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ON THE THERMAL STABILITY OF SOME POLYNUCLEAR COORDINATION COMPOUNDS OF Ni(II) AND Fe(III) GENERATING NICKEL FERRITE

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ABSTRACT

The authors present their results concerning the thermal conversion of some polynuclear coordination compounds of Ni(II) and Fe(III) into nickel ferrite.

INTRODUCTION

Following our research concerning the thermal stability of polynuclear coordination compounds (PCC) [1], in this paper we present the results concerning the thermal stability of four such PCC of Ni(II) and Fe(III).

EXPERIMENTAL

Powders of the following PCC: $[Fe_2NiO(CH_3COO)_6(H_2O)_3]_3 \cdot 3H_2O$; $[Fe_2NiO(HCOO)_8(H_2O)](NH_4)_2 \cdot 2H_2O$; $[Fe_2Ni(C_2O_4)_8(H_2O)_2](NH_4)_8 \cdot 6H_2O$; $[Fe_2Ni(C_2O_4)(OH)_8(H_2O)_2]\ (NH_4)_2$, synthesized according to methods described elsewhere [2], were used.

The decomposition curves in air for the temperature interval 20–1000°C were recorded by help of a Paulik–Paulik–Erdey type MOM derivatograph (Budapest) with various heating rates (1, 2.5, 5 and 10 K min^{-1}).

The linear dimensions of the powder grains determined by help of a Stereoscan (150) microscope varied between 2 and 5 μm.

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RESULTS AND DISCUSSION

On the derivatograms obtained under the above conditions one can distinguish 2–4 solid–gas decomposition steps in the temperature interval 60–200°C, which consist of dehydration and ammonia, carbon monoxide, carbon dioxide, oxygen or acetone loss. A final exothermic decomposition step, during which the ligand is evolved, occurs in the temperature interval 200–450°C. As the DTA curves do not exhibit any crystallization peak, we came to the conclusion that the solid-state reaction between NiO and Fe_2O_3 (ferritization) occurs simultaneously with the last step between 200 and 450°C. Some of the decomposition steps are not single, thus, the important overlapping between them, even at low heating rates, did not allow us to determine the kinetic parameters. The non-isothermal kinetic parameters were equally not determined for the strong exothermic decomposition steps which are probably heat-transfer limited.

Thermal decomposition of $[Fe_2NiO(CH_3COO)_6(H_2O)_3]\cdot 3H_2O$

According to the derivatographic data, the decomposition of this PCC occurs in the following sequence of decomposition steps

$$[Fe_2NiO(CH_3COO)_6(H_2O)_3]\cdot 3H_2O(s) \rightarrow [Fe_2NiO(CH_3COO)_6(H_2O)_3](s) + 3H_2O(g) \qquad (I)$$

$$[Fe_2NiO(CH_3COO)_6(H_2O)_3](s) \rightarrow [Fe_2NiO(CH_3COO)_4CO_3](s) + 3H_2O(g) + (CH_3)_2CO(g) \qquad (II)$$

$$[Fe_2NiO(CH_3COO)_4CO_3](s) \rightarrow [Fe_2NiO(CO_3)_3](s) + 2(CH_3)_2CO(g) \qquad (III)$$

$$[Fe_2NiO(CO_3)_3](s) \rightarrow Fe_2NiO_4(s) + 3CO_2(g) \qquad (IV)$$

The decomposition of the acetic anions from neighbour positions with acetone as a reaction product is well known as a classical method to obtain ketones [3]. Other literature data [4,5] confirm the given sequence. To confirm the nature of the gas products evolved during thermal decomposition, various samples were heated in air and inert atmosphere. Thermal decomposition with mass spectrometry was also applied. All these measurements showed that the evolved gases were acetone and carbon dioxide.

Thermal decomposition of $[Fe_2NiO(HCOO)_8(H_2O)](NH_4)_2\cdot 2H_2O$

The thermal decomposition of this PCC occurs in the temperature interval 70–300°C according to the following sequences

$$[Fe_2NiO(HCOO)_8(H_2O)](NH_4)_2\cdot 2H_2O(s) \rightarrow [Fe_2NiO(HCOO)_8](NH_4)_2(s) + 3H_2O(g) \qquad (V)$$

$$[Fe_2NiO(HCOO)_8](NH_4)_2(s)$$
$$\rightarrow [Fe_2NiO(HCOO)_6](s) + 2NH_3(g) + 2CO(g) + 2H_2O(g) \quad \text{(VI)}$$
$$[Fe_2NiO(HCOO)_6](s) \rightarrow Fe_2NiO_4(s) + 6CO(g) + 3H_2O(g) \quad \text{(VII)}$$

The above techniques allowed us to confirm the validity of the proposed sequence.

