Lattice Inclusion of Copper Ions in Ammonium Perchlorate through Co-crystallization: Impact on Lattice, Physical, and Thermal Characteristics

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ABSTRACT: Ammonium perchlorate (AP) is an important oxidizer extensively used in composite solid propellants. Any alterations in the lattice configuration of AP could bring in a dramatic change in its physical, thermal, and ballistic characteristics though the basic thermodynamic properties could remain unaltered. In this work, we attempt to dope AP with copper nitrate through co-crystallization and examine its impact on the lattice, physical, and thermal characteristics. The effect of copper ion on the crystal morphology, bulk density, friability, moisture content, and the decomposition behavior is compared with normal propellant-grade AP. The incorporation of copper ion into AP resulted in an increase in bulk density and aspect ratio and a marginal decrease in the average particle size. The shape factor remained intact. The presence of copper ion remarkably decreased both the low- and high-temperature decomposition and reduced the activation energy for both stages, confirming the catalytic nature of copper-doped AP.

1. INTRODUCTION

Ammonium perchlorate (AP) is the common oxidizer used in composite solid propellant for launch vehicles. The composite propellant is a heterogeneous mixture of an oxidizer (usually AP), a metallic fuel like aluminum powder, and hydroxyl-terminated polybutadiene, which acts as both fuel and propellant binder. AP has the highest effective oxygen content among the oxidizers, i.e., its oxygen balance is up to +34%, which results in the oxidization of aluminum and the binder during the combustion of propellants. For an optimum solid loading of 86% by weight in the solid propellant, AP contributes approximately 68–70% by weight. Since AP is the major constituent of composite propellant, the properties of AP directly affect the properties of composite solid propellant. Thus, while a new oxidizer is being developed, researchers focus mainly on replacing a part of AP with new compounds or elements.1

The burn rate of a composite solid propellant based on AP can be increased by reducing the oxidizer particle size, increasing its fine-to-coarse ratio, increasing the surface area of metallic fuel, and adding a burn rate modifier. The commonly used burn rate modifiers are iron oxide and copper chromite. A lot of studies have been carried out on doped AP, where the dopants are mechanically mixed. Transition metals and their oxides are found to be good catalysts that decrease the activation energy and decomposition temperature of oxidizer ammonium perchlorate.2–5 Copper and its salts and oxides are highly effective catalysts in the thermal decomposition of ammonium perchlorate.6–13

The studies related to the effect of foreign ion particles present in the lattice of AP, i.e., homogeneous doping of AP with compounds were reported earlier, but the kinetic, physical, and crystallographic details are not mentioned.3,4 The surface characteristics, purity, size, shape, crystal strength, crystal perfection, and particle size distribution of AP directly depend on the crystallization process, so it is the most critical step in the manufacture of AP.14–16 The present paper focuses on the effect of copper-ion inclusion into AP lattice during crystallization with specific focus on the crystal structure, average particle size, shape, bulk density, and friability. The catalytic effect of copper on lattice-modified AP was studied by thermogravimetric analysis (TGA) and TG–mass spectrometry (TG-MS), and the activation energy was determined by thermal analysis at different heating rates by the Flynn–Wall–Ozawa method.
2. EXPERIMENTAL SECTION

2.1. Materials. Ammonium perchlorate of >99.0% purity processed by sodium route, procured from Ammonium Perchlorate Experimental Plant, Aluva, Kerala was used for the preparation of doped AP. Analytical grade reagent copper nitrate trihydrate from Merck was used as received for doping of AP.

