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NON-ISOTHERMAL KINETIC STUDY OF THE DECOMPOSITION OF SOME Fe^{III} AND Cu^{II} COORDINATION COMPOUNDS

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ABSTRACT

This paper contains the non-isothermal kinetic analyses of ten solid–gas thermal decompositions. The values of the kinetic parameters estimated by using two groups of methods show a satisfactory agreement.

INTRODUCTION

In some previous notes we developed several methods for non-isothermal kinetic analysis [1–3]. This paper aims to check their validity on the non-isothermal kinetic analysis of the decomposition reactions of some coordination compounds.

EXPERIMENTAL

The following coordination compounds were used: $NH_4[Fe_2(HCOO)_7]\cdot H_2O$ (S_1); $(NH_4)_3[CuFe(C_2O_4)Cl_2(OH)_4]$ (S_2); $(NH_4)_3[CuFe_3(HCOO)_9Cl_5(H_2O)_6]$ (S_3).

The three compounds S_1, S_2 and S_3 were synthesised according to methods described elsewhere [4]. The thermal decomposition curves were recorded

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with a Paulik–Paulik–Erdey type derivatograph (MOM, Budapest) with various heating rates between 2.5 and 10 K $\min^{-1}$. To accommodate the limitation of lack of mass transfer, small amounts of powder (up to 0.1 g) were used.

The X-ray powder diffractograms were recorded with a Philips diffractometer (P.W. 1140/90) using chromium K_α radiation.

In Table 1 the Bragg angle, θ, interplanar distances, d, relative intensities of the line, i_r, and mean crystallite sizes, r, calculated according to Scherrer's formula are given [5].

The kinetic parameters of the decomposition were obtained by using:

(a) the method of integration over small temperature intervals, M_I [1],

(b) the method of integration over small temperature intervals, M_{II} [2],

(c) the improved Coats–Redfern method, M_{III} [3].

To check the accuracy of these methods, developed by two of the present authors, the non-isothermal kinetic parameters were alternatively evaluated with the methods of Coats–Redfern, M_1 [6], Freeman–Carroll, M_2 [7], and Achar–Brindley–Sharp, M_3 [8].

RESULTS AND DISCUSSION

Decomposition of S_1

According to thermogravimetric data the decomposition of S_1 exhibits the

TABLE 1

Preliminary X-ray diffraction data concerning the coordination compounds S_1–S_3

Compound S_1							
θ	10°24′	18°25′	21°18′	23°24′			
d (Å)	6.329	3.612	3.223	2.877			
i_r (%)	100	3.8	33	21			
r (μm)	0.051	–	–	–			
Compound S_2							
θ	11°39′	13°36′	16°48′	17°42′	24°30′		
d (Å)	5.652	4.859	3.953	3.758	2.755		
i_r (%)	43	38	19	31	100		
r (μm)	–	–	–	–	0.061		
Compound S_3							
θ	10°42′	12°	18°24′	18°36′	21°30′	23°36′	24°36′
d (Å)	6.154	5.496	3.620	3.582	3.118	2.854	2.745
i_r (%)	100	53	28	28	32	33	32
r (μm)	0.054	–	–	–	–	–	–

TABLE 2

Thermogravimetric data for reactions I and II

Reaction I									
T (K)	333	343	353	363	373	383	393	403	413
α[a]	0.094	0.153	0.241	0.341	0.471	0.606	0.753	0.859	0.888
$\frac{d\alpha}{dT}\times10^3$ (K^{-1})	5.3	7.4	9.4	11.5	13.3	14.1	12.7	6.8	5.0
Reaction II									
T (K)	433	443	453	463	473	483	493	503	
α[a]	0.019	0.046	0.081	0.143	0.243	0.370	0.576	0.957	
$\frac{d\alpha}{dT}\times10^3$ (K^{-1})	2.3	3.1	4.9	8.1	11.4	16.7	29.4	22.5	

[a] Conversion degree.

following steps

$$NH_4[Fe_2(HCOO)_7]\cdot H_2O(s) \rightarrow 2Fe(HCOO)_3(s) + NH_3(g) + 2H_2O(g) + CO(g) \qquad (I)$$

$$2Fe(HCOO)_3(s) \rightarrow Fe_2O_3(s) + 3H_2O(g) + 6CO(g) \qquad (II)$$

The TG, DTG and T data, worked in terms of the conversion, are given in Table 2.

The non-isothermal kinetic parameters for reactions I and II are given in Table 3.

An inspection of the results given in Table 3 shows a satisfactory agreement between the values of the non-isothermal kinetic parameters obtained by our methods and those obtained by other methods given in the literature.

