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Review

A physico-geometric approach to the kinetics of solid-state reactions as exemplified by the thermal dehydration and decomposition of inorganic solids

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Abstract

By reviewing various microscopic studies on the mechanisms of the thermal dehydration and/or decomposition reactions of inorganic solids, the physico-geometric and chemical features of the solid-state reactions were investigated. A model of reaction interface and a classification of interfacial chemical behavior for the thermal dehydration of solids, which have extensively been studied by professors Galwey and Brown, were introduced in order to evaluate the significance of such mechanistic understandings on the solid-state reactions. The meanings of the kinetic models and kinetic equations, which have been employed conventionally for analyzing the overall kinetics of solid-state reactions, were discussed in relation to the complicated physico-geometric and chemical behaviors of the solid-state reactions revealed by the mechanistic investigations. Possible extensions of the conventional kinetic theory by incorporating various physico-geometric and chemical features were examined for an advanced kinetic understanding of the solid-state reactions. The kinetic data required for the advanced kinetic analysis of the solid-state reactions were discussed by emphasizing the usefulness of the controlled rate thermal analysis (CRTA). The present status and future subjects of the kinetic and mechanistic studies on the solid-state reactions were summarized briefly through the present review. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Solid-state reaction; Reaction mechanism; Kinetics; Microscopy; Thermal analysis

1. Introduction

Thermal decomposition including dehydration is one of the most popular processes in material synthesis. Kinetic and mechanistic studies on such processes have widely been carried out for obtaining fundamental kinetic data, as well as for characterizing the thermophysical properties of the materials. Various kinds of thermoanalytical techniques have been employed for the kinetic measurements [1–3]. In the respective kinetic studies on such processes, the kinetic parameters and reaction mechanisms are estimated on the basis of theoretical fundamentals on the solid-state reaction kinetics [4–6]. At the same time, numerous new aspects of the kinetic behavior, characteristic for the solid-state reactions, have been found through such kinetic studies of very widely distributed kinds of materials and processes under various reaction conditions. The newly found kinetic behavior and/or characteristics are expected to contribute notably towards the provision of a theoretical foundation for the further understanding of solid-state reactions. In order to analyze qualitatively and quantitatively the

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newly found kinetic behavior, it is sometimes required to improve and develop the thermoanalytical techniques and methodology of kinetic analysis. The kinetic theory of solid-state reactions has been developed as the result of compensative contributions by the practical kinetic studies for various materials and processes with the individually orientated purposes and the methodological studies for the kinetic analysis.

Distinguished contributions to our field of kinetics of solid-state reactions by Brown et al. [5], and Galwey and co-workers are recognized by noting their achievements in reconstructing the kinetic and mechanistic theory of solid-state reactions through logical integration of the widely distributed kinetic results for various processes of the thermal dehydration and decomposition of solids [7–12], in addition to their highly valued results of the sophisticated practical kinetic studies on the thermal dehydration of crystalline solids and systematic investigations on the methodology of the kinetic analysis. Among others, their proposal of classifying types of the reaction mechanism from a physico-geometric view point [5,7–12], taking account of the relationships between the characteristics of rate processes in the nucleation and advancement of reaction interface and the morphology as exemplified by the thermal dehydration of crystalline hydrates, seems to provide a rigid guiding principle for future studies on the mechanism and kinetics of solid-state reactions.

Their comprehensive understanding of the kinetics and mechanism of the solid-state reactions has been obviously achieved by their skillful experimental techniques to reveal unknown surfaces of the characteristics of the solid-state reaction. Especially, the microscopic observations [13–16] of the reaction processes for the thermal dehydration of various crystalline hydrates provided us with significant information on the classification of the reaction mechanisms from the physico-geometric viewpoint.

In the practical kinetic analysis of the solid-state reactions, estimation of the possible kinetic model from experimental thermoanalytical curves is important as a basis for a detailed characterization of the reaction mechanism. Brown and co-workers [17–22] have examined thoroughly the methodology of the kinetic model determination. Concerning the significance of the kinetic parameters obtained by the kinetic analysis using the thermoanalytical curves, it was suggested [23] that the establishment of a rational procedure for obtaining the reliable kinetic parameters and these methods evaluating the reliability are required for the theoretical interpretation of the physical meaning of the kinetic parameters. The present status of the methodology and practical usefulness of the kinetic analysis of the solid-state reactions were shown clearly through the project of round robin tests organized by the kinetic committee of the international confederation of thermal analysis and calorimetry (ICTAC) by Brown et al. and others [24–28].

In the present article, several practical reaction processes of the thermal dehydration and decomposition of inorganic solids are reviewed on the basis of the physico-geometric kinetics. Characteristic reaction behaviors of the solid-state reactions are discussed from the morphological viewpoints of surface nucleation and advancement of reaction interface using the results of microscopic observation. The significance of the classification of physico-geometric reaction mechanisms proposed by Galwey [12] is reviewed and evaluated in comparison with the conventional kinetic models for the solid-state reactions. In order to evaluate the correspondence to the physico-geometric kinetics of the solid-state reaction, methodologies of determining the kinetic model and kinetic parameters from thermoanalytical curves are reinvestigated. Expected orientations of the future developments of the physico-geometric kinetics and thermoanalytical approaches to the kinetics of the solid-state reaction are discussed on the basis of the above investigations.

2. Surface nucleation

In the thermal dehydration and decomposition of inorganic solid compounds, the reactant surfaces can be recognized as one of the most reactive sites and, in many cases, the reaction is initiated by nucleation of the solid product on the reactant surfaces. On the surface, the reactive sites are closely connected with the crystal structure characteristics of the reactant and with the existence of defects and dislocations. Optical microscopic observations have been conducted to find the relationship between the surface dislocations and nucleation sites during the thermal dehydration and decomposition of solids [29–31]. Because the reactant surfaces are exposed to the reaction atmosphere, the product nucleation processes and the kinetics are directly influenced by the atmospheric conditions. Frequency of nucleation and shape of the product nuclei produced over the reactant surface during thermal dehydration and/or decomposition of solids are very important in discussing the overall reaction kinetics, because the surface nucleation and growth result in the formations of reaction interface for the established reaction and of solid product layers, which play important roles in the chemical events and diffusion process of the evolved gas products, respectively, during the overall reaction process. Observations on the surface nucleation processes for the thermal dehydration and decomposition of solids have been long carried out and considerable information about the nucleation sites and shape of nuclei has been collected in relation to the reactant crystallography and reaction atmosphere.

