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Influence of water vapor on the thermal dehydration of $Li_2SO_4 \cdot H_2O$ [a]

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Abstract

Kinetics of thermal dehydration of lithium sulfate monohydrate have been studied by using TG and DSC for $Li_2SO_4 \cdot H_2O$ samples with different characteristics, i.e., powdered sample, pressed pellet, plate crystal and cubic crystal. The TG measurements in N_2 saturated with water and dry N_2 showed that the dehydration of $Li_2SO_4 \cdot H_2O$ was affected by the presence of water, particularly for the powdered sample at the early stage of dehydration. This phenomenon is explained by consideration of H_2O diffusion. The apparent activation energies were calculated based on the Ozawa method from TG data obtained at different heating rates. No significant difference was found in the apparent activation energy due to the presence of external water vapor. DSC measurements on the dehydration of all four samples were also performed, and the apparent activation energies, obtained from analyzing partial areas by the Ozawa method, are comparable to those obtained from TG.

INTRODUCTION

The kinetics of the thermal dehydration of lithium sulfate monohydrate have been studied by several workers because of the simplicity of its single stage reaction [1–5]. The vast majority of work has centered on dry atmosphere or vacuum dehydration and relatively little work has been done to examine the influence of external water vapor on the dehydration kinetics. The reaction is reversible so diffusion of the water molecules produced away from the reaction site plays an important role in the dehydration of $Li_2SO_4 \cdot H_2O$. A study of the influence of external water vapor should help to better understand the role of the removal of water in the kinetics of dehydration. The method of sample preparation, rate of change of temperature, and purging gas (type and flow rate) used are generally factors.

In this paper, the kinetics of dehydration have been studied using four samples of lithium sulfate monohydrate, i.e. powder, pressed pellet, thin

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platelet crystal and cubic shaped crystal, in flows of dry N_2 and N_2 saturated with water. It is hoped that this study will lead to a better understanding of the role of water in the kinetics of the dehydration reaction of $Li_2SO_4 \cdot H_2O$ by considering other parameters affecting the kinetics, such as sample geometry, heating rates and purging gas. DSC experiments in a dry atmosphere were also performed because the atmosphere in the DSC more closely resembles a self generated atmosphere, and it provides a different set of conditions for comparison with the TG measurements.

EXPERIMENTAL PROCEDURES

Sample preparation

Powdered $Li_2SO_4 \cdot H_2O$ was obtained from the Alfa Chemical Co., with a purity of 99.99%. Each pellet was made by pressing the as-received powder in a die 1.0 cm in diameter under a pressure of 10000 lbf in^{-2}. The pressed disk (thickness 1 mm) was then cut into small cubes with dimensions of about 2 mm × 2 mm. Single crystals of $Li_2SO_4 \cdot H_2O$ were grown through solvent vaporization from a saturated aqueous solution at 50 °C. The cubic crystals used in the TG and DSC experiments were made by grinding and polishing the large grown crystals to dimensions of approximately 2 mm × 2 mm × 1 mm. Platelet crystals were obtained from the as-received powder by sieving. These thin platelet crystals had a thickness in the range 0.1–0.3 mm.

Thermal analysis

The TG instrument used was the Perkin-Elmer 7 series TG. Samples with weights ranging from 36 to 38 mg were loaded at 50 °C. Heating experiments were performed from 90 to 260 °C at rates of 0.5, 2, and 10 °C min^{-1}. The sample-purging gas for the dry atmosphere was N_2 with a standard flow rate of 20 cm^3 min^{-1}. For the wet atmosphere the nitrogen was saturated with water at room temperature. The gas was at atmospheric pressure. The balance chamber was also constantly purged with dry nitrogen, so the total flow over the sample was a combination of both the sample and the balance purges, 35 cm^3 min^{-1}. The sample temperature was calibrated using the Curie temperature of alumel as 163 °C. The resulting correction factors (+0.32, +2.01 and +2.11 °C at the heating rates of 10, 2, 0.5 °C min^{-1} respectively) were applied prior to the analysis of the kinetic data.