TABLE 3

Non-isothermal kinetic parameters of reactions I and II

Method	n[a]	A (s^{-1})	E (kcal mol^{-1})
Reaction I			
M_{II}	1	5.5×10^3	10.4
M_{III}	1	2.4×10^3	9.8
M_1	1	3.3×10^3	10.1
M_3	1	1.6×10^3	9.5
Reaction II			
M_{II}	0	1.5×10^7	21.4
M_{III}	0	1.2×10^7	21.2
M_1	0	6.3×10^6	20.7
M_3	0	2.8×10^6	19.9

[a] Reaction order.

Decomposition of S_2

The TG curves exhibit the following decomposition steps which occur by heating the samples from room temperature to 600°C.

$$(NH_4)_3[CuFe(C_2O_4)Cl_2(OH)_4](s) \rightarrow (NH_4)_3[CuFe(C_2O_4)Cl_2O(OH)_2](s) + H_2O(g) \qquad \text{(III)}$$

$$(NH_4)_3[CuFe(C_2O_4)Cl_2O(OH)_2](s) \xrightarrow{1/2O_2(g)} [CuFe(CO_3)Cl_2O_{0.5}](s) + 3NH_3(g) + 2.5\ H_2O(g) + CO_2(g) \qquad \text{(IV)}$$

$$[CuFe(CO_3)Cl_2O_{0.5}](s) \xrightarrow{1/4O_2} [CuFeO_2Cl](s) + CO_2(g) + \tfrac{1}{2}Cl_2(g) \qquad \text{(V)}$$

$$[CuFeO_2Cl](s) \xrightarrow{1/4O_2} CuFeO_{2.5}(s) + \tfrac{1}{2}Cl_2(g) \qquad \text{(VI)}$$

The thermogravimetric data and the values of the non-isothermal kinetic parameters of reactions III–VI are given in Tables 4 and 5, respectively.

These results also show for reactions III–VI a quite satisfactory agreement between the non-isothermal kinetic parameter values obtained by various methods.

TABLE 4

Thermogravimetric data for reactions III–VI

Reaction III								
T (K)	303	313	323	333	343	353	363	373
α	0.06	0.14	0.24	0.36	0.52	0.66	0.82	0.92
$\frac{d\alpha}{dT} \times 10^3$ (K^{-1})	6	9	11	14	15	15	13	8
Reaction IV								
T (K)	438	448	458	468	478	488	498	
α	0.031	0.079	0.157	0.317	0.561	0.861	0.999	
$\frac{d\alpha}{dT} \times 10^3$ (K^{-1})	4	6.3	11.4	20.4	27.7	31.4	14.1	
Reaction V								
T (K)	523	533	543	553	563	573	583	
α	0.101	0.169	0.278	0.435	0.634	0.851	0.981	
$\frac{d\alpha}{dT} \times 10^3$ (K^{-1})	5.5	8.9	13.3	17.8	20.8	17.3	7.5	
Reaction VI								
T (K)	663	683	703	723	743	763	783	
α	0.061	0.146	0.272	0.473	0.708	0.902	0.998	
$\frac{d\alpha}{dT} \times 10^3$ (K^{-1})	3.1	5.2	8.5	11.4	11.1	6.1	4.5	

Decomposition of S_3

The thermogravimetric data show the following decomposition steps of the binuclear coordination compound S_3

$$(NH_4)_3[CuFe_3(HCOO)_9Cl_5(H_2O)_6](s)$$

$$\rightarrow (NH_4)_3[CuFe_3(HCOO)_9Cl_5(H_2O)_2](s) + 4H_2O(g) \qquad \text{(VII)}$$

$$(NH_4)_3[CuFe_3(HCOO)_9Cl_5(H_2O)_2](s)$$

$$\rightarrow [CuFe_3Cl_5(CO_3)O_2](s) + 3NH_3(g) + 8H_2O(g) + 4CO(g) + 4CO_2(g) \qquad \text{(VIII)}$$

$$[CuFe_3Cl_5(CO_3)O_2](s) \xrightarrow{1/2O_2} [CuFe_3Cl_3(CO_3)O_3](s) + Cl_2(g) \qquad \text{(IX)}$$

$$[CuFe_3Cl_3(CO_3)O_3](s) \xrightarrow{1/2O_2} [CuFe_3ClO_5](s) + CO_2(g) + Cl_2(g) \qquad \text{(X)}$$

The thermogravimetric data and the values of the non-isothermal kinetic parameters for reactions VII–X are given in Tables 6 and 7, respectively.

