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THERMAL DECOMPOSITION OF AMMONIUM COPPER CHROMATE: EFFECT OF THE ADDITION OF BARIUM

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ABSTRACT

The influence of the addition of barium (as barium chromate) to ammonium copper chromate on its thermal decomposition has been investigated by TG, DTG and DTA in the temperature range 303–1273 K. The solid products formed in the decomposition at different temperatures were characterised by X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy and also by measuring their specific surface area. The addition of $BaCrO_4$ at different concentrations (0–19.8%) was found not to change the general trend in the decomposition of ammonium copper chromate (which occurs in four distinct steps), except small changes in the temperature corresponding to DTG and DTA peaks. However, the sintering (or crystal growth) of the solid product is largely reduced by the presence of $BaCrO_4$.

INTRODUCTION

The thermal decomposition of ammonium copper chromate is one of the important steps in the preparation of active copper chromite [1], which is an industrially important hydrogenation catalyst [2] because of its ability to hydrogenate functional groups in aliphatic and aromatic compounds selectively. Copper chromite is also an effective oxidation catalyst for the conversion of carbon monoxide to carbon dioxide in an automobile exhaust emission control [3].

Barium-promoted copper chromite is often used in industrial practice for the hydrogenation processes [2]. The addition of barium was found [4,5] to stabilize the copper chromite catalyst against reduction [Cu(II) to Cu(I)] and prevent consequent deactivation, and it also enhanced its catalytic activity. The barium-promoted copper chromite can be prepared by thermal decomposition of coprecipitated ammonium copper chromate and barium chromate [4].

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Investigations of the decomposition of ammonium copper chromate have been carried out in detail [6–8], but the influence of the presence of barium on the decomposition and the characteristics of the solid products formed have not been investigated so far. Since barium plays a very important role in stabilizing the copper chromite catalyst, it is also interesting to know the influence of its presence on the surface properties of the catalyst formed in the decomposition. In our earlier studies [6,7], the thermal decomposition of ammonium copper chromate was thoroughly investigated. The present work is concerned with the above matter.

EXPERIMENTAL

Preparation of ammonium copper chromate containing barium

Ammonium copper chromate containing barium chromate at different concentrations (0–19.8 wt%) was prepared by a method similar to that described elsewhere [4,9] by coprecipitating it from a solution containing cupric nitrate and the required amount of barium nitrate with an ammoniacal solution of ammonium dichromate at room temperature and at a pH of 7–7.5. The precipitate was aged for 3 h. During the ageing period, the pH of the slurry was adjusted by the addition of ammonia solution. After the precipitate was aged, it was filtered under vacuum using a Buchner funnel, and washed with distilled water until it was free from nitrate ions. The filtered cake was dried in an air oven at 333–373 K overnight. The dried mass was crushed to 200–300 mesh and stored in a desiccator.

The concentration of barium in the coprecipitated complex was determined by a gravimetric method [10].

The chemicals used in the preparation were of laboratory reagent grade (BDH).

γ-Irradiation

γ-Irradiation of the complex was done by irradiating the coprecipitated complex (containing 11.84 wt% $BaCrO_4$) by γ-rays using a Gamma Cell-220 at a dose rate 22.65 Krcel h^{-1} for 72 h.

Thermal analysis

The TG, DTG and DTA thermograms of coprecipitated complex of ammonium copper chromate–barium chromate were carried out on an automatic unit (Mom derivatograph, Budapest, Type 00-102-B) with the following specifications: sample size, 200 mg; reference compound, α-alumina; sample pretreatment, sample dried at 353 K for 2 h before use;

sample holder, platinum crucible resting on thermocouple lead; temperature range, 303–1273 K; heating rate, 10 K min^{-1}; atmosphere, air under suction.

Characterization of solid products of decomposition

Samples of the solid products of decomposition were prepared by heating the coprecipitated complex for 4 h in a muffle furnace (in air) at different temperatures (viz. 598, 673, 773, 973 and 1273 K). These temperatures were chosen by examining the TG, DTG and DTA thermograms.