The DSC instrument used was the Perkin–Elmer 7 series DSC. All the measurements were performed without a sample cover. The purge gas was N_2 at a pressure of 1 atmosphere and the flow-rate was kept constant at 20 cc min^{-1}. The temperature was programed to rise rapidly to 70 °C after loading the sample at room temperature, to then hold for one minute to stabilize, and then to increase at the desired rates of either 10, 5, or 2 °C

min^{-1}. The sample temperature was calibrated using the melting point of indium as 156.6°C. The resulting correction factors (+1.70, +2.37 and +2.59°C at the heating rates of 10, 5, and 2°C min^{-1} respectively) were applied to the analysis of the kinetic data.

RESULTS AND DISCUSSION

Thermogravimetry

The results were obtained as plots of percentage weight loss vs. temperature. The theoretical weight loss associated with the loss of a molecule of water from the monohydrate is 14.08 wt.%. For powdered samples, the dehydration takes place at a lower temperature than it does for the denser pressed pellet and single crystals, as shown in Fig. 1. This can be easily explained by the fact that the powdered sample has the highest effective surface area of all three and probably a greater proportion of defects in the structure than single crystals. This loose structure allows the water molecules produced to diffuse out more easily. In the pellet, the diffusion of evolved H_2O is restrained by its dense structure, which builds up an unfavorable high partial pressure of water at the reaction interface inside the sample. For crystals, the diffusion of water molecules inside the crystal is far more difficult, and the number of defects are also fewer than in powder or pellet, so the higher dehydration temperature is expected, especially for the cubic shaped crystal. A very high internal pressure of water vapor may need to be established before cracks and fissures form to allow the escape of water into the atmosphere.

When water vapor is introduced into the purging gas, the dehydration curve is shifted to higher temperatures, as shown in Fig. 2. The dehydration process is described by the following simple reaction, in which water

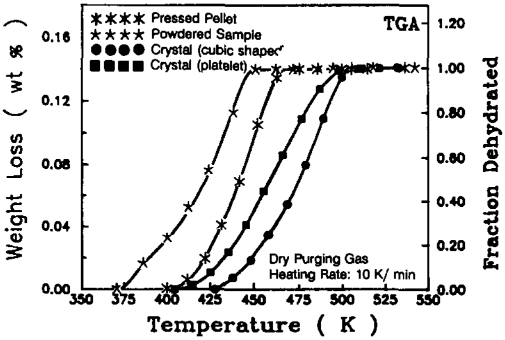

Fig. 1. Plots of weight loss vs. temperature for powdered sample, pressed pellet, platelet crystal, and cubic shaped crystal at a heating rate of 10 K min^{-1} for the dry atmosphere.

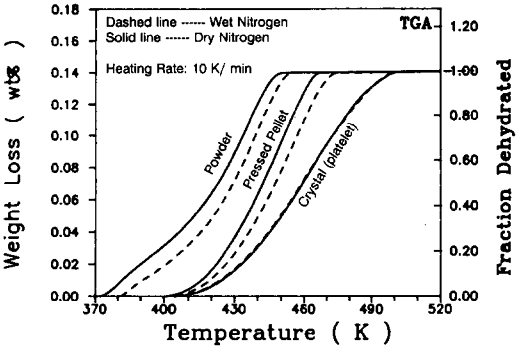

Fig. 2. Effect of water vapor on lithium sulfate monohydrate dehydration with regard to sample characteristics, i.e. powder, pressed pellet, and single crystal.

molecules are released as the reaction proceeds

$$Li_2SO_4 \cdot H_2O = Li_2SO_4 + H_2O \qquad (1)$$

Equation (1) is reversible so the extent of the dehydration at a given temperature is inversely proportional to the partial pressure of the water. Thus, removal of the liberated water molecule from the reaction interface is essential for the dehydration to proceed. The water molecules released at the reaction site have to travel from the reaction interface to the surface of the sample through the dehydrated portion. This is followed by desorption from the surface to the atmosphere. If water vapor is introduced into the atmosphere, the concentration gradient of H_2O required for diffusion through the dehydrated portion is reduced, and in addition, the desorption from the surface to the atmosphere is also discouraged. Both of these effects prevent further dehydration at the reaction interface until a higher temperature is reached. This combined effect is reduced when a slower heating rate is used, as shown in Fig. 3, because the time allowed for the removal of water molecules from the reaction site is increased.