2.1. *Effect of the reactant crystallography*

Thermal dehydration of plate-like single crystals of inorganic hydrates with stacking layer structure can be mentioned as a typical example that indicates the unambiguous relationship between the crystallographic characteristics and the reactive sites on the reactant surfaces. In the thermal dehydrations of single crystalline magnesium oxalate dihydrate [32] and zinc acetate dihydrate [33], surface nucleation is taking place selectively at the edge surface of the plate-like crystals.

Fig. 1(a) represents an optical microscopic view of the partially dehydrated edge surface of single crystalline zinc acetate dihydrate. The solid product can be observed on the edge surface, at the sites of linear alignment, being evenly spaced, parallel to the most developed surface (0 1 0) [33]. The reactivity of the sites on the edge surfaces can be explained by the structure of the reactant, in which the single crystals assume the form of thin plates which are stacked together to form prisms, with the prism surface (1 0 0) and (0 0 1) [34]. Similarly, single crystalline magnesium oxalate dihydrate is a monoclinic plate-like crystal with the most developed surface (1 0 0), where water molecules lie parallel with (1 0 0) planes [32]. The higher reactivity of the edge surface during the thermal dehydration of magnesium oxalate dihydrate is also ascribed to such characteristics of the reactant crystal structure. In both the reactions, the reaction interfaces produced by the product nucleation at the edge surface proceed toward the center of the plate-like crystal two-dimensionally. Fig. 1(b) shows a typical internal (0 1 0) face of the partially dehydrated single crystalline $Zn(CH_3COO)_2{\cdot}2H_2O$. The two-dimensional shrinkage of the reaction interface indicates that the reactant crystals are composed of extended planar units that are sufficiently stable to the reaction [12]. It was reported that the thermal dehydration of zinc formate dihydrate could also be classified as this type of dehydration [35].

2.2. *Effect of the reaction atmosphere*

Thermal dehydration of single crystalline copper(II) sulfate pentahydrate has frequently been subjected to microscopic observations [16,36–45]. In relation to the crystallographic structure of the reactant, it was reported [37] that product nuclei with different shapes form on the reactant surfaces of different crystallographic directions. Although the reaction pathway of the thermal dehydration to the anhydrous salt has so far been examined repeatedly, it is generally accepted that the dehydration proceeds via the monhydrate under reduced atmospheric pressure and proceeds via the trihydrate and monohydrate under the higher water vapor pressure (>100 Pa H_2O vapor) [39,40].

Fig. 2(a) and (b) show microscopic views of the product nuclei produced on the (1 0 0) original surface during the isothermal dehydration of single crystalline copper(II) sulfate pentahydrate under flowing nitrogen and reduced atmospheric pressure (1.5 h Pa), respectively. The scanning electron microscopic view of the product nuclei produced under flowing nitrogen is also presented in Fig. 2(c). The crater-like product nuclei of the trihydrate produced under flowing nitrogen grow hemispherically over the surface and inward into the reactant crystal. On the other hand, the product nucleus of monohydrate produced under reduced atmospheric pressure shows a parallelogram with a cross crack at the center and grow only two-dimensionally over the reactant surface. In this example, the atmosphere-dependent change in the product phase is accompanied by the change in the morphology and structure of the product nuclei.

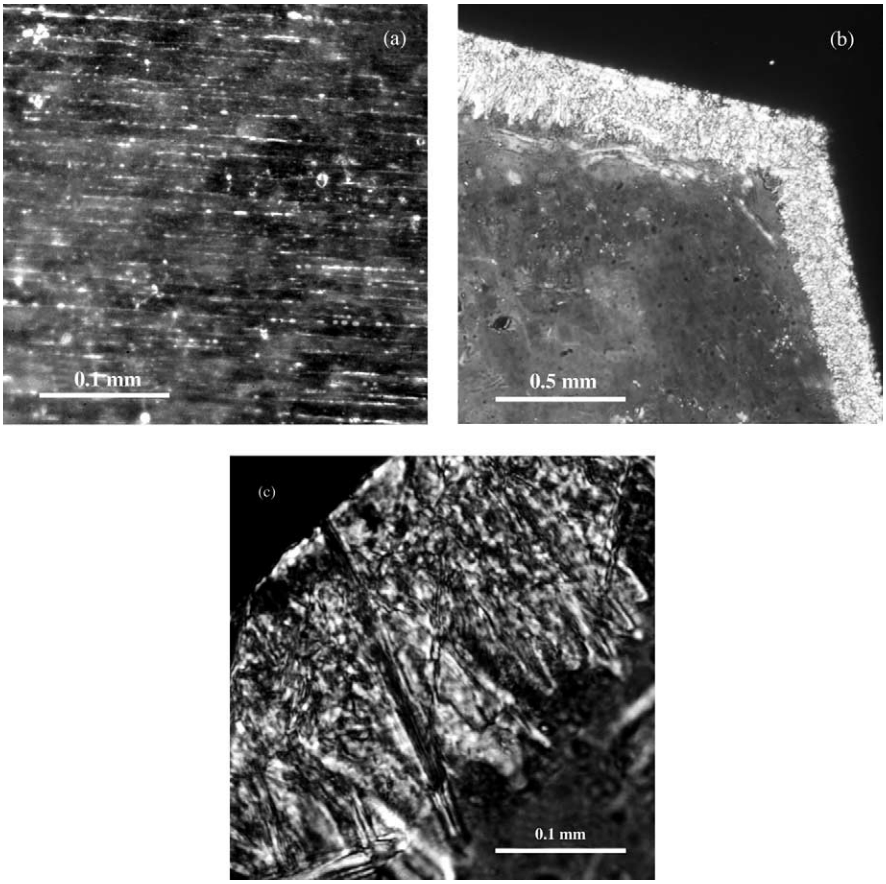

Fig. 1. Typical microscopic views of the thermal dehydration processes of single crystalline zinc acetate dihydrate: (a) an optical microscopic view of the edge surface at the beginning of the dehydration; (b) a polarizing microscopic view of internal (0 1 0) face of the partially dehydrated sample; and (c) a polarizing microscopic view of the reaction front and solid product layer.

2.3. Function of product nuclei

Both the center of the crater-like nuclei and cross crack of the parallelogram nuclei, observed during the thermal dehydration of copper(II) sulfate pentahydrate under flowing nitrogen and under reduced atmospheric pressure, respectively, are likely to play an important role, as a possible diffusion route of evolved water vapor, in the established reaction of advancing a reaction interface toward the center of the reactant crystal. Direct observation of the dehydration process under flowing nitrogen using a hot stage microscope indicated that the water vapor evolved in the interior of the reactant crystal is released through the center of the crater-like product nuclei on the surface [16,44]. Because the extent of the water vapor release varied periodically, it was expected that the water vapor pressure at the reaction interface would also change periodically. A typical polarizing microscopic view of the (1 0 0) internal surface of single crystalline copper(II) sulfate pentahydrate dehydrated partially under flowing nitrogen is shown in Fig. 2(d). The reaction interface shows the saw-like shape, and the product layer is constructed by a repeated stacking of dense and coarse aggregates of the product crystallites [44]. Such a structure of the product layer seems to result from the change in the size of product crystallites with the water vapor pressure at the reaction interface.

