Thermochimica Acta, 198 (1992) 61–70
Elsevier Science Publishers B.V., Amsterdam

Non-linear compositional dependence of the thermal stability of copper–cobalt hydroxide nitrates

N. Zotov [a], K. Petrov [b] and S. Hrisov [a]

[a] *Institute of Applied Mineralogy, Bulgarian Academy of Sciences, Rakovski Street 92, Sofia 1000 (Bulgaria)*
[b] *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia 1113 (Bulgaria)*

(Received 12 August 1991)

Abstract

A study of the thermal decomposition of $Cu_xCo_{2-x}(OH)_3NO_3$ solid solutions, $0.0 \leq x \leq 2.0$, was performed by differential thermal analysis, thermogravimetric analysis and differential scanning calorimetry under non-isothermal conditions. It was found that the onset temperature, the endothermic peak temperature and the enthalpy of decomposition increase non-linearly with x. Kinetic analysis of the thermal decomposition was also made by the Flynn and Wall, Kissinger and Takhor methods. The values of the activation energy determined by the three methods are very close and also indicate non-linear dependence of the thermal stability on composition. It is suggested that the behaviour of the investigated thermodynamic and kinetic parameters is related to the variation of the strength of the hydrogen bonds in the structure and the polarisation ability of the cations.

INTRODUCTION

Layered copper–cobalt hydroxide nitrates, along with other solid solutions of the same structural type, are commonly used as precursor compounds for the synthesis of active metal oxides with interesting properties. However, data on their thermal behaviour are very scarce. The thermal decomposition of the end members, $Cu_2(OH)_3NO_3$ and $Co_2(OH)_3NO_3$, has been investigated by several authors [1–5]. Recently, Petrov et al. [6] have carried out systematic investigation of the effect of composition on the lattice parameters and the thermal behaviour of copper(II)–cobalt(II) hydroxide nitrate solid solutions, $Cu_xCo_{2-x}(OH)_3NO_3$, over the whole compositional range $0.0 \leq x \leq 2.0$. Their results have shown that the decomposition of the solid solutions is a complex process consisting of several stages, the sequence being determined by the composition of the samples.

Correspondence to: N. Zotov, Institute of Applied Mineralogy, Bulgarian Academy of Sciences, Rakovski Street 92, Sofia 1000, Bulgaria.

However, they concentrated their attention on the high-temperature decomposition stages.

In the present paper we report the systematic investigation of the low-temperature stage of the decomposition process.

EXPERIMENTAL

Sample preparation

Solid solutions $Cu_xCo_{2-x}(OH)_3NO_3$, where $0.0 \leq x \leq 2.0$, were prepared by rapid co-precipitation. Sodium hydroxide and copper(II) nitrate solutions of preset concentrations were added simultaneously and at the same rate to a boiling solution of cobalt(II) nitrate. The process finished when the atomic ratio $[OH]^-/Me^{2+}$ in the system reached a value of 1.3. The precipitates were filtered and washed with distilled water and ethanol, and dried at 60°C for 48 h. A more detailed description of the preparation procedure was published elsewhere [5]. Eleven $Cu_xCo_{2-x}(OH)_3NO_3$ samples were synthesised, where $x = 0.00$, 0.19 ± 0.03, 0.29 ± 0.03, 0.34 ± 0.02, 0.40 ± 0.02, 0.51 ± 0.02, 0.88 ± 0.05, 1.13 ± 0.05, 1.34 ± 0.03, 1.62 ± 0.01 and 2.00. The copper and cobalt contents were determined by atomic absorption spectroscopy as well as by an appropriate combination of complexometric and iodometric methods; the results obtained were averaged. The molar content of the nitrate groups per formula unit, determined by the method of Dewarda, was practically independent of x and equal to 1.01 ± 0.02.