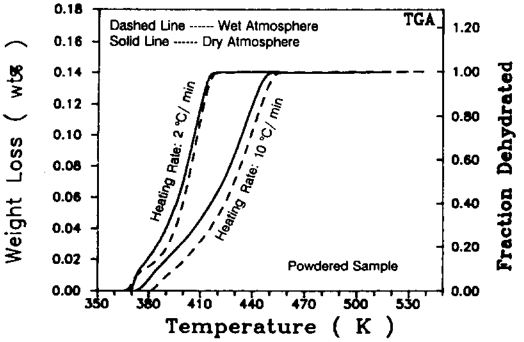

Fig. 3. Effect of water vapor on lithium sulfate monohydrate dehydration with regard to heating rates.

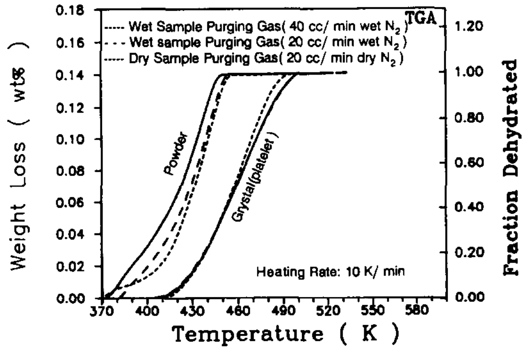

Fig. 4. Effects of water vapor on lithium sulfate monohydrate dehydration with regard to different gas flow rates.

For single crystals, however, the diffusion of water molecules inside the dehydrated solid is very difficult. The slow-down in the diffusion caused by the presence of water vapor in the atmosphere will not change the overall diffusion rate of water molecules inside the dehydrated solid much. Thus the weight loss curve remains almost unchanged, as shown in Fig. 3. For the pelletized sample, the influence of external water vapor on the dehydration rate is intermediate between that of powdered samples and single crystals.

When the purge rate of the nitrogen saturated with water vapor is increased, the slow-down in the overall rate of water removal is significant for the powdered sample, and a higher temperature is required to dehydrate the same amount of $Li_2SO_4 \cdot H_2O$. For crystals, the effect on the dehydration is again very limited in the early stages of dehydration, as explained above; however, at the later stages, when the crystal has been extensively disrupted, the diffusion of water molecule inside the dehydrated solid is no longer very small, and the diffusion rate at a higher temperature is increased. The increased purging gas flow rate will promote the removal of water molecules from the surface to the atmosphere, and the overall reaction speed is thus increased, as seen in Fig. 4.

In determining the Arrhenius parameters from the TG data, the Ozawa method was applied [6]. In this method, the temperature associated with a particular fraction reacted α is determined at different heating rates. A plot of log(heating rate) vs. reciprocal temperature has a slope corresponding to the apparent activation energy. Figure 5 shows such an analysis. The apparent activation energies are listed in Tables 1–4. It is seen that a higher apparent activation energy is associated with a small α, that the powdered sample has the highest apparent activation energy, and that the single crystal has a smaller apparent activation energy for the same fraction reacted (see Figs. 6 and 7). Such phenomena are also reported by Koga and Tanaka [2]. It is implied that the kinetic mechanism changes during the course of the dehydration. It is also seen from the apparent activation energies that the

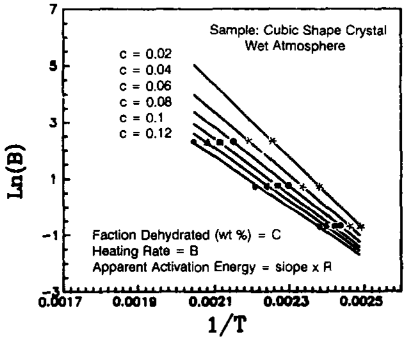

Fig. 5. Typical plot of the analysis of TG data by the Ozawa method.

presence of external water vapor has little effect on the later stage of the dehydration, in which the water has to diffuse through the entire dehydrated solid; the influence on the diffusion of water of external water vapor is very limited.

