

Thermal decomposition studies.
Part 19. Kinetics and mechanism of thermal
decomposition of copper ammonium chromate precursor
to copper chromite catalyst and correlation of surface
parameters of the catalyst with propellant burning rate

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Abstract

The thermal decomposition of copper ammonium chromate (CAC), which is a precursor of copper chromite (CC) catalyst (used as a ballistic modifier in solid propellants), has been thoroughly studied. The DTG curves show that there are three main peaks at about 286, 440 and 740°C, whereas DTA gives peaks at 254 (endo), 278 (exo), 408 (exo) and 699°C (endo). The kinetic parameters for the prominent and clear-cut first stage in TG (DTG peak at 286°C) are $E = 236 \text{ kJ mol}^{-1}$, $A = 1.51 \times 10^{21} \text{ s}^{-1}$, and $\Delta S = 136 \text{ J K}^{-1} \text{ mol}^{-1}$. The mechanism of this decomposition reaction is identified as a phase boundary reaction with spherical symmetry, as per the equation $g(\alpha) = 1 - (1 - \alpha)^{1/3}$. The surface parameters of the CC samples obtained by calcination of CAC, at different temperature regimes compatible with TG data, have been determined. The surface area of the CC decreases when the calcination temperature increases. The surface area also decreases when CC samples are washed with acetic acid. X-ray diffraction (XRD) patterns of CC samples obtained from higher temperature calcinations of CAC differ from those obtained at lower temperatures. The propellant burning rate is enhanced by the addition of CC and increases when the Lewis acid amounts of the catalyst sample increase. These correlations have been established for the first time for CC catalysts used in propellant technology.

Keywords: Catalyst; Copper ammonium chromate; DSC; DTA; DTG; Kinetics; Mechanism

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1. Introduction

As part of our continuing programme of studying thermal decomposition reactions from the kinetic and mechanistic points of view [1], we report here the results of a study on the thermal conversion of basic copper ammonium chromate (CAC) precursor to copper chromite catalyst. Although the phenomenological aspects of the thermal decomposition of CAC have been the subject of some previous investigations [2,3], a search of the literature showed that no studies have been reported on the kinetic parameters (energy of activation, pre-exponential factor and entropy of activation). Interest in CAC arises from the fact that CAC is the usual precursor for the preparation of the important catalyst “copper chromite”. Copper chromite (CC) is really a mixed copper–chromium oxide, with a spinel structure. A literature survey also showed that information about surface parameters of CC is scanty, whereas no studies have been reported on the concentration of Lewis acid sites in CC.

In addition to the well known use of CC as a catalyst in synthetic organic chemistry (catalytic hydrogenolysis, for example), much recent focus on CC has been due to its catalytic activity in modifying the burning rate (“ballistic modifier”) of composite solid propellants. Of particular interest to us was the use of CC as a catalyst to enhance the burning rate of composite solid propellants based on hydroxy terminated polybutadiene (HTPB), ammonium perchlorate (AP) and aluminium (Al). Addition of a small amount (0.2% to 0.4% by mass) of CC to the propellant formulations enhances the burning rate (BR) of the propellant to a considerable extent. It was felt that a better understanding of the kinetics and mechanism of the thermal decomposition of precursor CAC to the catalyst CC, and greater information about the surface properties (surface area and Lewis acid amounts) of CC, would be of use in formulating (tailoring) the propellant–catalyst compositions used in solid fuel propelled rockets.

In this paper we present the results of our studies on (1) the thermal decomposition of CAC using TG, DTG, DTA and DSC techniques, (2) surface area of CC samples and their Lewis acid site concentrations, (3) the X-ray diffraction (XRD) pattern of the CC samples and (4) the burning rate pattern of our propellant–catalyst formulations using CC.