2.2. Preparation of AP Crystals. A glass-jacketed crystallizer with glass agitator having a Teflon paddle was used for the crystallization. A solution of AP was prepared in distilled water at 75 °C, and the concentration of the solution corresponds to supersaturation. The temperature of ammonium perchlorate solution was maintained at 80 °C to prevent secondary nucleation in the system. The temperature coefficient of solubility is high for AP in water. The solubility of AP in distilled water is also high. The concentration of copper nitrate in mother liquor is varied from 5 to 20% moles of AP. A cooling crystallization up to 5 °C was carried out at different rates of cooling and varying rpm values. The optimum doping condition was found to be fast cooling at low rpm, which was used for crystallization since the concentration of dopant in the crystals is maximum in this mode. The prepared AP crystals were filtered out using a funnel with filter paper, and it is washed with acetone to remove the traces of water. The washed AP crystals were spread in glass trays to prevent agglomeration of crystals. The doped crystals were then dried at 60 °C for 4 h in a laboratory hot-air oven.

2.3. Instrumentation. The particle size distribution of the doped AP was measured by sieve analysis. The ASTM standard sieves of sieve size from 500 to 45 μm were used on a ROTAP sieve shaker. The weighted average particle size was calculated from the differential particle size distribution obtained from the sieve analysis. The copper content in the AP crystals was measured using atomic absorption spectroscopy.

The specific surface areas of the particles were measured using a Quantachrome NOVA 1200e surface area analyzer. About 2–2.5 g of AP was taken in a bulb cell with rod, and a degassing time of 4 h was given at a temperature of 100 °C. Multipoint Brunauer–Emmett–Teller (BET) was taken using nitrogen gas adsorbate with an effective molecular diameter of 3.54 Å and density of 0.806 g/cc, and the adsorption was carried out at a temperature of 77 K using liquid nitrogen.

The friability of AP crystals was measured using crystals of particle size >125 μ. After measuring the initial weight of AP, the crystals underwent rotation and gyration for 30 min along with 100 glass beads of size 3 mm. The percentage weight loss is measured as the friability of the crystals. The digital bulk density (DBK) apparatus with a 100 mL measuring cylinder was used for the measurement of bulk density of the crystals. The bulk density is the ratio of the mass to the total volume of the crystals after 100 tapping. The total moisture content in AP is measured using an instrument based on infrared (IR) heating, which is very accurate and can determine very low percentages of moisture in a sample.

The surface morphology of the samples was analyzed using a Carl Zeiss, Supra 55 model field emission scanning electron microscope (SEM). The crystallographic properties of the samples were examined from the powder X-ray diffraction (XRD) data of the samples on a Bruker D8-Discover powder X-ray diffractometer with Cu Ka (λ = 1.5418 Å) at a scan rate of 2.5°/min. Crystalline phases were identified by comparing the experimental diffraction patterns to Joint Committee on Powder Diffraction Standards (JCPDS).

Table 1. Physical Characteristics of Normal and Copper-Doped AP

| Sample | % of copper | % of moisture | Average particle size (μm) | % of friability | Bulk density (g/cm³) | Specific surface area (m²/g) |
|--------|-------------|---------------|-----------------------------|-----------------|---------------------|-------------------------------|
| AP     | 0           | 0.11          | 312                         | 0.04            | 1.30                | 0.18                          |
| APCu-1 | 0.16        | 0.12          | 302                         | 0.06            | 1.31                | 0.19                          |
| APCu-2 | 0.31        | 0.14          | 300                         | 0.06            | 1.31                | 0.21                          |
| APCu-3 | 0.43        | 0.14          | 296                         | 0.06            | 1.33                | 0.21                          |
| APCu-4 | 0.59        | 0.17          | 294                         | 0.06            | 1.33                | 0.23                          |

The kinetic analysis was done by the Flynn–Wall–Ozawa (FWO) method, an isocconversional method, the final equation of which is given below

\[ \ln \beta = \ln \left( \frac{AE}{Rg(\alpha)} \right) = 5.523 - 1.0518 \left( \frac{E_a}{RT_d} \right) \]  \hspace{1cm} (1)

where \( E_a \) is the activation energy for the percentage conversion \( \alpha \) and \( R \) is the universal gas constant. A plot of \( \ln \beta \) vs \( 1/T_d \) gives straight lines. The slopes of the straight lines were used for the estimation of activation energy.

