

STUDY OF COPPER–CHROMIUM OXIDE CATALYST. Part IV. Thermal decomposition of basic copper(II)–ammine ammonium chromate *

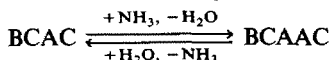
G. PLESCH, F. HANIC and K. PUTYERA

*Institute of Inorganic Chemistry, Slovak Academy of Sciences,
CS-842 36 Bratislava (Czechoslovakia)*

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ABSTRACT

Basic copper(II)–ammine ammonium chromate (BCAAC) of the composition $[(\text{Cu}^{2+})_{1+x}(\text{NH}_4^+)_y(\text{OH}^-)_{2x+y}(\text{NH}_3)_z(\text{CrO}_4^{2-})]$ was prepared by the reaction of basic copper(II)–ammonium chromate (BCAC) with ammonia. Compounds with coefficients x , y , z varying in the approximate intervals $0 < x < 0.3$, $0 < y < 0.2$, $3 < z < 4$ were obtained in dependence on p_{NH_3} . According to the results of IR, electronic and EPR spectra, NH_3 substitutes for oxygen and hydroxyl groups bound to Cu(II) and $[\text{Cu}(\text{NH}_3)_4]^{2+}$ complex cations are formed in BCAAC. This reaction is reversible at room temperature and it can be written schematically as



At 130 °C and 180 °C ammonia desorption takes place in the process of the thermal decomposition. At ca. 205 °C an explosive Cr(VI) to Cr(III) reduction leads to copper–chromium oxide catalyst with highly disordered structure. After its heating to 500 °C a system, which contains crystalline CuO and a metastable CuCr_2O_4 with a unit cell of orthorhombic symmetry ($a = 0.593$ nm, $b = 0.603$ nm, $c = 0.779$ nm) was obtained. The activity of the catalyst in the hydrogenation–alkylation reaction is lower than the activity of the one prepared from BCAC at 270 °C.

INTRODUCTION

Copper–chromium oxide catalyst can be prepared by various methods. Its synthesis by thermal decomposition of basic copper(II) ammonium chromate (BCAC) was first described by Adkins and Connor [1] and has been widely used to date [2–4]. Our recent paper [5] showed that BCAC has the character of a solid solution, the composition of which can be represented by the formula $[(\text{Cu}^{2+})_{1+x}(\text{NH}_4^+)_y(\text{OH}^-)_{2x+y}(\text{NH}_3)_z(\text{CrO}_4^{2-})]$. The coeffi-

* For preceding part see ref. 5

cients x , y , z vary in intervals $0 < x < 0.3$, $0.6 < y < 0.9$, and $0 < z < 0.2$, depending on the pH value at the precipitation reaction of Cu^{2+} with CrO_4^{2-} in the presence of aqueous ammonia.

The thermal decomposition of CuCrO_4 occurs at 460°C . This is a significantly higher temperature than the decomposition temperature of BCAC (270°C). Both thermal decompositions lead to copper–chromium oxide catalysts, but the activity in hydrogenation–alkylation reaction of the first product is significantly lower [6,7].

Preparation of tetraamine copper(II) chromate from BCAC and ammonia has been reported [8]. In the process of thermal decomposition at 220°C reduction of Cr(VI) to Cr(III) takes place, analogous to the above chromates. Because of its comparatively low decomposition temperature, formation of active copper–chromium oxide catalyst could be expected.

To prove this assumption the reaction of BCAC with ammonia was studied and the properties and thermal decomposition of the prepared products were investigated. The catalytic activity of the copper–chromium oxide catalyst obtained was tested.

EXPERIMENTAL

BCAC was prepared according to ref. 5. Its composition can be described by the formula $\text{CuCrO}_4[\text{Cu}(\text{OH})_2]_{0.1}[(\text{NH}_4)(\text{OH})]_{0.8}[\text{NH}_3]_{0.1}$.

Basic copper(II)–ammine ammonium chromate (BCAAC) was prepared by the reaction of 6 g BCAC, which was suspended in 15 ml of acetone, and 15 ml of aqueous ammonia (~ 27 wt.% NH_3) was added. The red-brown suspension turned immediately to green. It was stirred for 4 h. The product was filtered, washed with a small amount of acetone and dried quickly. However, the color of the green powder returned to red-brown within some hours in open air. In closed vessels the sample did not decompose even after some months.

