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Formation of copper oxide through $NaNO_3$–KNO_3 eutectic melt and its catalytic activity in the decomposition of ammonium perchlorate

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Abstract

The decomposition of basic copper carbonate in the presence and absence of $NaNO_3$–KNO_3 eutectic melt has been studied by employing isothermal TG and dynamic TG/DSC techniques. The rate constants for the decomposition in the presence of eutectic melt were found to be higher than when carbonate was heated alone. In both the cases copper oxide was found to be the end product. Catalytic activity of copper oxide obtained by the two methods were tested for the decomposition of ammonium perchlorate.

Keywords: Copper oxide; $NaNO_3$–KNO_3 eutectic melt; Ammonium perchlorate

1. Introduction

There are large number of transition metal salts which when heated above their decompostion temperatures are converted to corresponding metal oxides. The temperature of formation of these oxides is generally very high. However, when the metal salts are heated in suitable molten electrolytes, oxides are formed relatively at much lower temperatures [1]. Decomposition of number of metal salts forming metal oxides through nitrate eutectic melts has been reported [2–5]. The kinetics and mechanism of such reactions have been discussed. However, the role of oxides obtained through nitrate eutectic melts as catalysts has not been studied so far.

In the present paper kinetics of decomposition of basic copper carbonate through $NaNO_3$–KNO_3 eutectic melt has been discussed. The role of CuO as a catalyst during the decomposition of ammonium perchlorate (AP) has also been studied.

2. Experimental

2.1. Materials

$NaNO_3$, KNO_3 and $CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$ all from Qualigence were used. AP of 99.1% purity was received from Central Electrochemical Research Institute, Karaikudi, Tamil Nadu. It was crushed gently in an agate mortar to avoid explosion and sieved through 100–200–400 mesh.

2.2. Methods

2.2.1. Preparation of $NaNO_3$–KNO_3 eutectic mixture

Dried samples of sodium nitrate and potassium nitrate were mixed in 45:55 percent ratio (wt.%) in

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a clean test tube. The mouth of the test tube containing the nitrate mixture was sealed and kept in a furnace at a temperature slightly higher than the melting points of the components. When the entire mass melted, the molten liquid was quenched suddenly to room temperature. The process of heating and cooling was repeated several times and ultimately the solidified material was removed from the test tube and crushed into fine powder. This was done to produce a homogeneous mixture of the two components. The melting point of the eutectic mixture was found to be 226 °C.

2.3. Isothermal TG studies

Isothermal TG experiment on copper carbonate alone and in presence of $NaNO_3$–KNO_3 eutectic mixture were performed with a manual thermo-gravimetric analyser under ambient conditions, in an atmosphere of air. Gold crucible was used in the experiment and hung in an electric furnace with gold wire. The temperature was recorded with a temperature indicator PI (LC-40). The sample was maintained at constant temperature with the help of a dimerstat. The mass loss was noted as a function of time. Each experiment was repeated three times at different temperature.

2.4. TG–DSC studies

Simultaneous TG–DSC studies on basic copper carbonate, copper carbonate in $NaNO_3$–KNO_3 eutectic, AP with 2% CuO and AP with 2% CuO prepared through $NaNO_3$–KNO_3 eutectic were performed with thermal analyser STA 409 EP apparatus at HEMRL, Pune, under an atmosphere of air at a heating rate of 10 °C min^{-1}.

2.5. Powder X-ray diffraction studies

The X-ray powder diffraction patterns of the residues after TG were recorded with a X-ray diffractograph (XRD-5 General Electic, USA) using Cu Kα radiation.

2.6. Analysis of the gaseous product

The evolved gas was tested in the usual way and found to be CO_2 and water vapour. CO_2 was tested by passing through lime water where as water vapour was tested by anhydrous copper sulphate.

2.7. Gravimetric estimation

Solid reaction products obtained from thermogravimetric studies were washed with water to separate insoluble oxide. Copper was estimated gravimetrically as an oxide by a standard method [6].

2.8. Ignition delay studies of AP

Ignition delay (D_E) studies of AP and ammonium perchlorate + CuO were undertaken by tube furnace technique. The sample (weight = 15 mg; 100–400 mesh) was taken in ignition tube (5 cm length and 0.4 cm diameter) and the time interval between the insertion of the tube into the tube furnace and the time of ignition was noted with the help of stop watch with an accuracy of 0.1 s. This gave the value of ignition delay D_E.