3. RESULTS AND DISCUSSION

3.1. Physical Characteristics. During crystal formation in the crystallizer, the growth of phase of AP may be inhibited due to the presence of copper. The inclusion of copper ion into AP crystals diminishes the strength of the latter, which results in a slight increase in friability and reduction in the particle size of AP. The physical characteristics of normal AP and copper-doped AP are given in Table 1. There is a possibility of 1% error in the measurement of physical characteristics like average particle size, copper, moisture, friability, bulk density, and specific surface area.

The specific surface area is in the range of 0.17–0.19 m²/g for normal AP and 0.19–0.23 m²/g for copper-doped AP. The reduction in average particle size results in a slight increase of specific surface area. A better packing and compactness of smaller particles leads to higher bulk density, i.e., the bulk density usually increases with decrease in the particle size of the material. Copper salts are more soluble than AP. Therefore, it should precipitate at a slower rate compared to AP. As AP crystallizes at a nominal speed, the inclusion of copper ion in AP lattice enhances the lattice entropy. Crystallization is an exothermic phenomenon. Exothermicity and entropy increases are conducive factors for co-crystallization. The bulk density of AP crystals steadily increases with an increase in copper concentration, which implies reduction in the number of voids.
or pores. Thus, the bulk density is found to be increased due to the reduction in defects/voids and average particle size. The mother liquor included in the crystal during crystal formation cannot be removed by drying, and it can be measured as the moisture content available inside the crystal. The occluded moisture present in the crystal may diffuse to the surface of the crystal during storage and get condensed in humid atmosphere. Although the moisture content increases with an increase in copper concentration, it is within specification for propellant-grade AP.

Surface characteristics like shape factor and aspect ratio are obtained by dynamic laser imaging. Being a measure of sphericity, a shape factor of unity corresponds to spherical and round particles and zero corresponds to rough and elongated particles. Figure 1 shows the average aspect ratio and average shape factor for normal AP and doped AP (APCu-1, APCu-2, APCu-3, APCu-4). With an increase in copper concentration, an increasing trend in the aspect ratio and shape factor is observed. At low concentration, the average aspect ratio and average shape factor of doped AP are found to be less than those of normal AP. But the trend is changed when the concentration of copper exceeds 0.16%, irregular growth of the bigger crystals is hindered by secondary nucleation and thus results in increase in the sphericity and regularity of the crystals. Both the shape factor and aspect ratio show the same trend for all of the AP crystals. An average shape factor of 0.73 and an average aspect ratio of 0.61 were obtained for the Cu-doped AP crystals.

Scanning electron microscopy was taken for normal AP and copper-doped AP particles for comparison of their surface morphologies. Figure 2 shows the SEM images of normal AP and APCu-4. The SEM image shows the regularity and spherical nature of the particles for normal AP and doped AP. The cooling pattern selected for crystallization was the fast cooling mode. Cooling up to 5 °C was done to get maximum yield. After reaching the minimum temperature at the fixed cooling rate, the agitation was maintained for an additional 20 min, which reduces the irregular growth of the crystals and results in more spherical nature. The SEM results show homogeneous doping of copper nitrate as it cannot be differentiated from AP in the images. With an increase in copper-ion concentration, the spherical nature of crystals is maintained and is comparable to normal AP. The energy-dispersive X-ray spectroscopy (EDS) characterization of APCu-4, as shown in Figure 3, confirms that the co-crystallized crystals are composed of copper in addition to nitrogen, oxygen, chlorine, and hydrogen.

### 3.2. Crystallographic Characteristics

The doping of AP up to a concentration of 0.6% of copper is found to modify the XRD pattern of AP. According to the ASTM data of AP, the main peaks appear for AP at 2θ values of 15.3, 19.4, 22.7, 23.9, 24.6, 27.4, 30.1, 30.8, and 34.6°, which are assigned to the (101), (011), (201), (002), (210), (211), (112), (202), and (212) crystal planes, respectively. Figure 4a compares the XRD peaks of normal AP and the AP doped with copper ion. Figure 4b compares the XRD peaks of normal AP (AP), doped AP by

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**Figure 1.** Average aspect ratio and average shape factor of normal AP and Doped AP (APCu-1, APCu-2, APCu-3, APCu-4).