Thermal analysis

Two independent series of DTA measurements were made using a Stanton STA 781 apparatus. Small amounts of the samples (about 15 mg) were used for each run, using α-Al_2O_3 as a reference material. The measurements were performed in an atmosphere of static air in the temperature range from 25 to 350°C at a heating rate of 10°C min^{-1}, in platinum crucibles. A separate series of experiments was performed using a Stanton DSC 1500 apparatus in a flow of dry nitrogen (45 ml min^{-1}) at a heating rate of 10°C min^{-1} in order to diminish the self-cooling effects. Additional DSC and temperature calibrations were made by measuring the heats of melting of In, Pb, Sn and Zn standards. Decomposition kinetics measurements under non-isothermal conditions were carried out at four different heating rates (10, 20, 30 and 40°C min^{-1}) in static air. In this case in particular, the samples were also compressed in order to improve their thermal contact with the platinum cruicible and to standardise the conditions for diffusion of the gaseous products of the reaction. The results were analysed by the computer program TRACE [7].

RESULTS AND DISCUSSION

The TG and DTA curves of all the investigated samples are quite similar. They show only one endothermic peak in the temperature range from 200 to 350°C [6]. Typical DTA and TG curves for the composition $x = 0.0$ are shown in Fig. 1.

Thermogravimetric analysis

The proposed decomposition reactions for each composition, represented by the corresponding eqns. (1)–(4) below are presented in Table 1. A monophase or two-phase mixture of metal oxides is obtained as a result of the decomposition, depending on the composition, x.

(a) $x = 0$

$$3Co_2(OH)_3NO_3 \rightarrow 2Co_3O_4 + 4.5H_2O + NO + 2NO_2 + 0.5O \tag{1}$$

The only solid product is the cobalt spinel phase Co_3O_4.

(b) $0.0 \leq x \leq 2/3$

$$3Cu_xCo_{2-x}(OH)_3NO_3 \rightarrow 2Cu_yCo_{3-y}O_4 + 4.5H_2O + NO + 2NO_2 + 0.5O \tag{2}$$

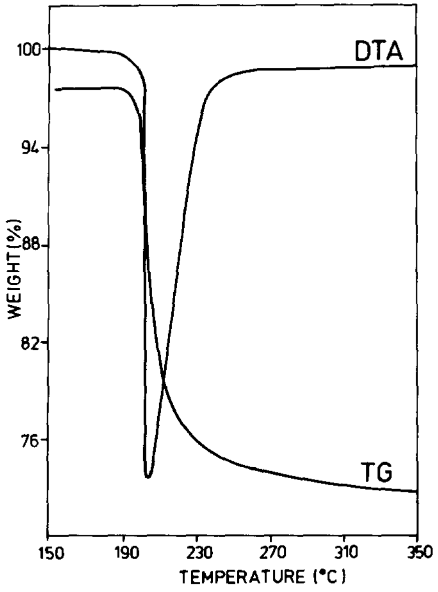

Fig. 1. DTA and TG curves for $Co_2(OH)_3NO_3$.

TABLE 1

Thermogravimetric data

Composition (x)	Weight losses (%)			Reaction type [a]
	Obs.	Calc.	Δ	
0.00	29.0	30.5	1.5	1
0.19	26.0	30.4	4.4	2
0.29	25.8	30.3	4.5	2
0.34	26.3	30.3	4.0	2
0.40	26.7	30.2	3.5	2
0.51	27.2	30.2	3.0	2
0.88	28.8	30.8	2.0	3
1.13	29.6	31.4	1.8	3
1.34	30.4	32.0	1.6	3
1.62	31.8	32.7	0.9	3
2.00	32.8	33.7	0.9	4

[a] The reaction types correspond to eqns. (1)–(4) in the text.

The only solid product is a mixed copper–cobalt spinel phase $Cu_yCo_{3-y}O_4$, where $0 < y = 3x/2 \leq 1.0$.

(c) $2/3 < x < 2.0$

$$2Cu_xCo_{2-x}(OH)_3NO_3 \rightarrow (2-x)CuCo_2O_4 + (3x-2)CuO + 3H_2O + (2-x)NO_2 + xNO_2 + 0.5O_2 \quad (3)$$

In contrast with case (b), the solid products of the reaction are $CuCo_2O_4$ and CuO oxides.

