DECOMPOSITION MECHANISM OF COPPER AMMONIUM CHROMATE: A BASIC MATERIAL FOR COPPER CHROMITE CATALYST

PRADYOT PATNAIK, D. YOGESWARA RAO, PRABUDDHA GANGULI and
R. SREERAMA MURTHY

Hindustan Lever Research Centre, Chakala, Andheri (East), Bombay 400 099 (India)

(Received 21 March 1983)

ABSTRACT

The mechanism of thermal decomposition of basic copper ammonium chromate has been investigated using TG/DTG/DSC and X-ray studies. The decomposition is a three-step process. Calcination at lower temperatures can be achieved by taking advantage of the exothermicity of the decomposition process.

INTRODUCTION

Fatty alcohols can be prepared from fatty esters by a catalytic hydro-genolysis under high pressure. It has been fairly well established that among the wide range of catalysts available for this reaction, copper chromite and its promoted analogues are the most active and extensively used [1–6]. Copper chromite is generally obtained by calcination of copper ammonium chromate (CAC) between 300 and 500°C [5]. The calcination conditions are very crucial as they determine the formation of various phases, crystallinity, hardness, particle sizes, etc. Though an exhaustive amount of literature is available on copper chromite catalyst, the decomposition mechanism of the CAC is not very well understood. The present study, using TG/DTG, DSC, XRD, etc., aims at filling this gap, and optimising the calcination conditions of CAC to prepare promoted and unpromoted copper chromite catalysts.

EXPERIMENTAL

Copper ammonium chromate preparation

The basic material, copper ammonium chromate (CAC) was precipitated by adding warm (80°C) copper nitrate solution to a well-stirred solution of

sodium dichromate and 25% ammoniacal solution [5]. In the case of 10% barium-doped CAC, the required amount of barium nitrate was added to the copper nitrate solution. Two sets of CAC were prepared by controlling the precipitating time to 5 and 35 min. The CAC was subjected to XRD, TG/DTG and DSC. Copper chromite catalysts were also prepared from CAC by calcination at 300, 400 and 500°C for 3 h and 6 h.

Chemical analysis

The copper and chromium in the catalysts were estimated by a slight modification of a procedure reported in the literature [7]. 0.5 g of sample were mixed with about 8 g of sodium peroxide in a nickel crucible. 4–5 pellets of sodium hydroxide were added and then the crucible was heated on a flame for about 30 min. The molten black mass was extracted with 200 ml of water and filtered through a sintered crucible. The filtrate was concentrated to 150 ml and acidified using 9 N H_2SO_4. The solution was made up to 250 ml in a volumetric flask. This solution was used for estimation of Cr. The precipitate in the crucible was washed with water, dissolved in conc. HCl and the solution made up to 250 ml with water. This solution was used for estimation of copper. The copper was estimated by iodometry and the chromium by titration against ferrous ammonium sulphate [7].

Thermal and X-ray measurements

The TG/DSC experiments were carried out on a duPont 990 thermal analyser. The heating rate was kept to 10°C min^{-1}. Approximately 10 mg samples were taken for all the experiments. X-Ray powder diffractograms were recorded with a Siemens D-500 diffractometer using CuK_α radiation. The scan speed was kept at 2° min^{-1}.

RESULTS AND DISCUSSION

Chemical analysis

The results of chemical analysis are shown in Table 1. A wide range of values for the Cu : Cr ratio have been reported in the literature. The catalysts prepared in the laboratory had Cu : Cr $\simeq$ 1. This is important, since some CuO phase on the $CuCr_2O_4$ is desirable for catalytic activity. Any catalyst prepared from the precipitate with 5 min precipitation time had a higher copper/chromium ratio. The Ba content was $\simeq$ 10% in both cases and was quantitatively precipitated.

