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Kinetic study of the dehydration reaction of lithium sulfate monohydrate crystals using microscopy and modeling

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ABSTRACT

Simulation of gas–solid reactions occurring in industrial processes requires a robust kinetic model to be applicable in a wide range of complicated reaction conditions. However, in literature it is often seen that even the same reaction under specific controlled conditions is interpreted with different kinetic models. In the present work, a phenomenological model based on nucleation and nuclei growth processes is presented to study the kinetics of the dehydration reaction of lithium sulfate monohydrate single crystals. The two elementary processes of the reaction, nucleation and nuclei growth, are characterized and quantified as a function of temperature by using optical microscopy experiments. The *in-situ* measured characteristics of the dehydration reaction provided confirmatory evidence that the rate of nucleation obeys an exponential law and the rate of nuclei growth is approximately constant. With knowledge acquired from the optical observations as inputs of the kinetic model, the fractional conversion of the dehydration reaction was calculated and compared with experimental results from thermogravimetric analysis (TGA). A satisfactory comparison was found both in isothermal and non-isothermal conditions. It is demonstrated that this knowledge-based model has a great potential to represent the gas–solid reaction kinetics in a wide range of process conditions regarding temperature, pressure and particle geometry.

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1. Introduction

Kinetic models play a central role in simulation of gas–solid reactions, which can be considered as the core of numerous techniques in industry. A particular example is thermo-chemical heat storage using salt hydrates for long term heat storage. From material characterization experiments by thermal analysis, several salt hydrates were identified as promising candidates with very high heat storage density, such as $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ [1]. Then, a prototype heat storage system using $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ was built successfully at the Energy Research Center in the Netherlands, but the overall energy density achieved ($\approx 0.5 \text{ GJ/m}^3$) was lower than the theoretical value of $\approx 1 \text{ GJ/m}^3$ [2]. To optimize and improve the energy storage system, comprehensive understanding of the reactions under complicated operating conditions is needed. Numerical tools based on reliable kinetic models are particularly helpful for the analysis and later improvement.

In the present study lithium sulfate monohydrate ($\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$), a model material for salt hydrate studies, was chosen for an examination of the dehydration kinetics. A large number of studies on the thermal dehydration reactions of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ crystals have been carried out. Its overall reaction kinetics has been extensively investigated by using conventional thermoanalytical techniques [3–18]. From previous studies, it is evident that the overall kinetics of this thermal dehydration reaction is largely dependent on experimental conditions and samples. This complexity gives rise to difficulties in providing coherent models to match the overall kinetics. As shown in Table A.1, there is a list of typical alternatives of reaction models derived theoretically from a single or combined mechanistic assumptions. They are usually used to fit kinetic curves from TGA in order to interpret the reaction with certain reaction mechanisms and to derive kinetic parameters, e.g. activation energy. Unfortunately, this approach leads to a wide selection of kinetic models in different studies. A main reason of the variation could be that this kind of analytical models attempts to reproduce the overall effect, instead of involving detailed analysis of elementary mechanisms. For example, a geometrical contraction model (Rn) was chosen to fit the overall kinetics of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ dehydration reactions in several papers [10,11], while an Avrami–Erofev model (An) for the first

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part of the kinetic curve and a geometrical contraction model (Rn) for the second part were used in other papers [3,8,12,13]. In principle, the index number n is associated to the degree of symmetry of the reactant solid particles. However, various values of the index number n in the kinetic model such as 2.5 [10] or 1.5 and 3.1 [3] can be found. This is because the values are products of mathematical adjustments instead of physical examinations. The inconsistency, both in choice of kinetic models and in kinetic parameters, could give rise to problems in simulation of gas–solid reactions where the reaction kinetics is essential for reliable predictions. As emphasized by Galwey and his coworkers [19–21], more detailed and more extensive kinetic observations are required in order to gain insights into the chemistry, controls and mechanisms of solid-state decompositions.

In contrast to the analytical models, phenomenological models can be much more robust and coherent as they rely in essence on a detailed description of the reaction. The overall kinetics of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ dehydration reactions can be generally separated into several elementary processes. It was demonstrated by examining the textural changes of partially dehydrated crystals that the dehydration reaction proceeds by nucleation and nuclei growth mechanisms [10]. Nucleation is the process responsible for the initial formation of the reactant/product interface which is often accompanied by structural reorganization. Identification of the appearance of nuclei is difficult in experiments and, consequently, quantitative studies on the nucleation process are difficult to find in literature. Recently, numerical work has been done to study the mechanism of nucleation, where a microscopic model was developed to simulate the origin, diffusion, and aggregation of point defects by using a probabilistic approach [17]. Experimentally, the influence of water vapor pressure on the appearance of nuclei during $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ single crystals dehydration was studied by means of both isothermal thermogravimetry and environmental scanning electron microscopy [18]. The other elementary process, the growth process (also known as interface advance), has been studied with more effort due to its dominant role in the overall kinetics [4–6,15]. It was found that chemical changes were active at the reactant–product interface (thickness ca. $150 \mu\text{m}$) [5] and rates of the interface advance were constant [15]. In addition, all areas of the reaction interface are usually regarded as identical. Thus, the rate of dehydration reaction is directly proportional to the total reactant–product area.