The presence of various crystal phases in the solid products was studied by X-ray powder diffraction using a Philips PW/1730 X-ray generator with Ni-filtered CuK_α radiation and a scintillation counter. The surface composition of the solid products was determined by XPS (X-ray photoelectron spectroscopy) using a VG scientific ESCA-3 MK II electron spectrometer. The size and morphology of the crystals of the solid products were studied with a Cambridge Steroscan Model 150 scanning electron microscope.

The specific surface area of the solid products was determined by the single-point BET method by measuring the adsorption of nitrogen at liquid nitrogen temperature and at a nitrogen concentration of 0.3 mol% (balance Helium) using a Monosorb surface area analyser (Quantochrome Corp., U.S.A.) based on the dynamic adsorption/desorption technique.

RESULTS AND DISCUSSION

The coprecipitated mass obtained by treating the solution of barium nitrate and cupric nitrate with an ammoniacal solution of ammonium dichromate is expected to be a mixture of ammonium copper chromate [$NH_4Cu(OH)CrO_4$] and barium chromate.

The formation of barium chromate during the coprecipitation was confirmed by precipitating out chromium in the absence of cupric nitrate with an ammoniacal solution of ammonium dichromate under conditions similar to those used in the preparation of the barium-containing ammonium copper chromate and analysing the precipitate formed by chemical and thermal methods. The thermal analysis of the chromium compound showed a negligible weight loss (1%) in the temperature range 303–1273 K which is characteristic of barium chromate. In the presence of cupric nitrate, chromium is also expected to be coprecipitated by the ammoniacal solution of ammonium dichromate as barium chromate. This is further confirmed by the decrease in the weight loss of the coprecipitated complex containing barium with the increase in the concentration of barium in the complex, as discussed later.