Similar crater-like product nuclei have been observed for the thermal dehydration of alums [13–16]. Galwey and co-workers succeeded in observing the

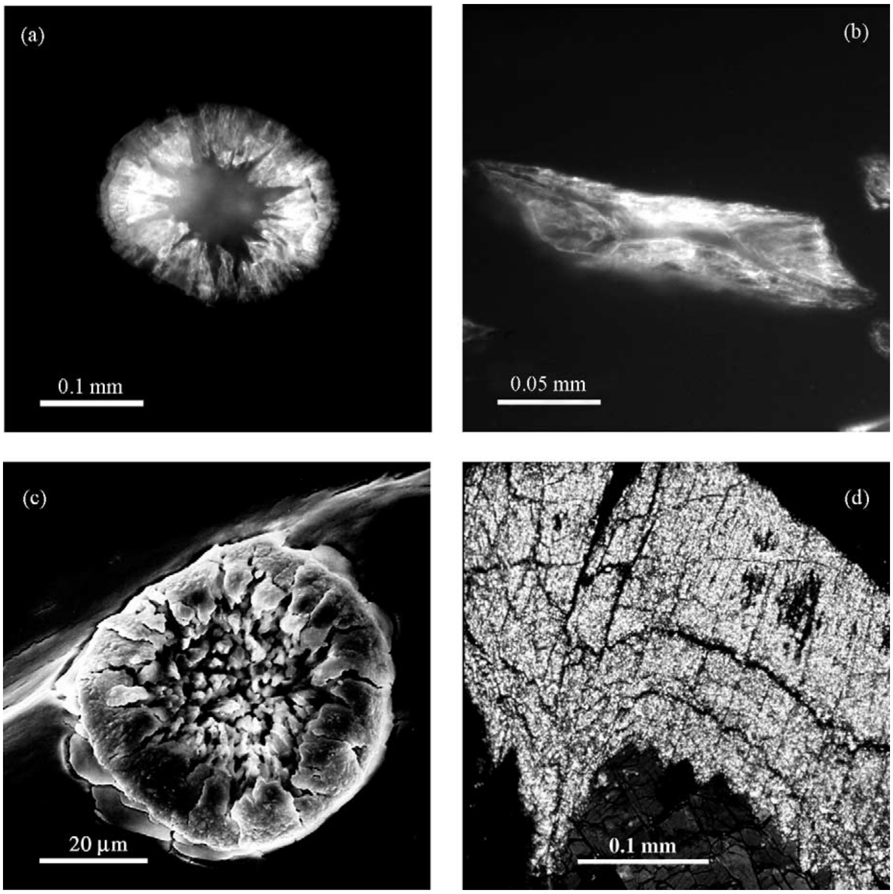

Fig. 2. Typical microscopic views of the thermal dehydration processes of single crystalline copper(II) sulfate pentahydrate: an optical microscopic view of the product nucleus produced at the reactant surface under (a) flowing N_2; (b) reduced pressure of 1.5 h Pa; (c) a scanning electron microscopic view of the product nucleus produced at the reactant surface under flowing N_2; and (d) a polarizing microscopic view of internal (1 0 0) face of the partially dehydrated sample.

internal crack structure of the crater-like nuclei produced at the (1 1 1) cleaved surface during the thermal dehydration of $KAl(SO_4)_2 \cdot 12H_2O$ and $KCr(SO_4)_2 \cdot 12H_2O$ by scanning electron microscopy using a replication technique [13–16] and revealed that the internal crack system is developed by radiating from the center of the crater-like nuclei and indicating a honey-combed shape. It was assumed that the dehydration during the nucleus growth was ascribed to retexturing/recrystallization of water-depleted salt facilitated by some product water vapor temporarily retained within each nucleus [14,46], because the nucleation and retexturing of the alum surface were enhanced by exposing temporarily the reactant surface to water vapor. By considering such a function of the product nuclei on the reaction advancement, Galwey classified [7] such nuclei as ‘‘fluid-flux nuclei’’ [14,47,48]. The proposal of classifying the nuclei from the viewpoints of morphology and function seems to be very important in approaching physico-geometrical to the kinetics and mechanism of the solid-state reaction. In addition to ‘‘fluid-flux nuclei’’ described above, ‘‘fusion nuclei’’ [49,50], ‘‘functional nuclei’’ [51–54], and ‘‘flux-filigree nuclei’’ [55] have been proposed to classify the nuclei from morphological and functional aspects. The characteristics of the respective type of nuclei classified by Galwey and co-workers are summarized briefly in Table 1 [7,55].

Table 1
Classification scheme for the product nuclei of the thermal dehydration of solids based on the structural and functional characteristics [7,55]

Classification	Structural and functional characteristics	Example
Fluid-flux nuclei	Nuclei retain temporarily a proportion of a volatile product at the interface condensed as a liquid within which chemical reactions and/or recrystallizations occur	Dehydration of alums [14,47]; $KBr + Cl_2 \rightarrow KCl + BrCl$ [48]
Fusion nuclei	Product melting, accompanied by eutectic formation on dissolution of the reactant in the expanding fluid formed, facilitates the reaction	Decomposition of ammonium dichromate [49] and copper(II) malonate [50]
Functional nuclei	Reaction occurs at the reactant-product interface induced by strain and/or heterogeneous catalytic breakdown of a chemisorbed intermediate at the reaction interface, which is directly promoted by product nuclei	Decomposition of copper(II) formate [51], nickel formate [52], nickel squarate [53] and silver malonate [54]
Flux-filigree nuclei	The reaction takes place at the reaction interface of two-zone structure, where the reactant at the nucleus periphery is strained, as a consequence of water loss, and the freshly dehydrated material is an irregular disposition of small particles of recrystallized product	Dehydration of lithium sulfate monohydrate [55]

3. Advancement of reaction interface

The reaction interface, characterized as a zone of locally enhanced reactivity located at the reactant/product contact, is formed inevitably by the surface nucleation. Various chemical and/or physical events, such as destruction of reactant crystal structure, breaking of chemical bonds, recrystallization of solid product, diffusional removal of gaseous product and so on, are expected to take place at the reaction interface [5,7–12]. At the reaction stage when all the surfaces are covered by the solid product, the reaction interfaces located at the growth front of the respective nucleus are overlapped and a chained reaction interface advancing inwards toward the center of reactant crystal is formed. Shape of the reaction interface may depend on the frequency of surface nucleation, crystal structure of the reactant, degree of strain at the plane of contact between the crystalline reactant and product phases, and so on. The linear rate of advancement of the reaction front is likely to be influenced by the structural factors of the reaction interface and the kinetics of chemical process and of gaseous diffusion at the reaction interface [5,7–12]. The chemistry of the reaction interface is not fully clarified due to the difficulty of experimental approaches.