With the essential characteristics of nucleation and growth processes, the reaction kinetics in terms of systematic changes in area of active interface can be calculated. This kind of kinetic models is generally recognized as nucleation and growth models. Among all nucleation and growth models, the most often used is the Avrami–Erofev model [22], see Table A.1. The success of the Avrami–Erofev model could be attributed to its sigmoidal feature of the kinetic curve which is often observed in experiments but seldom available in other typical models as shown in Fig. A.1. As most of the other analytical models, the advantage of the Avrami–Erofev model is its ease of use in mathematics, while the disadvantage is the lack of physical meaning in terms of separated processes of nucleation and growth instead of a global contribution to the overall kinetics. More important, this model is even invalid in gas–solid reactions with surface nucleation, since nucleation in the bulk of particles is an essential assumption for the model derivation. In contrast, Mampel's model [23] was derived theoretically with the assumption that reaction takes place in the form of random nucleation at the surface of grains and their isotropic growth. This model was further developed with a stochastic approach for non-isothermal and non-isobaric conditions [24]. Later, it was used to study the dehydration of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ single crystals [16], where the rates of nucleation and growth were assumed to be constant

under isothermal and isobaric conditions and can be estimated by model-fitting of the corresponding TGA results.

In this work, an integrated approach to study the reaction kinetics of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ monocrystals is proposed. Instead of using optical microscopy to provide complementary information for the selection of kinetic models, we made a kinetic model based on kinetics of the elementary processes of the reaction which are characterized from optical observation. Firstly, a numerical model based on Mampel's assumptions is presented to describe the surface nucleation and nuclei growth processes during the dehydration reaction. Secondly, parameters needed in the phenomena-based model are quantified by optical observation experiments under isothermal conditions with the aid of hot-stage microscopy experiments. Thirdly, the overall rate of the reaction is computed and compared to TGA results.

2. Microscopy experiments

For the purpose of optical observations, especially the characterization of nucleation, large $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ monocrystals were grown from commercial $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ powder (SIGMA–ALDRICH, $\geq 99.0\%$). The commercial reactant was first dissolved in distilled water at room temperature with a recipe of 27 g $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ in 100 g H_2O . The solution was thoroughly mixed by using a magnetic stirrer. After filtration through filter papers (particle retention 5–13 μm), the under-saturated solution was poured into a crystallizer with a diameter of 140 mm. The crystallizer was then covered by a piece of plastic wrap in which a large number of holes were pierced in order to control the solvent evaporation from the aqueous solution of the salt. After around 10 days, plate-like crystals, recrystallized along the crystallographic orientation [0 1 0], were collected with typical dimensions: $L = 4\text{--}5 \text{ mm}$, $W = 2\text{--}3 \text{ mm}$ and $e = 0.5\text{--}1 \text{ mm}$ (see Fig. 1(a)).

In order to measure the rate of nuclei growth into the crystal bulk, preparation of crystals was needed to prevent surface nucleation from obscuring the bulk effects. The idea was proposed by Okhotnikov et al. [9] and developed by Modestov et al. [15] where crystals were encapsulated by metal grease on all the surfaces except one. In our case, a transparent epoxy was used such that the growth rate in the bulk of crystals could be observed using a microscope. Crystals were embedded at room temperature in a liquid resin called EpoFix, which hardened within 10 h after it was mixed with its hardener. Hence, encapsulated crystals were polished with water using abrasive papers of grit 600–4000 in order to increase the visibility of crystals through the microscope. After that, an end surface in the direction [0 1 0] was ground using abrasive papers of grid 1200 to remove the resin, which made that single surface open to the environment (see Fig. 1(b)). For grinding of the contact surface, it is worth noting that no water was used because water dissolves the salt crystal. Besides, grinding is also beneficial to activate the instantaneous nucleation at that entire face. Further growth of nuclei will form a flat reactant/product interface.

The experimental system used for microscopic observations is presented in Fig. 2. Investigations of kinetics of the nucleation and growth processes were carried out in the heating stage facility with a Zeiss microscope (SteREO Discovery V20). The heating stage consists of a metal base with a cavity ceiled by a piece of glass, within which the reaction environment including both temperature and water vapor pressure are well controlled. Compressed air was used as humidity carrier. Gas controllers (EL-FLOW, Bronkhorst) were used to control the gas flows. The humidity of the air flow was determined by mixing two flows: one dry flow and the other one water saturated at ambient temperature. Before the humidified air entered the reaction chamber, it was heated to a desired temperature by passing the air through a long channel inside the metal

Fig. 1. (a) Sketch of a recrystallized single crystal of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$; (b) example of a $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ crystal encapsulated by epoxy resin except the right surface indicated by the arrow (the crystal shape is indicated by the dashed line).