Analysis is given here for a typical sample (Cu, Cr were determined by atomic absorption and H, N by elemental analysis). Calculated for $\text{CuCrO}_4[\text{Cu}(\text{OH})_2]_{0.1}[(\text{NH}_4)(\text{OH})]_{0.2}(\text{NH}_3)_{3.3}$ 27.69% Cu, 20.59% Cr, 19.42% N, 4.43% H. Found 27.78% Cu, 20.41% Cr, 19.48% N, 4.38% H.

Physical and thermal measurements

The IR spectra were scanned on a Perkin Elmer 983 G instrument in the $400\text{--}4000\text{ cm}^{-1}$ range, using KBr pellets.

The electronic spectra were measured on a Specord M 40 instrument (C. Zeiss, Jena) in the range $12\,000\text{--}30\,000\text{ cm}^{-1}$ in Nujol mulls.

The powder EPR spectra were taken on the Varian E-4 device in X band at room temperature.

The X-ray powder diffraction patterns were obtained on a Philips 1540 diffractometer, using Cu K_α radiation.

The thermal decomposition of BCAAC was studied in air with a Derivatograph Q 1500 using 300 mg of sample at the heating rate of 5°C min^{-1} .

Catalytic activity

Copper–chromium oxide catalysts were prepared by heating BCAAC in air at 220 and 250°C for 1/2, 1 and 2 h, respectively.

The catalyzed, hydrogenation–alkylation reaction of *p*-aminodiphenylamine with acetone was performed as described in ref. 7.

The standard was prepared by heating BCAC in air at 270°C for 1 h.

RESULTS AND DISCUSSION

BCAC, which is a solid solution characterized by the formula $[(\text{Cu}^{2+})_{1+x}(\text{NH}_4^+)_y(\text{OH}^-)_{2x+y}(\text{NH}_3)_z(\text{CrO}_4^{2-})]$ ($0 < x < 0.3$, $0.6 < y < 0.9$, $0 < z < 0.2$) [5], reacts readily with ammonia in an exothermic reaction. In the IR spectra this process is manifested by the significant increase of the weak bending vibration bands of ammonia coordinated to Cu(II) at 1630 cm^{-1} and at 1250 cm^{-1} (Fig. 1a, b). A shift of the later band from 1272 cm^{-1} in BCAC to 1250 cm^{-1} in the obtained product is observed. Simultaneously the amount of NH_4^+ and OH^- groups is reduced. The intensity of the strong absorption of NH_4^+ at 1406 cm^{-1} decreases to nearly zero. The valence OH vibration band at 3460 cm^{-1} is also strongly reduced. The above data indicate that in the course of the BCAC reaction with ammonia NH_3 molecules substitute for oxygen and hydroxyl bridging groups bound to Cu(II) and a Cu(II)–ammonia complex is formed. For a description of this process, the reaction of the liberated OH^- groups with NH_4^+ and a release of water molecule must be assumed. Finally the BCAC structure is transformed and a quite new diffraction pattern is developed. The obtained product, basic copper(II)–ammine ammonium chromate (BCAAC), can be characterized by the same formula as BCAC: $[(\text{Cu}^{2+})_{1+x}(\text{NH}_4^+)_y(\text{OH}^-)_{2x+y}(\text{NH}_3)_z(\text{CrO}_4^{2-})]$. However, the values of y and z coefficients for both compounds are very different (x is related to the Cu:Cr ratio, which does not change in this reaction). Since in BCAAC only a small amount of NH_4^+ was detected, y approaches zero. According to visible and EPR spectra (see below) tetraammine copper(II) complex is formed in BCAAC; thus a z value approaching four can be expected.

The above reaction proceeds very quickly in ammonia vapour, as well as in aqueous ammonia or in an aqueous ammonia–acetone mixture. On the other hand, it is reversible under suitable conditions and it can be written