3.1. Formation of reaction interface

Fig. 3 shows a typical polarizing microscopic view of internal (0 1 0) section of the partially dehydrated single crystalline lithium sulfate monohydrate. The thin section of Fig. 3(a) was prepared for the sample in which the nucleus formation was observed on the original reactant surface. It is seen that several nuclei formed on the original reactant surface are growing hemispherically inwards to the interior of the reactant to form the reaction interface by overlapping each other at the growth fronts of the respective nuclei [56,57]. As is seen in Fig. 3(b), the reaction interface advancing inward toward the center of the reactant is established in the further dehydrated sample (ca. 40%). It is worth noting [56,57] that a wavy front forms on the reaction interface proceeding along the *c*-axis, whereas a flat front does so along the *a*-axis. The wavy front may result from the generation of fewer nuclei on the original (0 0 1) surface during the early stage of reaction followed by more rapid growth, resulting in nucleus overlap. On the original (1 0 0) surface, however, it appears that there is relatively denser nucleation.

3.2. Structure of reaction interface

Investigation of the shape of reaction front advancing inwards, which may be related to the crystallographic characteristics of the reactant crystal and its destruction mechanism, provides valuable information in discussing chemistry of the reaction interface. Fig. 4(a) shows a typical polarizing microscopic view of the internal (0 1 0) face of the thin section of copper(II) acetate monohydrate dehydrated partially

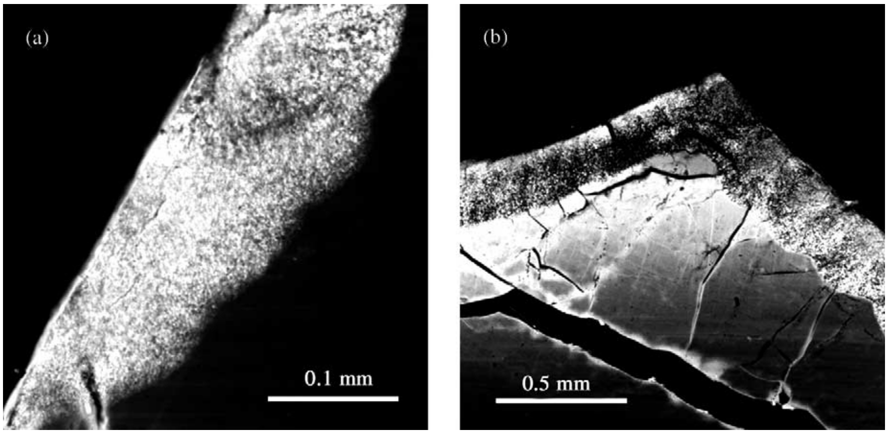

Fig. 3. Typical polarizing microscopic views of the thermal dehydration processes of single crystalline lithium sulfate monohydrate: (a) a cross section of the product nuclei; and (b) an internal (0 1 0) face of the partially dehydrated sample.

under an isothermal condition. A reaction front with a saw-like shape is found proceeding along the direction of cleavage (*c*-axis), whereas the reaction fronts advancing in the other crystallographic directions show different morphologies [58]. These observations indicate the possibility that the kinetics and mechanism of advancement of reaction front varies depending on the crystallographic characteristics.

Only a few works succeeded in measuring the thickness of the reaction interface for the thermal dehydration of crystalline hydrates. Boldyrev et al. measured the thickness of the reaction interface for the thermal dehydration of lithium sulfate monohydrate and copper(II) sulfate pentahydrate by diffractometry of synchrotron radiation [59]. By scanning on the coordinate near the reaction interface by a collimated beam of synchrotron radiation, it was reported the thickness of the reaction interface is 100–200 μm. Using scanning electron microscopy, the reaction interface for the thermal dehydration of *d*-LiK-$C_4H_4O_6{\cdot}H_2O$ was described by Galwey et al. [60, 61], as a water-depletion layer of up to 10 μm thickness followed by a discontinuous advance of the recrystallization zone. Fig. 4(b) represents the polarizing microscopic views of the reaction interface advancing along the *c*-axis during the thermal dehydration of

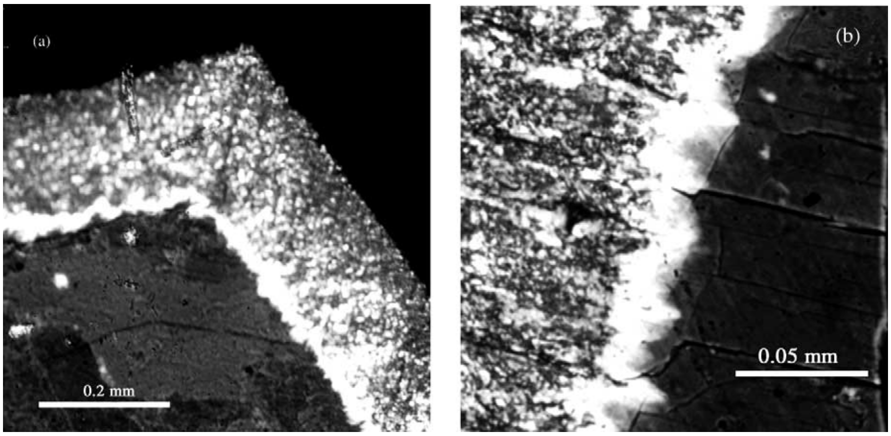

Fig. 4. Typical polarizing microscopic views of the thermal dehydration processes of single crystalline copper(II) acetate monohydrate: (a) an internal (0 1 0) face of the partially dehydrated sample; and (b) the reaction interface and solid product layer.

