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Solid State Chemistry of Copper Chromite Used as a Catalyst for the Burning of Ammonium Perchlorate/Polystyrene Propellants

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The formation of copper chromite by solid-state reaction between basic copper carbonate and chromium carbonate has been investigated. It has been established that the extent of reaction is 98% even when the reactants are heated for 15 min at 800°C. The burning rate of polystyrene/ammonium perchlorate propellants containing mixtures of basic copper carbonate and chromium carbonate as additives was measured after prior heating at 800°C for different times. The catalytic action depends on the formation of fine grains of copper chromite. Although this is favored by high temperature, higher temperatures and longer duration of prior heating are unfavorable factors since these promote greater sintering. Experimental results show that optimization is obtained when copper chromite is prepared by heating a mixture of the carbonates in the weight ratio 1 : 2.37 at 800°C for 2 hr.

INTRODUCTION

It has been reported (*1–8*) that copper chromite enhances the decomposition and deflagration rate of ammonium perchlorate (AP). The effect of copper chromite on the deflagration rate of propellants has also been reported in some earlier communications (*9–12*). However, the chemistry of copper chromite catalyst is not clear. Based on chemical analysis it has been recently reported (*13*) that none of the commercial catalysts is copper chromite. For example, the empirical formula 9 $CuO \cdot Cr_2O_3$ or 8 $CuO \cdot CuCr_2O_4$ has been suggested for Harshaw CuO202 catalyst. Strahle *et al.* (*14*) have reported that Harshaw catalyst CuO202 is a mixture of approximately 82% of CuO and 17% of Cr_2O_3. It has been reported that copper chromite is formed during the calcination of mixtures of nitrates (*15*) of copper and chromium at 900°C for 24 hr and mixture of basic copper carbonate and Cr_2O_3 (*16*) at 700°C for 2 hr. Very recently, calcined mixtures of basic copper carbonate and chromium carbonate have been found to be more effective burning rate catalysts (*17*).

Hence, it was thought interesting to undertake studies on (i) the solid-state reaction between a mixture of basic copper carbonate (BCC) and chromium carbonate (CC), (ii) the chemistry of copper chromite, and (iii) the catalytic action of copper chromite as a burning rate catalyst. In the context of (i), the time required for the formation of copper chromite at 800°C has been studied. The products were analyzed by chemical analysis and X-ray diffraction. TG studies on BCC, CC, and BCC/CC mixture in the weight ratio 1 : 2.37 was undertaken in order to understand the mechanism of the reaction.

The burning rate of polystyrene (PS)–AP propellants was measured in the presence of these catalysts. The effect of the time of heating of the mixture of carbonates on the catalytic activity has also been investigated.

EXPERIMENTAL

Materials. Ammonium perchlorate (Central Electro-chemical Research Institute, Karaikudi, Madras, India) was used without any purification. Basic copper carbonate, chromium carbonate, CuO, and Cr_2O_3

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were obtained commercially and were used in the form of fine powders as received. Styrene (Synthetics and chemicals Ltd., Bareilly, India) monomer was purified by fractional distillation and polymerized as reported earlier (*18*).

PREPARATION OF COPPER CHROMITE

Mixtures of BCC and CC were prepared in the weight ratios of 1 : 2.37, 1 : 1, and 3 : 1. The mixtures were homogenized in an agate mortar using acetone and allowed to dry. The dried mass was heated for different time intervals, e.g., 0.25, 1, 2, 5, 10, and 24 hr, in a furnace which was maintained at 800°C and controlled to ±10°C. This temperature was chosen since the surface temperature of burning propellants is of the order of 800°C. Samples were taken out of the furnace two or three times during heating. These were crushed and homogenized with acetone and again calcined at the same temperature in order to ensure complete solid-state reaction.

Chemical analysis. Reaction products were treated with boiling conc. HCl in order to assess the percentage of copper chromite formed after calcination. The percentage of residues, i.e., copper chromite, formed at various times are reported in Table 1. Copper chromite was confirmed by chemical analysis for copper and chromium. Copper was estimated as CuSCN gravimetrically and chromium volumetrically (*19*). The results are given in Table 1, which correspond to the calculated values (theor. Cu = 27.4%, Cr = 44.9%) within the experimental error.

X-Ray diffraction studies. X-Ray diffraction patterns of the reaction products obtained by calcining BCC/CC in the weight ratio 1 : 2.37 for 0.25, 2, and 24 hr at 800°C were obtained with the help of an X-ray diffractometer at BARC, Bombay, India using CuK_α radiation. The products were found to be copper chromite since the *d* values in each case correspond to those reported for copper chromite in the powder X-ray diffraction file.