base. A flow rate of about 230 ml/min for the humidified air was used, which can fill the reaction chamber quickly (less than a half minute). The heating stage was controlled by a thermometer and was stabilized at a setpoint temperature in advance. After introduction of the sample, it takes less than one minute for the salt crystal to reach an isothermal condition based on analytical estimations. The propagation of reaction front is observed by the optical microscope together with a camera system. Reorganization of the crystal structure after elimination of water yields small dehydrated particles with crystallite textures and cracks that scatter light. This makes the product material opaque and recognizable under the optical microscope. Before the start of each measurement, the environment in the heating stage has to be stabilized until reaching the setting temperature and humidity. Then, a crystal sample is quickly placed on the heating stage. The dehydration reaction is documented by periodic photomicrographs. In this work, all measurements including microscopic observations and following TGA measurements were performed at a water vapor pressure 13 ± 1 mbar, which is a practical value for application of thermo-chemical heat storage [25].

Quantitative measurements of numbers of nuclei per unit area and propagation of the reactant/product interface as a function of time are made. It is clear that the formation of nuclei is highly sensitive to the crystalline structure and accurate quantification has been recognized as a big challenge. To reduce the complexity but still get a reliable estimation of the nucleation rate, the following selections are made for all observation measurements of the nucleation rate. First, all pictures recorded are under the same magnification of the microscope ($100\times$) and an area of about 1 mm^2 of crystal surfaces (001) is selected for investigation under this magnification (see Fig. 3). Secondly, borders of the selected area are at a distance of at least 0.2 mm from the edges of the crystal. Thirdly, and most importantly, the surface selected is without

visible defects including dusts, cracks and grain boundaries. After a series of pictures is produced in one measurement, the number of nuclei is counted from their appearance based on the pixel jump from transparent to opaque. White spots without growth are not taken into account. In contrast, the calculation of interface motion in the encapsulated crystals is much simpler, since the reaction front moves approximately as a flat plate as shown in Fig. 11. In the post-processing, a straight line is drawn to fit the interface so that a mean distance between the reaction front and the open surface of the encapsulated crystals is calculated.

The same protocol for the microscopic observations is followed for the TGA measurements. The TG50 M3 measuring module (METTLER TOLEDO) was stabilized first at the desired experimental conditions, both for temperature and partial water vapor pressure. The same carrier gas at the same flow rate as used in the microscopic observations was used. After the isothermal and isobaric conditions were reached, the salt sample was placed into the TGA module. Similarly, with analytical estimations it is expected that the sample and its surrounding can reach the isothermal and isobaric conditions within one minute after the introduction of samples. This period of one minute is relatively short compared to the period of a complete TGA measurement (typically 1–2 h).

3. Nucleation and nuclei growth model

A typical example of the dehydration reaction observed through the microscope is shown in Fig. 4. The dehydration reaction of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ crystals initiates as the formation of nuclei on the crystal surface and their growth converts the parent phase into an anhydrous phase (white phase in the picture). The nucleation and growth model used in this work is developed by Helbert et al. [24]. According to the assumptions of Mampel's model [23], first, reactions of crystals are assumed to lead to nuclei at random localized spots in the reactant surface and proceed by an inward deterministic growth. Secondly, the rate-limiting step takes place at the internal interface between the initial phase and the new phase. Thirdly, crystal sizes do not change during the course of the chemical reaction: no expansion or shrinkage is considered. So, the overall reaction kinetics is determined by these two elementary processes simultaneously with a systematic change of reactant-product interface area. With sufficient knowledge of the two processes, the fractional conversion can be calculated from the appearance of nucleation to completion of reaction, which is equivalent to the definition of the fractional conversion in a thermogravimetric measurement as:

$$\alpha(t) = \frac{m_0 - m_t}{m_0 - m_\infty} \quad (1)$$

Fig. 2. A schematic drawing of the heating stage in combination with the microscope.

Fig. 3. (a) Selected crystal surface without visible imperfections; (b) typical picture of nucleation at 110°C and 13 mbar.

where α is the fractional conversion, m_0 is the initial weight, m_t is the weight at time t and m_∞ is the final weight.

Fig. 5 shows a snapshot of the simulation based on Mampel's model, where the transformation process takes place in the form of surface nucleation and nuclei growth. The numerical implementation is realized in such a way that a crystal is represented by a large number of discrete points. At the beginning, the crystal is in an untransformed state (in blue). Then a random number of nuclei (in red) appears on the crystal surface. The rate of nucleation is assumed to be a space-time Poisson process, with a mean frequency of nucleation γ , which is expressed as a number of nuclei per unit of time and per unit of surface area. New nuclei are initiated randomly at grid points both in transformed and untransformed phase of the

crystal. Information of each nucleus including central position and time of appearance is recorded at each time-step. The radial growth (in black) of each nucleus is deterministic, with the rate of radial growth ϕ , and isotropic until the crystal is totally reacted. In general, the fractional conversion can be written as

$$\alpha(t) = f(\gamma, \phi) \quad (2)$$

where γ is the nucleation rate ($1/(m^2s)$) and ϕ is the growth rate (m/s). The material is reacted if there is at least one nucleus which covers it. During the course of transformation, both ingestion and coalescence phenomena take place. In order to avoid the complexity in calculation, the fractional conversion as the output of this model is determined by evaluating grid points which are untouched

Fig. 4. Surface growth sequence of the anhydrous nuclei formed during the dehydration reaction of a single $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ crystal at 90°C and 13 mbar.