3. Results and discussion

TG curve for the decomposition of basic copper carbonate is given in Fig. 1. The figure shows the gradual weight loss up to 290 °C (about 10%). This may be due to removal of adsorbed water molecules and water of crystallization. After this temperature there is rapid weight loss up to 300 °C (31.5%) and then the weight became constant. The theoretical weight loss for the conversion of basic copper carbonate to copper oxide is 33.1% which is in good agreement with the experimental value. From the results it appears that both the carbonate and hydroxide component decompose at one temperature or there is very little temperature difference in the decomposition of the two components.

DSC curve for the decomposition of basic copper carbonate is shown in Fig. 2. It gives a small endothermic peak at 60 °C due to removal of adsorbed water molecule. A sharp endothermic peak at 297.6 °C and an endothermic hump at 315 °C are due to decomposition of carbonate and hydroxide component of basic copper carbonate. The results show that there is very little temperature difference between the decomposition of carbonate and hydroxide part of the basic copper carbonate and the results are in conformity to that of TG.

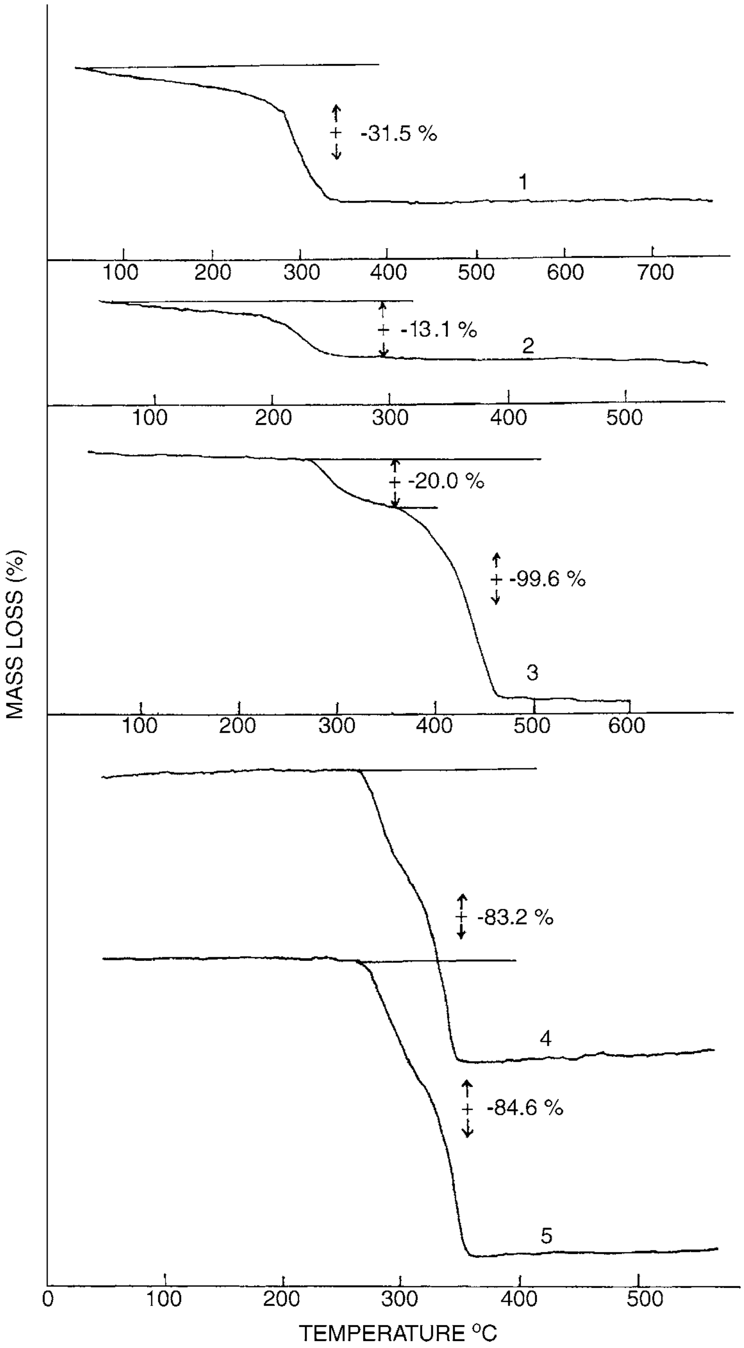

Fig. 1. TG curve for: (1) basic copper carbonate; (2) basic copper carbonate in $NaNO_3$–KNO_3 eutectic; (3) AP; (4) AP in presence of CuO prepared directly; (5) AP in presence of CuO prepared from eutectic.

