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Note

ON THE THERMAL STABILITY AND NON-ISOTHERMAL DECOMPOSITION KINETICS OF A BINUCLEAR COORDINATION COMPOUND PRECURSOR OF MIXED OXIDES

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ABSTRACT

Results are presented concerning the thermal decomposition of $[Fe_4Mn(CH_3COO)_6(OH)_8] \cdot 12H_2O$, characterized by chemical analysis, IR spectrometry and X-ray diffractometry. Non-isothermal kinetic parameters for the solid–gas dehydration were evaluated by four different methods.

INTRODUCTION

Following our research concerning the decomposition of polynuclear coordination compounds [1–3], the present paper reports some results concerning the thermal behaviour of the compound $[Fe_4Mn(CH_3COO)_6(OH)_8] \cdot 12H_2O$.

EXPERIMENTAL

The powdery compound $[Fe_4Mn(CH_3COO)_6(OH)_8] \cdot 12H_2O$ was synthesized according to a method described elsewhere [4]. Its composition was checked by chemical analysis and IR spectrometry. The mean size of the crystallites, evaluated by X-ray diffractometry using Scherrer's formula [5], is 58 Å.

The IR spectra were recorded using a Specord 72 Karl–Zeiss–Yena RDG spectrometer.

The thermal curves were recorded, for the interval 20–500 °C, using a MOM–Budapest Paulik–Paulik–Erdey type derivatograph in a static air atmosphere at various heating rates within the range 2.5–13.5 K min^{-1}.

Four methods were used to obtain the values of the non-isothermal kinetic parameters: the Freeman–Carroll [6], Coats–Redfern [7], Ozawa–Flynn–Wall [8,9] and Kissinger [10] methods. The experimental data were processed automatically using programs written by Coseac and Segal for a TI 66 minicomputer [11] as well as a versatile program written in BASIC for the TIM S and ZX Spectrum computers [12].

RESULTS AND DISCUSSION

The derivatogram of the compound under investigation recorded at 2.5 K min^{-1}, given in Fig. 1, exhibits the decomposition steps described by the chemical equations

$$[Fe_4Mn(CH_3COO)_6(OH)_8] \cdot 12H_2O(s) \xrightarrow{90\,°C} [Fe_4Mn(CH_3COO)_6(OH)_8] \cdot 8H_2O(s) + 4H_2O(g) \qquad (1)$$

$$[Fe_4Mn(CH_3COO)_6(OH)_8] \cdot 8H_2O(s) \xrightarrow{150\,°C} [Fe_4Mn(CH_3COO)_6(OH)_8] \cdot 2H_2O(s) + 6H_2O(g) \qquad (2)$$

(The temperatures above the arrows correspond to the maximum decomposition rate.)

As shown by the derivatogram, the third decomposition step is not a simple one. This step can be described by the following overall chemical equation.

$$4[Fe_4Mn(CH_3COO)_6(OH)_8] \cdot 2H_2O(s) + 47.5O_2(g) \xrightarrow{220\,°C} 2Fe_3O_4(s) + 4MnFe_2O_4(s) + \gamma Fe_2O_3(s) + 60H_2O(g) + 48CO_2(g) \qquad (3)$$

The formulae of the solid dehydrated intermediates are supported by derivatographic data (TG curve), chemical analysis and IR spectra (Fig. 2), the only differences being recorded within the range of frequencies corresponding to the coordinated water [13].

According to the derivatogram, the compound is totally decomposed at 280 °C. As far as the solid products of the decomposition are concerned, X-ray diffractograms recorded for the initial compound as well as for the

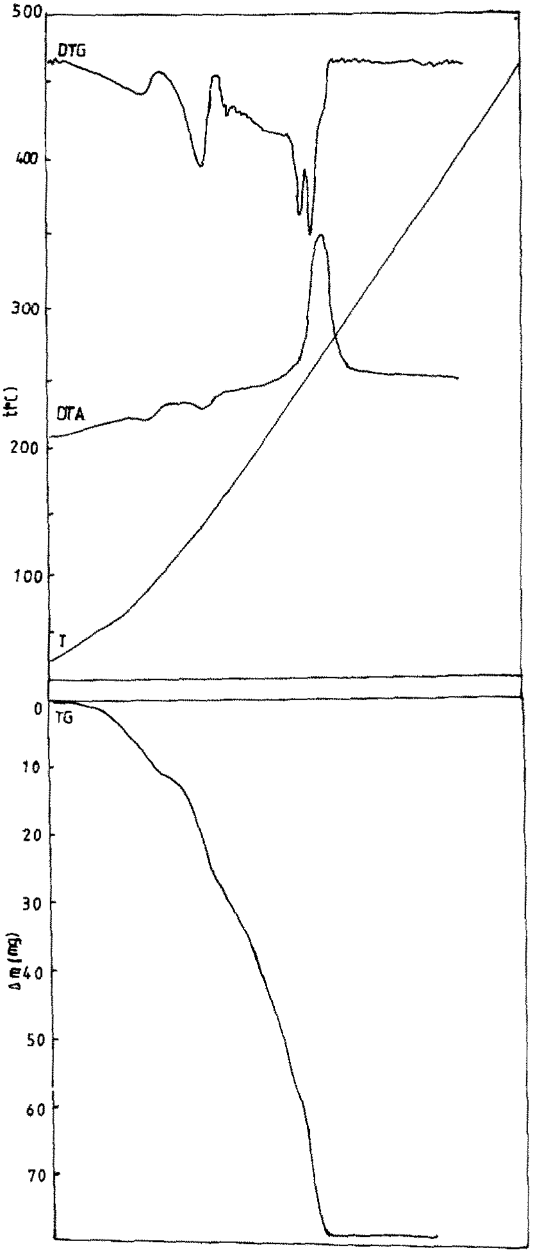

Fig. 1. The derivatogram of $[Fe_4Mn(CH_3COO)_6(OH)_8]\cdot 12H_2O$.

solid products formed on heating at 220, 270 and 350 °C indicate the gradual formation of $Fe_3O_4 + MnFe_2O_4$ and γ-Fe_2O_3.