Fig. 5. Snapshots of the transformation of a typical crystal by surface nucleation and isotropic growth processes at various stages (reactant phase in blue, product phase in black, edges and nuclei in red for emphasis). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

by the new phase. So, the formation of nuclei in already transformed material and the overlapping regions do not contribute to the rate of transformation.

The obvious advantages of this model are that in principle it is applicable to arbitrary geometries, and also valid in more complicated situations such as non-isothermal and non-isobaric conditions as long as sufficient information of nucleation and growth is gained. Compared to the Avrami–Erofev model, the calculation of fractional conversion in Mampel’s model is relatively complicated. However, more important, Mampel’s model is a knowledge-based model, which makes it more reliable and consistent under different reaction conditions. Most kinetic features including the sigmoid-shape shown in Fig. A.1 can be covered in this model, while those analytical models are fixed to a certain kinetic feature due to the assumptions made for the theoretical derivation.

4. Results and discussion

In this section, the numerical model is first validated with an analytical solution for a spherical geometry. Then, characterization of nucleation and growth processes of the $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ dehydration reaction is performed under isothermal and isobaric conditions. With measured rates of the nucleation and growth as inputs for the kinetic model, rates of dehydration reactions both in isothermal and non-isothermal conditions are calculated and compared to rates obtained from TGA measurements.

4.1. Analytical validation

An analytical solution using the Mampel model can be derived when the geometry of the crystal is a sphere, a cylinder or an infinite plate and rates of nucleation and growth are constant [26]. In order to evaluate the relative significance of nucleation and growth processes, a dimensionless parameter based on the nucleation rate γ and growth rate ϕ is defined as:

$$K = \frac{S_0 r_0 \gamma}{\phi} \quad (3)$$

where S_0 is the surface area and r_0 is the radius of a sphere. This dimensionless parameter K is an indicator of competition between nucleation and growth processes and has an important effect on the

overall kinetics. When the K value is small, the rate of growth is relatively large compared to the rate of nucleation, which means that a few nuclei will dominate the transformation and the kinetics of the overall reaction is mainly determined by those nuclei. When the K value is large, a large number of nuclei will cover the grain surface rapidly; the effect of nucleation on the overall kinetics finishes in a short time period. The major transformation is then determined by the growth process. Both of these two extreme cases can be regarded as one-process kinetics, which usually can be described by an analytical model. However, it was demonstrated that the dehydration reaction of lithium sulphate monohydrate involves both nucleation and growth processes simultaneously [8,10]. It is necessary to involve the competition when the nucleation and growth process are comparable, just as described in the Mampel’s model.

With the analytical solution for a spherical particle (see Appendix B), comparison of fractional conversion at various K values between numerical solutions and analytical solutions are carried out and results are shown in Fig. 6(a). All of these fractional conversion curves for various values of K show that the numerical solutions are in good agreement with the analytical solutions. As discussed above, the competition between nucleation and growth as indicated by the K parameters can represent various mechanistic assumptions involved in analytical models. For example, a sigmoidal shape of the kinetic curve is obtained in the main range of K values which is a characteristic feature as in the Avrami–Erofev models (An). On the other hand, when nucleation is so fast that it can be considered as “instantaneous” compared to the growth of the nuclei (large K value), the Mampel model should be identical to the contracting volume model (R3). The corresponding reaction rate can be simply determined by the shrinking radius of the unreacted core. As one can notice in Fig. 6(b), the present kinetic model approaches the contracting volume model (R3) when K gets larger.

4.2. Characterization of nucleation and growth

Characterization of the dehydration reaction of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ monocrystals using optical microscopy is carried out for the two elementary processes: surface nucleation and nuclei growth. A quantitative study of these phenomena is made for various temperatures and a fixed water vapor pressure (13 mbar).

Fig. 6. (a) Fractional conversion as a function of time for various K values; numerical solutions are shown in dashed lines and analytical solutions in solid lines; (b) comparison between the numerical solutions from the nucleation model for different nucleation rates and the solution derived from the contracting volume (R3) model.

4.2.1. Kinetics of nucleation

In heterogeneous nucleation, it is generally agreed that nucleation happens preferably at imperfections of crystals, where the activation energy for transformation is lower. As shown in Fig. 4, there are many imperfections on the two ends of the initial crystal (enclosed areas). In contrast, the central area is much clean so that scratches from the background (surface of the copper heating stage) are visible. Therefore, there are more nucleation events on the two ends than in the central area of the surface under given reaction conditions. Moreover, edges of the crystal are regarded as linear defects and therefore more favorable to nucleation than the regular crystalline structure, e.g., the central area. The total number of imperfections could be regarded as the limit of potential nucleation sites. Also, the rate of nucleation must decrease with time as these sites become exhausted or get ingested by growing nuclei. The rate of nucleation as a function of time can be described by the following relation (neglecting ingestion)[22]

$$\gamma = \frac{dN}{dt} = k_n N_0 \exp(-k_n t) \quad (4)$$

where

$$k_n = \nu \exp\left(-\frac{E_a}{RT}\right) \quad (5)$$

with N the number of nuclei per unit area, N_0 the initial number of sites per unit area, ν the frequency factor, E_a the activation energy, R is the universal gas constant and T the temperature.