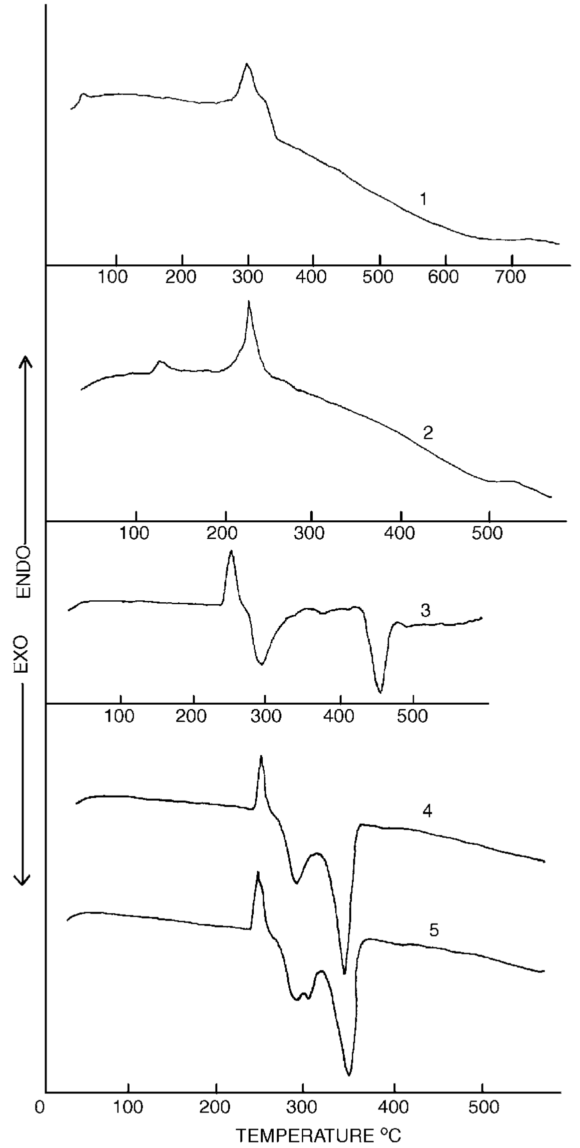

Fig. 2. DSC curve for: (1) basic copper carbonate; (2) basic copper carbonate in $NaNO_3$–KNO_3 eutectic; (3) AP; (4) AP in presence of CuO prepared directly; (5) AP in presence of CuO prepared from eutectic.

The end product of the reaction was analysed by chemical analysis and powder X-ray diffraction technique and was found to be CuO.

Isothermal TG studies (230–320 °C) showed that the kinetic data obey Eq. (1).

$$1 - (1 - \alpha)^{1/3} = k_1 t \qquad (1)$$

where α is the fraction decomposed at any time t and k_1 the rate constant. The values of α are given in Table 1. When $[1 - (1 - \alpha)^{1/3}]$ is plotted against t straight lines (Fig. 3) are obtained showing the validity of Eq. (1). From the slope of the lines the values of k_1 were calculated and are given in Table 2. The energy of activation was calculated from Arrhenius plot and is given in the same table.

The TG curve for the basic copper carbonate in $NaNO_3$–KNO_3 eutectic is shown in Fig. 1. There is a continuous weight loss up to about 58 °C which may be due to removal of adsorb water molecules and water of crystallization and after that there is rapid weight loss up to 200 °C. The theoretical weight loss for the formation of CuO in this mixture is 12.5% where as experimentally observed value is 13.1%. The DSC curve shows two endothermic peaks at 125 and 227.4 °C. The first one is due to phase transformation of KNO_3 whereas the second endotherm is due to melting of eutectic as well as decomposition of basic copper carbonate.

When basic copper carbonate was heated (230–320 °C) with molten $NaNO_3$–KNO_3 eutectic, it decomposed to CuO. This was confirmed by powder X-ray diffraction technique. Kinetics of the reaction was studied by isothermal TG and data obeyed Jander's equation (2).

$$[1 - (1 - \alpha)^{1/3}]^2 = k_2 t \qquad (2)$$

where k_2 is the rate constant. The values of α are given in Table 1. When $[1 - (1 - \alpha)^{1/3}]^2$ is plotted against t straight lines showing the validity of Eq. (2) are obtained (Fig. 4). The rate constant k_2 were calculated from the slope of the lines and are given in Table 3. The energy of activation was calculated from Arrhenius plot and the value is given in Table 3. The results show that basic copper carbonate in $NaNO_3$–KNO_3 eutectic decompose at a much faster rate involving lesser amount of energy of activation.

