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Kinetic analysis of the nonisothermal dehydration of lithium sulfate monohydrate

Nobuyoshi Koga and Haruhiko Tanaka

Chemistry Laboratory, Faculty of School Education, Hiroshima University, Shinonome, Minami-ku, Hiroshima 734 (Japan)

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Abstract

Kinetic data of the title dehydration obtained from simultaneous TG–DSC measurements were compared between the single crystals and crushed crystal material. The kinetics were interpreted in relation to the reaction geometry observed by polarizing microscopy. The kinetic compensation effect established for the Arrhenius parameters evaluated by the Ozawa method was discussed in terms of the temperature interval analyzed.

INTRODUCTION

The process of thermal decomposition of those solids that yield solid and gaseous products consists of several stages, e.g., the chemical act of breaking of bonds, followed by destruction of the reactant crystal lattice, formation of nuclei of the solid product and growth of these nuclei, adsorption–desorption of gaseous products, diffusion of gases, and heat transfer [1]. On the other hand, thermoanalytical (TA) measurements, which have been widely used for kinetic study of solid-state reactions, provide a certain macroscopic information averaged over the process depending on the physical quantity measured. Recently, we reported that some differences are observed between the kinetic results obtained from TG and DSC for the process in which crystallization of the solid product and diffusion of gaseous product through the solid product layer play an important role [2,3]. Also, it is important to link the kinetic results assessed thermoanalytically, which reflect macroscopic behavior, with direct observation of the relevant texture, which is centered on a localized site [4], by such techniques as scanning electron microscopy [5], optical microscopy [6] and polarizing microscopy [7].

In this study, simultaneous TG–DSC data for the nonisothermal dehydration of lithium sulfate monohydrate, as reported earlier [8], were further analyzed to compare the kinetic results derived from TG and DSC. The results are interpreted in connection with the reaction morphology and/or geometry observed by polarizing microscopy.

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EXPERIMENTAL

Sample preparation and simultaneous TG–DSC measurements were described earlier [8]. Thin sections of the single crystals and crushed crystals ($-48+100$ mesh) dehydrated to various fractional extents of reaction α in the above TG–DSC system under conditions identical with those of TA measurements were prepared by using the techniques reported elsewhere [2,7–9]. These thin sections were observed by a polarizing microscope and photographed.

RESULTS AND DISCUSSION

Figure 1 shows typical plots of α against temperature T, obtained from the simultaneous TG and DSC measurements of the nonisothermal dehydration of the single crystals at various heating rates. We see that (1) the α–T curves derived from TG shift to higher temperatures than those from DSC during the initial reaction, in particular for the lowest heating rate, and that (2) there is no apparent difference in the α–T curves in the subsequent reaction ($0.1 \leqslant \alpha \leqslant 0.9$). A similar tendency was observed irrespective of the sample preparation examined. This does not correspond to the results obtained for the nonisothermal dehydration of $K_2CuCl_4 \cdot 2H_2O$ [2], where crystallization of the solid product and diffusion of the gaseous product play important roles [7]. It is a marked contrast that there is a diffusion controlled process for the dehydration of $K_2CuCl_4 \cdot 2H_2O$ during the later stage of reaction. Fact (1) may be related to an abrupt retardation of rate of reaction observed for the isothermal dehydration in a constant-volume glass apparatus initially evacuated [10] and possibly under dynamic vacuum [11]. It is thus likely that the process is regulated by diffusion of the evolved water vapor from a metastable intermediate [11]. It must also be noted here that the initial and final parts of the integrated DSC curves are appreciably

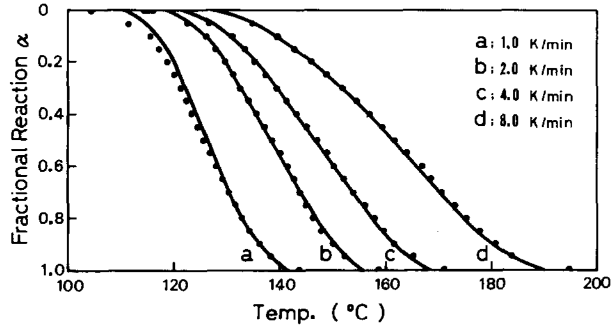

Fig. 1. Plots of α against T obtained from TG (———) and DSC (●) for the nonisothermal dehydration of single crystals of $Li_2SO_4 \cdot H_2O$.