Fig. 7(a) shows nuclei density from six different crystals at 100 °C and 13 mbar plotted as a function of time. Because of the similar shape of all kinetic profiles, the exponential nucleation law as presented in Eq. (4) can be confirmed. The number of nuclei eventually reaches a limit, which is directly associated to the total number of surface imperfections. Small variations among different samples are observed in terms of both the rate of nucleation and the maximum number. Fig. 7(b) shows the influence of temperature on the nucleation kinetics. The nucleation rate shows a large increase in the temperature range from 90 °C to 110 °C. The profile at 90 °C is nearly linear before it reaches the limit. At 110 °C the nucleation occurs much faster with a large number of nuclei covering the crystal surface quickly.

It can be concluded from Eq. (4) that at low temperatures k_n values are relatively small. The exponential law can then be simplified to a linear relationship at a certain temperature

$$\gamma = k_n N_0 = \nu N_0 \exp\left(-\frac{E_a}{RT}\right) \quad (6)$$

Even at high temperatures, about 80% of the final total number of nuclei are formed approximately at a constant rate. In the later stage of nucleation, the rate considerably decreases due to the depletion of the reactant surface. Therefore, a linear estimation of nucleation rate is adopted. The constant nucleation rate at constant temperature is calculated and results are plotted as a function of temperature in Fig. 8. Large variation at 110 °C can be seen in Fig. 8(a). This is because the nucleation process at higher

Fig. 7. (a) Nuclei density against time at 100 °C from six different measurements on crystal surface (001); (b) nuclei density against time at different temperatures.

Fig. 8. (a) Nucleation rate as a function of temperature; (b) plot $\ln(\gamma)$ against reciprocal temperature.

temperatures tends to be completed in a short time. This enhances the influence of the initial period of measurement preparation, which is not well controlled. In Fig. 8(b) the nucleation rate as a function of temperature is fitted by Eq. (6) as

$$\gamma \text{ (1/(mm}^2 \text{ min))} = \exp(78.1 \pm 8.3) \exp\left(\frac{-(240.0 \pm 25.8) \times 10^3}{RT}\right) \quad (7)$$

where A is the pre-exponential factor and equal to νN_0 in this case, and the activation energy is 240.0 kJ/mol. This relationship will be used in the subsequent calculation of the fractional conservation in the non-isothermal condition.

4.2.2. Kinetics of growth of surface nuclei

Fig. 9(a) shows established nuclei on the crystal surface. Two marked features of the nucleus growth are worthy to stress. The first noticeable feature is the star-shaped nuclei with a central hole and radial cracks as indicated by arrows in the photograph. The holes are identified as nuclei and radial channels are developed around them, which is caused by volume shrinkage and crack formation after water elimination. As also demonstrated in [10] by electron microscopic examinations, the individual systems of micro-channels connect each other during the growth and coalescence of separate nuclei, which forms a micro-channel network further facilitating the escape of the volatile water. The second major feature is that the shape of individual nuclei is an ellipse with a preferable growth in the crystallographic direction [010]. This observation is different from the nucleus shape of dehydration reaction of alums, where an approximately circular shape of nuclei was observed [27].

(a)

(b)

Fig. 9. (a) Structure of star-shaped nuclei indicated by arrows; (b) effective radius as a function of time at various temperatures.

From the previous observations, it is clear that the growth of nuclei in this reaction is in three dimensions, which means that the reactant/product interface expands outwards in all directions, generating hemispheres of product. To simplify the calculation of the growth rate, the surface shape of nuclei is assumed to be circular and an effective radius is calculated based on the area of each nucleus. Fig. 9(b) shows a typical plot of data for the growth of nuclei at various temperatures up to radial dimension of 70 μm . Growth of larger nuclei could not be followed since they overlap with neighbours. From these microscopic measurements, it can be concluded that rates of nucleus growth are constant at constant temperatures and water vapor pressures. The velocity of nucleus growth at each temperature was calculated and is plotted in Fig. 10(a). The experimental data, connected by straight lines, show a nearly exponential increase in velocity at higher temperatures. By fitting the data with an Arrhenius equation, the activation energy was deduced as shown in Fig. 10(b).

However, the interface motion observed in these measurements is probably still within the reaction zone, since the reaction interface of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ dehydration has a thickness of ca. 150 μm [5]. For a quantitative study of the growth kinetics, experiments are needed tracking the reaction front over larger distances, typically in the order of millimeters.