TABLE 1

Analysis of Products Obtained on Heating BCC/CC Mixtures at 800°C for Different Time Intervals and Their Catalytic Activity

BCC/CC (wt ratio)	Time of calcination (hr)	Copper chromite formed (%)	Chemical analysis of copper chromite		Catalytic activity (C_A)[a]
			Copper (%)	Chromium (%)	
1 : 2.37	0.25	98.6	26.9	45.3	1.08
	1	—	—	—	1.77
	2	99.1	26.8	44.4	2.56
	5	99.1	—	—	1.53
	10	99.1	—	—	1.38
	24	99.9	27.6	44.4	1.37
1 : 1	0.25	49.0	—	—	1.40
	2	49.1	—	—	1.52
	5	50.4	—	—	1.34
	10	51.8	—	—	1.33
	24	52.4	26.8	45.9	1.16
3 : 1	0.25	27.7	—	—	1.29
	2	27.4	—	—	1.63
	5	28.5	—	—	1.49
	10	29.1	—	—	1.45
	24	30.7	27.2	45.2	1.19

[a] C_A = Burning rate of propellant + catalyst/Burning rate of pure propellant.

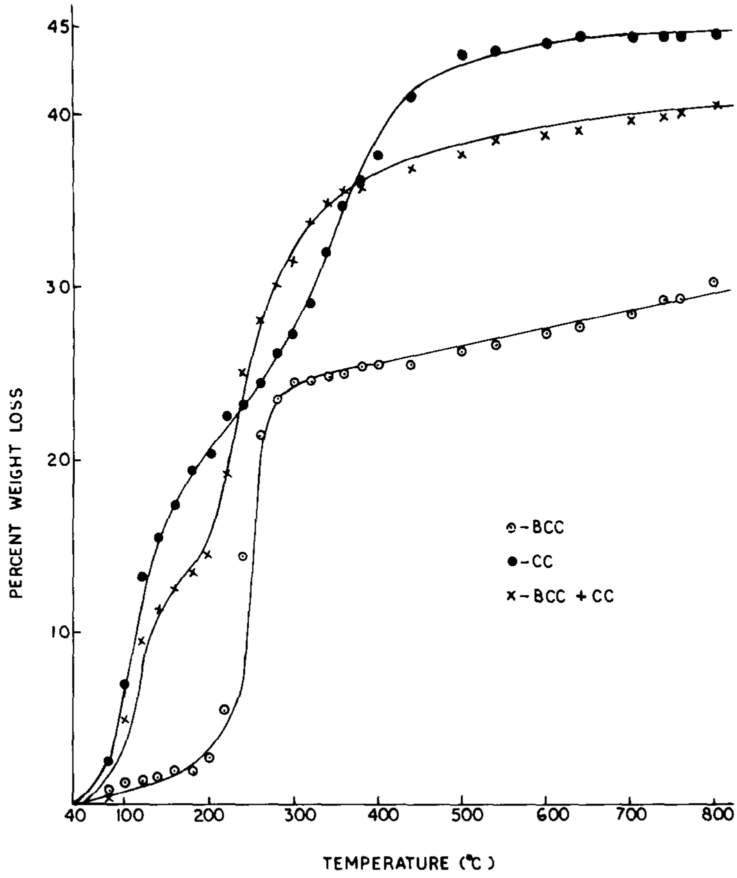

FIG. 1. TG plots for BCC, CC, and BCC + CC (1 : 2.37 by wt) at a heating rate of 4°C min^{-1}.

TG STUDIES ON BCC, CC, AND BCC/CC (1 : 2.37 BY WT)

TG of (i) BCC, (ii) CC, and (iii) mixture of BCC/CC (weight ratio = 1 : 2.37) was carried out using a dynamic thermogravimetric analyzer (P & D Division, F.C.I. Ltd., Sindri, India) at a heating rate of 4°C min^{-1}. The percentage weight loss is plotted against temperature in Fig. 1. The isothermal TG for BCC, CC, and (BCC + CC) at 275 ± 1°C was also undertaken and plots are given in Fig. 2.

PREPARATION OF PROPELLANTS AND MEASUREMENTS OF BURNING RATES

Catalysts. The products obtained by calcining BCC/CC in the weight ratio of 1 : 2.37, 1 : 1, and 3 : 1 for 0.25, 1, 2, 5, 10, and 24 hr at 800°C were used as catalysts. It may be noted that products obtained from 1 : 2.37 contain $CuCr_2O_4$ whereas 1 : 1 and 3 : 1 contain mixtures of $CuCr_2O_4$ and CuO. Depending upon the time of calcination of the mixtures of carbonates, traces of Cr_2O_3 can be present due to incomplete solid-state reaction.