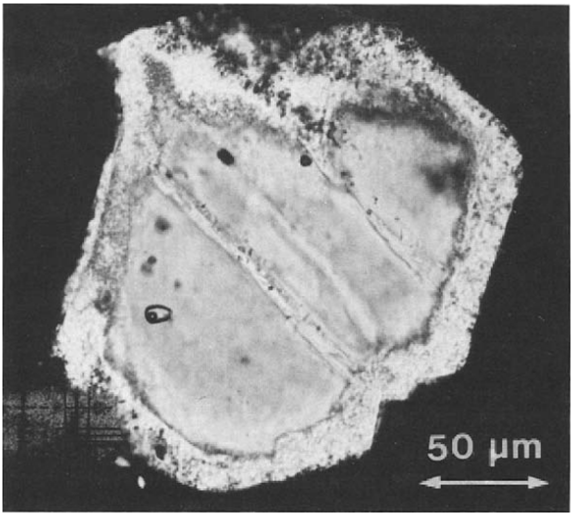

Fig. 2. Typical polarizing microscopic view of the internal surface of 50% dehydrated crushed crystal of $Li_2SO_4 \cdot H_2O$ of $-48+100$ mesh sieve fraction.

affected by the base-line assumed. Fact (2) is related to the earlier finding that the dehydration results in the generation of an extensive irregular crack and pore structure penetrating the coherent assemblage of product (Li_2SO_4) crystallites, ca. 0.2–1.0 μm in diameter. This intercrystalline system of connected channels is possibly the escape route for removal of the gaseous product [10].

A typical polarizing microscopic view of a 50% dehydrated crushed crystal at a heating rate of 4 K min^{-1} is shown in Fig. 2. As is the case for the single crystals [8], it is evident that the reaction proceeds according to the advance of the reaction front from the surface towards the center of the crystal.

Table 1 shows the most appropriate kinetic model function $F(\alpha)$ and Arrhenius parameters determined by the Ozawa method [12] across the various ranges of α. Although the R_n law with $n > 3$ has no physical meaning, such laws were not ruled out in the present study [8]. As is expected from the α–T curves, no apparent difference is observed between the kinetic parameters derived from TG and DSC. The kinetic results show that the kinetic curves are expressed, on the whole, by a combination of an Avrami–Erofeyev (A_m) model, $[-\ln(1-\alpha)]^{1/m} = kt$, which is representative during the earlier stage of reaction, with a phase-boundary controlled (R_n) model, $1-(1-\alpha)^{1/n} = kt$, which in turn becomes predominant as the reaction proceeds [8]. The obedience to the R_n law with $2 < n < 3$ during the later stage of the reaction is in good agreement with the reaction geometry observed by polarizing microscopy, in accordance with the usual correspondence of the kinetic results obtained from TA data to the geometry factor [13].

TABLE 1

Comparison of the kinetic parameters $F(\alpha)$, E and log A derived by the Ozawa method for the nonisothermal dehydration of $Li_2SO_4 \cdot H_2O$

Particle size, mesh	Range of α	TG				DSC			
		$F(\alpha)$	E (kJ mol^{-1})	log A (s^{-1})	γ [a]	$F(\alpha)$	E (kJ mol^{-1})	log A (s^{-1})	γ [a]
−170+200	0.1–0.9	$R_{3.0}$	135±2	15.5	0.9999	$R_{2.8}$	137±3	15.8	0.9999
	0.1–0.5	$A_{1.0}$	154±2	18.8	0.9998	$A_{1.0}$	155±4	18.7	0.9998
	0.2–0.6	$A_{1.1}$	141±1	16.7	0.9998	$A_{1.0}$	143±4	17.0	0.9998
	0.3–0.7	$R_{2.2}$	131±1	15.0	0.9999	$R_{2.5}$	133±3	15.2	0.9999
	0.4–0.8	$R_{2.5}$	124±2	14.0	0.9999	$R_{2.0}$	126±3	14.3	0.9999
	0.5–0.9	$R_{2.4}$	117±2	13.1	0.9999	$R_{2.0}$	120±2	13.4	0.9999
−48+100	0.1–0.9	$R_{2.6}$	115±1	12.6	0.9999	$R_{2.6}$	116±1	12.6	0.9999
	0.1–0.5	$A_{1.2}$	127±1	14.6	0.9999	$A_{1.2}$	128±1	14.8	0.9999
	0.2–0.6	$A_{1.2}$	119±1	13.5	0.9999	$A_{1.3}$	120±1	13.6	0.9999
	0.3–0.7	$R_{2.4}$	113±1	12.2	0.9999	$A_{1.2}$	113±1	12.7	0.9999
	0.4–0.8	$R_{2.1}$	108±1	11.6	0.9999	$R_{2.5}$	108±1	11.6	0.9998
	0.5–0.9	$R_{2.6}$	103±1	11.0	0.9999	$R_{2.1}$	104±1	11.0	0.9999
Single crystal	0.1–0.9	$R_{4.8}$	93±2	8.4	0.9998	$R_{5.0}$	92±2	8.2	0.9998
	0.1–0.5	$A_{1.0}$	104±2	10.6	0.9995	$A_{1.0}$	103±2	10.4	0.9993
	0.2–0.6	$A_{1.0}$	96±2	9.5	0.9999	$A_{1.0}$	95±2	9.4	0.9998
	0.3–0.7	$R_{4.3}$	90±2	8.1	0.9999	$R_{4.6}$	89±2	7.9	0.9999
	0.4–0.8	$R_{2.9}$	86±2	7.6	0.9999	$R_{3.1}$	85±2	7.5	0.9999
	0.5–0.9	$R_{3.0}$	82±2	7.2	0.9999	$R_{3.0}$	81±2	7.0	0.9999