4.2.3. Kinetics of growth in the bulk

In the next experiments, encapsulated crystals were used in the microscopy experiments and the nuclei were forced to grow in a single direction. A typical example of the dehydration reaction of an encapsulated $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ monocrystal is shown in Fig. 11. The reaction originated at the surface where epoxy resin was removed, the

Fig. 10. (a) Velocity of nucleus growth as a function of temperature; (b) rates of nucleus growth at various temperatures are fitted by the Arrhenius equation.

right surface in this case. It can be seen that the reaction interface was propagating into the crystal in the $[0\ 1\ 0]$ direction, while reaction on the other faces was restricted during the early stage of the dehydration process. The reaction front was recorded photographically and the distance of the reaction front to the right surface was estimated as indicated X_c in Fig. 11.

Data of the interface advance at various temperatures are shown in Fig. 12(a). A complete prevention of surface nucleation cannot be achieved by the epoxy encapsulation. In particular when the reaction temperature is high, the restriction from the epoxy resin layer was diminished by expansion of the layer itself. The interface advance at a later stage was obscured by undesired nuclei and only the first part of the reaction was adopted for calculation with acceptable accuracy. The advancing distance going up to values of $2500\ \mu\text{m}$ is, however, already much larger than the reported thickness of reaction zone ($150\ \mu\text{m}$). It is evident that the

displacement of the reaction front is almost linear as a function of time in isothermal and isobaric conditions. Thus, a constant rate of interface propagation is derived at each temperature by using the least square fitting method. Several measurements were conducted under the same experimental conditions and results of growth rate are plotted together with error bars in Fig. 12(b). Compared to the surface growth rate (see Fig. 10(a)), the growth rate into crystal bulk is smaller. For example, the growth rate into crystal bulk at $110\ ^{\circ}\text{C}$ is only about 0.51 times of the surface growth rate. With the same fitting method, Fig. 13 shows the rate of interface propagation fitted as a function of temperature by equation:

$$\phi\ (\mu\text{m}/\text{min}) = \exp(29.0 \pm 2.6) \exp\left(\frac{-(88.4 \pm 8.4) \times 10^3}{RT}\right) \quad (8)$$

where the activation energy obtained in this way is 88.4 kJ/mol .

Fig. 11. Typical sequence of the interface advance in the bulk of an encapsulated $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ monocystal during dehydration at $120\ ^{\circ}\text{C}$.

Fig. 12. (a) Interface position as a function of time at various temperatures; (b) rates of interface advance at various temperatures with error bars.

Next, a direct comparison with previous studies is made with respect to the reaction rate constant:

$$k \text{ (s}^{-1}\text{)} = A \exp\left(-\frac{E_a}{RT}\right) \quad (9)$$

where A is the pre-exponential factor in units of frequency. In most cases, this parameter, as mentioned in the introduction, is derived from fitting the overall kinetic data by certain kinetic models. However, in the present work and also works from Okhotnikov et al. [4] and Kirdyashkina et al. [6], the rate of interface advance was measured by optical observation in our case and by thermal analysis in their cases. The transformation from the advance rate to the conventional rate constant can be done as follows:

$$k \text{ (s}^{-1}\text{)} = \frac{d\alpha}{dt} = \frac{1}{\Delta m_{\text{H}_2\text{O}}} \frac{dm}{dt} = \frac{\rho_{\text{H}_2\text{O}} S}{\rho_{\text{H}_2\text{O}} S L} \frac{dX_c}{dt} = \frac{1}{L} \frac{dX_c}{dt} = \frac{\phi}{L} \quad (10)$$

where S is the area of the open face, L is the length of single crystals and $\rho_{\text{H}_2\text{O}}$ is the density of water in lithium sulfate monohydrate ($\rho_{\text{H}_2\text{O}} = 290 \text{ kg/m}^3$).

Results from the present work and literature are shown in Table 1, where group (a) presents data based on measuring the interface propagation and group (b) presents data based on measuring the overall reaction kinetics of single crystals. The activation energy from our result is in good agreement with the other two group (a) members, Okhotnikov et al. [4] and Kirdyashkina et al. [6]. The pre-factor matches the result from the experiment (a3) rather well, but is one-order smaller than the value deduced in experiment (a2). The reaction rate as a function of temperature is calculated and presented in Fig. 14. The result (a3) is in relatively good agreement with all results in group (b). However, it is larger than our result and

smaller than result (a2). The difference could be related to the sample size, particularly in group (a), where the reaction rate decreases as the sample size is increasing. Moreover, it was demonstrated by Galwey et al. [10] that during the dehydration of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ there was pore penetration beyond the reaction interface attributable to shrinkage following water loss from the unrecrystallized reactant beyond the textural discontinuity. This means that the water loss deduced from interface advance measured by optical observation (our result) is probably delayed compared to the water loss measured by TGA (all other results). Thus this could explain why our k -result is smaller than all other results obtained by TGA.