(d) $x = 2.0$

$$2Cu_2(OH)_3NO_3 \rightarrow 4CuO + 3H_2O + 2NO_2 + 0.5O_2 \quad (4)$$

The weight losses calculated on the basis of eqns. (1)–(4) are slightly lower than the observed ones, the differences decreasing with increasing copper content x (Table 1). This can be explained by the fact that the observed weight losses are determined in the temperature range from the beginning to the end of the DTA peak. However, for temperatures greater than the terminal temperature T_e, an additional small loss of weight is observed (Fig. 1) which is not accompanied by any thermal effect. This is due to the slow desorption of the gaseous products from the finely dispersed spinel phases as well as to the fact that the oxides of cobalt, prepared at low temperatures, are non-stoichiometric compounds containing an excess of oxygen. This extra oxygen is released slowly at higher temperatures [8,9]. That is why the differences between the observed and calculated weight losses decrease with decreasing the relative amounts of cobalt.

TABLE 2

Thermoanalytical and kinetic data for $Cu_2(OH)_3NO_3$

Ref.	T_O (°C)	T_P (°C)	T_e (°C)	ΔH_d [a] (kcal mol^{-1})	E [a] (kcal mol^{-1})
2	240	285	310	33.47	32.85
3	205	290	400	–	43.2
4	160	–	210	41.17	–
5	–	270	–	–	–
This study	244	262	310	40.3	40.1

[a] The enthalpy of decomposition and the activation energies are given in kcal mol^{-1} for direct comparison with previously published data.

DTA and calorimetric analysis

The low-temperature endothermic peaks are narrow and no splitting is observed for all compositions investigated. This confirms the conclusions made on the basis of X-ray diffraction [10] and IR spectroscopy [11] studies that the investigated copper–cobalt hydroxide nitrates form homogeneous solid solutions.

The results obtained for the pure copper hydroxide nitrate are generally compatible with the data published by other authors (Table 2). The differences are, most probably, connected with the different DTA/TG apparatus and sample loadings used.

The DTA and calorimetric results for all investigated compositions are given in Table 3. The onset (T_O) and peak (T_P) temperatures, determined by the DSC and DTA measurements, are practically identical within

TABLE 3

DTA and calorimetric results

x	T_O (°C)		T_P (°C)			ΔH_d (kcal mol^{-1})
	DSC	DTA [b]	DTA [a]	DTA [b]	DSC	
0.00	200	198	206	206	213	22.2
0.19	207	209	211	208	216	23.2
0.29	214	–	226	–	220	25.6
0.34	224	224	237	236	227	33.1
0.40	234	232	239	240	237	30.6
0.51	237	242	250	–	241	37.4
0.88	253	–	258	–	264	42.8
1.13	250	–	258	257	257	42.6
1.34	249	–	258	–	255	42.1
1.62	238	–	258	255	247	44.0
2.00	244	–	264	262	255	40.3

[a] First series of measurements [6].

[b] Present series of measurements.

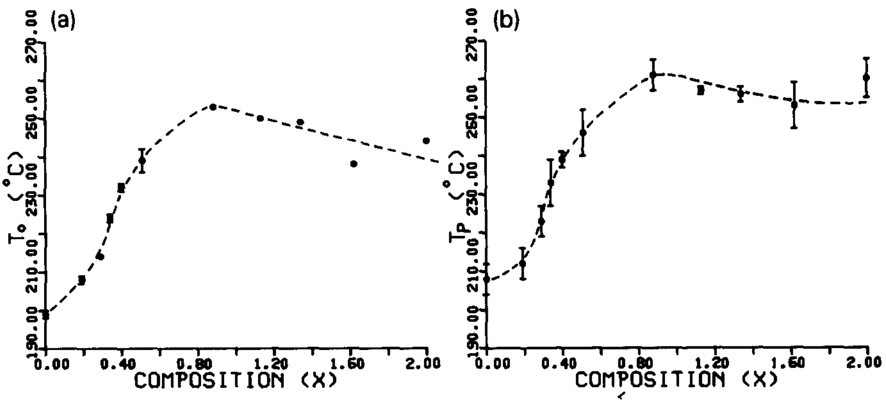

Fig. 2. (a) Dependence of the onset temperature T_O versus the copper content x. (b) Dependence of the peak temperature T_P versus the copper content x.

