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THE SIMULTANEOUS DETERMINATION OF THE KINETICS AND THERMODYNAMICS OF $Cu(OH)_2$ DECOMPOSITION BY MEANS OF TG AND DSC

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ABSTRACT

The kinetics and thermodynamics of the thermal decomposition of powdered copper(II) hydroxide to copper(II) oxide and water were studied by means of TG–DSC recorded simultaneously at constant temperatures as well as TG at linearly increasing temperature. The thermal decomposition is regulated by one of random nucleation and subsequent growth mechanisms (an Avrami–Erofeyev law). The activation energy for the decomposition was considerably larger than the corresponding enthalpy change. The kinetic parameters estimated isothermally are smaller than those estimated dynamically. The cause of these differences is discussed.

INTRODUCTION

Although there have appeared a number of kinetic studies of solid decompositions by means of dynamic thermal analyses, it still seems difficult to obtain reliable kinetic parameters from a single dynamic run. In order to obtain the meaningful parameters from these analyses, it is in general necessary to analyze various data recorded under different conditions, e.g., under various heating rates and particle sizes, etc. [1]. In addition, a conventional isothermal method is properly used to check the kinetic parameters obtained dynamically.

Recently, we have reported the kinetic study of the thermal dehydration of calcium oxalate monohydrate, using TG both at constant and linearly increasing temperatures [2]. It was concluded that, contrary to the result of earlier works, the dehydration of this hydrate follows not a phase-boundary reaction but one of random nucleation and subsequent growth mechanisms (an Avrami–Erofeyev law). We have also studied the dehydration stages of barium chloride dihydrate systematically by means of TG–DSC recorded simultaneously [3]. It was suggested that the

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dehydration stages of this dihydrate should also proceed both at constant and increasing temperatures according to an Avrami–Erofeyev law. On the other hand, other workers reported that the dehydration follows an Avrami–Erofeyev law at constant temperature but follows a contracting-circle law at increasing temperature [4].

It is thus worth examining systematically the kinetics of thermal decomposition of solids along these lines. The present paper deals with the kinetics and thermodynamics of the thermal decomposition from $Cu(OH)_2$ to CuO and H_2O by means of dynamic TG–DSC at different heating rates as well as TG–DSC at constant temperature.

EXPERIMENTAL

Copper(II) hydroxide was precipitated by the addition of 10% aqueous ammonia solution to 0.5 M aqueous $CuSO_4$ solution until the solution became deep blue; 1.0 M aqueous NaOH solution was then added dropwise at 50°C to the resulting solution [5]. The precipitate was dried in air at 60°C. The hydroxide was identified by means of IR and TG. The mean weight loss due to the thermal dehydroxylation was ca. 18.0% (theoretically 18.47%). The hydroxide was ground in a mortar with a pestle and sieved to the fraction 170–200 mesh.

TG–DSC traces were obtained simultaneously at various heating rates in a stream of dry nitrogen at a flow rate of 30 ml min^{-1}, using a Rigaku Thermoflex TG–DSC 8085E1 type instrument. About 10.0 mg of the sample were weighed into a platinum crucible of 5 mm diameter and 2.5 mm depth. α-Alumina was used as reference material. TG–DSC at constant temperatures were also recorded under the same sample conditions as those in the dynamic run. The calibrations of temperature and enthalpy change were made with the phase transition of KNO_3 at 128°C.

The peak areas of DSC traces were measured with a polar planimeter. Computer work was done with a micro-computer. Graphical plots were obtained using a plotter connected to the computer.

RESULTS AND DISCUSSION

Thermodynamics

Figure 1 shows typical TG–DSC traces obtained simultaneously for the decomposition from $Cu(OH)_2$ to CuO and $H_2O(g)$. Table 1 shows the extrapolated onset temperature, T_{eo}, and the peak temperature, T_p, for the decomposition at various heating rates by means of DSC. The decomposition temperature is in good agreement with that of Endoh et al. [5], taking into account the slightly decreasing temperature with decreasing heating rates.

The enthalpy change, ΔH, for the decomposition was determined as 11.27 ± 0.06

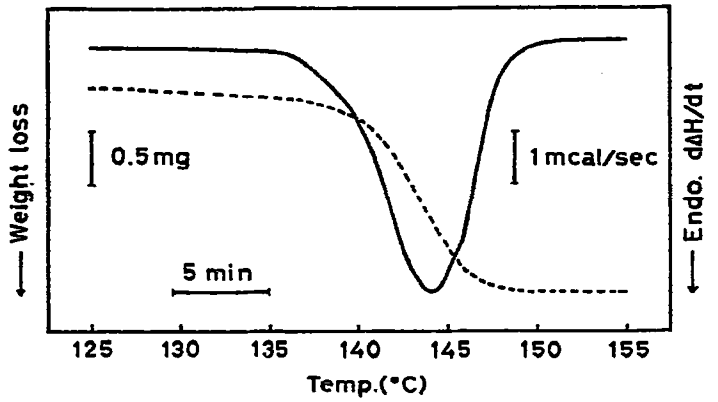

Fig. 1. Typical traces of TG (- - - - - -) and DSC (————) recorded simultaneously for the dehydration of $Cu(OH)_2$.

kcal mole^{-1} by means of DSC at a heating rate of 1.06°C min^{-1}. This value is comparable with previous values [5,6] and with the theoretical value calculated from the standard heat of formation at 25°C [7].

