shift to the right hand side. The surface reactions will, in fact, remove the N_2O as N_2, and this will lead to the production of more amount of H_2O, a step which does not occur during the AP decomposition. Then the heat release and kinetics could be influenced by the water condensation. In this situation, the kinetics of heat released in the system under high pressure becomes very complicated. Consequently, the inhibitors of the reactions are not separated from the crystal leading to the adsorption or occlusion of water. In an open system, water is eliminated at a faster rate and does not influence the development of decomposition.[27] This would apparently start governing the decomposition phenomena at high pressures and costs heavily on the E_α values at higher pressures.

Conclusions

The effect of pressure on the catalyzed and non-catalyzed decomposition kinetics of AP was studied using high pressure DSC. Two different behaviours were exhibited by the AP and AP in presence of CuO nanorod under different pressure conditions. Although the exact mechanistic reason for this change in behaviour is not clear, the encouragement of gas phase reaction between the species originated from the sublimation of AP by the nitrogen seems to enhance the decomposition rate at higher pressures. With CuO addition the catalytic effect was immediately recognizable from the α-T kinetic curves. The shift in temperature to higher values for catalyzed decomposition of AP is attributed to the formation of water as a by-product of surface reaction and subsequent adsorption or occlusion into the crystal. Also, the competition between a heat generating process–decomposition of perchloric acid, and a heat absorbing process–the oxidation of ammonia, lead to different thermal behaviours in presence and absence of surface reactions. Hence, the study shows that surface reactions and the reaction by-product play different roles at different pressure conditions and influence the kinetic parameters. In conclusion, the water formation, adsorption and desorption seem to govern the decomposition reaction of AP at elevated pressures.

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