TABLE 1

Apparent activation energies E and constants A calculated by the Ozawa method for nonisothermal dehydration of powdered samples of lithium sulfate monohydrate by TG

Fraction reacted	Dry nitrogen		Wet nitrogen	
	E (kJ mol^{-1})	Log A	E (kJ mol^{-1})	Log A
0.14	219.74	70.2	114.09	36.0
0.28	131.14	41.2	101.22	31.3
0.43	110.62	34.2	93.44	28.6
0.57	99.24	30.3	87.57	26.6
0.71	91.82	27.8	83.43	25.1
0.85	85.62	25.7	79.97	23.9

TABLE 2

Apparent activation energies E and constants A calculated by the Ozawa method for nonisothermal dehydration of pressed pellets of lithium sulfate monohydrate by TG

Fraction reacted	Dry nitrogen		Wet nitrogen	
	E (kJ mol^{-1})	Log A	E (kJ mol^{-1})	Log A
0.14	93.84	29.2	96.00	29.3
0.28	82.87	25.5	87.49	26.4
0.43	75.21	23.0	81.32	24.3
0.57	69.98	21.3	77.37	22.9
0.71	65.59	19.9	72.06	21.2
0.85	61.31	18.5	70.79	20.7

TABLE 3

Apparent activation energies *E* and constants *A* calculated by the Ozawa method for nonisothermal dehydration of plate crystals of lithium sulfate monohydrate by TG

Fraction reacted	Dry nitrogen		Wet nitrogen	
	E (kJ mol^{-1})	Log A	E (kJ mol^{-1})	Log A
0.14	105.18	31.6	116.93	34.8
0.28	93.09	27.5	101.65	29.9
0.43	85.74	25.0	93.16	27.1
0.57	80.58	23.2	87.37	25.1
0.71	76.28	21.7	83.44	23.8
0.85	73.90	20.5	80.83	22.7

TABLE 4

Apparent activation energies *E* and constants *A* calculated by the Ozawa method for nonisothermal dehydration of cubic crystal of lithium sulfate monohydrate by TG

Fraction reacted	Dry nitrogen		Wet nitrogen	
	E (kJ mol^{-1})	Log A	E (kJ mol^{-1})	Log A
0.14	88.49	26.1	107.60	31.5
0.28	81.79	23.7	94.15	27.1
0.43	77.40	22.1	86.86	24.7
0.57	74.98	21.2	82.02	23.1
0.71	73.07	20.5	78.00	21.8
0.85	71.44	19.8	74.47	20.6

Differential scanning calorimetry

Figure 8 demonstrates the same result as shown by the TG experiment; that the powdered sample starts to dehydrate at the lowest temperature,

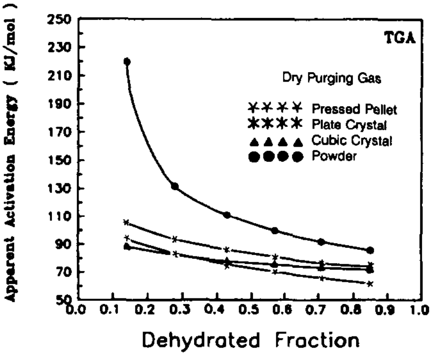

Fig. 6. Plots of apparent activation energy vs. fraction dehydrated for the dry atmosphere.

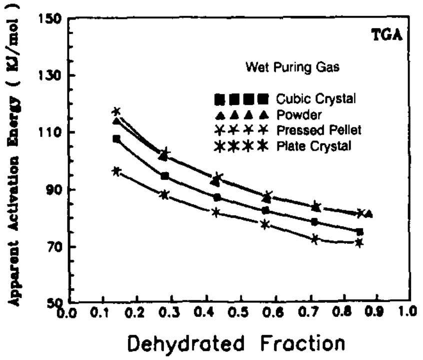

Fig. 7. Plots of apparent activation energy vs. fraction dehydrated for the wet atmosphere.