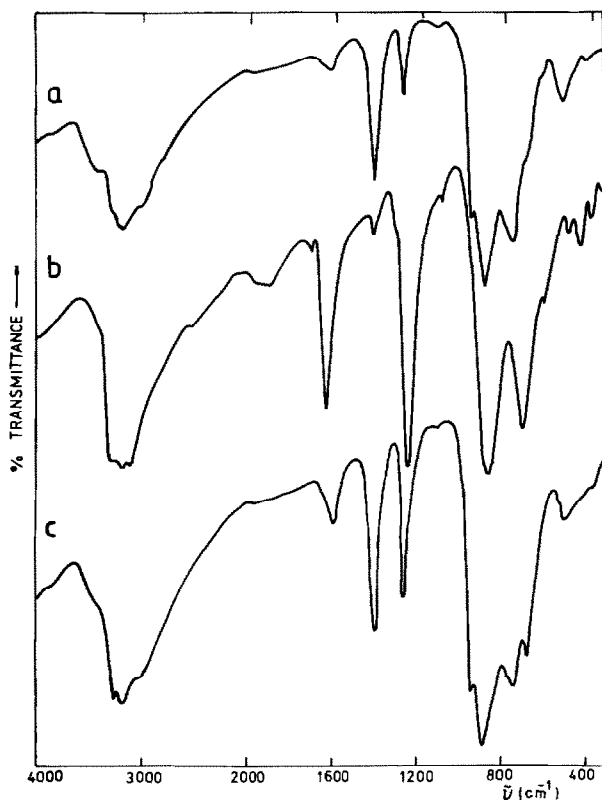


Fig. 1. IR spectra of (a) BCAC, (b) BCAAC, (c) BCAC obtained by decomposition of BCAAC at room temperature.

schematically as



In open air at room temperature, BCAAC is converted back to BCAC within some hours. The original diffraction pattern of BCAC is restored; only small shifts in the positions of some diffractions indicate small modifications in the BCAC solid solution structure. In the IR spectra after the NH_3 desorption intense NH_4^+ and weak NH_3 bands are observed (Fig. 1c). These bands, however, do not return to their original intensity, indicating that the coefficient z in BCAC so obtained is somewhat higher and y is somewhat lower than in the starting BCAC substance. Since for the formation of NH_4^+ and OH^- in BCAC a water molecule is needed, the presence of moisture in the media is necessary for this reaction. Therefore the transformation of BCAAC to BCAC does not occur in dry atmosphere. It is remarkable that BCAAC is stable even in vacuo at room temperature.

The analytical data of BCAAC differ slightly from sample to sample. The value of $z = 3.3$ in a typical case indicates that ammonia was partly

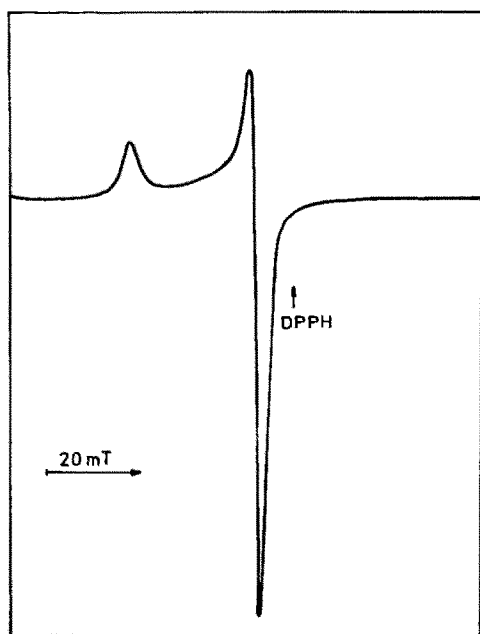


Fig. 2. EPR spectrum of BCAAC.

desorbed from the investigated sample, probably during the manipulations in open air. The results of physical measurements, however, do not give any evidence for the inhomogeneity of the BCAAC products. They allow us to assume that BCAAC has the character of a solid solution, where the coefficients x , y and z vary in the approximate intervals $0 < x < 0.3$, $0 < y < 0.2$ and $3 < z < 4$.

The assymmetric $d-d$ absorption band in the electronic spectra, which shows a maximum at $13\,200\text{ cm}^{-1}$ in BCAC [5], is shifted to $17\,800\text{ cm}^{-1}$ in BCAAC. It indicates a change from tetragonal-bipyramidal Cu(II) coordination by oxygen atoms to a tetragonal coordination by four ammonia molecules.

In contrast to BCAC which, as a consequence of Cu(II)–Cu(II) superexchange interactions via oxygen atoms, is practically EPR silent, the coordinated ammonia molecules cancel this interaction in the BCAAC structure. BCAAC shows a sharp axial EPR spectrum (Fig. 2) with the parameters $g_{\parallel} = 2.222$ and $g_{\perp} = 2.049$. These g factors are consistent with tetragonal $[\text{Cu}(\text{NH}_3)_4]^{2+}$ complex cation in the structure [9]. The value of $G(g_{\parallel} - 2.002)/(g_{\perp} - 2.002) = 4.7$, together with the sharp lines, indicate ferrodistorptive ordering, where the tetragonal axes of the $[\text{Cu}(\text{NH}_3)_4]^{2+}$ units are oriented parallel.