Preparation of propellants. The propellant samples were prepared by adding 1% (by wt) of the above catalysts to the PS/AP (1/3 ratio by wt) system as reported earlier (*20*). These were cured in a thermostat maintained at 50°C for about 10–20 days. It may be noted that a processing difficulty was encountered in preparing the propellants with these catalysts. The matrix sticks to the glass moulds during curing of the propellants. However, propellant samples

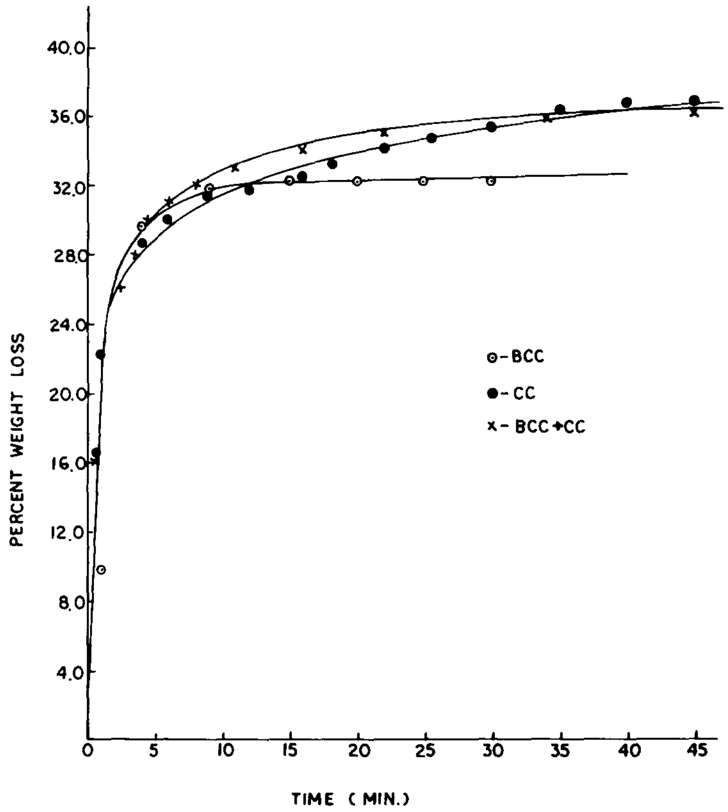

FIG. 2. Isothermal TG for BCC, CC, and BCC + CC (1 : 2.37 by wt) at 275°C.

were removed by breaking the glass moulds.

Measurement of burning rate. The burning rates of cured samples were measured in the manner reported (*17*) earlier. The propellant strands were inhibited by applying PVC tape to check the side burning. The strands were held vertically and ignited electrically with the help of a nichrome wire at the top. The time required for a certain length of burning of the strand was recorded by a stop watch. The burning rate has been calculated by taking l/t where l is length of propellant strand (cm) and t the time (sec) of burning. The burning rate data are plotted in Fig. 3.

DISCUSSION

Table 1 clearly shows that 98.6–99.9, 49.0–52.4, and 27.7–30.7% of copper chromite are formed when the BCC/CC ratios were taken to be 1 : 2.37, 1 : 1, and 3 : 1 (by wt), respectively, and calcined at 800°C for different time intervals. However, the percentage of copper chromite formed depends on the time of calcination. Copper chromite (98%) has been found to be formed within 15 min when BCC/CC mixture in the weight ratio of 1 : 2.37 was heated at 800°C.

The reaction between BCC and CC can take place in either of the following two ways:

(i) $$CuCO_3 \cdot Cu(OH)_2 \cdot H_2O \rightleftharpoons 2\,CuO + CO_2 + 2H_2O \quad \text{(A)}$$

$$Cr_2(CO_3)_3 \rightleftharpoons Cr_2O_3 + 3CO_2 \quad \text{(B)}$$

$$CuO + Cr_2O_3 \rightarrow Cu\,Cr_2O_4 \quad \text{(C)}$$

(ii) $$CuCO_3 \cdot Cu(OH)_2 \cdot H_2O + 2\,Cr_2(CO_3)_3 \rightarrow 2\,CuCr_2O_4 + 7\,CO_2 + 2H_2O$$