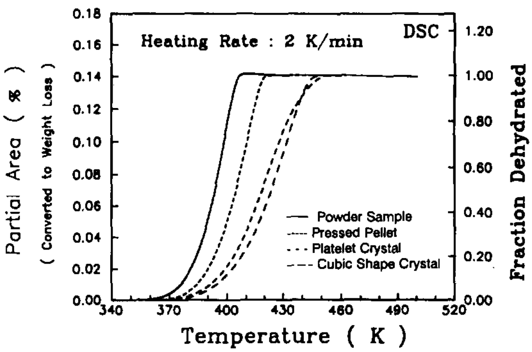

Fig. 8. Plots of fraction dehydrated vs. temperature in DSC by analyzing partial areas.

followed by the pressed pellet, then the platelet crystal, and finally the cubic shaped crystal, which dehydrates at the highest temperature. Converting heat flow vs. temperature results into partial area vs. temperature results, a presentation similar to that for the TG can be obtained, which demonstrates the progress of dehydration during the heating experiments. Figure 9 is such a presentation for the platelet crystal. A comparison of such a graph with

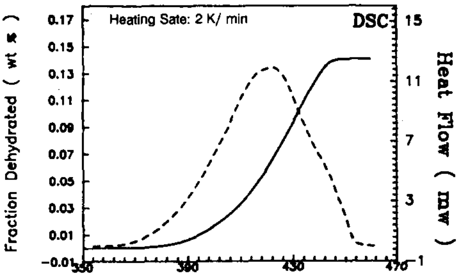

Fig. 9. Typical plot of partial area converted from enthalpy peak vs. temperature.

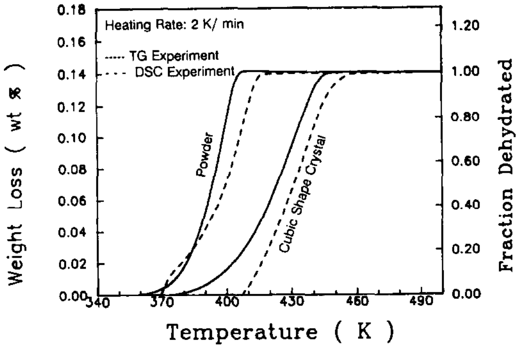

Fig. 10. Comparison of lithium sulfate monohydrate dehydration in TG and DSC.

TG data for the same type of sample is shown in Fig. 10. The geometries and flow patterns of each apparatus are different, and the starting temperature in DSC (70 ° C) is also higher than that used in TG (50 ° C) to minimize the dehydration during the stabilizing period, so it is difficult to obtain a perfect match between the two sets of curves. In analyzing the DSC partial area vs. temperature data, the Ozawa method was also applied, after converting the DSC curve to fraction reacted vs. temperature. The apparent activation energies are listed in Table 5. It is seen that a higher apparent activation energy is again associated with a small α, as shown in Fig. 11. The apparent activation energies are slightly lower than those obtained from TG data, and they do not vary as much as for the TG measurements during the course of dehydration. This may be attributed to the slower removal of released water in the DSC, because the DSC cell is much smaller than the TG furnace tube and may have a different flow pattern relative to the sample. When high heating rates are used, large amounts of water cannot be swept away by the purging gas in time. This is turn extends the whole reaction to higher temperatures, as shown in Fig. 12. The same explanation

TABLE 5

Apparent activation energies E[a] and constants A calculated by the Ozawa method for nonisothermal dehydration of lithium sulfate monohydrate by DSC

Fraction reacted	Powder		Pellet		Cubic crystal		Plate crystal	
	E	Log A	E	Log A	E	Log A	E	Log A
0.14	84.56	27.4	72.08	22.9	78.28	24.1	84.37	26.2
0.28	80.53	25.7	69.39	21.7	76.77	23.1	79.23	24.1
0.43	78.02	24.7	67.08	20.8	74.98	22.2	75.67	22.7
0.57	76.08	23.9	64.43	19.8	73.48	21.5	72.33	21.4
0.71	74.77	23.3	61.39	18.7	72.38	20.9	69.65	20.4
0.85	72.81	22.5	51.29	15.6	70.10	20.0	65.59	18.9

[a] In kJ mol^{-1}.