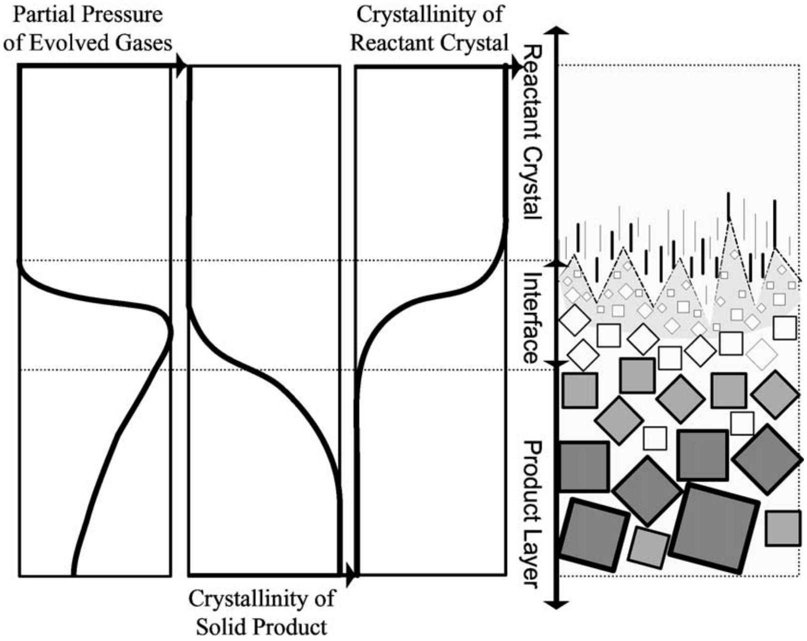

Fig. 5. A schematic illustration of the reaction interface recognized for the thermal dehydration of solids, where three interface processes are taking place, i.e. (1) destruction of reactant crystalline structure; (2) diffusional removal of the gaseous product; and (3) progressive recrystallization of solid product.

copper(II) acetate monohydrate. It is noted that there is an optically different layer of 20–50 μm thicknesses on the reactant side adjacent to the reaction front [58].

Fig. 5 illustrates schematically a typical model of reaction interface for the thermal dehydration and decomposition of solids [5,7–12]. In this model, the reaction interface is recognized as a strain zone of appreciable thickness within the reactant extending beyond the interface. On the basis of the representative investigations of reaction interface as described above, Brown et al. [5], and Galwey and co-workers suggested the following processes as participating in the thermal dehydration of solids [7–12].

(1) Water mobility within the crystalline reactant.
(2) Diffusive migration of water to crystal edge or interface.
(3) Water volatilization at the crystal edge or interface.
(4) Chemical reactions, if any.
(5) Recrystallization of solid reactant to product structure.
(6) Water vapor adsorption/desorption on product solid.
(7) Intranuclear diffusive escape of water and loss beyond crystal.

3.3. Recrystallization of solid product

Recrystallization of the solid product is a concurrent and/or consecutive process with the destruction of crystal structure of reactant accompanied by breaking of chemical bonds at the reaction interface and elimination of the gaseous product from the reaction interface [5,7–12]. The diffusion of the gaseous product through the solid product layer seems to be influenced largely by the degree of recrystallization and size of product crystallites. It is also expected that the relationships between time and space of the respective interface processes: (1) destruction of the reactant crystalline structure; (2) diffusional removal of the gaseous product; and (3) recrystallization of the solid product, vary from reaction to reaction depending on the reaction conditions.

Fig. 1(c) shows a typical polarizing microscopic view of the reaction interface advancing in the direction of *c*-axis and of the solid product layer during the isothermal dehydration of single crystalline zinc acetate dihydrate. The product layer is constructed by the needle-like crystallites of the solid product [33]. Penetration of the product crystallites to the reactant phase indicates that the advancement of the reaction interface is controlled by the crystal growth of the solid product. In such a reaction, the respective interface processes of (1), (2), and (3) are likely to be relatively close to each other in time and space. On the other hand, when the interface processes are separated in time and space, it is probable that an amorphous phase appears at the reaction interface, which will recrystallize during the course of reaction. It has been reported that certain time lags among the respective interface processes have been deduced experimentally in the thermal decompositions of calcium hydroxide [62] and copper(II) hydroxycarbonate [63,64]. In the thermal decomposition of copper(II) hydroxycarbonate, the extent of the lags of the respective interface processes may change depending on the partial pressure of water vapor [63,64].

When the recrystallization of solid products is further separated remarkably from the other interface processes of (1) and (2) in time and space and also in the reaction temperature, an amorphous phase could be produced as the stable solid product of the reaction. Many examples of this type can be seen for the thermal dehydration and decomposition of solids. As an example, Fig. 6 shows typical TG–DTA curves for the thermal dehydration of lithium metaborate dihydrate [65]. The dehydration reaction is completed at around 650 K producing the amorphous anhydride. Crystallization of the amorphous product takes place at around 750 K as can be seen from an exothermic peak in DTA. Although the reaction mechanism of producing a stable amorphous product has not fully been discussed, a complicated reaction behavior is likely to result from the interactions among the respective processes at the reaction interface. For example, Masuda and Nagagata reported on the thermal dehydrations of zinc(II) formate dihydrate [66] and yttrium formate dihydrate [67] that the solid products of these reactions under reduced atmospheric pressure are amorphous with respect to X-ray diffractometry, whereas crystalline anhydrides are produced by the dehydrations under relatively higher water vapor pressure. The change in the recrystallization behavior depending on the partial pressure of water vapor has been pointed out as one of the possible reasons of Smith–Topley effect [66–68], known as anomalous water vapor dependence of the dehydration rate [69,70].

Another example of formation of non-crystalline products can be seen during the thermal dehydration of magnesium acetate tetrahydrate [71]. Fig. 7 shows a

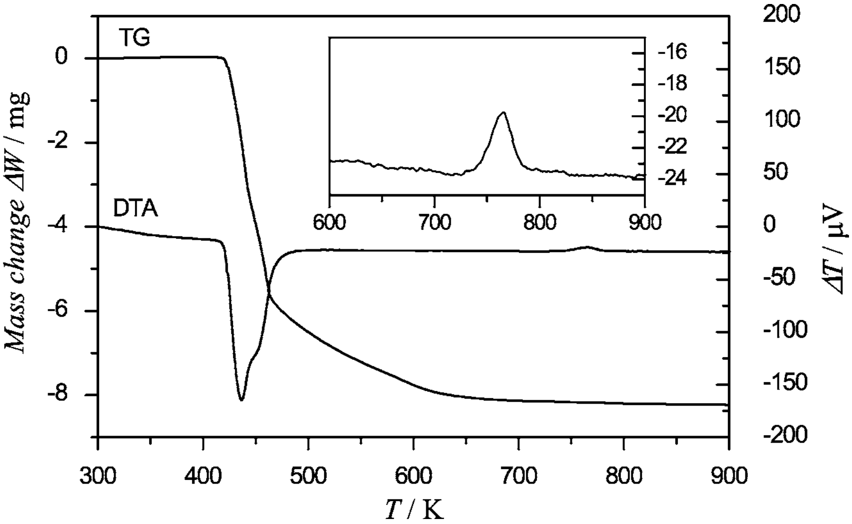

Fig. 6. Typical TG–DTA curves for the thermal dehydration of lithium metaborate dihydrate.

