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NON-ISOTHERMAL DECOMPOSITION KINETICS OF POLYNUCLEAR COORDINATION COMPOUNDS

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ABSTRACT

Results concerning the thermal stability and decomposition kinetics of four polynuclear coordination compounds are presented.

INTRODUCTION

In the last two decades polynuclear coordination compounds (PCC) have become particularly interesting in connection with the synthesis of double oxides [1]. Indeed by a convenient choice of the cations and ligands one can obtain PCCs whose thermal decomposition leads either to a mixture of oxides, or directly to the double oxide. This paper presents results concerning the thermal kinetic stability of some PCCs generating, through thermal decomposition and subsequent heating, double oxides of spinelic ferrite type.

EXPERIMENTAL

The following PCCs were used, synthesised and characterized by previously described methods [2]: $(NH_4)_8[MgFe_2(C_2O_4)_8] \cdot 4(NH_4)_2C_2O_4$; $(NH_4)_8[MgFe_2(C_2O_4)_8]$; $(NH_4)_2[MgFe_2(C_2O_4)_2(OH)_6]$; $(NH_4)_4[MgFe_2(C_2O_4)_4(OH)_4]$.

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The heating curves of the powdered materials were recorded with a Paulik–Paulik–Erdey type derivatograph (MOM Budapest) in air at various heating rates. The decomposition products were characterized by X-ray diffractometry using a Philips P.W. 1140/90 diffractometer with Cu K_α radiation. To obtain values of the kinetic parameters the experimental data were processed by use of the Coats–Redfern [3] method.

RESULTS AND DISCUSSION

The decomposition of $(NH_4)_8[MgFe_2(C_2O_4)_8] \cdot 4(NH_4)_2C_2O_4$

The derivatographic data recorded at 10 K min^{-1} (Fig. 1) indicated the

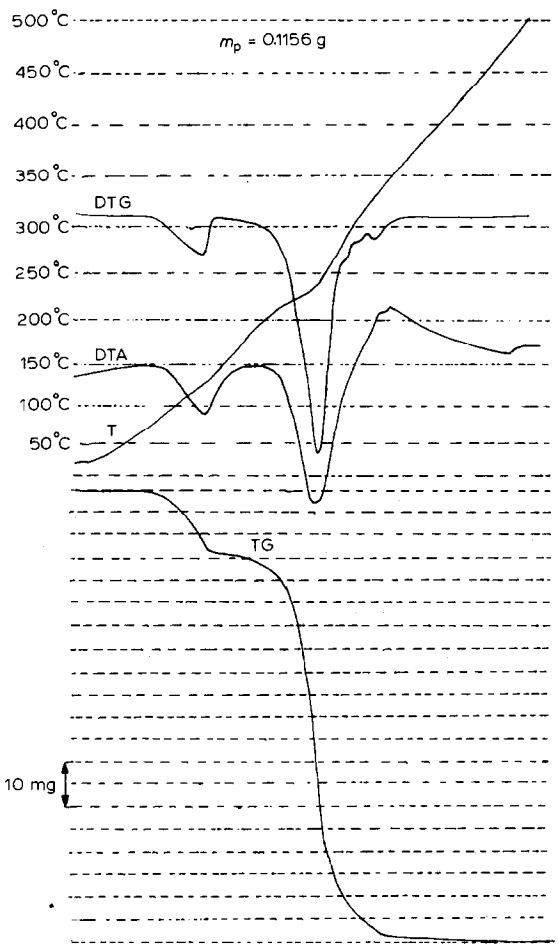

Fig. 1. The derivatogram of $(NH_4)_8[MgFe_2(C_2O_4)_8]\cdot 4\ (NH_4)_2C_2O_4$. m_p is the weight (g) of the powdered material before heating.

following decomposition steps which occur on heating the sample

$$(NH_4)_8[MgFe_2(C_2O_4)_8] \cdot 4(NH_4)_2C_2O_{4(s)} \rightarrow (NH_4)_8[MgFe_2(C_2O_4)_8] \cdot 2.5(NH_4)_2C_2O_{4(s)} + 1.5\ CO_{(g)} + 1.5\ CO_{2(g)} + 1.5\ H_2O_{(g)} + 3\ NH_{3(g)} \quad (I)$$

$$(NH_4)_8[MgFe_2(C_2O_4)_8] \cdot 2.5\ (NH_4)_2C_2O_{4(s)} \rightarrow Fe_2O_{3(s)} + MgO_{(s)} + 13\ NH_{3(g)} + 6.5\ H_2O_{(g)} + 10.5\ CO_{(g)} + 10.5\ CO_{2(g)} \quad (II)$$

Step I occurs with maximum rate at 125 °C, which could be considered as the reaction temperature. As far as step II is concerned its maximum rate occurs at 230 °C. Although not elementary, step I behaves like a unique reaction as shown by the DTA and DTG curves which exhibit only one peak. The same curves for step II exhibit several secondary peaks indicating a complex process. Therefore, only the kinetic parameters of step I were determined. Their values are given in Table 1. The values obtained for the reaction order, n, show a diffusional mechanism [4]. The pre-exponential factor A is expressed in s^{-1} because we started from the isothermal zero order reaction rate $d\alpha/dt = k$. The constancy of the kinetic parameters by changing the heating rate shows no heat transfer limitation.