2. Experimental

2.1. Preparation of copper ammonium chromate (CAC)

The composition of CAC has been represented by the general formula $(\text{Cu}^{2+})_{1+x}(\text{NH}_4^+)_y(\text{OH}^-)_{2x+y}(\text{NH}_3)_z(\text{CrO}_4^{2-})$, by Plesch et al. [3]. It is reported that the coefficients x , y and z vary depending upon the pH of the precipitating medium, the variation being $0 < x < 0.3$, $0.6 < y < 0.9$ and $0 < z < 0.2$. Patnaik et al. [2] have also reported that under ideal conditions it is possible to obtain a compound of the composition $\text{Cu}(\text{NH}_4)(\text{OH})\text{CrO}_4$ (in this case $x = 0$, $y = 1$ and

Table 1
Analytical results for CAC and CAC-B

Sample	CAC		CAC-B
	Exptl.	Theoretical	Exptl.
Copper %	29.8	29.6	27.8
Chromium %	24.1	24.2	23.6
Nitrogen %	6.3	6.5	6.6
Barium %	—	—	4.9
Cu/Cr	1.24	1.22	1.18

Table 2
Effect of washing of CC catalyst with 10% acetic acid ^a

Sample	No. of washing	CuO lost from sample/%
CC	First	12.2
	Second	9.8
	Third	2.0
	Fourth	1.5
	Fifth	1.5
CC-B	First	11.6
	Second	5.0
	Third	1.4
	Fourth	1.4
	Fifth	1.4

^a Conditions: mass of sample, 5 g; washing solution, 50 ml of 10% v/v acetic acid; stirring time, 10 min; settling time, 10 min.

$z = 0$). We have followed the procedure of Patnaik et al. [2], for the preparation of CAC.

Barium doped copper ammonium chromate (CAC-B) was also prepared according to the method of Patnaik et al. [2].

The chemical analysis results for the samples of CAC and CAC-B are given in Table 1.

2.2. Preparation of copper chromite (CC)

About 50 g samples of CAC were taken in porcelain china dishes and heated under two temperature regimes (350–400°C and 500–600°C) in a thermostatic muffle furnace for 1 h. (This duration was found to be sufficient for complete decomposition.) In this process, the yellowish brown CAC is converted to black CC. In some experiments, the CC prepared as above was also used without any treatment such as washing with acetic acid (CC unwashed). In other experiments

Table 3
Analytical results for copper chromite samples

No.	Sample ^a	Cu/%	Cr/%	Ba/%	Cu/Cr
1	CC washed (350–450°C)	35.2	35.9	—	0.98
2	CC unwashed (350–450°C)	39.0	32.4	—	1.20
3	CC-B washed (350–450°C)	32.5	33.0	6.6	0.98
4	CC-B unwashed (350–450°C)	34.0	30.0	5.9	1.13
5	CC-B washed (550–600°C)	32.3	33.2	6.5	0.97
6	CC unwashed Theoretical	40.9	33.4	—	1.22

^a The temperatures given in parentheses refer to the temperatures at which the precursor CAC samples were calcined to obtain the catalyst CC samples.

CC was washed twice with 500 ml of 10% acetic acid, then six times with water and finally dried at 120°C for 2 h (CC washed). (The above washing programme was chosen because it is the one employed in the procedures for the preparation of industrial grade CC catalyst [4,5].) Details of the amounts of CuO leached out during washing are given in Table 2.

Barium doped copper chromite (CC-B) was prepared in a manner similar to the above, giving samples of “CC-B washed” and “CC-B unwashed”.

All the samples were subjected to chemical analysis. The results are presented in Table 3.

3. Instrumentation

The TG–DTG and DTA studies were carried out using a DuPont model 2000 Thermal Analyst in conjunction with 951 thermogravimetric analyser and 1200 DTA cell. DSC curves were recorded using Mettler TA 3000 system in conjunction with a DSC 20 standard cell and a TC10A TA processor. The experiments were carried out in ultra pure nitrogen atmosphere at a flow rate of 50 cm³ min⁻¹. The heating rate employed was 10°C min⁻¹ and the sample mass was 10 ± 0.1 mg. In separate experiments, the samples were pyrolysed using a Pyrolyser PYR-2A and the evolved gases were analysed by a Shimadzu gas chromatograph GC 5A coupled to the pyrolyser. Helium was used as carrier gas.

The Lewis acid amounts (LAA) were determined using a butylamine sorption technique by adopting the method of Araujo et al. [6]. The surface area measurements were carried out with a Quantachrome Monosorb Surface Area Analyser.