TABLE 1

Chemical analysis of copper chromite catalyst

Catalyst	Copper (%)	Chromium (%)	Cu/Cr
Ba promoted (commercial)	29.64	26.29	1.13
Ba promoted (lab. prepared) (5 min ppt. time)	30.24	24.00	1.26
Without Ba (lab., prepared) (5 min ppt. time)	36.47	29.02	1.26
Without Ba (lab. prepared) (35 min ppt. time)	38.75	31.65	1.22

Thermal analysis and X-ray studies

The X-ray diffractograms of the basic copper–chromium intermediate and the barium-promoted analogues with 5 and 35 min precipitation times are given in Fig. 1. It is identified conclusively as $Cu(OH) \cdot NH_4CrO_4$ ($2\theta = 26.9$, 30.1, 35.1) based on ASTM data [8]. The barium-doped CAC is identified as $Cu(OH) \cdot NH_4CrO_4$ and $BaCr_2O_4$ ($2\theta = 41.6$, 28.2, 30.8) phases.

Thermogravimetry (TG) and derivative thermogravimetry (DTG) experiments on CAC between room temperature and 1000°C in air and nitrogen and differential scanning calorimetry (DSC) in air were carried out. The thermograms are shown in Figs. 2–4, and Table 2 lists the relevant experimental observations. The X-ray diffractograms of the products calcined at 300, 400, 500, and 900°C and at 300°C with varying calcination times are given in Figs. 5–7.

The weight losses in the case of CAC and BaCAC are 28% and 25%, respectively. This difference in the two cases can be accounted for by the fact that the $BaCr_2O_4$ in BaCAC does not undergo any thermal decomposition. The following conclusions can be drawn from the thermal studies.

(i) The initial loss ($\simeq 100$°C) of $\simeq 2\%$ and 6% in the case of CAC precipitated at 35 min and 5 min, respectively (which is endothermic), can be attributed to the free moisture in the precipitate.

(ii) The main decomposition of the precipitate is initiated at ~ 200°C and is endothermic: this is followed by a highly exothermic step between 220 and 350°C. The weight loss as this stage is $\sim 20\%$ and $\sim 18\%$ in the case of CAC and BaCAC, respectively. This weight loss can be attributed to the rupture of the basic precipitate liberating 4 water molecules and one N_2 molecule.
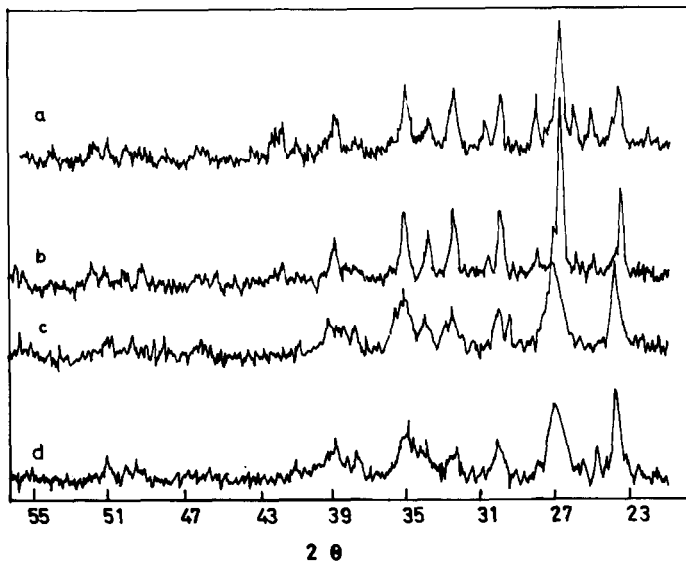
Fig. 1. X-Ray powder diffraction patterns of BaCAC with precipitation times of (a) 35 min and (b) 5 min and CAC with precipitation times of (c) 5 min and (d) 35 min.
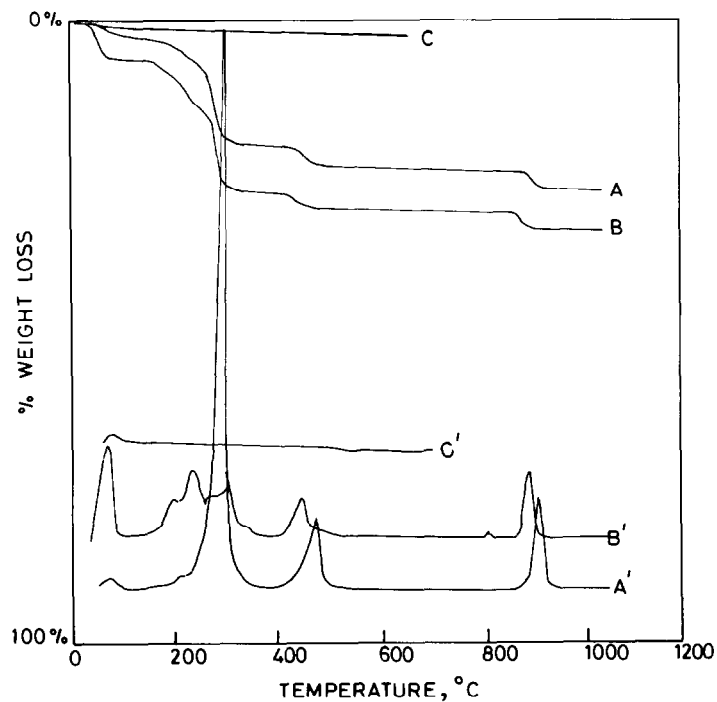