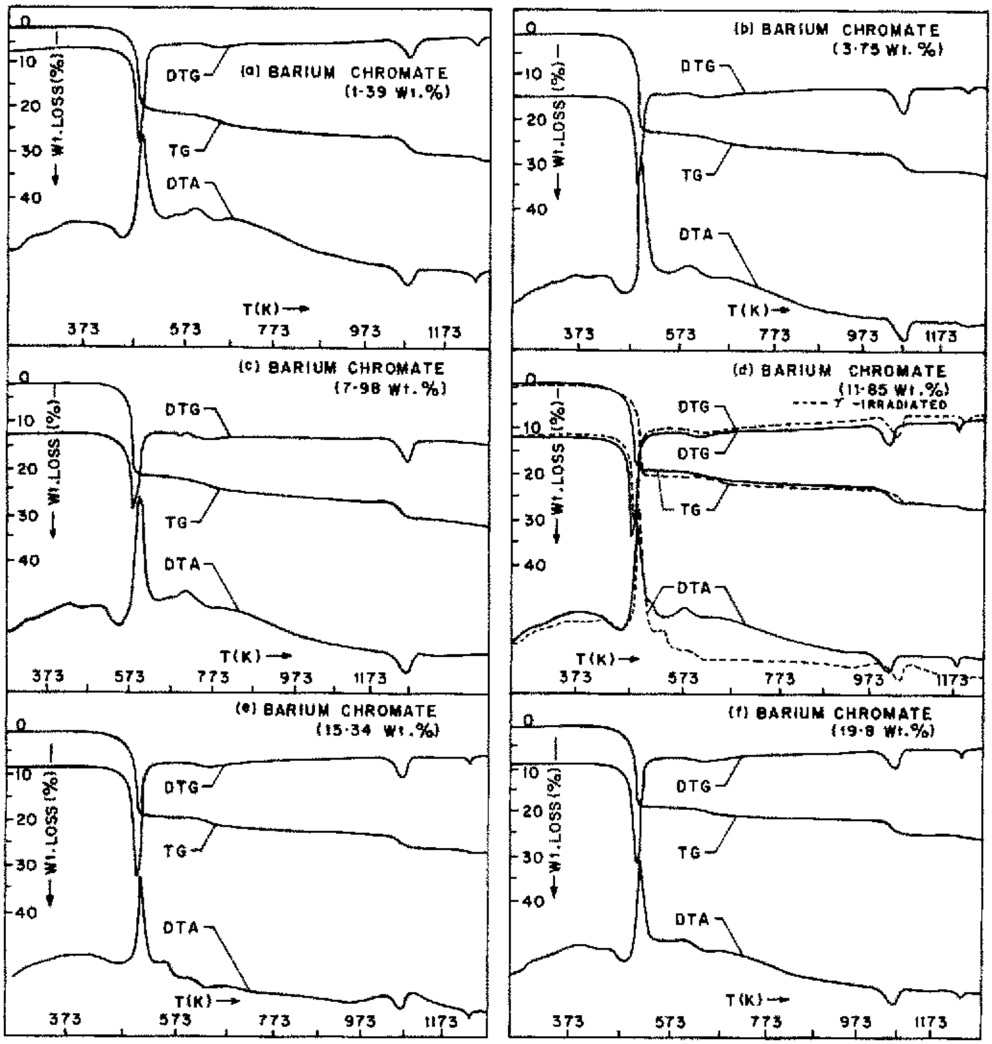


Fig. 1. TG/DTG/DTA curves for decomposition of ammonium copper chromate in the presence of barium chromate at different concentrations.

Thermal analysis

The TG, DTG and DTA curves for the barium chromate–ammonium copper chromate with different concentrations of barium chromate (1.39–19.84 wt%) are presented in Fig. 1. It can be seen that the decomposition occurs in four stages of which stages I and III are very distinct. The decomposition in the first stage is exothermic (as indicated by a maximum in the DTA curve), while in the other stages it is endothermic. The thermal curves (Fig. 1) are very similar to those observed in the case of the decomposition of ammonium copper chromate in the absence of barium [6].

The data of the thermal analysis are given in Table 1. It can be noted from the results that, in general, the weight loss at the different stages of the decomposition decreases with the increase in the concentration of $BaCrO_4$ in the coprecipitated complex. This observation is consistant with the fact that $BaCrO_4$ does not decompose at the temperature of the study (303–1273 K). The theoretical weight loss during decomposition according to the reaction: $2NH_4Cu(OH)CrO_4 \rightarrow CuO \cdot CuCr_2O_4 + 5H_2O + N_2\uparrow$, which is completed in the second stage of decomposition [6], is expected to be 27.1, 26.5, 25.3, 24.2, 23.3 and 22.0% for the coprecipitated complex containing 1.4, 3.8, 8.0, 11.9, 15.3 and 19.84 wt% $BaCrO_4$, respectively. The total weight loss of the second stage of decomposition (Table 1) is quite close to the corresponding expected values given above. A comparison of the TG data of the coprecipitated complex containing barium chromate at the different concentrations with that without barium chromate (i.e., pure ammonium copper chromate) indicates that the mechanism of the decomposition of ammonium copper chromate is not affected by the presence of barium chromate. However, the DTA/DTG peak temperatures, or the extent of decomposition at different temperatures, are changed to a small extent. The DTA/DTG peaks for the complex containing 7.98 wt% $BaCrO_4$ are shifted considerably towards the higher temperature side. The data for this complex were collected repeatedly in order to confirm these results. There is probably a critical concentration of $BaCrO_4$ in the coprecipitated complex at which the decomposition is delayed to an appreciable extent.

The thermal curves for the γ-irradiated barium chromate–ammonium copper chromate are presented in Fig. 1d. The decomposition of γ-irradiated barium chromate–ammonium copper chromate also occurs in four stages, of which stages I and III are quite distinct. The decomposition in the first stage is exothermic, while in the other three stages it is endothermic. The thermal decomposition data are included in Table I.

A comparison of the results of the thermal analysis of the complex with and without γ-irradiation (Table 1) shows that, due to the γ-irradiation, there is no significant change in the total weight loss at the different stages of decomposition, but the temperature corresponding to the DTA and DTG peaks has shifted to higher values for all stages of decomposition. Thus, γ-irradiation increases the thermal stability of the complex and its solid decomposition products.