Kinetics at constant temperatures

For the isothermal decomposition of $Cu(OH)_2$, the equation

$$F(\alpha) = kt \tag{1}$$

is assumed, where $F(\alpha)$ is a function depending on the decomposition mechanism, α is the fraction decomposed at time t, and k is the rate constant. Table 2 lists the kinetic functions commonly used for the solid decomposition [8]. The $F(\alpha)$ pertinent to the decomposition can be searched by plotting it against t; the appropriate one should give a straight line with a slope k [8,9]. The correlation coefficient r and error δ as a measure of the linearity are shown in Table 3 for the least squares fitting in the various $F(\alpha)$ vs. t plots. It may be deduced from Table 3 that the decomposition of $Cu(OH)_2$ should follow an Avrami–Erofeyev law of A_4. The best $F(\alpha)$ was estimated actually as $A_{4.8}$ and $A_{4.6}$ by means of TG and DSC, respectively, over the temperature range 134.5–150.2°C, using a computer.

TABLE 1

The dehydration temperature of $Cu(OH)_2$ at various heating rates

Heating rate (°C min^{-1})	T_{eo} (°C)	T_p (°C)
0.50	133.6	137.8
1.06	138.0±0.4 [a]	144.0±0.4 [a]
2.13	143.8	151.3
4.52	153.8	164.4

[a] Mean value of six measurements and its probable error.

TABLE 2

Various mechanistic functions F(α) used in the isothermal decomposition of solids

Symbol	F(α)
D_1	α^2
D_2	$\alpha+(1-\alpha)\ln(1-\alpha)$
D_3	$[1-(1-\alpha)^{1/3}]^2$
D_4	$1-2\alpha/3-(1-\alpha)^{2/3}$
A_u	$\ln[\alpha/(1-\alpha)]$
A_m	$[-\ln(1-\alpha)]^{1/m}$; $m=1, 2, 3, 4$
R_n	$1-(1-\alpha)^{1/n}$; $n=1, 2, 3$

It is noted that the m value is slightly larger than the usual maximum value of four. Such a higher value was also found for $KMnO_4$ [10]. The physical meaning of the higher value is not clear at this stage. The m value is assumed here to be simply a parameter that enables the experimental data to fit into the generalized Avrami–Erofeyev law [11].

Tables 4 and 5 list the rate constants, k, at various temperatures by means of TG and DSC, respectively, together with the value of r. Table 6 shows the activation energy, E, and $\log_{10}$ of the frequency factor, A, derived from the Arrhenius plot, together with the value of r for the least squares fitting. It is interesting that the values of E and $\log A$ from TG are little smaller than those from DSC. Our values of E and $\log A$ are compatible with those of other workers [6], although the kinetic model assumed is different. Such a pattern was also found for other solid decompositions [2,12].

Kinetics at increasing temperature

It is well known that Coats and Redfern's method of evaluating kinetic parameters by means of a dynamic run is one of the most reliable [2,13]. The following equation is used

$$\ln\left[F(\alpha)/T^2\right] = \ln\frac{AR}{aE}\left(1-\frac{2RT}{E}\right)-\frac{E}{RT} \tag{2}$$

where T is the absolute temperature, R is the gas constant, and a is the linear heating rate. Table 7 shows the kinetic parameters derived in terms of all F(α) listed in Table 2 except A_u using eqn. (2).

Assuming for the moment that F(α) selected isothermally can be applied to the non-isothermal decomposition [2], the kinetic parameters at various heating rates listed in Table 8 are obtained. It is seen that the parameters increase with decreasing heating rates, whereas the rate constant is nearly constant. This may be explained by the kinetic compensation law [14]. The variation in the parameters can be explained by the change in dehydration temperature, as is shown in Table 1 [15]. It is seen

TABLE 3

Coefficient as a measure of linearity for the least squares fitting in the $F(\alpha)$ vs. t plot at 137.3°C in the α range 0.1–0.9