Fig. 2. TG and DTG curves of CAC with precipitation times of (A) 35 min, (B) 5 min and (C) catalyst calcined at 300°C. (A'), (B') and (C') are the DTG curves of (A), (B) and (C).
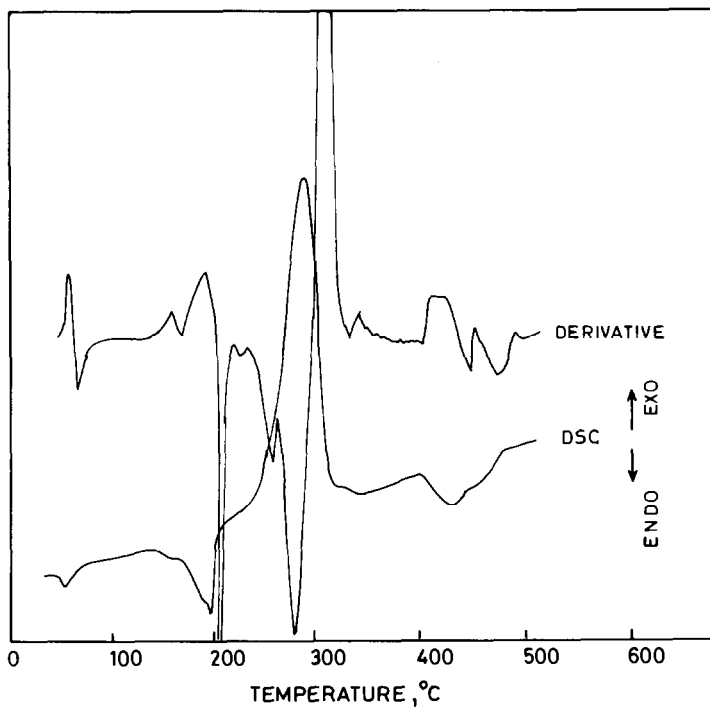
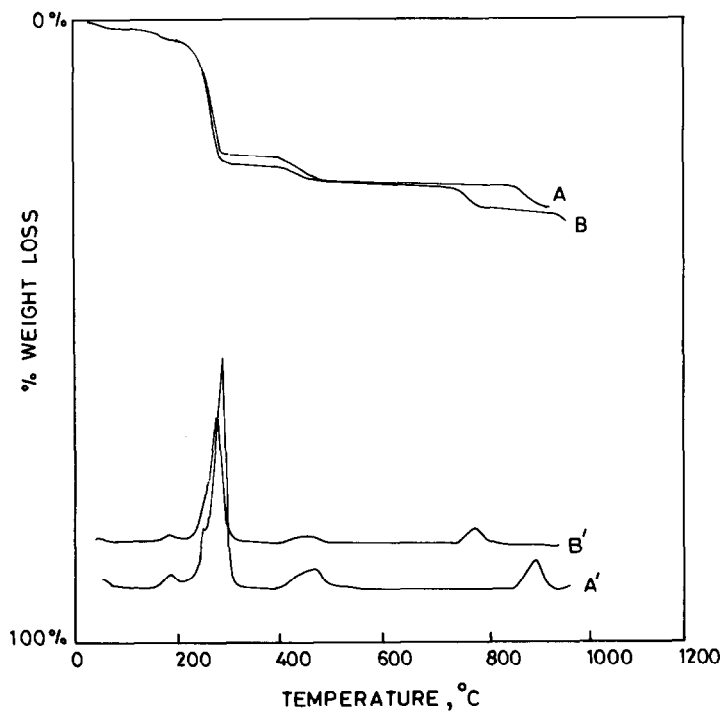Fig. 3. DSC of copper ammonium chromate precipitate.