The values obtained for the non-isothermal kinetic parameters reaction order n, activation energy E, and pre-exponential factor A for reactions (1) and (2)—the only ones which are feasible kinetically—are given in Table 1.

Inspection of these results shows that for both dehydration steps the

TABLE 1

Values of non-isothermal kinetic parameters for reactions (1) and (2)

Decom-position step	β (min)	Method									
		Freeman–Carroll				Coats–Redfern				Kissinger	Ozawa–Flynn–Wall
		n	E (kcal mol^{-1})	A (s^{-1})	k (s^{-1})	n	E (kcal mol^{-1})	A (s^{-1})	k (s^{-1})	E (kcal mol^{-1})	E (kcal mol^{-1})
1	2.79	–	–	–	–	1	11.85	4.5×10^{4}	–		
	5.56	–	–	–	–	1	12.69	2.80×10^{5}	–	13.04	12.31
	11.6	–	–	–	–	1	12.86	4.29×10^{4}	–		
2	3.38	0.89	27.85	9.86×10^{11}	4.03×10^{-3}	1	30.20	3.10×10^{13}	7.7×10^{-3}		
	5.65	–	–	–	–	1	30.75	8.66×10^{13}	8.31×10^{-3}	26.44	27.06
	13.1	0.94	27.04	6.67×10^{11}	7.12×10^{-3}	1	28.30	4.01×10^{12}	9.56×10^{-3}		

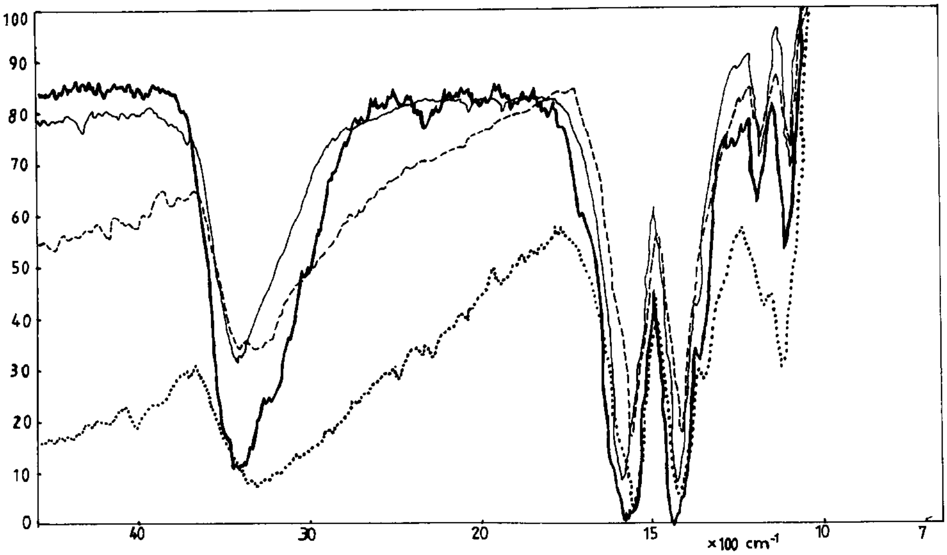

Fig. 2. IR spectra of the: initial compound (▬▬); initial compound heated in air at 90 °C (———); initial compound heated in air at 150 °C (— — —); initial compound heated in air at 220 °C (······).

values of the 'reaction order' are equal to unity. In the case of reaction (2), the value of the pre-exponential factor agrees satisfactorily with the value predicted by transition state theory [14]. For reaction (1), the value of the pre-exponential factor is about seven-eighths orders of magnitude lower than the value predicted by transition state theory for $n = 1$. In this case the value $n = 1$ is only the apparent one, the reaction being better described by the JMAYK equation [15]

$$-\ln(1-\alpha) = kt^r \quad \text{with } r = 1 \tag{4}$$

There is satisfactory agreement among the values of the kinetic parameters obtained by the various methods and at the various heating rates. The small differences between them can be evened out by calculating the value of the rate constant k for a given temperature. In the case of reaction (2), this was done for $t = 150$ °C. It can be seen that the values of the kinetic constants obtained by two methods and for three heating rates differ by a factor whose maximum value is 2.37. Thus the slightly different values of A and E exhibit a kind of apparent compensation effect with respect to the heating rate, as well as to the method used to evaluate the non-isothermal kinetic parameters.

CONCLUSIONS

(1) The thermal decomposition of the compound under investigation occurs in three steps. Two of these steps, recorded at lower temperature, are

endothermic and simple. The final step, recorded at higher temperature, is exothermic and complex.

(2) The values of the non-isothermal kinetic parameters obtained by the four methods are in satisfactory agreement.

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