4.3. Experimental validation

In order to determine the fractional conversion by the nucleation and growth model, the growth rate in other crystallographic directions is needed. Based on both surface nuclei growth and one-dimension interface advance, the growth rate in $[100]$ direction was measured. The ratio between the velocity in $[010]$ direction and in $[100]$ direction is plotted in Fig. 15. The average ratio from surface nuclei growth is about 1.54 and the value from interface advance is about 1.45. Due to the limit of the crystal thickness, measurements in the third direction $[001]$ of interface advance are not possible. After the rates of nucleation and growth were estimated from the optical observations, the fractional conversion α in isothermal and non-isothermal conditions was calculated by

Fig. 13. (a) Rates of interface advance at various temperatures are fitted by the Arrhenius equation.

Fig. 14. Reaction rate as a function of temperature from different studies as shown in Table 1.

Table 1Kinetic parameters for the thermal dehydration of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$.

T range (K)	L (mm)	E_a (kJ/mol)	A (s^{-1})	Reference
(a1) 373–413	2	88.4	1.9×10^7 (c)	Present work
(a2) 300–400	0.3	87.1	1.4×10^8 (c)	Okhotnikov et al. [4,28]
(a3) 315–362	1	84.9	1.3×10^7 (c)	Kirdyashkina et al. [6,28]
(b1) 360–400	1.6	79.9	6.6×10^6	Galwey et al. [10]
(b2) 362–402	1.6	106.3	2.8×10^{10}	Brown et al. [11]
(b3) 385–400	1.2	111.8	2.0×10^{11}	Koga et al. [8]

a. Parameters are derived by fitting the rate of interface propagation, which is constant at isothermal and isobaric conditions.

b. Parameters are derived by fitting the overall kinetics of reaction with certain kinetic models.

c. A values are in units of the mass density of water in lithium sulfate monohydrate (290 kg/m^3).

using the nucleation and growth model. To validate the model, TGA measurements were performed by using regular crystals as shown in Fig. 1(a). The comparison between numerical results and TGA results is shown in Fig. 16.

In the isothermal condition ($T=100^\circ\text{C}$), the nucleation rate and mean growth rate obtained from previous microscopic measurements are used for calculation. Their values are $\gamma = 1.79 \text{ 1/(mm}^2 \text{ min)}$ and $\phi = 1.36 \mu\text{m/min}$, respectively. A typical sigmoidal shape of the kinetic curve in Fig. 16(a) can be seen from the numerical result, but this shape is not that obvious from the TGA result. This difference is especially originating from the first part of the curves, where the nucleation process is involved. The corresponding dimensionless parameter K is about 2.8×10^4 when

a typical length $r_0 = 1 \text{ mm}$ is chosen. Compared to the growth rate, the nucleation rate is relatively large. It can be expected that the nucleation rate over entire crystal surface with many imperfections like impurities and crystal edges will be larger than the rate quantified from the selected area in our microscopy experiments, which means a larger K value. Therefore, the numerical result is corresponding to a smaller K value than the TGA result because an underestimated nucleation rate is used in the calculation. As a result, the numerical result shows a sigmoidal feature just as the Avrami–Erofev models, while the TGA result with larger K value is approaching the contracting volume (R3) expression.

The result for the non-isothermal condition with a heating rate of 1°C/min is shown in Fig. 16(b). Except the delay due to

Fig. 15. Ratio between the velocity in [0 1 0] direction and in [1 0 0] direction at different temperatures (horizontal lines are the averages): (a) from surface nuclei growth; (b) from interface advance in the crystal bulk.

Fig. 16. Fractional conversion of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ dehydration reactions: (a) comparison between the numerical and TGA result in the isothermal condition (100°C); (b) comparison for the non-isothermal condition with a heating rate of 1°C/min .

underestimation of the nucleation rate, the kinetic curves of the numerical result and the TGA result are in good agreement. The main part of the curve is approximately linear, which indicates a constant rate of reaction kinetics as the reaction temperature increases. This could be explained by the dynamic balance between the increase of reactivity as a function of temperature and the decrease of active reaction area during the course of the reaction.

Moreover, it is noteworthy that the lag of the structural reorganization from the mass loss as discussed in relation to Fig. 14 may be also associated with the obvious delay of the numerical result compared to the TGA result in both isothermal and non-isothermal cases. It is evident from Galwey's study [10] that water loss from reactant can be in the zone beyond the phase transformation interface, which could lead to an under-estimation of the mass loss deduced from interface advance.

Overall, it is safe to say that the fractional conversion in $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ dehydration reactions both in isothermal and non-isothermal conditions can be represented by the present nucleation and growth model as long as sufficient knowledge of the elementary processes is available. The extension of the kinetic model to cover non-isobaric conditions is straightforward after studying the influence of pressure on the kinetics of the nucleation and growth processes, which will make the kinetic model applicable in even more complex reaction conditions.