Fig. 4. TG and DTG curves of copper ammonium chromate precipitate in (A) air and (B) nitrogen. (A') and (B') are the DTG curves of (A) and (B).

TABLE 2

Thermal studies on basic copper ammonium chromates

Intermediate	Observations	
	Temperature (°C)	% Weight loss
$Cu(OH) \cdot NH_4CrO_4$	Up to 75	2
	150–350	20
		in two steps
	450	4
	900	4
$Cu(OH) \cdot NH_4CrO_4$	Up to 75	2
$+ BaCr_2O_4$ (35 min	125–300	18
precipitation)	475	4
	900	3
$Cu(OH) \cdot NH_4CrO_4$	Up to 75	6
$+ BaCr_2O_4$	150–300	19
(5 min precipitation	450	3
	875	3

(iii) A further weight loss of ~ 4% at 450°C is accompanied by an endothermic process. This is due to the loss of one more water molecule.

(iv) Another weight loss of ~ 3–4% at 880°C is probably due to loss of oxygen from the system.
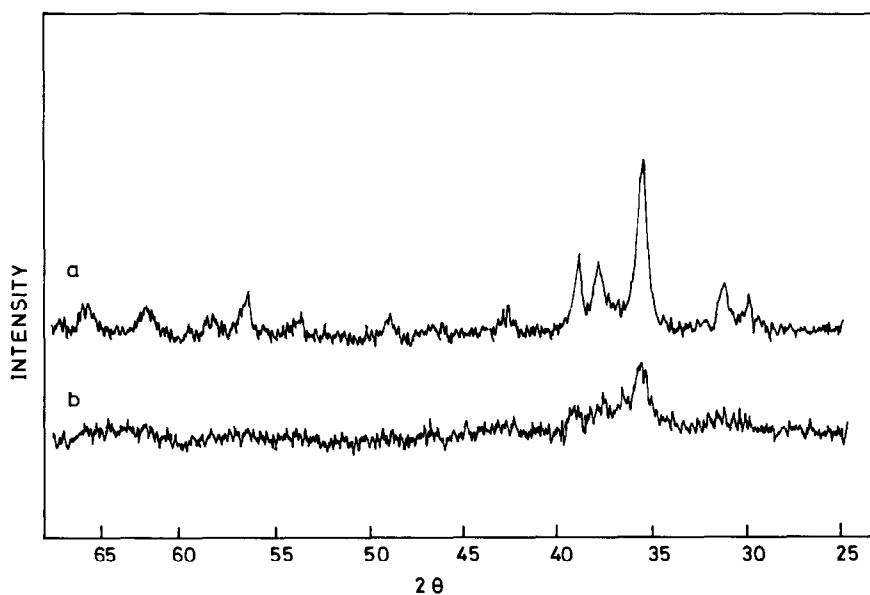