experimental error limits. The dependences of the onset temperature and the peak temperature as a function of the composition x are given in Fig. 2. As can be seen from Fig. 2, both T_O and T_P increase with increasing x in the compositional range $0.0 \leq x \leq 1.0$. Therefore we may conclude that the thermal stability of the investigated compounds increases with increasing copper content for $x \leq 1.0$ and remains practically unchanged for $x \geq 1.0$.

In order to examine this effect further, Fig. 3 shows the enthalpy of decomposition ΔH_O, plotted as a function of x. The form of the curve is similar to that of $T_O(x)$ and $T_P(x)$.

The observed non-linear thermal stability of the copper–cobalt hydroxide nitrates as a function of the composition x can be associated with the structural peculiarities of the investigated solid solutions. The pure copper hydroxide nitrate has a layered structure, consisting of two-dimensional octahedral layers, which are held together by hydrogen bonds [12]. The X-ray diffraction studies of Feitknecht et al. [13] and Zotov and Petrov [10] have shown that the copper–cobalt solid solutions also have the same type of structure. The substitution of cobalt for copper in this system leads to a

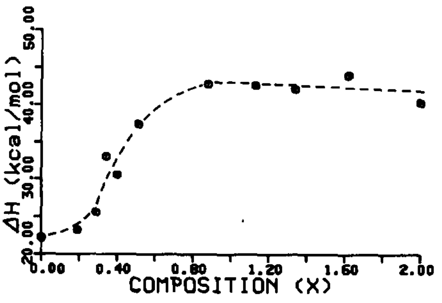

Fig. 3. Dependence of the enthalpy of decomposition ΔH versus the copper content x.

change in the strength of the hydrogen bonds and the polarisation of the nitrate groups [11]. The strength of the hydrogen bonds, as determined by the shift $\Delta\nu$(OH) of the OH streching vibrations, have the same dependence on x as $T_O(x)$ and $T_P(x)$. This is direct evidence for the influence of the strength of the hydrogen bonds on the thermal stability in the compositional range $0.0 < x < 1.0$. It has also been established that the polarisation of the nitrate groups increases for $x < 1.0$. Taking into account that the polarisation ability of the cation influences strongly the thermal stability of other salts (formates, oxalates, perchlorates, etc. [14]) of divalent transition metals, we may assume that the change in the polarisation ability of the cations with composition is also responsible for the observed compositional dependence of the thermal stability of the investigated solid solutions.

Decomposition kinetics

It is generally assumed that an increase in the activation energy shifts the beginning of the decomposition process to higher temperatures [15]. Therefore, on the basis of the compositional dependence of the onset temperature (Fig. 2), one can expect that the activation energy E will increase with increasing copper content in the compositional range $0.0 \leq x \leq 1.0$. In order to verify this suggestion we carried out a non-isothermal decomposition kinetic study.

In the present paper, we have used three different methods which are based on the employment of multiple heating rates — the thermogravimetric method of Flynn and Wall (FW) [16], the method of Takhor [17], based on plotting $\ln Q$ verus $1/T_P$, where Q is the heating rate, and the analogous method of Kissinger [18] in which $\ln(Q/T_P^2)$ is plotted versus $1/T_P$. These latter two methods should yield a straight line with a slope