The thermal decomposition of BCAAC starts with two endothermic reactions at 130 and 180°C , which correspond to desorption of ammonia (Fig. 3). They are followed by an intense exothermic reaction at ca. 205°C .

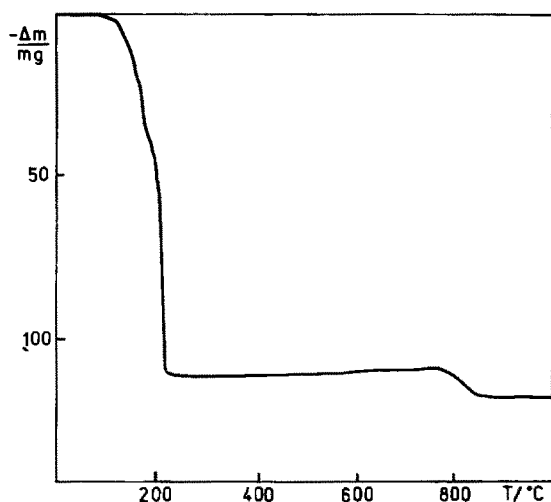
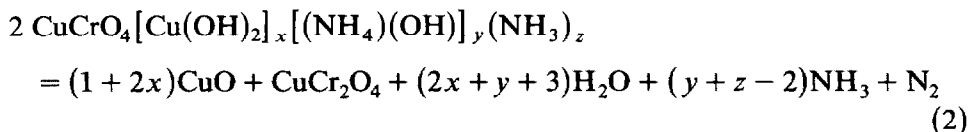


Fig. 3. TG curve for the thermal decomposition of BCAAC (using 307.2 mg of sample).

In some experiments the violent ignition even partially blew the finely powdered sample out of the crucible. In this reaction step, reduction of Cr(VI) to Cr(III) and oxidation of ammonia to N_2 proceeds. Similar results were reported for the thermal decomposition of tetraammine copper(II) chromate [8]. The sum of the above processes can be described by the scheme



For the BCAAC sample with values of $x = 0.1$, $y = 0.2$ and $z = 3.3$, we observed a weight loss of 35.9 wt.% (calc. 35.2 wt.%). The product of the thermal decomposition is a highly disordered system, for which diffuse diffractions at $2\theta = 31.5^\circ$ and 36.5° can be clearly identified (Fig. 4a). The term "protospinel" was introduced for such intermediates in the process of CuCr_2O_4 spinel formation [10]. For "protospinel" obtained as a product of the thermal decomposition of BCAC at 270°C , a different structure with very broad diffractions in the ranges $2\theta = 30\text{--}39^\circ$ and $40\text{--}48^\circ$ has been observed [7]. The absence of CuO diffractions can be explained in both cases by dissolution of CuO in the "protospinel" solid solution [10].

At higher temperatures (about $450\text{--}500^\circ\text{C}$) a recrystallization under formation of crystalline CuCr_2O_4 and CuO proceeds (Fig. 4b). The indexing of the diffraction pattern of the CuCr_2O_4 component of this system led to the parameters of the orthorhombic unit cell, $a = 0.593$ nm, $b = 0.603$ nm, $c = 0.779$ nm (Table 1). This structure is distorted from the usually observed tetragonal CuCr_2O_4 spinel ($a = b = 0.6033$ nm and $c = 0.7788$ nm [11]) in