[a] Correlation coefficient for linear regression analysis of the $F(\alpha)$ vs. generalized time θ plot.

It was also reported that the A_m law with $m = 1$ (i.e., the first order equation) can be applied to the diffusion kinetics of "gas–solid small particles" reactions [14]. The obedience to the A_m law with $m \approx 1$ determined by TG for the thermal dehydration of crushed crystals of $Li_2SO_4 \cdot H_2O$ (−170 + 200 mesh) in a flow of N_2 [15] was explained on the basis of such diffusion of water vapor from the crystal lattice [14]. On the other hand, it was shown that nucleation and growth of the solid product play an important role during the initial part of the reaction [8,10]. Both of these different findings suggest the possibility of obedience to the A_m law, although kinetic obedience to a particular rate law does not always provide unambiguous information concerning the chemistry of the processes involved [16]. At the same time, such kinetic obedience is also affected by the distribution of the particle size [2], the anisotropy of the reaction [8] and the atmosphere (the vapor pressure of evolved water). Because the kinetic obedience also varies with α, it is difficult to specify a single kinetic function appropriate to the actual process, in particular over a wide range of α, e.g., $0.1 \leqslant \alpha \leqslant 0.9$. It must be also be noted that the kinetic data obtained from TA measurements include more or less error, which makes the kinetic obedience ambiguous [17,18].

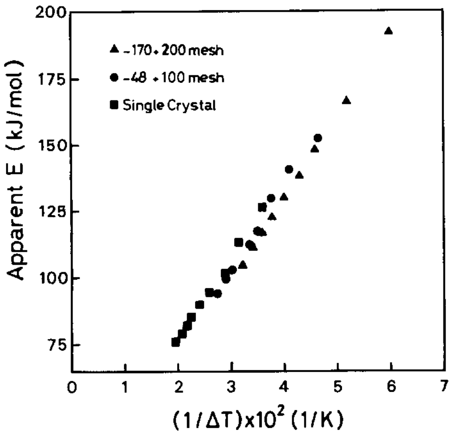

Fig. 3. Plots of the apparent E against the reciprocal of ΔT (see text).

The change in the Arrhenius parameters depending on the sample preparation and α can be interpreted by the so-called kinetic compensation effect (KCE) [19,20]

$$\log A = aE + b \tag{1}$$

where a and b are constants. From a mathematical viewpoint, the KCE seems to be due to the short temperature interval analyzed, ΔT [21]. In the present case, where a multi-heating rate method was used to evaluate the Arrhenius parameters, ΔT corresponds to the temperature interval between the lowest and highest heating rates at a given α. Figure 3 shows the plot of the apparent activation energies E against the reciprocal of ΔT. It may be noted that the following relationship is established [22]

$$E = c \cdot \frac{1}{\Delta T} + d \tag{2}$$

Combining eqn. (1) with eqn. (2), the change in log A is expressed by the equation [22]

$$\log A = ac \cdot \frac{1}{\Delta T} + (ad + b) \tag{3}$$

Simple mathematical analysis for the Ozawa method gives [23]

$$E = \frac{RT_{\mathrm{L}}T_{\mathrm{H}}}{\Delta T} \cdot \ln\left[\frac{T_{\mathrm{L}}^2}{T_{\mathrm{H}}^2} \cdot \frac{\phi_{\mathrm{H}}}{\phi_{\mathrm{L}}}\right] \tag{4}$$

where T_{L} and T_{H} are the temperatures at the lowest and highest heating rates, ϕ_{L} and ϕ_{H}, respectively. The linear interdependence expressed by eqn. (2) seems to be due also to the small difference between T_{L} and T_{H}. On the other hand, constant Arrhenius parameters can be obtained if $F(\alpha)$ and ΔT remain constant [22]. The variation in ΔT implies not only the complex nature of the kinetic process, but also the deviation of the reaction condition from that idealized [11,18,21].

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