Fig. 5. XRD patterns showing the effect of (a) 6 h and (b) 3 h calcination on the crystallinity.
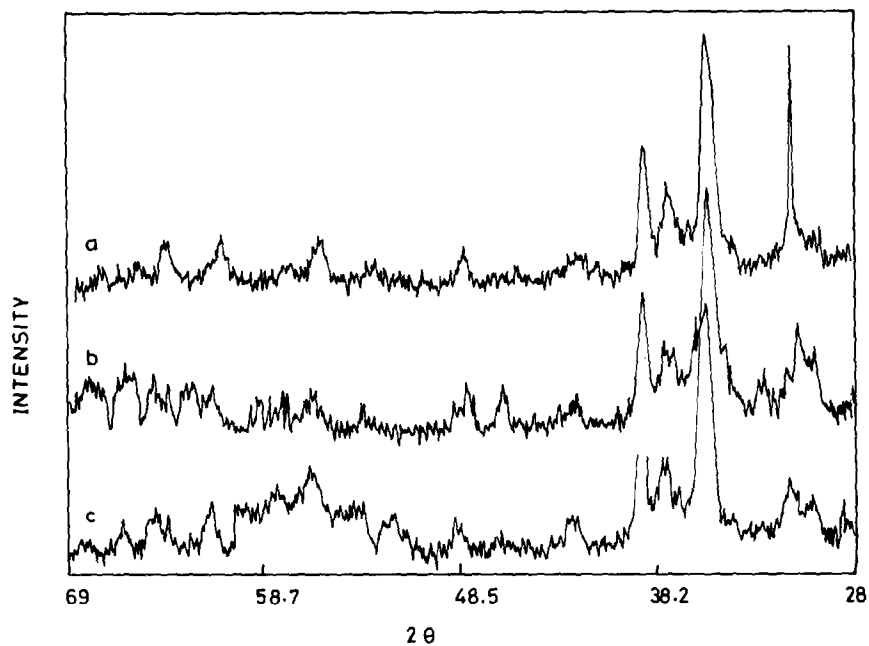
Fig. 6. XRD patterns showing the effect of calcination temperature on the crystallinity. (a) 500°C; (b) 400°C; (c) 300°C.
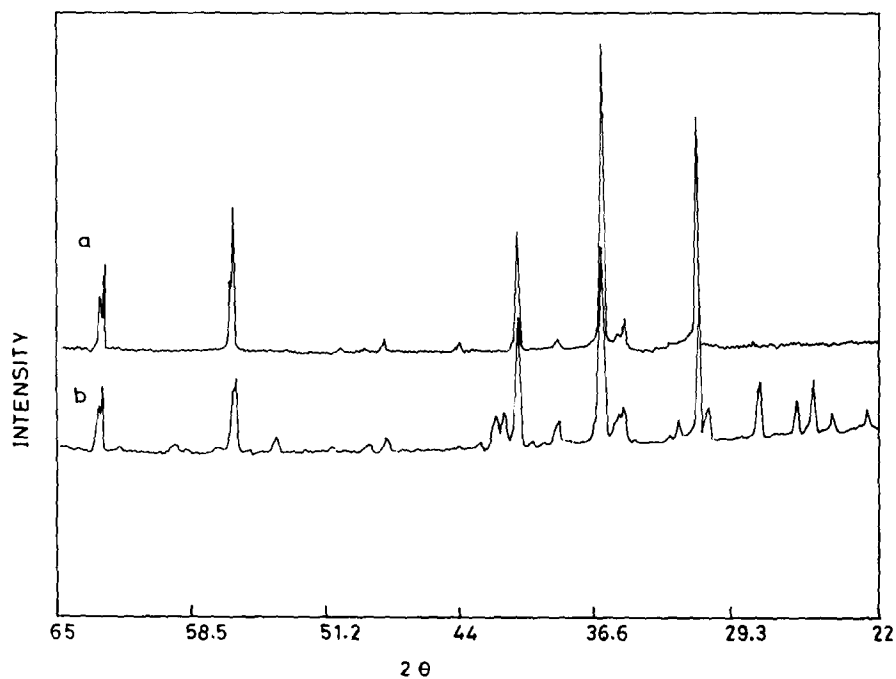

Fig. 7. XRD patterns of (a) CAC and (b) BaCAC calcined at 900°C.

The complete decomposition of the copper–chromium basic precipitate can be understood in terms of a set of reactions as given.