TABLE 5

Non-isothermal kinetic parameters of reactions III–VI

Method	n	A (s^{-1})	E (kcal mol^{-1})
Reaction III			
M_{II}	1.0	2.7×10^3	8.9
M_{III}	1.0	1.1×10^4	9.8
M_1	1.0	1.5×10^4	10.1
M_2	1.1	3.8×10^4	9.2
Reaction IV			
M_I	0.61	1.5×10^{10}	26.8
M_{II}	0.66	2.5×10^{11}	29.4
M_{III}	0.66	1.1×10^{11}	28.7
M_1	0.66	1.4×10^{11}	28.9
M_2	0.60	1.0×10^{11}	28.5
Reaction V			
M_I	0.70	2.4×10^9	29.6
M_{II}	0.66	8.5×10^8	28.8
M_{III}	0.66	2.3×10^9	29.7
M_1	0.66	1.2×10^9	28.9
M_2	0.72	1.3×10^9	29.1
Reaction VII			
M_{II}	1	1.2×10^7	31.4
M_{III}	1	3.3×10^7	32.9
M_1	1	1.8×10^7	32.2
M_2	0.95	5.5×10^7	33.7

TABLE 6

Thermogravimetric data for reactions VIII–X

Reaction VII								
T (K)	353	363	373	383	393	403	413	423
α	0.12	0.189	0.303	0.432	0.591	0.727	0.833	0.924
$\frac{d\alpha}{dT} \times 10^3$ (K^{-1})	7.2	9.1	12.2	14.7	15.3	12.1	9.7	8.4
Reaction VIII								
T (K)	453	463	473	483	493	503	513	
α	0.047	0.112	0.253	0.453	0.694	0.859	0.970	
$\frac{d\alpha}{dt} \times 10^3$ (K^{-1})	4.7	10.3	17.1	22.1	20.3	13.8	7.1	
Reaction IX								
T (K)	523	533	543	553	563	573	583	
α	0.129	0.201	0.297	0.543	0.627	0.801	0.978	
$\frac{d\alpha}{dT} \times 10^3$ (K^{-1})	6	8.4	12.1	16.5	17.9	17.6	10.1	
Reaction X								
T (K)	673	683	693	703	713	723	733	743
α	0.101	0.153	0.222	0.323	0.443	0.591	0.755	0.901
$\frac{d\alpha}{dT} \times 10^3$ (K^{-1})	4.3	6.1	8.5	11.1	13.4	15.6	15.4	11.5

TABLE 7

Non-isothermal kinetic parameters of reactions VII–X

Method	n	A (s^{-1})	E (kcal mol^{-1})
Reaction VII			
M_I	0.96	1.5×10^3	9.8
M_{III}	1.00	3.4×10^4	12.1
M_1	1.00	1.9×10^4	11.7
M_2	0.97	5.7×10^3	10.7
Reaction VIII			
M_I	1.1	5.4×10^{10}	28.4
M_{II}	1.0	7.7×10^{10}	28.8
M_{III}	1.0	2.8×10^{11}	30.1
M_1	1.0	1.1×10^{11}	29.4
Reaction IX			
M_{II}	0.50	8.1×10^6	23.7
M_{III}	0.50	6.6×10^5	23.5
M_1	0.50	9.4×10^6	23.9
M_2	0.57	1.4×10^7	24.3
Reaction X			
M_I	0.60	1.4×10^7	31.3
M_{II}	0.66	8.3×10^7	34.3
M_{III}	0.66	4.4×10^8	36.8
M_1	0.66	2.4×10^8	35.8
M_2	0.66	6.8×10^7	33.7

For reactions VII–X a quite satisfactory agreement between the values of the non-isothermal kinetic parameters evaluated by various methods can also be noted.

The subunitary values of the reaction order 0, 1/2, 2/3 came from the general rate equation

$$\frac{d\alpha}{dt} = k\alpha^m(1-\alpha)^n \tag{1}$$

with $m = 0$. These values indicate either physical phenomena which are rate limiting ($n = 0$), or surface-controlled reactions ($n = 1/2,\ 2/3$) [9,10]. The values of n close to unity could be assigned to a chemical reaction limited decomposition (for A values close to 5×10^{12} as predicted by the transition state theory [11]). This is perhaps the case for reaction VIII.

As far as reactions I, III, VI and VII are concerned, the first-order kinetic equation which formally describes the decomposition should be treated as a particular form of Avrami–Erofeev [12,13] equation

$$\ln(1/1-\alpha) = kt^p \tag{2}$$

for $p = 1$.

CONCLUSIONS

The non-isothermal kinetic parameters of ten solid–gas decompositions have been evaluated by using newly worked methods and methods already known in the literature. A satisfactory agreement of the non-isothermal kinetic parameters obtained by the two groups of methods has been noted.

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