The catalytic activities of the copper oxide prepared through two routes were tested for the decomposition of AP.

TG curves for the decomposition of AP in presence of copper oxide are shown in Fig. 1. In the presence of copper oxide prepared directly from basic copper carbonate, there is a sharp weight loss between 255 and 365 °C with a hump at about 310 °C. The total

Table 1
The value of fraction decomposed (α) at different time interval at different temperatures in different systems

Temperature (°C)	5 min	10 min	15 min	20 min	25 min	30 min	35 min	40 min	45 min	50 min	55 min	60 min	65 min
$CuCO_3{\cdot}Cu(OH)_2{\cdot}H_2O$													
230	0.36	0.41	0.45	0.54	0.59	0.64	0.69	0.71	0.76	0.79	0.81	0.85	1
260	0.36	0.47	0.58	0.66	0.72	0.8	0.85	0.88	0.925	0.95	1		
290	0.51	0.65	0.75	0.85	0.89	0.94	0.97	1					
320	0.63	0.75	0.90	0.96	0.1								
	1 min	2 min	3 min	4 min	5 min	6 min	7 min	8 min	9 min	10 min	11 min	12 min	
$CuCO_3{\cdot}Cu(OH)_2{\cdot}H_2O$ + eutectic													
230	–	0.182	0.432	0.6	0.717	0.762	0.862	–	0.89	–	0.93	1	
260	0.135	0.327	0.597	0.81	0.894	0.927	1						
290	0.35	0.81	0.928	1									
320	0.433	0.85	0.952	1									

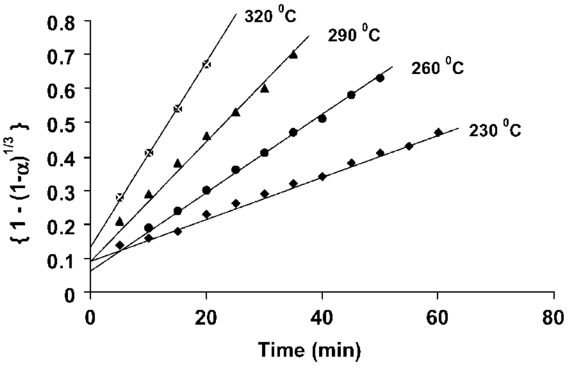

Fig. 3. Verification of kinetic equation (1) for the decomposition of $CuCO_3{\cdot}Cu(OH)_2{\cdot}H_2O$.

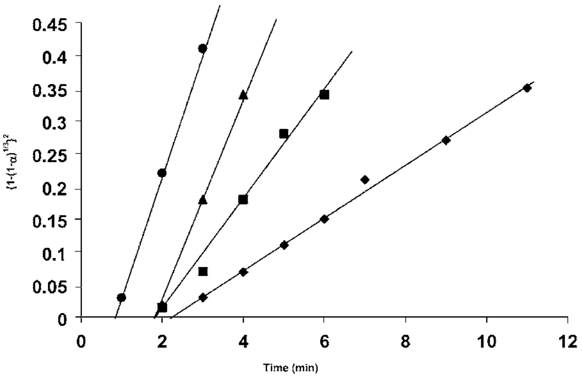

Fig. 4. Verification of kinetic equation (2) for the decomposition of $CuCO_3{\cdot}Cu(OH)_2{\cdot}H_2O$ in $NaNO_3$–KNO_3 eutectic melt.

weight loss correspond to 83.2%. However, in the presence of copper oxide prepared from eutectic, the weight loss starts at about 255 °C and the weight becomes constant at about 365 °C, with a weight loss of 84.6%. Again there is a hump at about 310 °C. The TG curves for the decomposition of AP in the presence of both the copper oxide are almost similar.

