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KINETICS AND THERMODYNAMICS OF THERMAL DEHYDRATION OF MAGNESIUM OXALATE DIHYDRATE

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The kinetics and thermodynamics of the thermal dehydration of crystalline powders of $MgC_2O_4 \cdot 2\,H_2O$ were studied by means of thermal analyses both at constant temperatures and at linearly increasing temperatures. The dehydration of the dihydrate is regulated by one of the Avrami–Erofeyev laws. The kinetic parameters from TG at constant temperatures are in good agreement with those from TG at the lowest rate of rising temperatures. The dynamic dehydration kinetics was also examined, using DSC recorded simultaneously with TG at linearly increasing temperatures. The validity of the estimated mechanism and kinetic parameters is briefly discussed.

Recently, we have reported kinetic studies on the thermal dehydration of several salt hydrates, using TG both at constant temperatures and at linearly increasing temperatures [1]. The dehydration of ground crystalline powders of these hydrates was found to obey a random nucleation and subsequent growth mechanism.

It seems worthwhile to examine such kinetics along these lines, since the results of different authors are often different. The present paper deals with an investigation of the kinetics and thermodynamics of the thermal dehydration of $MgC_2O_4 \cdot 2\,H_2O$ by means of dynamic TG–DSC, recorded simultaneously under various measuring conditions, as well as TG at constant temperatures.

Experimental

Magnesium oxalate dihydrate was prepared by the double decomposition of ammonium oxalate and magnesium chloride in hot aqueous solution. The dihydrate was identified from IR spectra and TG traces. The dihydrate was ground and sieved to four fractions: 100–170, 170–200, 200–280 and 280–350 meshes.

TG–DSC traces were recorded simultaneously at heating rates of 0.58, 1.22 and 2.33 degree min^{-1} in a flow of nitrogen at a rate of 25 ml min^{-1} for the fraction 170–200 mesh, using a TG–DSC (8085 E1) apparatus of Rigaku Denki Co. About 15.0 mg of the sample was weighed into a platinum crucible 5 mm in diameter and 2.5 mm in depth, without pressing. TG traces at constant temperatures were also

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recorded under the same measuring conditions as in the dynamic run. Other experimental procedures were the same as those described previously [1].

Results and discussion

Isothermal method

We can assume the following relation for the isothermal dehydration of $MgC_2O_4 \cdot 2\,H_2O$:

$$F(\alpha) = kt \qquad (1)$$

where $F(\alpha)$ is a function depending on the mechanism of isothermal dehydration, α is the fraction dehydrated at time t, and k is the rate constant. The correct $F(\alpha)$ can be estimated to some extent by plotting it against t. Various $F(\alpha)$ derived on the basis of theoretical models [2] have been examined. Table 1 lists such $F(\alpha)$. Table 2 shows the correlation coefficients r and standard deviations σ in the least square fitting of $F(\alpha)$ vs. t plots. In view of the values of r and σ, both R_n and A_m mechanisms are to be selected as the correct $F(\alpha)$. The mean values of n and m were determined to be 1.56±0.12 and 2.36±0.04, respectively, over the temperature range 159.8–175.0° by "scanning" the values with a computer. Typical plots of $F(\alpha)$ vs. t are shown in Fig. 1. Values of k at various temperatures, deduced from the plots using the mean values of n and m, are listed in Table 3. Table 4 shows the activation energy E and frequency factor A, together with the value of r derived from the Arrhenius plot. It is seen that the identical kinetic parameters result from either the A_m or R_n mechanism.

Our result is not compatible with those of other workers [3, 4], which may be due to the different sample and measuring conditions.