An earlier study [6] showed that γ-irradiation of ammonium copper chromate causes an increase in the total weight loss at every stage of decomposition. However, the γ-irradiation of barium chromate–ammonium copper chromate has been found to have no influence on the total weight loss at different stages of decomposition. These observations point to the fact that the presence of barium chromate has a stabilizing action on the effects produced by γ-irradiation on the extent of decomposition.

TABLE 1

Data on thermal analysis of coprecipitated ammonium copper chromate–barium chromate with different compositions

Conc. of $BaCrO_4$ (wt%)	Peak temperature (K)								Wt. loss (%) at each stage			
	DTA				DTG							
	I	II	III	IV	I	II	III	IV	I	II	III	IV
1.39	463	633	1063	1203	483	633	1053	1198	23.0	5.00	4.50	2.03
	(exo)	(endo)	(endo)	(endo)	(endo)	(endo)	(endo)	(endo)	(23.0) [a]	(26.0)	(30.5)	(32.0)
3.75	503	633	1053	1223	493	631	1051	1211	23.0	5.00	4.38	1.00
	(exo)	(endo)	(endo)	(endo)	(endo)	(endo)	(endo)	(endo)	(23.0)	(27.0)	(32.0)	(33.0)
7.98	583	753	1233	–	573	751	1231	–	22.0	7.48	5.01	—
	(exo)	(endo)	(endo)		(endo)	(endo)	(endo)		(22.0)	(26.5)	(31.0	
11.84	503	623	1011	1163	493	613	1011	1158	20.50	3.57	5.00	1.30
	(exo)	(endo)	(endo)	(endo)	(endo)	(endo)	(endo)	(endo)	(20.5)	(23.5)	(27.5)	(28.6)
11.84 (γ-irradiated)	513	633	1051	1203	503	633	1051	1195	21.0	3.39	5.50	0.69
	(exo)	(endo)	(endo)	(endo)	(endo)	(endo)	(endo)	(endo)	(21.0)	(23.5)	(27.5)	(28.3)
15.34	503	635	1063	1233	501	635	1063	1223	19.9	3.25	4.02	1.00
	(exo)	(endo)	(endo)	(endo)	(endo)	(endo)	(endo)	(endo)	(19.9)	(23.0)	(27.0)	(28.0)
19.84	513	643	1063	1233	508	643	1058	1223	19.5	3.20	4.00	0.93
	(exo)	(endo)	(endo)	(endo)	(endo)	(endo)	(endo)	(endo)	(19.5)	(22.0)	(26.0)	(26.6)
0.00 [b]	533	670	1101	1260	531	670	1101	1260	24.5	5.30	7.00	1.10
	(exo)	(endo)	(endo)	(endo)	(endo)	(endo)	(endo)	(endo)	(24.5)	(28.5)	(33.5)	(34.5)

[a] Values in parentheses indicate the total weight loss at the different stages of decomposition.

[b] Data from ref. 6.

TABLE 2

Crystalline phases in the solid products of the decomposition of ammonium copper chromate without and with barium chromate (11.84 wt%) at different temperatures

Decomposition temperature (K)	Crystalline phases	
	without $BaCrO_4$	with $BaCrO_4$
598	CuO and amorphous	$BaCrO_4$, CuO and amorphous
673	CuO and $CuCr_2O_4$	$CuCrO_4$, CuO and $BaCrO_4$
773	CuO and $CuCr_2O_4$	$CuCr_2O_4$, CuO and $BaCrO_4$
1023	CuO and $CuCr_2O_4$	$CuCr_2O_4$, CuO and $BaCrO_4$
1273	$Cu_2Cr_2O_4$ (CuO and $CuCr_2O_4$ in traces)	$Cu_2Cr_2O_4$ and $BaCrO_4$ (CuO and $CuCr_2O_4$ in traces)