5. Conclusions

In this work we developed an alternative approach to study the reaction kinetics of lithium sulfate monohydrate single crystals, based on the discrete approach proposed by Helbert et al. [24]. Compared to the conventional approach, fitting TGA results to typical kinetic models, our approach is different. Here, we characterized the elementary processes in dehydration reactions (nucleation and growth) by *in-situ* observations using an optical microscopy system, and calculated the fractional conversion based on the acquired knowledge of the elementary processes. After the number of nuclei on selected crystal surfaces was quantified, the applicability of a nucleation model described by a power law equation was confirmed. With a novel way of crystal encapsulation, nuclei growth rate into the crystal bulk is measured successfully over a much longer distance than the thickness of the reaction zone. Profiles of interface propagation at various temperatures are approximately linear. Both relations of nucleation rate and growth rate as a function of temperature are formulated with the Arrhenius equation and used as inputs in the kinetic model for further calculations. It is demonstrated that, by comparison of the calculated results and experimental results, the kinetic model provides a promising way to predict the overall kinetics for dehydration reactions under extensive experimental conditions.

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Appendix A. Typical list of reaction models

Table A.1

Solid-state rate and integral expressions for different reaction models.

Model	Differential form $f(\alpha) = (1/k)(d\alpha/dt)$	Integral form $g(\alpha) = kt$
Nucleation models		
Power law (P2)	$2\alpha^{1/2}$	$\alpha^{1/2}$
Power law (P3)	$3\alpha^{2/3}$	$\alpha^{1/3}$
Power law (P4)	$4\alpha^{3/4}$	$\alpha^{1/4}$
Avrami-Erofev (A2)	$2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$	$[- \ln(1-\alpha)]^{1/2}$
Avrami-Erofev (A3)	$3(1-\alpha)[- \ln(1-\alpha)]^{2/3}$	$[- \ln(1-\alpha)]^{1/3}$
Avrami-Erofev (A4)	$4(1-\alpha)[- \ln(1-\alpha)]^{3/4}$	$[- \ln(1-\alpha)]^{1/4}$
Prout-Tompkins (B1)	$\alpha(1-\alpha)$	$[\ln \alpha / (1-\alpha)] + c^a$
Geometrical contraction models		
Contracting area (R2)	$2(1-\alpha)^{1/2}$	$1 - (1-\alpha)^{1/2}$
Contracting volume (R3)	$3(1-\alpha)^{2/3}$	$1 - (1-\alpha)^{1/3}$
Diffusion models		
1-D diffusion (D1)	$1/(2\alpha)$	α^2
2-D diffusion (D2)	$-[1/\ln(1-\alpha)]$	$[(1-\alpha)\ln(1-\alpha)] + \alpha$
3-D diffusion (D3)	$[3(1-\alpha)^{2/3}]/[2(1-(1-\alpha)^{1/3})]$	$(1-(1-\alpha)^{1/3})^2$
Ginstling-Brounshtein (D4)	$3/[2((1-\alpha)^{-1/3} - 1)]$	$1 - (2/3)\alpha - (1-\alpha)^{2/3}$
Reaction-order models		
Zero-order (F0/R1)	1	α
First-order (F1)	$(1-\alpha)$	$-\ln(1-\alpha)$
Second-order (F2)	$(1-\alpha)^2$	$[1/(1-\alpha)] - 1$
Third-order (F3)	$(1-\alpha)^3$	$(1/2)[(1-\alpha)^{-2} - 1]$

Appendix B. Mampel model

In standard Mampel computations, rates of nucleation and growth are assumed to be constant with time. Dimensionless number K (called the model parameter), θ (reduced time replacing t) and φ are defined by:

$$K = \frac{\gamma 4\pi r_0^3}{\phi}, \quad \theta = \frac{\phi t}{r_0}, \quad \varphi = \frac{r_0 - \rho}{r_0} \quad (\text{B.1})$$

where ρ is the radius of an arbitrary thin spherical shell of the particle. The analytical solution for a spherical particle can be derived as following [26].

1st case: $\phi t \leq r_0$ ($\theta \leq 1$)

$$\alpha(\theta) = 1 - (1-\theta)^3 - 3 \int_0^\theta (1-\varphi)^2 \exp\left(-\frac{K}{12} \frac{\theta^3 - 3\varphi^2\theta + 2\varphi^3}{1-\varphi}\right) d\varphi \quad (\text{B.2})$$

2nd case: $r_0 < \phi t \leq 2r_0$ ($1 < \theta \leq 2$)

$$\alpha(\theta) = 1 - 3 \int_0^{2-\theta} (1-\varphi)^2 \exp\left(-\frac{K}{12} \frac{\theta^3 - 3\varphi^2\theta + 2\varphi^3}{1-\varphi}\right) d\varphi - 3 \exp(-K\theta) \int_{2-\theta}^1 (1-\varphi)^2 \exp\left(\frac{K}{3}(\varphi^2 - 2\varphi + 4)\right) d\varphi \quad (\text{B.3})$$

Fig. A.1. Typical examples of different kinetic models.

3rd case: $2r_0 \leq \phi t$ ($\theta \geq 2$)

$$\alpha(\theta) = 1 - 3 \exp(-K\theta) \int_0^1 (1 - \varphi)^2 \exp\left(\frac{K}{3}(\varphi^2 - 2\varphi + 4)\right) d\varphi \quad (\text{B.4})$$

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