Table 4
Mechanism-based equations

Equation	Form of $g(\alpha)$	Rate controlling process
(1)	α^2	One-dimensional diffusion
(2)	$\alpha + (1 - \alpha) \ln(1 - \alpha)$	Two-dimensional diffusion
(3)	$[1 - (1 - \alpha)^{1/3}]^2$	Three-dimensional diffusion, spherical symmetry; Jander equation
(4)	$(1 - 2/3\alpha) - (1 - \alpha)^{2/3}$	Three-dimensional diffusion, spherical symmetry; Ginstling–Brounshtein equation
(5)	$-\ln(1 - \alpha)$	Random nucleation, one nucleus on each particle; Mampel equation
(6)	$[-\ln(1 - \alpha)]^{1/2}$	Random nucleation; Avrami equation I
(7)	$[-\ln(1 - \alpha)]^{1/3}$	Random nucleation; Avrami equation II
(8)	$1 - (1 - \alpha)^{1/2}$	Phase boundary reaction, cylindrical symmetry
(9)	$1 - (1 - \alpha)^{1/3}$	Phase boundary reaction, spherical symmetry

The X-ray powder diffractograms were recorded using a Philips 1381 diffractometer with a PW 1140 X-ray generator using Cu $K\alpha$ radiation. Computational work was done with an IBM-PC/AT using a basic program.

4. Mathematical analysis of data

The kinetic analysis of the TG–DTG data were carried out using three non-mechanistic and nine mechanistic equations.

The non-mechanistic equations employed are the following:

(1) The Coats–Redfern (CR) equation [7]

$$\ln[g(\alpha)/T^2] = \ln[(AR/\phi E)(1 - 2RT/E)] - E/RT$$

(2) The MacCallum–Tanner (MT) equation [8]

$$\log_{10} g(\alpha) = \log_{10}[AE/\phi R] - 0.483E^{0.495} \frac{(0.449 + 0.217E) \times 10^3}{T}$$

(3) The Madhusudanan–Krishnan–Ninan (MKN) equation [9]

$$\ln[g(\alpha)/T^{1.9215}] = \ln[AE/\phi R] + 3.7721 - 1.9215 \ln E - \frac{0.12039E}{T}$$

where T is the temperature in K, A is the pre-exponential factor, ϕ is the heating rate in $^{\circ}\text{C min}^{-1}$, E is the energy of activation and R is the gas constant. In the above equations, the $g(\alpha)$ term for $n = 1$ is defined as

$$g(\alpha) = \frac{1 - (1 - \alpha)^{1-n}}{1 - n}$$

Table 5
Phenomenological data for the thermal decomposition of CAC and CAC-B; TG/DTG results

Sample	Stage	Decomposition behaviour ^a			
		$T_i/^\circ\text{C}$	$T_s/^\circ\text{C}$	$T_f/^\circ\text{C}$	Mass loss observed/%
CAC	I	200	286	340	22.6
	II	400	440	500	1.8
	III	700	740	800	3.6
CAC-B	I	200	293	340	20.9
	II	410	445	510	1.8
	III	750	780	820	3.1
	IV	850	892	910	1.6

^a T_i , temperature of initiation of decomposition; T_s , DTG peak temperature; T_f , temperature of completion of decomposition.

Table 6
Phenomenological data for the thermal decomposition of CAC and CAC-B; DTA results

Sample	Stage	Decomposition behaviour ^a			
		$T_i/^\circ\text{C}$	$T_s/^\circ\text{C}$	$T_f/^\circ\text{C}$	Endo/exo
CAC	I	220	254	260	Endo
	II	260	278	320	Exo
	III	380	408	430	Exo
	IV	650	699	710	Endo
CAC-B	I	220	254	260	Endo
	II	260	274	305	Exo
	III	400	429	450	Exo
	IV	670	721	750	Endo

^a Please see note to Table 5 for explanation of T_i and T_f ; T_s is the DTA peak temperature.

Table 7
Kinetic parameters for the decomposition of copper ammonium chromate using non-mechanistic equations from TG data

Equation ^a	$E/\text{kJ mol}^{-1}$	A/s^{-1}	$\Delta S/\text{J K}^{-1} \text{mol}^{-1}$	r ^b
CR	236.1	1.41×10^{20}	135.6	0.9989
MT	238.3	2.46×10^{20}	140.2	0.9991
MKN	236.1	1.51×10^{20}	136.2	0.9989

^a CR, Coats–Redfern equation; MT, MacCallum–Tanner equation; MKN, Madhusudanan–Krishnan–Ninan equation.