Table 2
Kinetic parameters of Eq. (1) for the decomposition of $CuCO_3{\cdot}Cu(OH)_2{\cdot}H_2O$

Temperature (°C)	k ($\times 10^2$ min^{-1})	E (kJ mol^{-1})	A (min^{-1})
230	0.6	42.0	132.5
260	1.1		
290	1.6		
320	2.6		

Pure AP is quite stable at room temperature but when heated at 249 °C undergoes a crystallographic modification with an exothermic peak in the DSC curve (Fig. 2). In this temperature range orthorhombic form is converted to cubic form. The process is accompanied by a simultaneous dissociative sublimation. The thermal decomposition of AP occurs in two

Table 3
Kinetic parameters of Eq. (2) for the thermal decomposition of $CuCO_3{\cdot}Cu(OH)_3{\cdot}H_2O$ in $NaNO_3{\cdot}KNO_3$ eutectic

Temperature (°C)	k ($\times 10^2$ min^{-1})	E (kJ mol^{-1})	A (min^{-1})
230	4.0	38.3	3019.9
260	8.0		
290	16.0		
320	19.0		

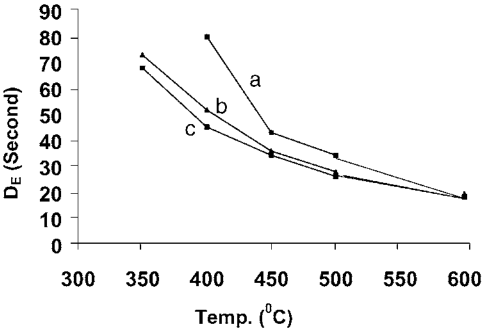

Fig. 5. Verification of ignition delay with temperature. (a) AP; (b) AP + CuO (prepared from eutectic); (c) AP + CuO (prepared directly).

steps [7,8]. The low temperature decomposition (LTD) up to about 300 °C (30%) and the higher temperature decomposition (HTD) above it with a second exothermic peak at 455 °C. The thermal stability of AP is extremely sensitive to additives. Catalysts are found to influence the reaction both in acceleratory and deceleratory periods.

In the presence of copper oxide prepared directly from basic copper carbonate the phase transformation temperature is decreased (246.4 °C) and the two exothermic peaks come much closer to each other and the temperatures are lowered.

DSC curve for the decomposition of AP in the presence of CuO prepared through $NaNO_3$–KNO_3 eutectic is shown in Fig. 2. The phase transition temperature of AP is shifted to lower temperature (246.3 °C). The first exothermic peak at 293.1 °C in the case of pure AP is splitted into two peaks at 287 and 304.8 °C. This indicates that probably CuO modifies the LTD process of AP. In the presence of CuO, AP (LTD) decomposes at 287 °C instead of 293.1 °C. Since the surface area of CuO prepared from eutectic is expected to be higher, the gases evolved may get adsorbed and when heated further desorption occurs at 304.8 °C. The second exothermic peak (HTD) is also lowered in the presence of CuO but the lowering is slightly less than that in the presence of CuO prepared directly. The results slow that the CuO prepared through nitrate eutectic have slightly higher catalytic activity towards the decomposition of AP.

Transition metal oxides are used as catalysts in enhancing the burn rate of solid propellants and they also enhance the decomposition [9]. Copper oxides lower down the ignition delay (Fig. 5). However the behaviour of the two CuO is almost similar.

From the overall results it can be concluded that basic copper carbonate decomposed at lower temperature and at a faster rate in $NaNO_3$–KNO_3 eutectic as compared to that when it is heated alone. The end product in the two cases is CuO and the effectiveness of the catalytic property of both the CuO is almost similar.

Acknowledgements

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References

[1] N.B. Singh, S.P. Pandey, P. Kumar, J. Sci. Ind. Res. 44 (1985) 533–543.
[2] D.H. Kerridge, A. Zellipour, Thermochem. Acta 159 (1990) 163–170.
[3] D.H. Keridge, W.M. Shakir, Thermochem. Acta 182 (1991) 107–122.
[4] N.B. Singh, S.P. Pandey, Thermochem. Acta 83 (1985) 203–211.
[5] N.B. Singh, S.P. Pandey, Indian J. Chem. A 28 (1989) 645–648.
[6] A.I. Vogel, A Text Book of Quantitative Inorganic Chemistry, Longman, New York, 1961.
[7] P.W.M. Jacobs, N.M. Whitehead, Chem. Rev. 69 (1969) 551.
[8] S. Ramamurth, P.S. Shrdri, J. Eng. Make. 14 (1996) 97.
[9] R. Rajeev, K. Ambikadevi, A. Abraham, K. Krishnan, T.E. Krishnan, K.N. Ninan, C.G. Nair, Thermochemi. Acta 145 (1995) 235.