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KINETICS OF THE MULTISTAGE DEHYDRATION OF ALUMINUM SULFATE HYDRATE

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ABSTRACT

The dehydration of aluminum sulfate hydrate is a consecutive four-stage thermal decomposition process. Reaction temperatures range from 50 to 230 °C and 250 to 430 °C. The kinetics of the individual stages are analyzed by a method proposed by Szuniewicz and Manitius, which utilizes the quasilinearization of nonlinear kinetic equations and the Marquardt iterative procedure to evaluate the best kinetic expression and its associated parameters which minimize the quadratic objective function J. Our results indicate that the nuclei–growth type of models, i.e., $\alpha = 1 - e^{-Kt^n}$, generally produce the smallest J values among many alternative kinetic expressions.

With $n = 1$ and optimized parameters, the experimental TG curves can be simulated well by a set of equations. The calculated activation energies vary from ca. 10.5 kcal mol^{-1} for the first stage reaction to ca. 25.0 kcal mol^{-1} for the last stage reaction. Variables such as heating rate and sample weight seem to have similar effects on the calculated activation energies as those discussed in an earlier paper for the calcination of anhydrous aluminum sulfate.

INTRODUCTION

The kinetics of multistage, consecutive thermal decompositions of a solid have been studied by a number of researchers [1–5]. The method proposed by Szuniewicz and Manitius [3] for processing experimental data obtained under non-isothermal conditions will enable the determination of the best kinetic models and corresponding parameters for the individual stages. In their method, a four-stage decomposition process can be described by the following set of equations

$$\Delta m(t) = m_0(K_1\alpha_1 + K_2\alpha_1\alpha_2 + K_3\alpha_1\alpha_2\alpha_3 + K_4\alpha_1\alpha_2\alpha_3\alpha_4) \tag{1}$$

$$\frac{d\alpha_i}{dt} = \exp\left(-\frac{E_i}{RT} + C_i\right)f_i(\alpha_i) \quad i = 1, 4 \tag{2}$$

where $\Delta m(t)$ = accumulated weight loss of the sample at time t, m_0 = initial sample weight, α_i = conversion in the ith stage, K_i = stoichiometric ratio, i.e., the ratio of the total weight loss in the ith stage to the initial sample weight,

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$f_i(\alpha_i)$ = best kinetic expression for the ith stage, E_i and exp C_i = activation energy and pre-exponential factor based on $f_i(\alpha_i)$, respectively.

The stoichiometric ratios of each stage are either known from the reaction itself or can be estimated along with other parameters. Since, in general, the DTG curves give a better resolution between consecutive stages of a decomposition process, they are therefore used for the selection of the best kinetic model and also for the preliminary determination of associated parameters, such as K_i, E_i and C_i, of the individual stages. The final optimization of these parameters will then involve the quasilinearization of nonlinear kinetic equations and the Marquardt iterative procedure to minimize the quadratic function J, defined as the sum of the squared deviations between experimental and theoretical results of the TG or DTG curves [3].

The dehydration process of aluminum sulfate hydrate was shown to consist of multistage consecutive reactions occurring between 50 and 500 °C [6.7]. Depending on the nature of the starting material, various amounts of water molecules would be evolved during each stage. The rates of dehydration were only analyzed for the overall decomposition process without distinguishing between different stages [6,7]. The kinetic models and corresponding parameters thus obtained were rather ambiguous. It is therefore the objective of this study to reexamine the kinetics of this multistage dehydration process of aluminum sulfate hydrate by a more rigorous method as outlined above.

EXPERIMENTAL PROCEDURE

Reagent grade aluminum sulfate hydrate ($Al_2(SO_4)_3 \cdot 16\text{–}18H_2O$, Osaka Hayashi Co.) was used in this work. The dynamic TG and DTG measurements were obtained with a Perkin-Elmer TGS-2 thermobalance, equipped with a FDC-1 first derivative computer. This unit was calibrated periodically with magnetic standards to ensure consistency. Powders of various weights were loosely packed in a platinum crucible of 5.8 mm diameter and 1.8 mm depth. Dry air flowing at 15 ml min^{-1} was used throughout this study. In Table 1, the specific experimental conditions of five runs are listed whose results are analyzed in this paper.