^b Correlation coefficient.

Table 8

Kinetic parameters for the decomposition of copper ammonium chromate using mechanistic equations from TG data

Mechanistic equation number ^a	$E/\text{kJ mol}^{-1}$	A/s^{-1}	$\Delta S/\text{J K}^{-1} \text{mol}^{-1}$	r
(1)	384.4	6.31×10^{33}	396.9	0.9920
(2)	423.6	2.30×10^{37}	465.1	0.9964
(3)	475.8	6.52×10^{41}	550.3	0.9989
(4)	440.6	2.97×10^{38}	486.3	0.9978
(5)	262.1	5.25×10^{22}	184.8	0.9975
(6)	126.5	5.37×10^9	-63.9	0.9974
(7)	81.3	2.04×10^5	-148.5	0.9971
(8)	220.5	2.04×10^{18}	100.4	0.9981
(9)	233.3	2.51×10^{19}	121.2	0.9989

^a The numbers (1) to (9) refer to the mechanisms given in Table 4.

where $\alpha = m_t/m_\infty$ and n is the order parameter; m_t is the mass loss at time t and m_∞ is the mass loss at the completion of the reaction in TG experiments.

The mechanistic equations used are based on $g(\alpha)$ values corresponding to different mechanisms proposed by Satava [10] for solid state reactions, as listed in Table 4.

5. Results and discussion

The phenomenological data for the thermal decomposition of CAC and CAC-B are presented in Table 5 (for TG) and in Table 6 (for DTA and DSC).

Kinetic parameters from non-mechanistic equations are listed in Table 7. Table 8 presents the kinetic parameters evaluated from mechanism based equations.

The XRD data are presented in Table 9. Table 10 presents the surface area values of some typical samples. The Lewis acid amount and burn rate values are given in Table 11.

5.1. Chemical analysis

Tables 1 and 2 show that CAC corresponds to the expected formula $\text{Cu}(\text{NH}_4)(\text{OH})(\text{CrO}_4)$ whereas CAC-B corresponds to an admixture of CAC and barium chromate.

The situation is rather different with CC, as may be seen from Table 3. Here the composition was found to be variable. This observation is in agreement with the findings of earlier workers. For example Patnaik et al. [2] report "a wide range of values for the Cu:Cr ratio in CC". Very wide variations in the Cu:Cr ratio in industrial CC have been reported by Pearson [11]. (In a typical case, Pearson gives

Table 9
XRD data for CC and CAC samples

Sample ^a	2 θ /deg
CC washed (350–450°C)	42.1, 37.5, 35.6, 32.5, 31.0, 26.4
CC unwashed (350–450°C)	42.2, 37.3, 35.6, 32.5, 31.0, 26.3
CC-B washed (350–450°C)	53.8, 42.1, 41.7, 37.0, 35.6, 32.5, 31.0, 28.3, 26.3, 25.4, 24.4
CC-B unwashed (350–450°C)	41.7, 35.6, 31.0, 28.3, 26.3, 25.4
CC-B washed (350–600°C)	65.2, 62.0, 53.8, 41.7, 38.5, 37.5, 35.6, 32.5, 31.0, 28.3, 26.3, 25.4
CAC	38.5, 35.6, 34.6, 33.5, 31.0, 26.5, 24.0
CAC-B	41.7, 36.0, 35.6, 34.6, 33.5, 31.0, 27.0, 24.0

^a Please see footnote to Table 3.

Table 10
Surface area values of some typical CC and CAC samples

No	Sample ^a	Surface area/ (m ² g ⁻¹)
1	CC unwashed/(350–450°C)	38.2
2	CC washed/(350–450°C)	53.6
3	CC-B unwashed/(350–450°C)	46.2
4	CC-B washed/(350–450°C)	42.1
5	CC-B washed/(550–600°C)	18.0
6	CAC, dried at 110°C	9.5
7	CAC-B dried at 110°C	10.4

^a Please see footnote to Table 3.

the values for Harshaw Chemical Co. copper chromite as 63.5% Cu and 12.1% Cr, while he reports the values 33.6% Cu and 29.9% Cr for Research Inorg. Chem. Co. copper chromite.)