The decomposition of $(NH_4)_8[Fe_2Mg(C_2O_4)_8]$

The heating curves of this PCC exhibit two decomposition steps according to the following reactions

$$(NH_4)_8[MgFe_2(C_2O_4)_8]_{(s)} \rightarrow (NH_4)_6[MgFe_2(C_2O_4)_7]_{(s)} + CO_{2(g)} + CO_{(g)} + H_2O_{(g)} + 2\ NH_{3(g)} \quad (III)$$

$$(NH_4)_6[MgFe_2(C_2O_4)_7]_{(s)} \rightarrow MgFe_2O_{4(s)} + 7\ CO_{(g)} + 7\ CO_{2(g)} + 6\ NH_{3(g)} + 3\ H_2O_{(g)} \quad (IV)$$

Step III with the maximum decomposition rate at 115 °C appears as a unique reaction while step IV with the maximum decomposition rate at 224 °C as shown by the DTG and DTA curves is a complex one. The values

TABLE 1

Values of the non-isothermal kinetic parameters of reaction I

β(K min^{-1})	n	E (kcal mol^{-1})	A (s^{-1})
2.4	0	30	6.7×10^{16}
5.5	0	30	1.7×10^{16}
8.1	0	33	5.8×10^{16}

TABLE 2

Values of the non-isothermal kinetic parameters of reaction III

β (K min^{-1})	n	E (kcal mol^{-1})	A (s^{-1})
3.5	1	18	8.3×10^{8}
6.5	1	22	6.6×10^{8}
8.4	1	20	6.0×10^{8}

of the kinetic parameters for step III are listed in Table 2. The kinetic parameters are, in the limit of experimental errors, independent of the heating rate showing no heat transfer limitations. The value of the reaction order shows an important contribution of the kinetic regime, the decomposition being limited by the chemical reaction.

The decomposition of $(NH_4)_2[MgFe_2(C_2O_4)_2(OH)_6]$

The recorded derivatogram shows the following decomposition steps

$$(NH_4)_2[MgFe_2(C_2O_4)_2(OH)_6]_{(s)} \rightarrow (NH_4)_2[MgFe_2(C_2O_4)_2(OH)_2O_2]_{(s)} + 2\ H_2O_{(g)} \quad \text{(V)}$$

$$(NH_4)_2[MgFe_2(C_2O_4)_2(OH)_2O_2]_{(s)} \rightarrow MgFe_2O_{4(s)} + 2\ CO_{(g)} + 2\ CO_{2(g)} + 2\ NH_{3(g)} + 2\ H_2O_{(g)} \quad \text{(VI)}$$

Step V occurs as a unique reaction with the maximum rate at 115 °C. Step VI occurs as a complex reaction with a maximum rate at 320 °C. In Table 3 the values of the kinetic parameters of reaction V are given.

This case exhibits neither heat transfer nor diffusional limitations but does exhibit chemical limitations. Like reaction III, reaction V occurs in the kinetic regime.

The decomposition of $(NH_4)_4[MgFe_2(C_2O_4)_4(OH)_4]$

As shown by the heating curves the decomposition occurs according to the following sequence

TABLE 3

Values of the non-isothermal kinetic parameters of reaction V

β (K min^{-1})	n	E (kcal mol^{-1})	A (s^{-1})
2.5	1	23	3.9×10^{10}
5.3	1	22	2.6×10^{10}
8.7	1	26	7.7×10^{10}

TABLE 4

Values of the non-isothermal kinetic parameters of reaction VII

β (K min^{-1})	n	E (kcal mol^{-1})	A (s^{-1})
2.4	1	23	1.6×10^{10}
6.3	1	22	3.1×10^{10}
9.0	1	21	2.4×10^{10}

$$(NH_4)_4[MgFe_2(C_2O_4)_4(OH)_4]_{(s)} \rightarrow (NH_4)_2[MgFe_2(C_2O_4)_3O_2]_{(s)} + CO(g) + CO_{2(g)} + 2\ NH_{3(g)} + 3\ H_2O_{(g)} \quad \text{(VII)}$$

$$(NH_4)_2[MgFe_2(C_2O_4)_3O_2] \rightarrow MgFe_2O_{4(s)} + 2\ NH_{3(g)} + H_2O_{(g)} + 3\ CO_{(g)} + 3\ CO_{2(g)} \quad \text{(VIII)}$$

As in the previous case, according to the heating curves only, step VII behaves like a unique reaction, its maximum rate occurring at 140 °C. For step VIII the DTG and DTA curves overlap several maxima the principal one occurring at 260 °C. Therefore, only the kinetic parameters for step VII were determined. The results are given in Table 4. Similar to the previous cases the values of the kinetic parameters are practically insensitive to changes in the heating rate. This fact and the value obtained for the reaction order suggests that the decomposition occurs in the kinetic regime.

CONCLUSIONS

(1) The non-isothermal kinetics of four PCC decompositions was investigated.

(2) The independence of the kinetic parameter values on the heating rate as well as the values obtained for the reaction order suggest the occurrence of reactions III, V and VII in the kinetic regime.

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