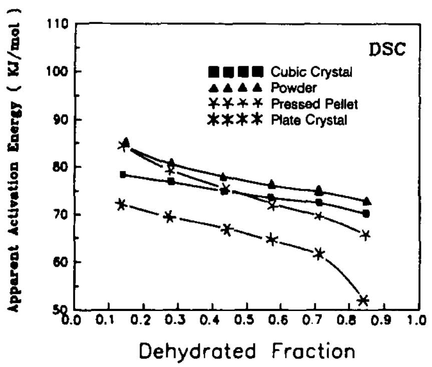

Fig. 11. Plots of apparent activation energy calculated from DSC data vs. fraction dehydrated.

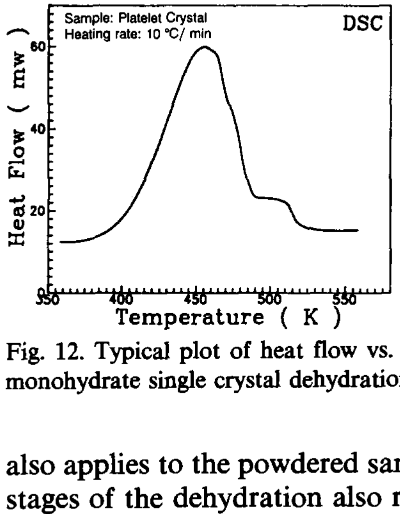

Fig. 12. Typical plot of heat flow vs. temperature in DSC measurements of lithium sulfate monohydrate single crystal dehydration at a high heating rate.

also applies to the powdered sample in TG, where a fast reaction in the early stages of the dehydration also releases large amounts of water.

CONCLUSIONS

On the basis of this study on the influence of external water vapor on the dehydration kinetics, we conclude that the dehydration of $Li_2SO_4 \cdot H_2O$ can be affected by the presence of a small amount of external water vapor, particularly during the early stage of the dehydration of those samples with an open structure. The dehydration of a single crystal is only marginally affected. It is recommended that future study of this material be performed on single crystals to avoid the unnecessary complexity of other parameters also affecting the kinetics. It is also found that DSC can give a reasonably good analysis of the dehydration of $Li_2SO_4 \cdot H_2O$, but one should note the possible influence from the self generated water vapor in the kinetics of the dehydration process. If one were to establish a set of criteria for the ideal

TABLE 6

Criteria for an ideal kinetic standard

Irreversible reaction	Minimum sample size
Very low enthalpy	Use slow rate range
No oxidation–reduction	Identical samples
Standard procedures	

kinetic study, clearly, reversible reactions should be avoided. Earlier work on the decomposition of $CaCO_3$ also described these problems and the self heating or cooling effects induced by the enthalpy of the reaction [7]. The criteria for an idealized kinetic study are set forth in Table 6.

REFERENCES

1 V.B. Okhotnikov, B.I. Yakobson and N.Z. Lyakhov., React. Kinet. Catal. Lett., 23 (1983) 125.
2 N. Koga and H. Tanaka, J. Phys. Chem., 93 (1989) 7793.
3 Yu.A. Gaponov et al., J. Therm. Anal., 33 (1988) 547.
4 N.A. Kirdyashkina and V.B. Okhotnikov, React. Kinet. Catal. Lett., 36 (1988) 417.
5 V.B. Okhotnikov, B.I. Yakobson and N.Z. Lyakhov, React. Kinet. Catal. Lett., 39 (1989) 345.
6 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 188; J. Therm. Anal., 2 (1970) 301.
7 P.K. Gallagher and D.W. Johnson, Jr., Thermochim. Acta, 6 (1973) 67.