We have also observed that the compositional variations are much less in the case of CC unwashed than CC washed. This observation conforms to expectations because we have experimentally confirmed that variable amounts of CuO are leached out during the washing process (Table 2). However, it was intriguing to find that even in the case of CC unwashed, there were variations. It is also found that the Cu:Cr ratio in CC unwashed is different from that of CAC. All this points to the possibility of partial loss of chromium due to volatilisation as CrO₃ during the calcination of CAC to CC.

Table 11
Lewis acid amounts and burn rate values of some typical copper chromite samples

Expt.	Sample ^a	Lewis acid amount in catalyst/ (sites g ⁻¹)	Burn rate of propellant– catalyst (0.3%) mixture/ (mm s ⁻¹)
1	CC washed (350–450°C)	3.70×10^{20}	7.69
2	CC unwashed (350–450°C)	5.80×10^{20}	7.84
3	CC-B washed (350–450°C)	2.35×10^{20}	7.69
4	CC-B unwashed (350–450°C)	6.03×10^{20}	8.02
5	Nil (absence of catalyst)	Not applicable	5.83

^a Please see footnote to Table 3.

5.2. Phenomenological aspects

5.2.1. TG and DTG data

Table 5 shows that CAC is stable up to 200°C (as seen from TG data). The first stage decomposition starts at 200°C and is completed at 340°C. Thereafter there is a stability plateau (340–400°C), followed by the second decomposition stage (400–500°C). At this stage, CAC is fully converted to CC. The stability plateau of CC extends from 500 to 700°C. Above 700°C, CC begins to decompose. The stability plateaus and decomposition ranges for CAC-B are only marginally different from those for CAC. These results are manifested as DTG peaks at 286, 440 and 740 for CAC and 293, 445, 780 and 892°C for CAC-B. The DTG peak at 892 for CAC-B (absent for CAC) obviously points to the decomposition of BaCrO₄ present in CAC-B, because independent experiments on BaCrO₄ showed a DTG peak at 892°C. In the catalyst preparation technology, we are not interested in this final stage. Our primary interest is related to the broad stability plateau of CC (500–700°C).

The fact that the decomposition stages and stability plateaus in TG for CAC-B are nearly the same as those for CAC is not surprising because in CAC-B the additional constituent is BaCrO₄ which begins to decompose only above 800°C.

It may be noted that data pertaining to the above temperature regions relate to dynamic thermogravimetry. In static muffle furnace conditions, it was observed that keeping CAC at 350–450°C for a period of 1 h leads to the complete conversion of CAC to CC (A sample taken from the muffle furnace, when subjected to a TG run, did not show any DTG peak at 440°C and showed only the TG plateau 500–700°C characteristic of CC.)

5.2.2. DTA and DSC data

The DTA data show similarities to the TG data. For CAC, there are four peaks in DTA. The peaks are at 254°C (endo), 278°C (exo), 408°C (exo) and 699°C

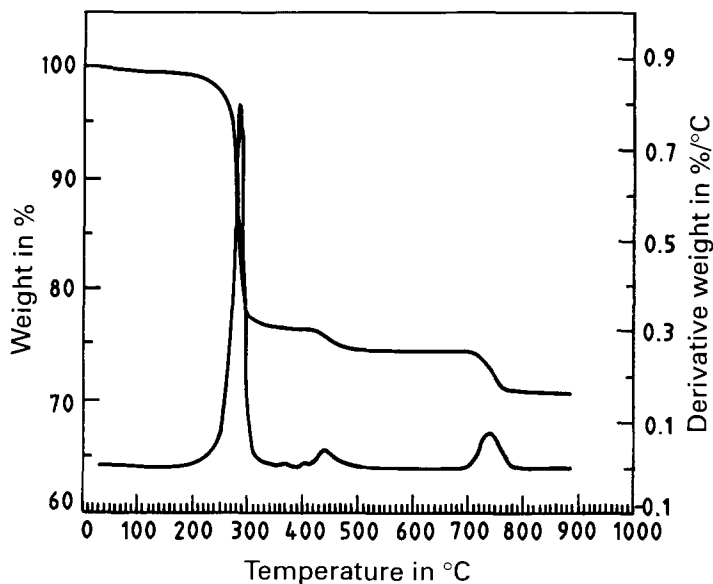


Fig. 1. TG and DTG curves of copper ammonium chromate (CAC).