Solid products of decomposition

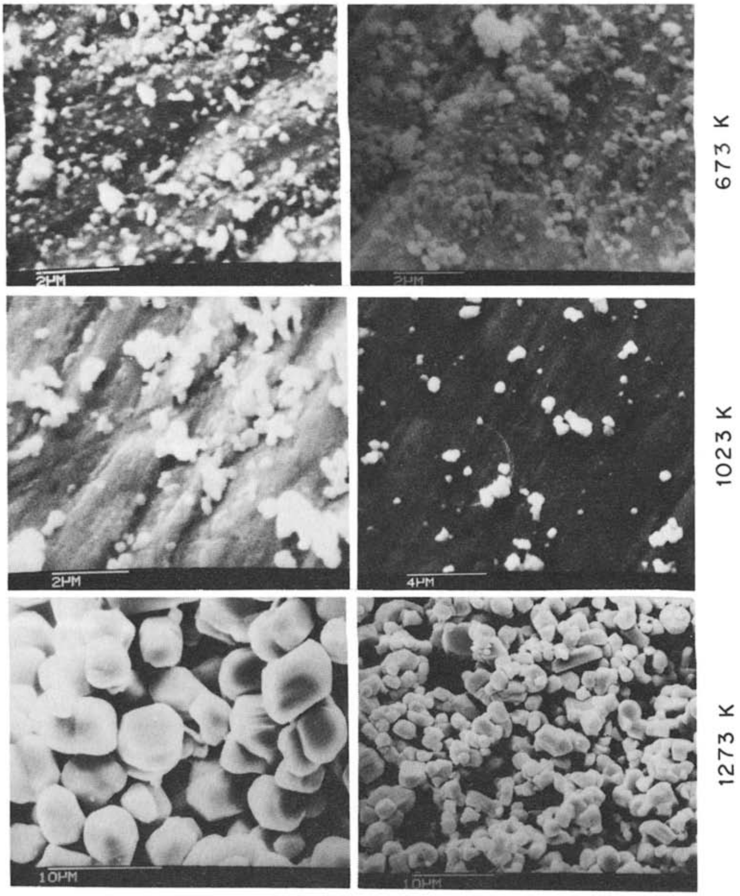
The solid products of the decomposition of barium chromate–ammonium copper chromate containing different concentrations of barium chromate (0–19.84 wt%) at 598, 673, 773, 1023 and 1273 K have been characterised for their crystalline phases, surface composition, morphology and crystal size, and specific surface area.

Crystalline phases

The results of the XRD analysis of the solid products of decomposition of ammonium copper chromate and barium chromate–ammonium copper chromate ($BaCrO_4$ 11.84 wt%) at the different temperatures are presented in Table 2.

The solid products obtained in the decomposition at 598 K are mostly amorphous. The crystallinity of the solid products was found to increase with the increase in the decomposition temperature.

A comparison of the results in Table 2 shows that the solid products formed on decomposition of barium chromate–ammonium copper chromate at the different temperatures are similar to those formed on decomposition of ammonium copper chromate at the corresponding temperature, except for the barium chromate present in the solid products of the decomposition of the former. This fact leads to the conclusion that the decomposition of ammonium copper chromate in the presence of barium chromate or in its absence occurs in the same way, that is, the decomposition in either case occurs in four distinct stages and involves the reactions described earlier [6].



(a) 0·0 wt. % $BaCrO_4$ (b) 11·84 wt. % $BaCrO_4$

Fig. 2. Scanning electron microphotographs of solid products of decomposition of ammonium copper chromate containing 0.0 and 11.84 wt% $BaCrO_4$.

Morphology and size of crystallites

Scanning electron microphotographs (SEM) of the solid products of the decomposition of ammonium copper chromate with 11.84 wt% $BaCrO_4$ and without it, at the different temperatures, are presented in Fig. 2. The examination of the SEMs revealed that: (i) the solid products of the decomposition at 598 K are mostly amorphous, which is consistent with the XRD results; (ii) the degree of crystallization of the solid products increases with the decomposition temperature; (iii) the increase in the decomposition temperature from 673 to 773 K causes a very small change in the crystal size, but a further increase in temperature causes a large increase in the crystal size of the solid products. The very significant increase in the crystal size with the increase in the decomposition temperature above 773 K points to the occurrence of the sintering and/or crystal growth of the solid products during the decomposition process.