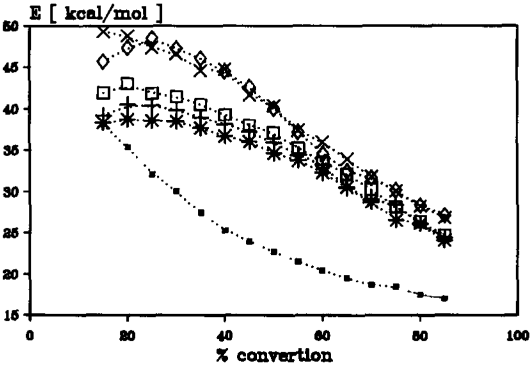

Fig. 4. Dependence of the activation energy E, determined by the method of Flynn and Wall [16], versus the degree of decomposition for different compositions: ■, $x = 0.00$; *, $x = 0.19$; +, $x = 0.34$; □, $x = 0.40$; ×, $x = 0.51$; ◇, $x = 2.0$.

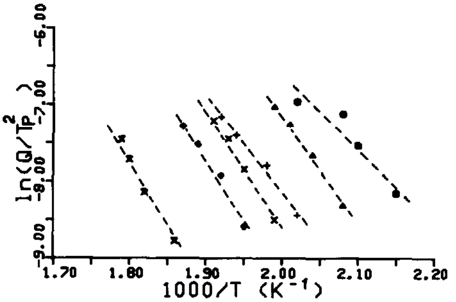

Fig. 5. Variation of $\ln(Q/T_P^2)$ versus $1/T$ for different compositions: ○, $x = 0.00$; △, $x = 0.19$; +, $x = 0.34$; ×, $x = 0.40$; ◆, $x = 0.51$; $\overline{\times}$, $x = 2.00$.

equal to E/R. A temperature range (T_O − 10°C, T_e + 10°C) was used in the FW method. The actual heating rates of the samples (10.7, 22.3, 35.3 and 46.7°C min^{-1}) were determined by averaging the derivative dT/dt in the same temperature range.

The Arrhenius plot based on the Kissinger method has the characteristic fan-like shape (Fig. 5). The scattering of the data points is greater only for the composition $x = 0.0$.

The values of the activation energy determined by the FW method depend on the degree of decomposition (Fig. 4). This indicates that the decomposition process cannot be described with one and the same equation over the whole temperature range. In order to obtain self-consistent results we have averaged for each composition, the activation energies corresponding to a degree of conversion α from 45% to 60%, because the peak temperatures determined at different heating rates fall just within this range of α values.

The activation energies calculated by the three methods and the pre-exponential factors, ln A, calculated by the FW method, are given in Table 4. It is interesting to note that the standard deviations for compositions with

TABLE 4

Decomposition kinetics data

x	Activation energy (kcal mol^{-1})			Average activation energy (kcal mol^{-1})	ln A (s^{-1})
	Takhor	Kissinger	Flynn and Wall		
0.00	23.1 ± 5	21.2 ± 5	22.2 ± 2	22.2 ± 1.0	28.5 ± 2
0.19	33.9 ± 1	31.9 ± 2	35.2 ± 2	33.7 ± 1.5	41.4 ± 2
0.34	33.3 ± 1	31.3 ± 2	34.2 ± 2	32.9 ± 1.5	39.1 ± 2
0.40	35.2 ± 2	33.2 ± 2	36.0 ± 2	34.8 ± 1.4	40.6 ± 2
0.51	37.6 ± 3	36.6 ± 2	38.9 ± 3	37.7 ± 1.2	43.2 ± 4
2.00	42.0 ± 4	39.8 ± 5	38.6 ± 4	40.1 ± 1.7	41.2 ± 4

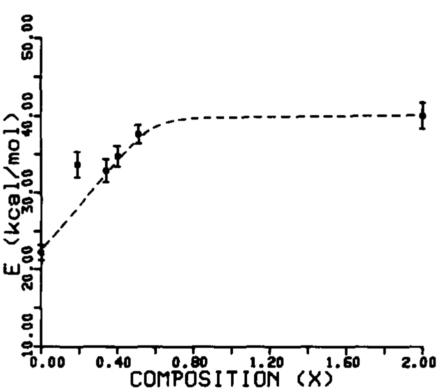

Fig. 6. Dependence of the average values of the activation energy E versus the copper content x.