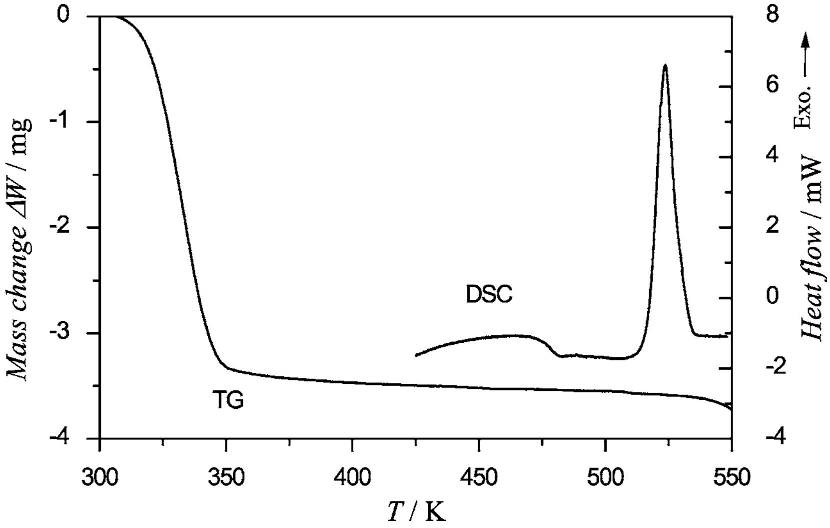

Fig. 7. A typical TG curve for the thermal dehydration of magnesium acetate tetrahydrate under reduced pressure, together with a typical DSC curve for the anhydrous product under flowing He.

typical TG curve for the non-isothermal dehydration of magnesium acetate tetrahyrate under reduced atmospheric pressure, together with a typical DSC curve for the dehydration product under flowing helium. The dehydration product indicates no distinguishable diffraction peak with respect to X-ray analysis. In the DSC curve of the non-crystalline product, a glass transition is observed and followed by an exothermic peak of crystallization. The glass formation process through the thermal dehydration is explained by a possible existence of a sol phase at the reaction interface, which subsequently is gelled due to diffusional removal of water [71].

3.4. Advancement rate of reaction interface

Kinetics of linear advancement of the reaction interface inward into the unreacted crystal is important in discussing the rate-limiting step of the overall reaction kinetics. Microscopic measurements of the linear advancement rate for the isothermal dehydration and decomposition of inorganic solids give evidence for this rate law [72]. Typical examples of such direct observation are given by the isothermal dehydrations of manganese(II) formate dihydrate [73] and zinc(II) formate dihydrate [35] and by the isothermal decomposition of ammonium perchlorate [74]. In all these studies, the linear advancement rates of the reaction interface were in agreement with the linear law, indicating a certain chemical event was the rate-limiting step for the overall kinetics. For the processes controlled by diffusion of evolved gases, the rate data might obey a parabolic law. Such processes, where the linear advancement rate throughout the reaction is expressed by a specified rate law, can be taken as an ideal case in formulating a kinetic model. For the practical processes, however, the kinetics and mechanisms of the linear advancements of the reaction interface sometimes vary depending on the crystallographic directions, as was deduced above from the change in the morphology of the reaction front with the crystallographic direction. Prodan performed kinetic modeling for thermal decompositions of the interface shrinkage type by considering the different kinetics of linear advancement of the reaction interface in the different crystallographic directions [75,76]. Even for the reaction process where the linear advancement rate of the reaction interface is well described by the linear law, it is often the case that the influence of the diffusion of gaseous product on the overall kinetics of the advancement becomes greater as reaction proceeds [33,58], due to increased difficulty of the diffusional removal of the gaseous products from the reaction interface with the increasing length of the diffusion pathway.

3.5. Structural and functional classification of reaction interface

By taking account of the crystallographic relation between reactant and solid products and of the structure and function of the reaction interface, Galwey proposed to classify the water evolution type (WET) for the thermal dehydration of crystalline solids into six different classes [12]. Such a classification of the reaction mechanism from a viewpoint of interface chemistry is useful in understanding systematically the characteristic behaviors of solid-state reactions. Table 2 summarizes the six classes of the WET.

4. Product layer and diffusion of evolved gases

4.1. Formation of surface product layer

Fig. 8 shows typical microscopic views of the reactant surface of nickel sulfate hexahydrate during the non-isothermal dehydration under flowing nitrogen. The product nuclei cover all the reactant surfaces by overlapping. It is expected that the retexturing and recrystallization on the reactant surface during the surface process may generate extensive strain. The dehydrated surface, however, is pseudomorphic with the original reactant and the initial nucleation sites cannot be distinguished [77]. It has been reported for some thermal dehydrations of inorganic hydrates that a characteristic surface texture like ‘‘orange peel’’ can be observed at this stage of reaction [14,43,78]. The surface product layer sometimes obstructs diffusional removal of the water vapor produced at the internal reaction interface. The behavior of obstructing the diffusional removal of the gaseous product by the surface product layer and the consequent superficial pause of the overall reaction are called by ‘‘impedance’’ and ‘‘arrest’’, respectively [79].

4.2. Crack formation and diffusion channel

On heating non-isothermally single crystalline potassium copper(II) chloride dihydrate under flowing nitrogen, the reaction initiates with the surface nucleation of the anhydride and produces an impermeable surface product layer [80]. Fig. 9(a) shows a typical polarizing microscopic view of the internal surface of the single crystal covered by the surface product layer. The surface layer impedes diffusion of the water vapor evolved at the reaction interface advancing inward toward the center of the reactant crystal. Consequently, advancement of the reaction interface stops by the increase of the partial pressure of evolved water vapor. Further intensive heating of the sample results in a structural rearrangement by a nucleation and growth of the product crystallites in the internal reactant crystal. A typical polarizing microscopic view of product crystallites produced by the internal process is shown in Fig. 9(b). The internal processes give rise to the further increase in the partial pressure of water vapor. As a result of the higher internal pressure and the strain resulted from recrystallization of the solid product, cracking takes place suddenly on the surface product layer and the internal water vapor is released through cracks to complete the reaction. This is a typical example that the crack formation on the surface product layer is a necessary condition to complete the reaction. The similar reaction behavior was seen for the thermal dehydration of nickel sulfate hexahydrate [77,81,82]. In the cases of smaller single crystals and/or crushed crystals of potassium copper(II) chloride dihydrate [77,83] and nickel sulfate hexahydrate [84], the thermal dehydration proceeded smoothly by the shrinkage of reaction interface. The shorter diffusion pathway of the water vapor evolved at the reaction interface is to be likely due to the smooth dehydration behavior for the smaller particles. This type of reaction can be classified into WET5 in Table 2.