It is very clear from a comparison of the SEMs (Fig. 2) that the presence of barium chromate strongly influences the sintering or crystal growth of the solid products at higher temperatures (above 773 K). The sintering (growth of the crystals) of the solid products is largely reduced by the presence of barium chromate. Thus, barium chromate acts as an inhibitor for the sintering of the copper chromite catalyst. The inhibition action is probably a result of the separation of the crystals of the solid products from each other by the presence of barium chromate.

It is known that the presence of barium chromate stabilizes the copper chromite catalyst against the reduction of Cu(II) to Cu(I) [4,5]. However, the present work shows that the presence of barium chromate also stabilizes the catalyst against sintering, which is one of the causes of catalyst deactivation, particularly in highly exothermic catalytic processes such as vapour-phase hydrogenation of nitroaromatics to their corresponding amines and oxidation of carbon monoxide, etc.

Surface area

Figure 3 shows the variation of the specific surface area of the solid products of the decomposition of ammonium copper chromate and barium chromate–ammonium copper chromate (11.84 wt% $BaCrO_4$) with the decomposition temperature. In both the cases of decomposition, the surface area of the solid products decreases with the increase in the decomposition temperature. However, the decrease in the surface area of the solid products containing barium chromate is much smaller than that for the solid products not containing barium chromate.

The decrease in the surface area with the increase in temperature is expected because of sintering, i.e., because of the increase in the crystal size due to crystal growth of the solid products of decomposition. The comparison of the results in Fig. 3 clearly indicates that the sintering of the solid products is largely reduced because of the presence of barium chromate.

Surface chemical analysis

The XPS data for the solid products of the decomposition of ammonium copper chromate with and without $BaCrO_4$ are given in Tables 3 and 4, respectively.

The XPS for O (1*s*) have been found to be very broad and composed of two unresolved peaks, the first corresponding to E_b (electron binding energy) of about 529 eV and the second corresponding to E_b of about 531 eV, indicating the presence of oxygen in two forms. The first peak is attributed to lattice oxygen (O^{2-}) and the second most probably to oxygen chemisorbed on the surface.