Reaction	Theoretical weight loss (%)
1 2 Cu(OH)·NH$_4$CrO$_4$ $\xrightarrow{300°C}$ (Intermediate)$+4$ H$_2$O$+$N$_2$	23
2 (Intermediate) $\rightarrow$ CuO·CuCr$_2$O$_4$ $+$H$_2$O	4
3 CuO·CuCr$_2$O$_4$ $\overset{880°C}{\rightleftharpoons}$ Cu$_2$Cr$_2$O$_4$ $+\frac{1}{2}$ O$_2$	3.7
Total weight loss	$\overline{30.7}$

The difference in weight loss between the experimentally observed and theoretically expected value can be explained as follows. The chemical analysis of the precipitate shows a Cu to Cr ratio of more than one. But from the chemical formula Cu(OH)·(NH$_4$)CrO$_4$, it is expected to be one. This means that Cu is present in excess (maybe as copper hydroxide) in the precipitate, and this phase is not undergoing the same weight loss as that of CAC/BaCAC. So it is obvious that the initial starting precipitate is a mixture of two phases with CAC/BaCAC constituting the bulk of it. The weight difference can be attributed to this impurity of the second phase.

The X-ray diffractogram of CAC, decomposed at 300°C for a few minutes did not show any crystallinity or phases. But the XRD patterns of the compound decomposed at 450°C showed CuO and CuCr$_2$O$_4$ phases. The XRD of the CAC decomposed at 900°C is shown in Fig. 7. This highly crystalline phase neither belongs to CuO nor to CuCr$_2$O$_4$. This phase has been identified by Stroupe [5] as Cu$_2$Cr$_2$O$_4$ and the d-values of the present study match well with his observations. The liberation of $\frac{1}{2}$ O$_2$ at this stage of decomposition is further confirmed by recording the TGA curve of the CAC in flowing nitrogen. If the decomposition step 3 is correct, then one would expect the decomposition temperature to decrease in a nitrogen atmosphere because of the decreasing partial pressure of oxygen. It can be seen from Fig. 4 that the decomposition temperature is lowered by 100°C, indicating the proposed reaction to be correct.

The thermal studies show that decomposition is complete only at 450°C. But the XRD of CAC/BaCAC decomposed at 300°C for more than one hour clearly showed two distinctive phases of CuO and CuCr$_2$O$_4$. And the TG curve of the decomposed compound did not show any weight loss up to 600°C (see Fig. 5). These experiments indicate that decomposition is complete at 300°C, contrary to the observation of thermal studies. However, this can be explained by considering the fact that the high exothermic nature of

the decomposition at 300°C (see Fig. 3) would increase the local temperature of the sample bulk sufficiently to remove the last water molecule when heated for an extended period.

The presence of two phases. Cu(II) oxide and Cu(II) chromite, as well as a certain degree of crystallinity in the catalyst is known to be essential for good catalytic activity. The XRD patterns, showing the effect of calcination time and temperature are portrayed in Figs. 5 and 6, respectively. It can be seen from the figures that the phases present in the catalysts are CuO ($2\theta = 35.1$, 37.4, 31.1, 42.4) and $CuCr_2O_4$ ($2\theta = 30.4$, 35.7, 57.6, 63.3). However, the product obtained by calcination for 3 h (see Fig. 5) is of poor crystallinity ($2\theta = 35.4$). But the crystallinity improves considerably when the calcination time is increased to 6 h. Similarly, the crystallinity increases with increase in temperature of calcination (see Fig. 6). The foregoing arguments are based on the intensities and line widths of the characteristic peaks ($2\theta = 31.0$, 35.7, 39.0, 56.3). Higher temperature and longer calcination time, however, have a sintering effect, thereby resulting in low surface area compounds. These parameters need to be optimised and their relationships with the catalytic activity need to be established.

CONCLUSIONS

These studies have shown that the thermal decomposition of the basic copper ammonium chromate takes place in three steps, the main one at 300°C being highly exothermic. The copper chromite catalyst of specific crystallinity can be prepared by either calcining the CAC at temperatures between 450 and 750°C or at 300–350°C for an extended period of about 6 h. In the case of barium-promoted CAC, $BaCr_2O_4$ is precipitated and remains unaltered during the calcination.

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