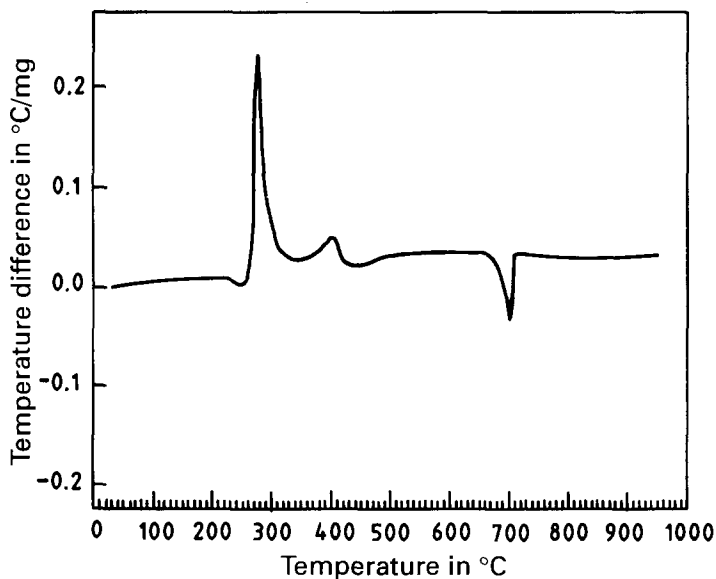


Fig. 2. DTA curve of copper ammonium chromate (CAC).

(endo). The DSC studies were confined to a temperature region up to 350°C (due to the limitation of the equipment). The DSC data for CAC give two peaks at 244°C (endo) and 264°C (exo). These correspond to the first two peaks in DTA. The values (in DTA) may be seen to be only marginally different for CAC-B.

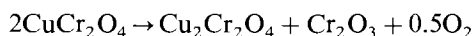
It is seen that while there are three decomposition peaks for CAC in DTG, there are four peaks in DTA (endo, exo, exo and endo in that order). It is reasonable to assume that the endotherm at 254°C and exotherm at 278°C correspond to the DTG peak at 286°C, the resolution being lost in TG.

5.2.3. Pyrolysis–GC studies

The pyrolysis–gas chromatographic analysis showed that H₂O, NH₃, O₂ and N₂ are the product gases evolved during the decomposition of CAC. In the light of the above information, it is possible to identify reactions occurring at the three stages in TG–DTG. The first stage (DTG peak at 286°C) refers to loss of water, ammonia and nitrogen. This itself is a composite reaction involving the endothermic processes of dehydration and deammonisation (DTA peak at 254°C, endo) and partial oxidation of the evolved NH₃ to N₂ and H₂O vapour by the chromate moiety (DTA peak 278°C, exo). Such an oxidation is eminently possible here because of the in situ generation of the catalyst (CC) during the decomposition process.

The second stage in DTG (440°C) corresponds to a small exotherm in DTA. This could be attributed to the decomposition of the remaining copper chromate to copper chromite and oxygen as verified by independent experiments on copper chromate.

The third stage (DTG 740°C, DTA 699°C endo) represents the decomposition of cupric chromite to cuprous chromite



The observed colour change from black (CuCr₂O₄) to dark green (due to the formation of Cr₂O₃) is also in agreement with this inference from TG.

5.2.4. Kinetics and mechanism

For the mathematical analysis, the TG–DTG data were preferred to the DTA–DSC data because the energy change manifestations in this case are rather complex, and the ΔT and ΔH values obtained are merely net values (depending on which step (endothermic or exothermic) dominates. Further the TG–DTG data are intrinsically simpler as they relate to mass changes.

Of the three stages of decomposition in TG, the first one (200–340°C) is the most prominent (Fig. 1) and therefore it was chosen for detailed kinetic analysis.

It may be seen from Table 7 that there is very good agreement among the values obtained using the three equations (CR, MT and MKN). The energy of activation amounts to between 236 and 238 kJ mol⁻¹ and A values lie between $1.41 \times 10^{20} \text{ s}^{-1}$ and $2.46 \times 10^{20} \text{ s}^{-1}$. The entropy of activation is 135.6–140.2 J K⁻¹ mol⁻¹. The positive values of ΔS indicate that the activated complex for this decomposition stage has a less ordered structure compared to the reactant. Further, the reaction may be described as “faster than normal”.