Table 1 The mechanistic functions $F(\alpha)$ examined for the thermal dehydration of $MgC_2O_4 \cdot 2\,H_2O$

$F(\alpha)$	Symbol	Rate-controlling process
α^2	D_1	One-dimensional diffusion
$\alpha + (1-\alpha)\ln(1-\alpha)$	D_2	Two-dimensional diffusion
$[1-(1-\alpha)^{1/3}]^2$	D_3	Three-dimensional diffusion (Jander function)
$1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}$	D_4	Three-dimensional diffusion (Ginstling–Broushtein function)
$\ln[\alpha/(1-\alpha)]$	A_u	Autocatalytic reaction (Prout–Tompkins function)
$1-(1-\alpha)^{1/n}$	R_n	Phase-boundary reaction; $n = 1, 2$ and 3 (one-, two- and three-dimensional, respectively)
$[-\ln(1-\alpha)]^{1/m}$	A_m	Random nucleation; $m = 1$ Random nucleation and subsequent growth; $m = 2, 3$ and 4 (Avrami–Erofeyev functions)

Table 2 The correlation coefficient r and standard deviation σ for the least square fitting of $F(\alpha)$ vs. t plot for the isothermal dehydration of $MgC_2O_4 \cdot 2\,H_2O$ at 159.8° in the α range 0.2–0.9

	D_1	D_2	D_3	D_4
r	0.9961	0.9847	0.9551	0.9764
$\sigma \times 10^2$	2.205	3.567	2.520	1.205
	A_u	R_1	R_2	R_3
r	0.9988	0.9952	0.9994	0.9968
$\sigma \times 10^2$	5.102	2.198	0.6219	1.133
	A_1	A_2	A_3	A_4
r	0.9845	0.9996	0.9992	0.9978
$\sigma \times 10^2$	10.90	0.9386	0.8762	1.080

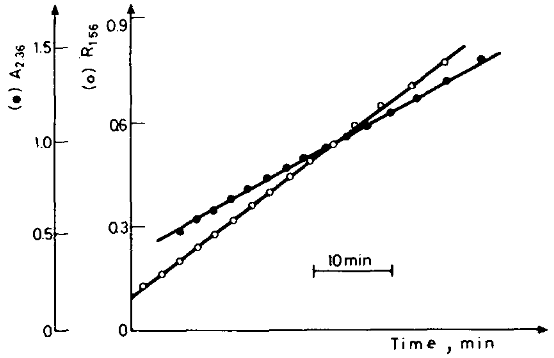

Fig. 1 Typical $F(\alpha)$ vs. t plots for the dehydration of $MgC_2O_4 \cdot 2\,H_2O$ at a constant temperature of 159.8° in the α range 0.2–0.9

Non-isothermal method

Typical TG–DSC traces obtained simultaneously for the thermal dehydration of $MgC_2O_4 \cdot 2\,H_2O$ are shown in Fig. 2. The kinetic parameters can be derived in terms of the equation [5, 6]:

$$\ln \frac{F(\alpha)}{T^2} = \ln \frac{AR}{aE}\left(1 - \frac{2RT}{E}\right) - \frac{E}{R}\frac{1}{T} \qquad (2)$$

where T is the absolute temperature, R is the gas constant, and a is the linear heating rate. If the correct $F(\alpha)$ is used, a plot of $\ln\,[F(\alpha)/T^2]$ vs. $1/T$ should give a straight

Table 3 The rate constants k for the isothermal dehydration of $MgC_2O_4 \cdot 2\,H_2O$ in terms of R_n and A_m functions

Temperature, °C	$k \times 10^4$, s^{-1}	
	R_n ($n = 1.56$)	A_m ($m = 2.36$)
159.8	2.7901	3.6105
161.4	2.8536	3.7212
162.5	3.5833	4.6168
165.7	3.9950	5.1473
166.1	4.1946	5.3842
170.7	5.8315	7.5647
170.9	5.7227	7.3466
175.0	7.1656	9.3802

Table 4 The Arrhenius parameters E and A, and the correlation coefficient r from the analysis of the isothermal dehydration of $MgC_2O_4 \cdot 2\,H_2O$