The second mechanism does not seem

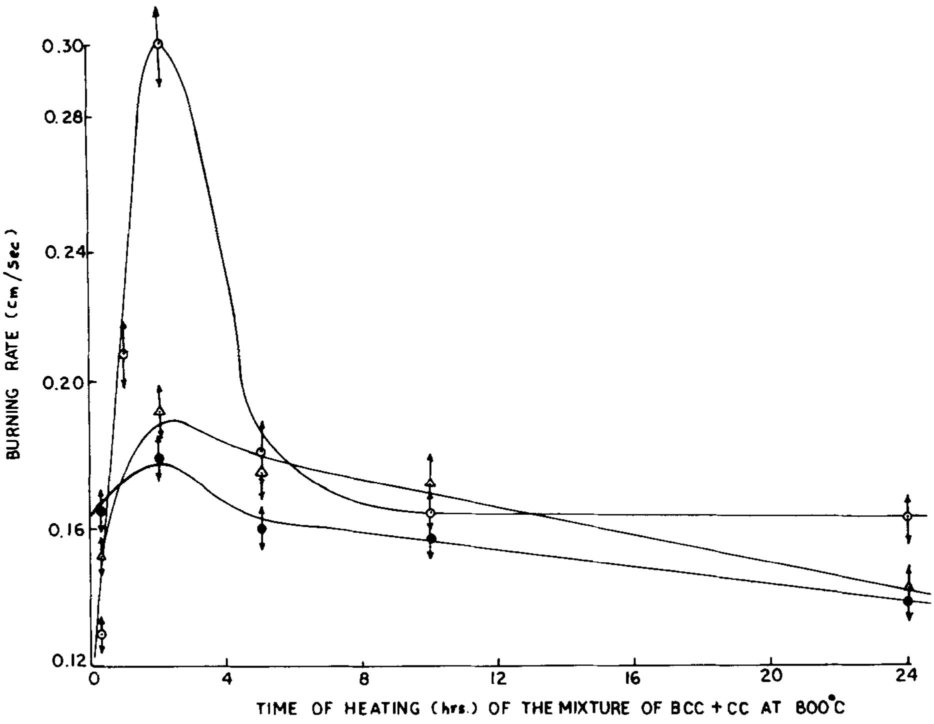

FIG. 3. Dependence of burning rate on the time of heating of the mixture of BCC/CC in the weight ratios ⊙, 1 : 2.37; ●, 1 : 1, and △, 3 : 1. Ambient temperature = 22°C. Catalyst added in the propellant (PS/AP = 1/3) = 1% (by wt). Burning rate of the propellant = 0.119 ± 0.005 cm/sec.

plausible since the reaction would be expected to proceed by the migration of ions. The carbonate ion is planar and it cannot easily take part in transport processes due to its bulky nature. The basic copper carbonate has a complex structure and hence the first mechanism involving three basic steps seems to be more acceptable. This is understandable since heterogeneous equilibria for BCC and CC would be represented by (A) and (B) and it is obvious that if CuO and Cr_2O_3 are constantly removed by the formation of copper chromite, the equilibria in both (A) and (B) would be shifted toward the right.

In order to find out whether decomposition of metal carbonates is enhanced in the presence of other metal carbonates or formation of copper chromite alone is enhanced, TG studies were undertaken. The experimental TG plots reported in Fig. 1 showed loss in weight for BCC, CC, and (BCC + CC) of the order of 30, 44, and 41%, respectively, up to 800°C which is in good agreement with the calculated values, i.e., carbonates are converted to their respective oxides. In order to check the enhancement in the decomposition of BCC + CC mixture, isothermal TG (Fig. 2) was studied at 275°C. It seems that neither the extent of decomposition nor the rate of decomposition is enhanced for individual carbonates in a mixed system. The copper chromite formation alone is enhanced since the reaction is found to be completed even in 15 min. This is understandable since the decomposition of BCC and CC would yield fresh particles of oxides which would contain a large number of defects and dislocations. Hence these would be more reactive and consequently copper chromite formation would be enhanced.

The catalytic activity (C_A) of copper chromite and the mixture of copper chromite, copper oxide, and Cr_2O_3 (in traces) has been measured where C_A is given by:

$$C_A = \frac{\text{Burning rate of propellant + catalyst}}{\text{Burning rate of pure propellant}}.$$

The values of C_A are given in the last column of Table 1. It has been found that the burning rate is enhanced in each case. Experimental results show that catalytic activity depends on the time of calcination. Figure 3 shows that it is true for all the catalysts prepared by calcining the mixture of carbonates (BCC/CC) in the weight ratio of 1 : 2.37, 1 : 1, and 3 : 1 at 800°C. Initially, the burning rate increases with the time of calcination after which it attains a maximum value and then decreases with increase in the time of calcination. This is due to the fact that because of the longer duration of heating, a greater extent of sintering takes place and the efficiency of the catalyst is gradually reduced. In the case of all the mixtures studied, the burning rate attains a maximum value when it is heated for 2 hr.

The extent of copper chromite formation would depend on temperature and duration of reaction. For efficient combustion catalysts, the particle size has to be controlled. Sintering and formation of aggregates of particles which are favored by higher temperature and duration of heating have to be avoided. In order to have an efficient copper chromite catalyst, it is necessary to optimize the temperature and duration of heating. From Fig. 3, it follows that optimum conditions are obtained when pure copper chromite (BCC/CC = 1 : 2.37) is prepared at 800°C and preheted for 2 hr.

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