**Figure 2.** SEM images (a) Normal AP and (b) APCu-4.

**Figure 3.** EDS spectrum of APCu-4.

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co-crystallization (APCu-1, APCu-2, APCu-3, APCu-4), and physical mixing (APCuM-4). Characteristic peaks of copper nitrate are at 18.59, 19.18, and 22.09°. The peaks at 18.59 and 19.18° disappear in the XRD pattern of doped AP sample due to the crystal modification of AP, at a very low concentration of copper nitrate. As the concentration of dopant is increased further, the XRD pattern is found to be similar to the physically mixed sample, due to excess concentration of copper nitrate outside the lattice. The presence of copper ion in the mother liquor prevents secondary nucleation. As the concentration of copper increases further, the effect becomes more pronounced. Therefore, it results in more sphericity and regularity at a higher concentration of copper. For the physically mixed AP sample, the XRD spectra show peak positions and relative intensities similar to that of normal AP. The peaks of the (210), (211), and (112) planes, at 2θ values of 24.6, 27.4, and 30.1°, are intensified for the doped AP sample produced by co-crystallization. The above results indicate that the doped AP by co-crystallization maintained a perfect crystalline structure like AP, and it is different from the crystallography pattern of the physically mixed sample.

3.3. Thermal Characteristics. Thermogravimetry (TG) and differential scanning calorimetry (DSC) measurements were used to examine the thermal characteristics of doped AP.
with reference to undoped AP (see Figure 5). The thermal decomposition of AP is a two-stage process, the first stage resulting in a 30% mass loss, i.e., low-temperature decomposition (LTD) starts at 240 °C and ends at 320 °C. The second stage accounts for complete decomposition, i.e., high-temperature decomposition (HTD), which immediately follows the LTD and completes at around 380 °C. The endotherm at 240 °C corresponds to the crystallographic transition from the orthorhombic to cubic form. Ammonia does not get completely oxidized during the LTD of AP, as reported elsewhere. This ammonia accumulated on the reactive surface of residual AP prevents it from further decomposition. As the temperature increases, the ammonia accumulated over the AP crystal surface gets oxidized and the high-temperature decomposition is initiated. The transition-metal compounds catalyze the decomposition of perchlorate ion and oxidation of ammonia.

The TG-DSC-derivative thermogravimetry (TG-DSC-DTG) curves of normal AP and doped AP are given in Figure 5a–5c, respectively. The TG profiles revealed the similarity in peaks for endothermic phase transformation, low-temperature decomposition, and high-temperature decomposition for all of the AP samples. The endothermic phase-transition peaks for all of the samples are within the range of 240–244 °C. The mass loss during low-temperature decomposition is found to be slightly more for AP with copper inclusion than the corresponding normal sample. The thermal decomposition starts from inside of the crystal and not at crystal surface for low-temperature decomposition. For high-temperature decomposition, the reaction proceeds at the surface.2 Copper is possibly converted to cupric oxide during the reaction, and both these act as a catalytic surface for the high-temperature decomposition of AP. The decomposition, starting on the surface, penetrated the copper ion into the lattice, which accounts for the effectiveness of the catalysis. For copper doping from 0.16 to 0.59%, the low-temperature decomposition is shifted toward the low-temperature regime (LTR) by 14–22 °C, and the high-temperature decomposition is highly catalyzed as the peak shifted toward LTR by 17–36 °C, as given in Table 2. The thermal analysis results are accurate, and there can be a difference of maximum 2° for repeated samples. The variation in mass loss percentage and decomposition temperature peak seen for copper-doped AP is due to the presence of copper in the crystal lattice.