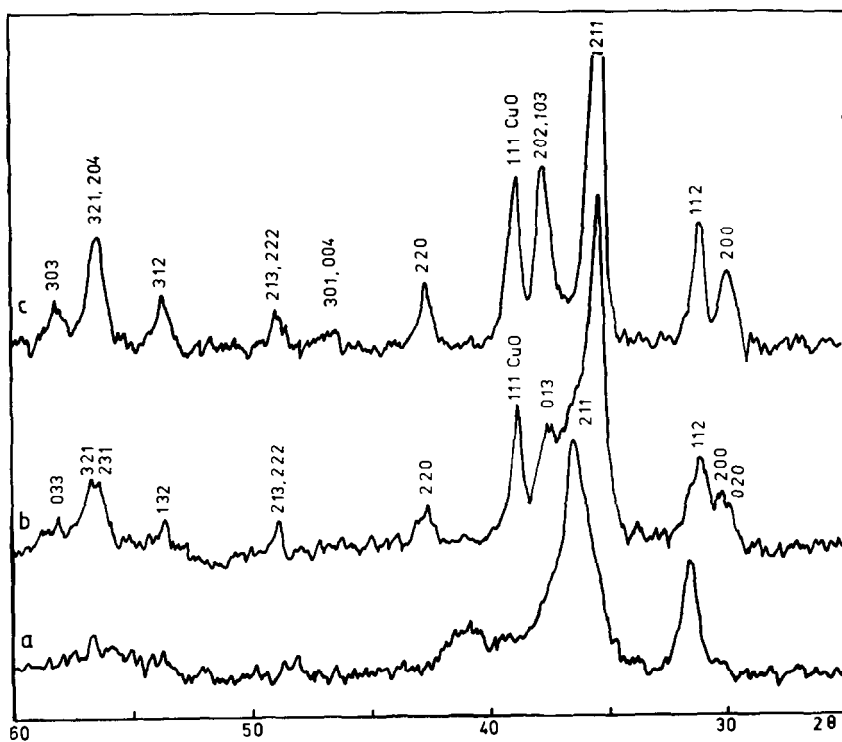


Fig. 4. X-Ray diffraction pattern of (a) BCAAC decomposed at 200 °C, (b) BCAAC decomposed at 500 °C (indices are for CuCr_2O_4 except (111) for CuO), (c) CuCrO_4 decomposed at 490 °C (indices are for CuCr_2O_4 except (111) for CuO).

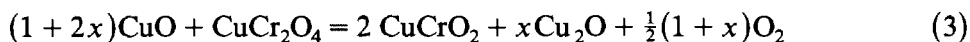
TABLE 1

Observed and calculated d_{hkl} values of diffractions h , k , l of CuCr_2O_4 in the system prepared from BCAAC at 500 °C (orthorhombic symmetry, $a = 0.593$ nm, $b = 0.603$ nm; $c = 0.779$ nm, $V = 0.2786$ nm³)

$(h \ k \ l)$	$d_{\text{obs.}}$ (nm)	$d_{\text{calc.}}$ (nm)
1 0 1	0.4710	0.4718
2 0 0	0.2948	0.2965
1 1 2	0.2858	0.2865
2 1 1	0.2518	0.2518
0 1 3	0.2388	0.2385
2 2 0	0.2117	0.2114
2 2 2	0.1859	0.1858
2 1 3	0.1859	0.1858
1 3 2	0.1706	0.1710
2 3 1	0.1628	0.1627
3 2 1	0.1619	0.1617
0 3 3	0.1584	0.1589

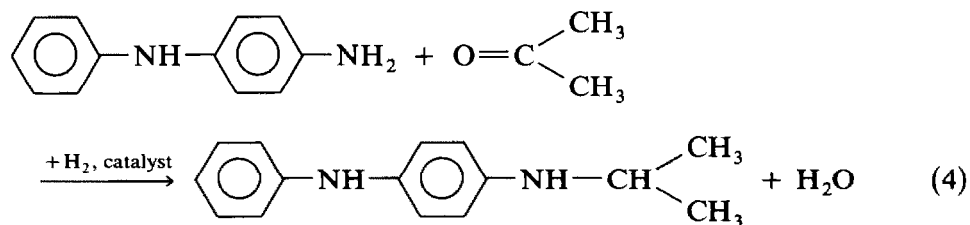
such a way that the parameter a is slightly reduced. Copper–chromium oxide catalyst, which contains CuO and CuCr_2O_4 with the orthorhombic unit cell ($a = 0.594$ nm, $b = 0.603$ nm, $c = 0.794$ nm) has been obtained in the process of the thermal decomposition of BCAC at 490°C [12]. It is remarkable that all observed modifications of CuCr_2O_4 show changes in a and c , but b remains constant. In both cases, the orthorhombic CuCr_2O_4 was transformed to the tetragonal form after heating at 650°C . The observed orthorhombic distortion is probably caused by the fact that a part of Cu(II) is distributed in octahedral and a part of Cr(III) in tetrahedral sites [11,13]. The spinel structure involves then two crystallographically distinct octahedral (and one tetrahedral) sites. The results obtained allow us to conclude that metastable orthorhombic modifications of CuCr_2O_4 arise in the process of thermal decomposition of “protospinel”. The thermal decomposition of CuCrO_4 , where no “protospinel” was observed as an intermediate product [6,7], leads at 500°C directly to a system containing CuO and tetragonal CuCr_2O_4 with the usual parameters (Fig. 4c). However, it is possible that the different $\text{Cu}:\text{Cr}$ ratios in the investigated samples play a certain role in the formation of various CuCr_2O_4 modifications.