Of the nine mechanistic equations examined (see Table 4) Eqs. (3) and (9) give kinetic plots with the highest linearity (highest correlation coefficients). However, the kinetic parameters calculated for mechanistic Eq. (9) show closest agreement with those evaluated from non-mechanistic equations. Thus, for mechanistic Eq.

(9), the values of E , A and ΔS are $233.3 \text{ kJ mol}^{-1}$, $2.51 \times 10^{19} \text{ s}^{-1}$ and $121.2 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively. Therefore, the rate controlling process would be a phase boundary reaction with spherical symmetry.

5.2.5. The XRD data

Table 9 presents typical XRD data for CAC (or CAC-B) and CC (or CC-B). The most prominent peaks for CAC and CAC-B correspond to 2θ values of 24 , 35.6 and 31° . The above peaks are common to CAC and CAC-B. It may be seen from Table 9 that all the CC and CC-B samples give a strong and sharp peak at about 35.6° and a medium sharp one at 31° . The peak at 35.6° has been attributed to CuCr_2O_4 by earlier workers [2], whereas the peak at 31° corresponds to CuO [12]. Thus it is seen that all the CC and CC-B samples contain free CuO in varying amounts in addition to the spinel CuCr_2O_4 .

It was interesting to observe that samples heated to 550 – 600°C show some additional peaks at 62° and 65.2° . These peaks are absent in CC samples prepared by calcination at 350 – 450°C . Because samples heated at 550 – 600°C have lower surface areas than those calcined at 350 – 450°C (vide infra, Table 10), and because a good catalyst should *prima facie* have a large surface area, absence of these peaks at 62° and 65.2° may be prescribed as a specification for special purpose commercial catalysts.

5.3. Surface area, Lewis acid amount and propellant burn rates

It was observed (see Table 10) that the surface area of the samples calcined at 350 – 450°C lie in the region 40 – $50 \text{ m}^2 \text{ g}^{-1}$ whereas for samples heated to 550 – 600°C the surface area is much lower ($18 \text{ m}^2 \text{ g}^{-1}$). This is not surprising because partial sintering may occur at the higher temperatures leading to particle agglomeration.

The Lewis acid amounts (LAA) are found to be in the region between 2.3×10^{20} and 3.7×10^{20} acid sites g^{-1} for washed samples, whereas for unwashed samples the acid amounts are higher (5.8×10^{20} to 6.0×10^{20} acid sites g^{-1}). This agrees with the observation that some free CuO is removed during the washing process (Table 2).

It was interesting to find that a correlation can be seen between the LAA and the burning rate (see Table 11). The burning rate increases with increase in LAA. Thus the BR is 8.02 mm s^{-1} with the samples having $\text{LAA} = 6.03 \times 10^{20}$ acid sites g^{-1} (Expt. 4); BR is 7.84 mm s^{-1} for $\text{LAA} = 5.80 \times 10^{20}$ acid sites g^{-1} (Expt. 2), both samples being unwashed CC calcined at 350 – 450°C . It is also seen that the presence of barium increases both LAA and BR (compare Expts. 2 and 4). Comparing Expts. 1 and 3, we see that both give the same BR of 7.69 mm s^{-1} , although the LAA is 3.70×10^{20} acid sites g^{-1} for sample 1 and 2.35×10^{20} acid sites g^{-1} for sample 3. Here we see the slight decrease in LAA is compensated by the presence of barium in Sample 3, which therefore gives the same BR as the barium-free Sample 1 with higher LAA. Further, comparing Expts. 1 and 3 on the one hand and Expts. 2 and 4 on the other, it is seen that washing with acetic acid decreases

both LAA and BR. This is understandable because independent experiments showed that more CuO than Cr₂O₃ is lost during washing. It is also known that CuO is a more potent catalyst in this context than Cr₂O₃. The results therefore indicate that, (1) the BR is increased when LAA is increased, (2) the BR is increased by the presence of barium, and (3) unwashed CC samples give higher LAA and BR values compared to washed CC samples.

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