Coefficient[a]	$F(\alpha)$											
	D_1	D_2	D_3	D_4	A_u	R_1	R_2	R_3	A_1	A_2	A_3	A_4
r	0.9631	0.9352	0.8864	0.9200	0.9981	0.9972	0.9833	0.9737	0.9463	0.9910	0.9981	0.9996
$\delta \times 10^2$	7.559	8.091	4.430	2.446	8.612	2.031	3.851	3.792	23.25	5.160	1.671	0.5759

[a] r is the so-called correlation coefficient and δ is the error defined by the equation

$$\delta=[\Sigma\epsilon_i^2/(N-1)]^{1/2}$$

where ϵ_i is the deviation from the straight line and N is the number of experimental data.

from Table 8 that the values of E and $\log A$ at increasing temperature are around 33.0 kcal mole^{-1} and 14.5 s^{-1}, respectively, since the parameters at the lowest heating rate are supposed to be the most reliable [2].

It is noted here that the parameters from the dynamic TG method are considerably larger than those from the isothermal method. This is one of the exceptions to the general trend that both methods give almost equal parameters, provided the small size of sample is heated very slowly in the case of the dynamic run [2]. Such a difference was also reported for the decomposition of a few solids [16,17].

The difference in the parameters between the isothermal and dynamic methods may be tentatively ascribed to the assumption that the exponent m for A_m functions

TABLE 4

The rate constants, k, derived from TG at different constant temperatures in terms of $A_{4.8}$ in the α range 0.1–0.9

Temp. (°C)	$k \times 10^4$ (s^{-1})	r
134.5	9.019	0.99972
137.3	10.97	0.99983
141.9	13.64	0.99987
143.4	15.14	0.99998
150.2	21.93	0.99992

TABLE 5

The rate constants, k, derived from DSC at different constant temperatures in terms of $A_{4.6}$ in the α range 0.1–0.9

Temp. (°C)	$k \times 10^4$ (s^{-1})	r
134.6	9.964	0.99995
137.4	12.70	0.99959
142.0	15.63	0.99966
143.5	18.76	0.99759
150.3	25.56	0.99944

TABLE 6

Kinetic parameters derived from the Arrhenius plot by means of isothermal TG and DSC

Method	E (kcal mole^{-1})	$\log A$ (s^{-1})	$-r$
TG	19.1 ± 0.2	7.2 ± 0.1	0.99884
DSC	20.3 ± 0.5	7.9 ± 0.3	0.99233

TABLE 7

Kinetic parameters derived from TG at a heating rate of 1.09°C min^{-1} using eqn. (2) in the α range 0.1–0.9

$F(\alpha)$	E (kcal mole^{-1})	log A (s^{-1})	$-r$
D_1	216	111	0.9875
D_2	239	123	0.9931
D_3	268	138	0.9977
D_4	249	128	0.9951
R_1	107	53.9	0.9873
R_2	126	63.8	0.9959
R_3	133	67.4	0.9977
A_1	149	76.4	0.9994
A_2	73.8	36.4	0.9994
A_3	48.6	23.0	0.9994
A_4	36.1	16.3	0.9994

TABLE 8

Kinetic parameters derived from TG at different heating rates in terms of $A_{4.8}$ using eqn. (2) in the α range 0.1–0.9

Heating rate (°C min^{-1})	T_{av} (°C) [a]	E (kcal mole^{-1})	log A (s^{-1})	$k \times 10^3$ (s^{-1}) [b]
0.50	136.7	33.0	14.5	1.41
1.06 [c]	142.7	28.6±0.7	12.2±0.4	1.42±0.03
2.13	149.9	22.4	8.92	1.38
4.52	161.5	12.6	3.78	1.38

[a] T_{av} refers to the temperature where α is 0.5.

[b] Value at 142.7°C.

[c] Mean of six observed values and its probable error.

is slightly different in each case; the decomposition mechanism varies within the A_m mechanism. As can be seen from Table 7, kinetic values closer to those of the isothermal method could be obtained if the larger value of m is adopted for the A_m function describing the dynamic decomposition. Alternatively, such a difference may be explained by the kinetic compensation law, the establishment of which can be seen from the comparison between Tables 4 and 8.

It is also worth comparing the observed value of E with the corresponding enthalpy change, ΔH. The large value of E in comparison with the value of ΔH is seen, contrary to the expected pattern for the endothermic solid decomposition in which E is nearly equal to the corresponding ΔH [18]. The difference may be ascribed to the assumption that the activation energy observed should include, at least in part, some proportion of the activation energy for nucleation of the solid product [19].

In conclusion, the thermal decomposition of $Cu(OH)_2$ to CuO and H_2O proceeds according to an A_m mechanism, both at constant and increasing temperatures. It is important in general that both isothermal and dynamic analyses should be made in order to examine the kinetics of solid decompositions. In this connection, many previous studies, in which a single dynamic run was analyzed especially using only an R_n type function, may not be necessarily meaningful.

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