At 820°C , an endothermic reduction Cu(II) to Cu(I) proceeds. It can be described by the scheme [5]



We observed a weight loss of 2.7 wt.% (calc. 3.5 wt.%). The product of the reaction showed the diffraction pattern of CuCrO_2 .

The decomposition products at 220 and 250°C (according to eqn. 2), were investigated for their catalytic activity in hydrogenation-alkylation reaction of *p*-aminodiphenylamine with acetone. The desired product here is *N*-phenyl-*N'*-isopropyl-*p*-phenylenediamine (AOCD), an important industrial antioxidant:



The results are summarized in Table 2. All samples show catalytic activity. However, it is lower than the activity of the standard prepared by thermal decomposition of BCAC at 270°C . In all cases the catalyzed reaction led to products with a smaller content of the desired AOCD and a greater content of unreacted *p*-aminodiphenylamine (ADPH), as well as of the intermediate non-hydrogenated product (Schiff base SB). It has been shown [7] that the catalyst prepared from BCAC at 270°C , at a temperature only slightly over

TABLE 2

Decomposition temperature, time of BCAAC heating and composition of the reaction product in catalyzed reaction

Temperature (°C)	Time (h)	Composition of the reaction products (wt.%)		
		ADPH ^a	SB ^b	AOCD ^c
220	0.5	39.0	39.3	21.4
220	1	38.4	37.8	23.5
220	2	35.8	41.8	22.0
250	0.5	35.8	38.6	25.3
250	1	35.3	38.1	26.2
250	2	36.6	38.8	24.2
Standard ^d		15.9	12.3	71.6

^a *p*-Aminodiphenylamine (starting substance).

^b Schiff base (intermediate product).

^c *N*-Phenyl-*N'*-isopropyl-*p*-phenylenediamine (desired product).

^d Prepared from BCAC (270°C, 1 h).

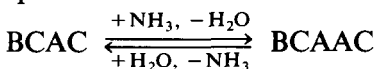
the threshold of the oxidation–reduction decomposition reaction, shows the highest catalytic activity. It decreases with increasing heating temperature. Thus, the assumption that catalysts with higher activity can be prepared by the thermal decomposition of copper(II) chromates with coordinated ammonia, where the threshold of the oxidation–reduction decomposition is shifted to lower temperature, was not confirmed by our measurements. In contrast, the increase of the BCAAC decomposition temperature from 220°C to 250°C leads to catalysts with slightly higher activities.

In the series of catalysts prepared at 220°C the best yield of the desired product AOCD was obtained with the sample heated for 1 h (Table 2). The catalysts heated for $\frac{1}{2}$ and 2 h, respectively, gave higher amounts of the non-hydrogenated intermediate product SB. No significant differences between the XRD patterns of the above catalysts were observed. The effects of the heating time were remarkably less pronounced in the series of the samples prepared at 250°C.

CONCLUSIONS

Ammonia readily enters into the crystal structure of BCAC, and $[\text{Cu}(\text{NH}_3)_4]^{2+}$ complex cations are formed in the obtained product BCAAC. During the chemisorption reaction the greatest part of NH_4^+ and OH^- groups is removed. We suppose that they are converted to NH_3 and H_2O . Although the composition of BCAC and BCAAC can be expressed by the same formula $[(\text{Cu}^{2+})_{1+x}(\text{NH}_4^+)_y(\text{OH}^-)_{2x+y}(\text{NH}_3)_z(\text{CrO}_4^{2-})]$, the ranges for y and z coefficients for stable BCAC and BCAAC solid solutions are significantly different. Their crystal and molecular structures also differ. The

above reaction is reversible at room temperature in the presence of atmospheric moisture and can be written schematically as



In the course of BCAAC thermal decomposition, ammonia is desorbed and at ca. 205 °C an explosive oxidation–reduction reaction leads to copper–chromium oxide catalyst with a highly disordered structure of “protospinel” containing dissolved CuO. Such systems lead after recrystallization at 500 °C to crystalline CuO and a CuCr₂O₄ with the unit cell of orthorhombic symmetry. Tetragonal CuCr₂O₄ is obtained after heating to 650 °C. However, the activity of the copper–chromium oxide catalysts in hydrogenation–alkylation reactions are lower than the activity of those prepared from BCAC at 270 °C.

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