TABLE 1

Experimental conditions

Run No.	1	2	3	4	5
Heating rate (°C min^{-1})	5.0	5.0	5.0	10.0	20.0
Sample weight (mg)	8.01	11.745	17.24	19.72	19.62

TABLE 2

List of kinetic equations considered in this work

Model	f(α)	Model	f(α)
R_1	α^0	A_3	$(1-\alpha)[-\ln(1-\alpha)]^{2/3}$
R_2	$(1-\alpha)^{1/2}$	A_4	$(1-\alpha)[-\ln(1-\alpha)]^{3/4}$
R_3	$(1-\alpha)^{2/3}$	D_1	α^{-1}
F_1	$(1-\alpha)$	D_2	$1/[-\ln(1-\alpha)]$
$A_{1.5}$	$(1-\alpha)[-\ln(1-\alpha)]^{1/3}$	D_3	$(1-\alpha)^{2/3}/[1-(1-\alpha)^{1/3}]$
A_2	$(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	D_4	$(1-\alpha)^{1/3}/[1-(1-\alpha)^{1/3}]$

RESULTS AND DISCUSSION

In Fig. 1, typical results of TG and DTG curves (based on Run 3 in this case) are shown. As can be seen, the dehydration process consists of four-stage consecutive reactions with overlapping between the first two and last two stages. Reaction temperatures range from 50 to 230 °C and 250 to 430 °C, respectively. These data are in good agreement with those reported by Gitis, et al. [6].

Since the overlapping of consecutive reactions is not very serious in this study, it is not difficult to draw hypothetical DTG curves for each stage as shown by the dashed lines in Fig. 1. By numerical integration of these curves, we find the following approximate values for K_1 to K_4: 0.24, 0.116, 0.0348 and 0.03771, respectively. With these values and the DTG curves for each stage, we can then use the Marquardt nonlinear algebraic regression to obtain the optimal initial estimation of the kinetic parameters, E_i and C_i, for every kinetic equation listed in Table 2. Results of calculated minimum J

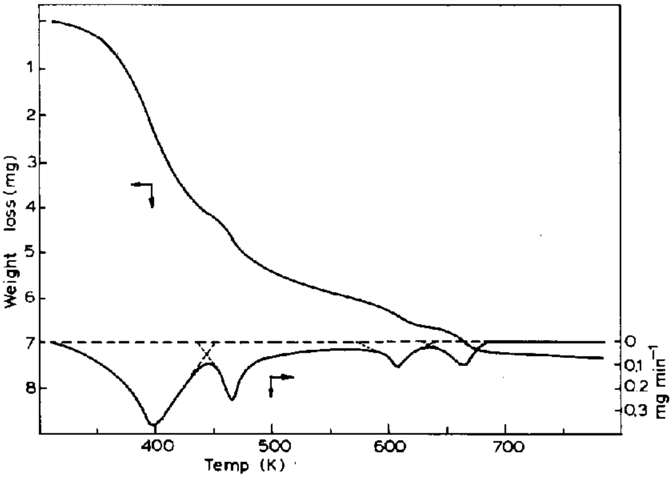

Fig. 1. Typical TG (above) and DTG (below) curves. (- - - - - -) Hypothetical DTG curve.

values for each model are summarized in Table 3.

From this table it is clear that the nuclei–growth model is generally better than either the phase boundary reaction or diffusion-controlled models in describing the reaction mechanism of this dehydration process. The F_1 model, also known as the first-order reaction model, was chosen to represent the reaction mechanisms of all stages in this study primarily for its simplicity. In some cases, other models, such as $A_{1.5}$ or A_2 might give lower J values than the F_1 model; yet the differences between these J values were never significant. By repeating this parameter-estimation method with the TG curve, furthur improvement can be achieved. The final kinetic model found through this procedure (for Run 3) is

$$\Delta m(t) = 17.24(0.238\alpha_1 + 0.118\alpha_1\alpha_2 + 0.0349\alpha_1\alpha_2\alpha_3 + 0.0376\alpha_1\alpha_2\alpha_3\alpha_4) \tag{3}$$