$F(\alpha)$	E, kJ mol^{-1}	$\log A$, s^{-1}	$-r$
$R_{1.56}$	103.5±1.4	8.93±0.16	0.9915
$A_{2.36}$	103.9±1.3	9.10±0.15	0.9927

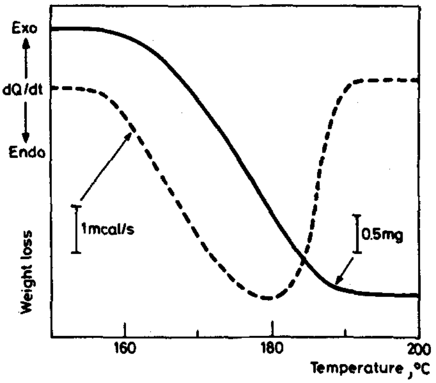

Fig. 2 Typical simultaneous traces of TG (———) and DSC (– – – –) for the dehydration of $MgC_2O_4 \cdot 2\,H_2O$ at a heating rate of 1.22 degree min^{-1}

line, from which the values of E and A are derived. Table 5 shows typical values of E and A, together with the value of r, for all $F(\alpha)$ listed in Table 1 except A_u. It seems, in view of the reasonable order of magnitude of E and A, and the reasonable value of r, that an A_m mechanism should regulate the dehydration of $MgC_2O_4 \cdot 2\,H_2O$.

If the isothermally-determined $F(\alpha)$, i.e. $R_{1.56}$ and $A_{2.36}$, are applied to Eq. (2), the values of E and A listed in Table 6 are obtained. It is seen that the parameters decrease with increase in the heating rate. This trend may be explained by a thermal lag between the furnace and the sample [7], as can be seen from the change in dehydration temperature [8]. The dehydration temperatures derived from DSC and TG traces are given in Table 7.

Table 5 The Arrhenius parameters E and A, and the correlation coefficient r for the dehydration of $MgC_2O_4 \cdot 2\,H_2O$ from a single TG trace at a heating rate of 1.22 degree min^{-1} in the α range 0.1–0.9

$F(\alpha)$	E, kJ mol^{-1}	log A, s^{-1}	$-r$
D_1	347	37.3	0.9730
D_2	385	41.7	0.9820
D_3	435	47.0	0.9904
D_4	402	43.0	0.9853
R_1	170	16.7	0.9718
R_2	202	20.3	0.9864
R_3	214	21.6	0.9901
A_1	241	25.3	0.9953
A_2	117	10.7	0.9949
A_3	75.3	5.71	0.9946
A_4	54.4	3.20	0.9942

Table 6 The Arrhenius parameters E and A for the dehydration of $MgC_2O_4 \cdot 2\,H_2O$ at various heating rates in the α range 0.1–0.9

$F(\alpha)$	Method	Heating rate (deg/min)					
		0.58		1.22		2.33	
		E, kJ mol^{-1}	log A, s^{-1}	E, kJ mol^{-1}	log A, s^{-1}	E, kJ mol^{-1}	log A, s^{-1}
$R_{1.56}$	TG	188	19.0	180	17.9	152	14.5
	DSC	217	22.5	201	20.3	167	16.3
$A_{2.36}$	TG	95.4	8.11	91.3	7.67	76.2	5.94
	DSC	108	9.68	101	8.81	81.2	6.53

It is noted here that the parameters for $A_{2.36}$ at the lowest heating rate are comparable with those from the isothermal method, whereas those for $R_{1.56}$ are not. We may thus assume that the dehydration of $MgC_2O_4 \cdot 2\,H_2O$ is regulated by an A_m mechanism [1]. The A_m mechanism is supported by the fact that the rate constant k is practically unaffected by the particle size. The effect of particle size on the values of E, A and k is shown in Table 8. The A_m mechanism seems to be probable too in that ground crystalline powder samples were used in the present study [9].