Except in the extreme cases that were seen for the thermal dehydrations of single crystalline potassium copper(II) dihydrate and nickel sulfate hexahydrate, it is important to understand the relationship between the crack system in the product layer and diffusion of the gaseous product in order to estimate the change in the partial pressure of evolved gases at the reaction interface and to consider its influence on the overall kinetics. Although the systematic study on the crack system of the product layer is very limited at present, the replication technique employed by Galwey et al. [13–16] seems useful for revealing the structure and role of the crack system.

Table 2
Classification scheme for the WET of the thermal dehydration of solids based on structural and interface characteristics [12] (reproduced partially from Table 1 in [12] with permission from Elsevier Science)

WET	Classification criteria	Structural and interface characteristics	Rate control	Dimension
1	Crystal structure maintained (no geometric rate controls)	Crystal spacing unchanged by dehydration	(a) Intercrystalline diffusion	(a) 1, 2, or 3
			(b) Surface desorption	(b) Surface
2	Diffusion across an adherent barrier layer	Topotactic reaction (lattice spacing reduced on dehydration without cracking)	Diffusion and geometric	1, 2, or 3
3	Interface advance: nucleation and growth, or contracting envelope	(a) Topotactic reaction (crystal spacings changed sufficiently to cause cracking within the reaction zone) (b) Product recrystallization (reaction may or may not be topotactic) (c) Amorphous product that subsequently recrystallize (d) Amorphous product that does not recrystallize	Interface reaction and geometric controls	1, 2, or 3
4	Homogeneous reactions in crystals	(a) Water is retained within a strong, impermeable structure until the temperature rise results in an internal pressure sufficient to cause explosive disintegration	(a) Explosive disintegration	(a) –
		(b) Systematic variations of lattice parameters occur with changes in equilibrium $p(H_2O)$	(b) Progressive structural change	(b) 1, 2, or 3
		(c) Crystal constituents react independently of each other and position within the crystal	(c) Homegeneous intracrystalline chemical change	(c) Homogeneous
5	Melting and formation of impervious outer layer	(a) During reaction of large crystals, water bursts from the surface during rapid reaction (b) In powders, an amorphous phase is formed initially which melts before recrystallization	Atypical kinetic characteristics	Particle size dependent
6	Comprehensive melting	Melting may be accompanied by reactions other than dehydrations	Chemical steps and/or diffusion	Homogeneous

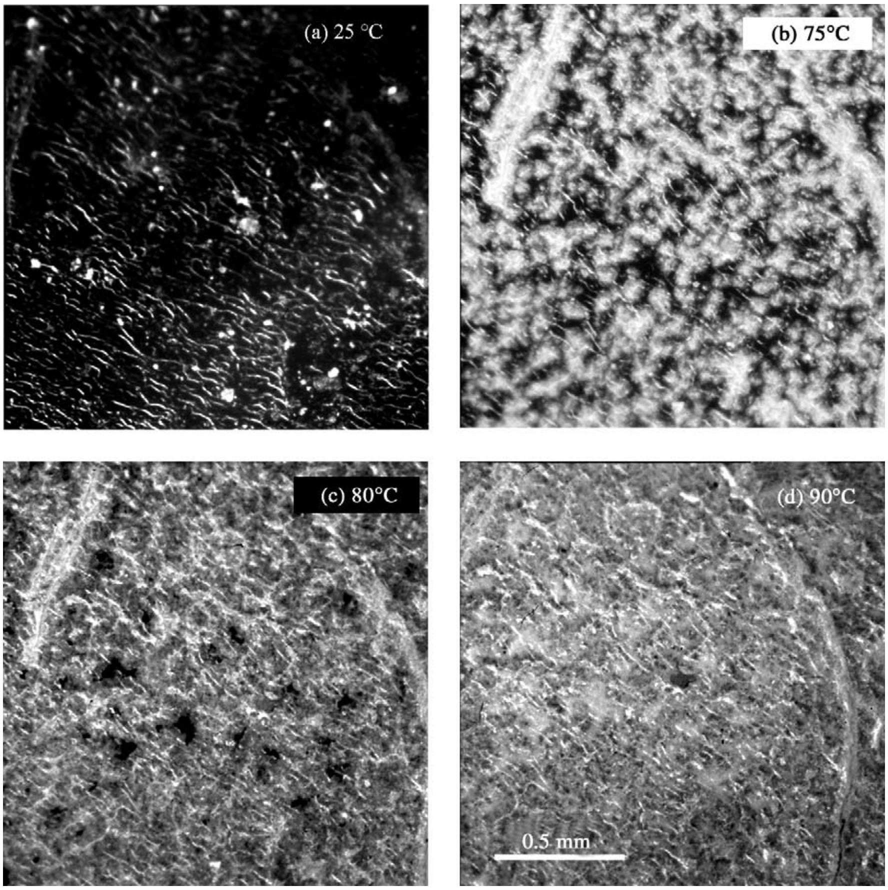

Fig. 8. Typical optical microscopic views of the surface nucleation and growth processes for the non-isothermal dehydration of single crystalline nickel sulfate hexahydrate under flowing N_2.

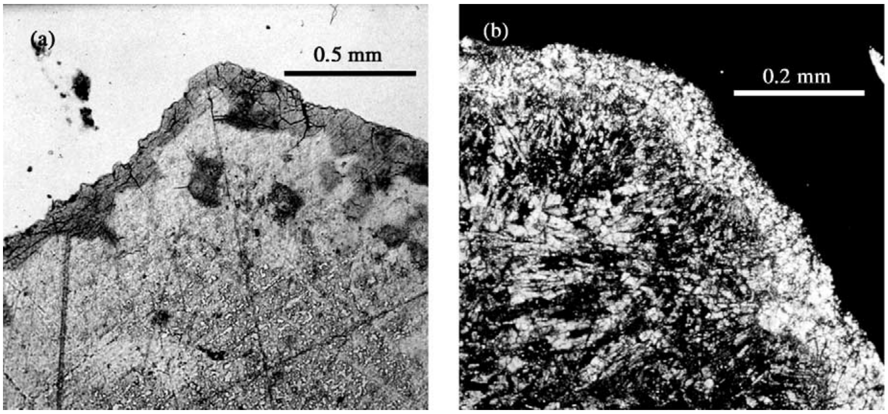

Fig. 9. Typical polarizing microscopic views of the thermal dehydration processes of single crystalline potassium copper(II) chloride dihydrate: (a) an internal (1 0 0) surface of the partially dehydrated sample; and (b) the impervious outer product layer and product crystallites in the bulk.