$$\mathrm{d}\alpha_1/\mathrm{d}t = \exp(-10410/RT + 11.21)(1-\alpha_1) \tag{4}$$

$$\mathrm{d}\alpha_2/\mathrm{d}t = \exp(-12350/RT + 11.03)(1-\alpha_2) \tag{5}$$

$$\mathrm{d}\alpha_3/\mathrm{d}t = \exp(-20840/RT + 15.02)(1-\alpha_3) \tag{6}$$

$$\mathrm{d}\alpha_4/\mathrm{d}t = \exp(-24440/RT + 16.78)(1-\alpha_4) \tag{7}$$

A comparison of the experimental data to the weight loss (Δm) calculated from the above set of equations is illustrated in Fig. 2. The agreement between these two curves is quite satisfactory.

Finally, the experimental data from other runs were also analyzed in the same manner. The kinetic parameters thus obtained are summarized in Table 4. It can be seen that the activation energies decrease as the heating rate or

TABLE 3

The minimum J values calculated for the individual stage according to the various models

Model	1st stage	2nd stage	3rd stage	4th stage
R_1	0.0121	0.0223	0.0145	0.0372
R_2	0.0086	0.0218	0.0129	0.0322
R_3	0.0054	0.0211	0.0121	0.0209
F_1 [a]	0.0018	0.0117	0.0053	0.0063
$A_{1.5}$	0.0019	0.0121	0.0057	0.0069
A_2	0.0021	0.0132	0.0068	0.0071
A_3	0.0024	0.0147	0.0072	0.0073
A_4	0.0024	0.0156	0.0072	0.0070
D_1	0.0192	0.0480	0.0490	0.0420
D_2	0.0170	0.0390	0.0370	0.0370
D_3	0.0510	0.0370	0.0280	0.0310
D_4	0.0128	0.0345	0.0215	0.0295

[a] The best fitting model based on these J values.

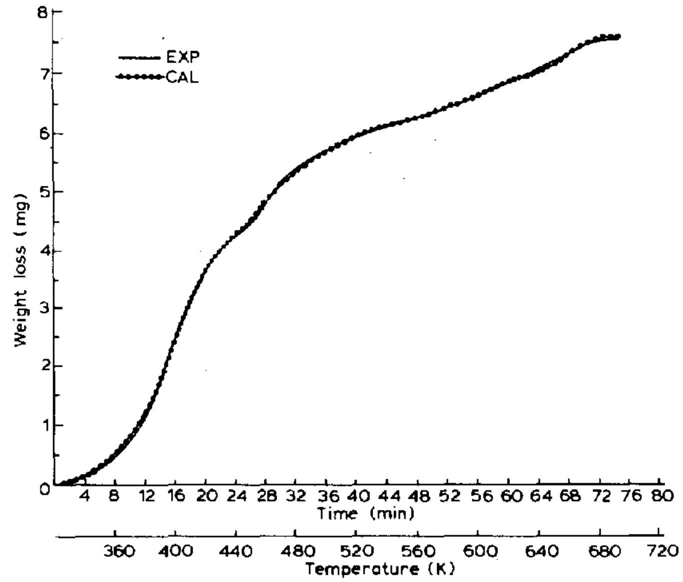

Fig. 2. Comparison of experimental and calculated weight loss.

TABLE 4

The kinetic parameters, based on model F_1, of the various stages of the dehydration process carried out under different experimental conditions (activation energy in kcal mol^{-1})

Run No.	1st stage		2nd stage		3rd stage		4th stage	
	E_1	C_1	E_2	C_2	E_3	C_3	E_4	C_4
1	10.78	11.32	13.07	11.69	22.56	16.20	26.27	17.56
2	10.66	11.18	12.55	11.27	21.35	15.40	24.98	17.02
3	10.41	11.21	12.35	11.03	20.84	15.02	24.44	16.78
4	8.67	9.08	10.78	10.72	18.73	14.27	22.47	15.51
5	8.13	8.72	10.47	10.45	18.24	13.97	21.71	15.17

sample weight increases, though the extent of variation differs for the different stages. This trend is generally very similar to that observed in an earlier paper [8] on the decomposition reaction of anhydrous aluminum sulfate.

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