Thermal decomposition of $[Fe_2Ni(C_2O_4)_8(H_2O)_2](NH_4)_8 \cdot 6H_2O$

The thermal decomposition of this PCC occurs in the temperature interval 60–450°C according to the reactions

$$[Fe_2Ni(C_2O_4)_8(H_2O)_2](NH_4)_8 \cdot 6H_2O(s)$$
$$\rightarrow [Fe_2Ni(C_2O_4)_8](NH_4)_8(s) + 8H_2O(g) \quad \text{(VIII)}$$
$$[Fe_2Ni(C_2O_4)_8](NH_4)_8(s)$$
$$\rightarrow Fe_2NiO_4(s) + 8CO(g) + 8CO_2(g) + 8NH_3(g) + 4H_2O(g) \quad \text{(IX)}$$

Thermal decomposition of $[Fe_2Ni(C_2O_4)(OH)_8(H_2O)_2](NH_4)_2$

The following decomposition steps were observed

$$[Fe_2Ni(C_2O_4)(OH)_8(H_2O)_2](NH_4)_2(s)$$
$$\rightarrow [Fe_2Ni(C_2O_4)(OH)_8](NH_4)_2(s) + 2H_2O(g) \quad \text{(X)}$$
$$[Fe_2Ni(C_2O_4)(OH)_8](NH_4)_2(s)$$
$$\rightarrow [Fe_2Ni(C_2O_4)(OH)_6(H_2O)_2](s) + 2NH_3(g) \quad \text{(XI)}$$
$$[Fe_2Ni(C_2O_4)(OH)_6(H_2O)_2](s)$$
$$\rightarrow [Fe_2Ni(C_2O_4)(OH)_4O](s) + 3H_2O(g) + 1/2O_2(g) \quad \text{(XII)}$$
$$[Fe_2Ni(C_2O_4)(OH)_4O](s)$$
$$\rightarrow Fe_2NiO_4(s) + 2CO(g) + 2H_2O(g) + 1/2O_2(g) \quad \text{(XIII)}$$

These decomposition steps were exhibited in the temperature interval 50–450°C.

The non-isothermal kinetic parameters were evaluated by help of the Coats–Redfern method [6]. The experimental data were automatically worked up with a programmable TI 66 calculator.

The values of the kinetic parameters, reaction order, n, activation energy, E, and the pre-exponential factor, A, are given in Table 1. For almost all the reactions, $n = 1$. The values of the pre-exponential factors of reactions(II) and (III) are in good agreement with those predicted by the transition-state theory [7]. Thus, the reaction order can be considered as a true one. As far as the rections (V), (VI), (VIII), (X)–(XI), are concerned, the reaction order is

TABLE 1

Values of the non-isothermal kinetic parameters for various decomposition steps

PCC	Reaction	n	E (kcal mol^{-1})	A (s^{-1})	Temp. interval (°C)	Thermal effect
$[Fe_2NiO(CH_3COO)_6(H_2O)_3]\cdot 3H_2O$	I	2/3	8.7	3×10^2	60–120	endothermic
	II	1	33	1.4×10^{14}	130–208	endothermic
	III	1	32.7	5.2×10^{14}	208–251	endothermic
	IV		heat-transfer limited		252–350	exothermic
$[Fe_2NiO(HCOO)_8(H_2O)_2](NH_4)_2\cdot 2H_2O$	V	1	8.4	1.1×10^2	70–175	endothermic
	VI	1	26.5	1×10^9	190–225	endothermic
	VII		heat-transfer limited		260–290	exothermic
$[Fe_2Ni(C_2O_4)_8(H_2O)_2](NH_4)_8\cdot 6H_2O$	VIII	1	11.0	3.20×10^2	60–200	endothermic
	IX		heat-transfer limited		200–450	exothermic
$[Fe_2Ni(C_2O_4)(OH)_8(H_2O)_2](NH_4)_2$	X	1	9.20	2.5×10^3	60–150	endothermic
	XI	1	21.0	6.2×10^6	160–220	endothermic
	XII	–	–	–	235–275	endothermic
	XIII		heat-transfer limited		280–450	exothermic

an apparent one. Actually, an integral kinetic equation corresponding to $n = 1$, can be considered as a particular case of the JMAYK (Johnson–Mehl–Avrami–Erofeev–Kolomogorov) equation [8] for instantaneous nucleation and unidimensional growth of the nuclei. For this case the experimental value of the activation energy equals the energy of growth. As for the value $n = 2/3$ for reaction (I), this corresponds to a contracting sphere with fast nucleation followed by surface growth of the nuclei [9].

CONCLUSIONS

(1) A derivatographic investigation concerning the thermal stability of four PCCs generating nickel ferrite was performed.

(2) The non-isothermal kinetic parameters for various decomposition steps were determined.

REFERENCES

1 M. Brezeanu, E. Safarica, E. Segal, L. Patron and T. Robu, Rev. Roum. Chim., 27 (1982) 137; M. Brezeanu, E. Tatu, S. Bocai, O. Brezeanu and E. Segal, Thermochim. Acta, 78 (1984) 351.
2 M. Brezeanu and I. Ilie, unpublished data.
3 C.D. Nenitescu, Organic Chemistry, Vol. I, Editura Technicǎ, Bucharest, 1960, p. 664 (in Romanian).
4 J.J. Ziolkonski, F. Bruchnik and T.S. Bozar, Inorg. Chim. Acta, 7 (1973) 473.
5 L. Patron, M. Brezeanu, G. Munteanu and E. Segal, unpublished data.
6 A.W. Coats and J.P. Redfern, Nature (London), 201 (1964) 68.
7 S. Glasstone, K.J. Laidler and H. Eyring, The Theory of Rate Processes, McGraw-Hill, New York, 1941, p. 296.
8 J. Šesták, Thermophysical Properties of Solids, Academia, Prague, 1984, pp. 190–191.
9 I.G. Murgulescu, T. Oncescu and E. Segal, Introduction to Physical Chemistry, Vol. II.2, Publishing House of the Academy of Socialist Republic of Romania, Bucharest, 1981, p. 703 (in Romanian).