$0.19 \leq x \leq 0.51$ are considerably lower than those for the two end members. This is most probably connected with the different reaction mechanisms involved. Nevertheless, the three estimates coincide within error limits. Therefore, Fig. 6 shows the average values of the three methods for the activation energy plotted as a function of the composition x. It should also be noted that the value of E for the pure copper hydroxide nitrate is in good agreement with those published previously (Table 2).

It is evident from Fig. 6 that the activation energy increases, although non-linearly, with increasing x. This substantiates our suggestion that the activation energy would increase when passing from the pure cobalt to the pure copper hydroxide nitrate. However, the extrapolated value of the activation energy of $Cu_2(OH)_3NO_3$, $E = 82$ kcal mol^{-1}, estimated from the slope of the line through the points with $x \leq 2/3$, is much higher than the experimentally obtained value. This is further confirmation of the already established effect of the non-linear compositional dependence of the thermal stability of the investigated compounds.

CONCLUSIONS

The thermoanalytical investigation of the mixed copper–cobalt hydroxide nitrates $Cu_xCo_{2-x}(OH)_3NO_3$, where $0.0 \leq x \leq 2.0$, has shown that their thermal decomposition is a complex process. The most curious and important feature is the non-linear dependence of the thermal stability of the solid solutions on the composition. This effect is inferred from the variation of the onset temperature, the peak temperature, the enthalpy of decomposition and the activation energy, with the copper content x; this can be associated with the change in the polarisation of the nitrate groups and the strength of the hydrogen bonds between the adjacent $[M_2(OH)_3ONO_2]$ layers in the structure.

REFERENCES

1 F. Boullon and A. Wafelaer, Bull. Soc. Chem. Belg., 65 (1955) 386.
2 P. Ramamurthy and E.A. Secco, Can. J. Chem., 65 (1970) 3510.
3 L. Ilcheva, M. Maneva and P. Bozadziev, J. Therm. Anal., 16 (1979) 305.
4 J.P. Auffredic, D. Louer and M. Louer, J. Therm. Anal., 16 (1979) 329.
5 L. Markov, K. Petrov and R. Joncheva, Russ. J. Inorg. Chem., 30 (1985) 3023.
6 K. Petrov, N. Zotov, O. Garcia-Martinez, P. Millan and R.M. Rojas, React. Solids, 7 (1989) 359.
7 Program TRACE 2, V4.2, Jan. 1989 Stanton Redcroft Ltd., Copper Mill Lane, London, UK.
8 L.R. Le Coustumier, A. d'Huysser, J.-P. Bonnelle, C.R. Acad. Sci. Paris Ser. C, 278 (1974) 989.
9 L.R. Le Coustumier, J.-P. Bonnelle and L.R. Beaufier, J. Chim. Phys. Phys. Chim. Biol., 72 (1975) 756.
10 N. Zotov and K. Petrov, Z. Kristallorgr., 190 (1990) 235.
11 N. Zotov, K. Petrov and M. Dimitrova-Pankova, J. Phys. Chem. Solids, 51 (1990) 1199.
12 H. Effenberger, Z. Kristallorgr., 165 (1983) 127.
13 W. Feitknecht, A. Kummer and J.W. Feitknecht, Proc. Int. Congr. Pure Appl. Chem., Paris, 1957, p. 243.
14 V.V. Boldirev, Influence of Defects in Crystals on the Rate of Thermal Decomposition of Solids, Tomsk Univ., Tomsk, 1963, in Russian.
15 J. Sestak, Thermophysical Properties of Solids. Their Measurement and Theoretical Thermal Analysis, Academia, Prague, 1984.
16 J.H. Flynn and L.A. Wall, Polym. Lett., 4 (1966) 323.
17 R.L. Takhor, in Advances in Nucleation and Crystallization of Glasses, Am. Ceram. Soc., Columbus, 1972, p. 166.
18 H.E. Kissinger, Anal. Chem., 20 (1957) 1702.