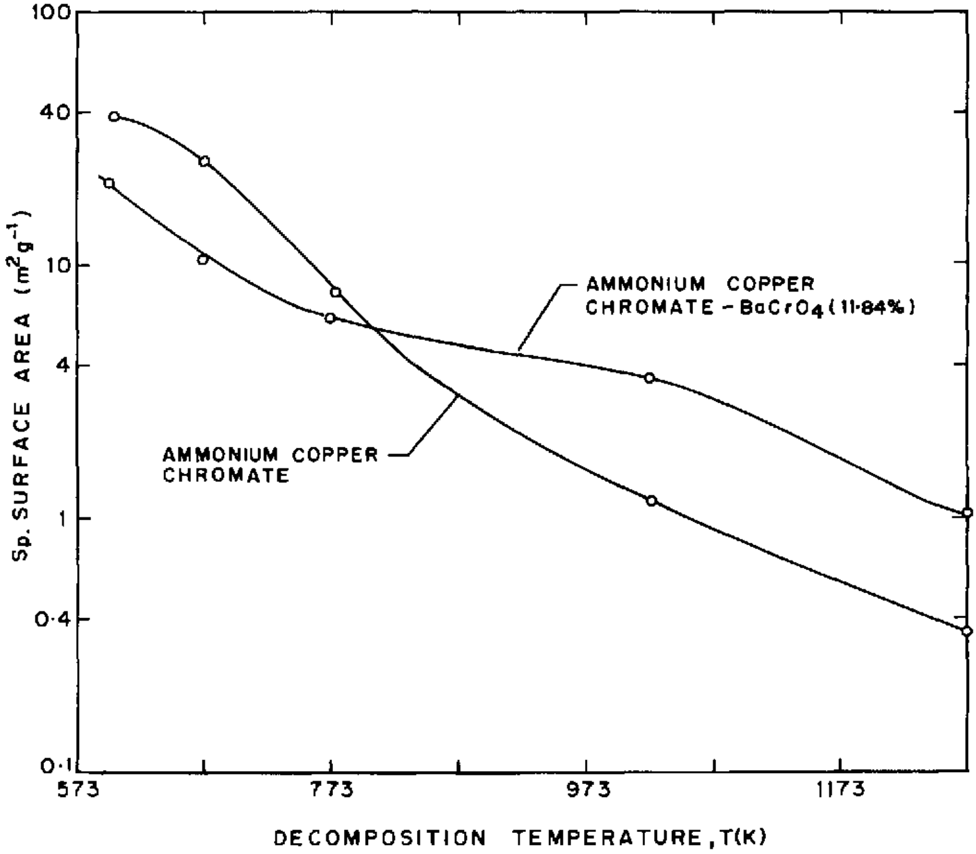


Fig. 3. Variation of surface area of the solid product(s) of decomposition of ammonium copper chromate and coprecipitated ammonium copper chromate and barium chromate with decomposition temperature.

TABLE 3

XPS data (eV) of solid products of decomposition of ammonium copper chromate at different temperatures

Decomposition temperature (K)	O (1*s*)		Cu ($2P_{3/2}$)		Cr ($2P_{3/2}$)	
	E_b	$\Delta E_{1/2}$	E_b	$\Delta E_{1/2}$	E_b	$\Delta E_{1/2}$
598	529.2	2.5	933.7	3.2	575.3	4.0
	531.3	1.9				
673	528.9	2.3	933.4	3.7	575.4	3.7
	531.2	1.4				
773	528.8	1.9	933.1	3.6	575.3	3.7
	530.6	2.2				
1023	529.2	1.9	933.1	3.7	575.5	3.6
	530.8	1.8				
1273	529.8	2.4	931.8	2.6	575.7	3.6
	531.4	2.6	933.6	2.4		

TABLE 4

XPS data (eV) on solid products of decomposition of coprecipitated ammonium copper chromate–barium chromate (11.84 wt% $BaCrO_4$) at different temperatures

Decomposition temperature (K)	O(1s)		Cu ($2P_{3/2}$)		Cr ($2P_{3/2}$)		Ba($3d_{5/2}$)	
	E_b	$\Delta E_{1/2}$	E_b	$\Delta E_{1/2}$	E_b	$\Delta E_{1/2}$	E_b	$\Delta E_{1/2}$
598	529.1	3.5	933.0	4.6	575.1	2.6	779.1	2.2
					578.2	2.2		
673	529.4	2.9	933.7	4.3	575.4	2.9	779.6	2.0
					578.6	2.4		
773	529.1	2.9	933.1	4.0	575.2	2.6	779.4	1.9
					578.3	2.4		
1023	530.9	2.8	933.6	4.0	575.6	2.6	781.0	2.6
					580.1	2.4		
1273	529.8	2.2	931.9	2.1	575.8	2.6	780.0	2.0
	531.9	2.6	934.8	2.3	579.8	2.2		

It can be noted from the XPS data for copper in Tables 3 and 4 that when the decomposition temperature is increased from 598 to 1273 K, E_b for Cu ($2P_{3/2}$) remains almost constant ($E_b = 933.4 \pm 0.3$ eV) up to 1023 K, but a further increase in temperature to 1273 K results in a significant decrease in E_b, indicating the transformation of Cu(II) to Cu(I). The second small, unresolved peak corresponding to a high E_b value for the decomposition products at 1273 K revealed the presence of a small amount of Cu(II). E_b for Cr ($2P_{3/2}$) of the solid products formed on decomposition of ammonium copper chromate containing $BaCrO_4$ at the different temperatures is 575.5 ± 0.2 eV (Table 3) which is very close to the value (575.6 eV) found for Cr(III) [10]. Whereas the two values observed for E_b of Cr ($2P_{3/2}$) (the first 575.4 ± 0.4 eV and the second about 579 eV (Table 4)) indicate the presence of Cr(III) and Cr(VI) in the solid products obtained by the decomposition of ammonium copper chromate containing $BaCrO_4$.

It may be noted that the conclusion drawn from the XPS studies about the presence of Cu and Cr in the different oxidation states is quite consistent with those derived from the thermal analysis and XRD studies.

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