It is interesting that the values of E and A from TG are smaller than those from DSC, whereas the values of k are practically equal. The compensation effect also seems to result in this case. The smaller values of E and A for TG may be ascribed to the fact that the volatilization of liberated water is not instantaneous, but a time lag may appear [7]. This may be seen in the effect of the particle size on the difference of E between TG and DSC analyses. Table 8 shows the tendency that the difference of E decreases with decrease in the particle size.

Table 7 The extrapolated onset temperature T_{eo} from the DSC trace, the temperature of half-dehydration $T_{1/2}$ from the TG trace, and the peak temperature T_p from the DSC trace for the dehydration of $MgC_2O_4 \cdot 2\,H_2O$

Dehydration temp., °C	Heating rate (degree/min)		
	0.58	1.22	2.33
T_{eo}	146.5	154.2	158.2
$T_{1/2}$	164.4	173.5	181.3
T_p	168.4	178.0	186.7

Table 8 The effect of particle size on the kinetic parameters E, A and k for the dehydration of $MgC_2O_4 \cdot 2\,H_2O$ at a heating rate of 1.22 degree min^{-1}

$F(\alpha)$	Kinetic parameter	Particle size fraction, mesh							
		100–170		170–200		200–280		280–350	
		TG	DSC	TG	DSC	TG	DSC	TG	DSC
$R_{1.56}$	E, kJ mol^{-1}	198	222	180	201	203	233	173	175
	$\log A$, s^{-1}	19.8	22.6	17.9	20.3	20.6	24.1	17.1	17.4
	$k \times 10^4$, s^{-1}	5.12	4.50	7.02	6.42	5.94	5.45	7.36	6.31
$A_{2.36}$	E, kJ mol^{-1}	100	111	91.3	101	104	113	87.1	90.4
	$\log A$, s^{-1}	8.65	9.95	7.67	8.81	9.09	10.2	7.17	7.57
	$k \times 10^4$, s^{-1}	8.64	8.60	9.91	10.0	9.53	9.50	9.88	9.53

It seems worthwhile to compare the value of E for the dehydration of $MgC_2O_4 \cdot 2 H_2O$ with the corresponding enthalpy change ΔH. The ΔH value per mole of water evolved was determined to be 61.20±0.21 kJ mol^{-1}. The isothermally-determined value of E (ca. 104 kJ mol^{-1}) is considerably larger than the ΔH value. This difference is explained by a possible contribution of nucleation of the solid product to the activation energy [10]. This can be regarded as another argument for the proposed dehydration mechanism: the random nucleation and its subsequent growth mechanism.

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Zusammenfassung — Kinetik und Thermodynamik der thermischen Dehydratisierung von kristallinen Pulvern von $MgC_2O_4 \cdot 2 H_2O$ wurde thermoanalytisch bei konstanter und linear ansteigender Temperatur untersucht. Die Dehydratisierung des Dihydrats folgt einem der Avrami—Erofeyev-Gesetzen. Die aus TG-Messungen bei konstanter und bei mit der geringsten Geschwindigkeit linear ansteigender Temperatur erhaltenen kinetischen Parameter stimmen gut überein. Die Kinetik der dynamischen Dehydratisierung wurde ebenfalls durch DSC und gleichzeitiger Registrierung der TG-Kurven untersucht. Die Zuverlässigkeit des ermittelten Mechanismus und der bestimmten kinetischen Parameter wird kurz diskutiert.

Резюме — Методом термического анализа при постоянных и линейно-возростающих температурах изучена кинетика и термодинамика термической дегидратации кристаллических порошков $MgC_2O_4 \cdot 2 H_2O$. Реакция дегидратации подчиняется одному из уравнений Аврами—Ерофеева. Кинетические параметри, установленные на основе ТГ при постоянном нагреве, хорошо согласуются с теми, которые были выведены из данных ТГ при самой низкой скорости подъема температур. Динамика кинетики дегидратации была исследована совмещенным методом ДСК—ТГ при линейном нагреве. Кратко обсужден механизм и параметры кинетики реакции дегидратации.