Normal physical mixing of AP with copper compounds catalyzes only high-temperature decomposition. The samples APCuM-2 and APCuM-4 are physically mixed ones with compositions similar to those of APCu-2 and APCu-4, respectively. The phenomenological data of thermal analysis of APCu-M-2 and APCu-M-4 are given in Table 3. But the doping of copper in AP crystals resulted in catalysis of low-temperature decomposition. Catalyzing both stages of AP decomposition will definitely increase the rate of decomposition of AP, thereby increasing the burn rate of AP containing propellants substantially.

The sample with maximum copper doping (APCu-4) was taken for kinetic analysis. Thermal analysis was done at three different heating rates—3, 5, and 10 °C/min—for kinetic study. For this particular sample, the peak temperature is decreased by 22 °C for LTD and by 36 °C for HTD. The activation energies calculated using the FWO method against percentage conversion for normal AP and doped AP for low- and high-temperature decompositions are given in Figure 6a,b respectively. The average activation energies for normal AP and copper-doped AP, respectively, are 149 and 137 for LTD, and 127 and 122 for HTD. There is a decrease in activation, which indicates the effectiveness of the catalytic process. The TGA results indicate the effect of copper ion as a good catalyst on thermal decomposition and associated kinetic parameters.

The thermal decomposition products for normal AP and copper-doped AP samples were analyzed by TG-MS (see Figure 7). The decomposition products of doped AP are found to be similar to the decomposition products of normal AP. In the LTD of normal AP, the concentration of HCl was very low. However, the concentrations of N2O and O2 are almost comparable, indicating the incomplete oxidation during LTD. For the doped AP sample, the concentrations of N2O and O2 are higher for LTD and the HCl concentration is slightly increased in HTD, indicating the catalyzed oxidation of ammonia.

Based on the crystallographic and thermal results, we can deduce that the doping of AP or lattice modification of AP with copper ion promotes both LTD and HTD. Gas-phase and solid-phase reactions are present in the low-temperature exothermic decomposition process. The controlling step is the electron transfer from ClO4− to NH4+, which may explain the mechanism of thermal decomposition of AP (Table 4).2–5 The mechanism proposed in the literature is given as follows.

A pair of ions is formed in the lattice in step I. In step II, decomposition starts with proton transfer from ammonium ion (cation) to perchlorate ion (anion) via a molecular complex formation. In step III, decomposition proceeds to form ammonia and perchloric acid. Low-temperature decomposition reactions start from the core and proceeds to the pores. The decomposition reactions of AP often involve both bond-breaking and bond-forming steps. Many reactions are involved in the presence of four elements, and a full range of oxidation states is utilized by chlorine and nitrogen.

In copper-doped AP crystals, the surface area is found to be increased due to copper inclusion. The copper ion modifies the
lattice of AP, makes the NH$_4^-$ClO$_4$ bond weak, due to the interaction of oxygen with copper, and the thermal decomposition occurs at a lower temperature. The presence of copper in the lattice favors both low-temperature and high-temperature decomposition. The partially filled Cu$^{2+}$ ion facilitates the electron transfer process. Positive holes in CuO can accept electrons, and the intermediate complex product formed favors the HTD. Copper acts as a catalyst and gives more surface area for the low-temperature decomposition to start, and the complex formed during the intermediate complex formation stage and cupric oxide favors the high-temperature decomposition.

4. CONCLUSIONS

The present investigation attempts incorporation of copper ion into AP crystal lattice through co-crystallization to study the effects on the crystal properties and physical and thermal characteristics. The difference in the thermal decomposition of doped AP by physical mixing and by co-crystallization suggests that the co-crystallization is more effective due to lattice modification, which is further confirmed by the difference in their XRD patterns. The copper-doped AP crystal has better decomposition characteristics, and the copper inclusion does not affect the crystal parameters. For copper-doped AP, there is a decrease in the average particle size and an increase in friability, bulk density, average shape factor, and average aspect
ratio. The co-crystallized AP with good particle size distribution and friability forms the basis of its application to achieve thermal decomposition at a lower temperature. The decrease in activation energy indicates the effectiveness of the catalytic process of the doped AP.

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