5. Bulk nucleation and growth

In addition to the reaction of interface shrinkage type characterized geometrically by the advancement of the reaction interface inward toward the center of reactant crystal, alternative reaction geometry of nucleation and growth type taking place in the bulk of the reactant crystal may be possible as was sometimes observed for the crystallization of non-crystalline solids [85]. For the thermal dehydration and/or decomposition processes, however, the reaction geometry of bulk nucleation and growth type is a very limited case, because of the higher reactivity of the reactant surface and the necessity of the diffusion route for the evolved gases.

In the practical kinetic analysis, the rate data for the thermal dehydration and/or decomposition of samples composed of assemblage of small reactant particles sometimes fits apparently one of the kinetic models of bulk nucleation and growth type. Such apparent fitting to one of the kinetic models of nucleation and growth type may result from the contributions from the occurrence of limited reactions across all surfaces, retention of water by adsorption on participating solids, generation of a pressure of product water, a contribution from the reverse reaction, and so on [10]. From a viewpoint of reaction geometry, the apparent agreement of rate data to the bulk nucleation and growth law is also expected when the reactions of the respective reactant particles behave superficially as if the reaction proceeds through the bulk nucleation and growth in the assemblage of the reactant particles [86]. It has been demonstrated mathematically that, if a remarkable distribution in fractional reaction α exists among the respective reactant particles reacting through an interface shrinkage, the apparent shape of the rate data is superficially in agreement with that for one of the bulk nucleation and growth models [87,88].

6. Kinetic model function

6.1. Fundamental kinetic model

As described above, the mechanistic investigations on the thermal dehydration and decomposition of solids have revealed that the solid-state reaction proceeds with features characteristic to the heterogeneous reaction in which there occurs a complexity of mutual dependence of the individual rate processes. It seems worth noting, however, that such interfacial chemical features are not always reflected by the measured rate data, because of the macroscopic character of thermoanalytical techniques [89]. The kinetic models for the solid-state reactions should incorporate ideally all the possible physico-geometric and chemical features, but at the same time the nature of information included in the kinetic models should be in accordance with that in the measured rate data. Fig. 10 illustrates schematically the physico-geometric features of solid-state reactions considered in deriving the conventional kinetic models for the solid-state reactions. As a result of an inductive modeling based on the mechanistic features, the reaction geometry and rate limiting step of the linear advancement of reaction interface had been considered in the conventional kinetic model, in addition to the kinetics of nucleation for the kinetic models of nucleation and growth type [90]. These simplified models are thus applicable to diverse solid-state reactions and widely used for the kinetic analysis. Table 3 lists the conventional kinetic model functions.

6.2. Extension of kinetic model function

When applying the kinetic model functions deductively to the actual process, it is sometimes necessary to reconsider the physico-geometric and interfacial chemical features of the reaction under investigation. An example is in connection with morphological anisotropies of the reactant and of the advancement of reaction interface. In the practical system, the shapes of the reactant crystals and the resulting reaction interface cannot be always described by a defined integral dimension. And also, the shape of the reaction front is not always planar, as was observed microscopically. In order to incorporate such geometric features in the kinetic model function, an extension of the kinetic model functions has been made by introducing fractal dimension [91,92].

Concerning the anisotropy of the linear advancement rate of reaction interface, Prodan proposed a kinetic model function taking account of three different rate components [75,76]. In the measurement of overall rate data carried out using thermal analysis, it

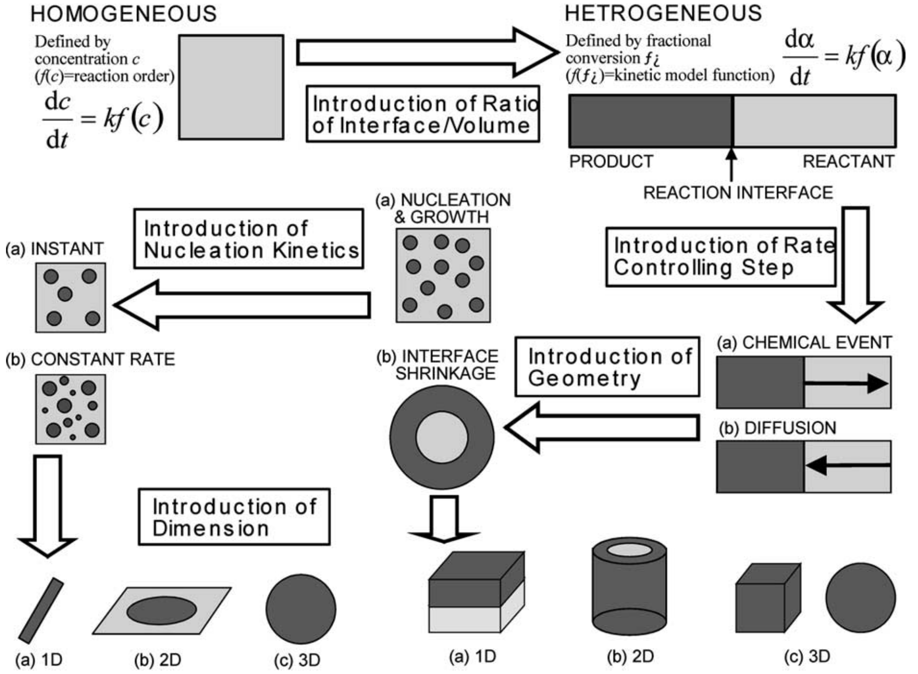

Fig. 10. Schematic diagram of a hypothetical transfer of the system geometry from the non-dimensional homogeneous-like model to the idealized heterogeneous model by introduction of dimensionality, due to the interface formation and interface growth.

is difficult to obtain the individual rate component of advancing in a specified direction. The rate data thus obtained reflect an averaged rate of reaction interface advancement in all the crystallographic directions of the reactant crystal. The averaged rate of reaction interface advancement may be not always in agreement to the linear law or parabolic law assumed on deriving the conventional kinetic model. Deviation of the rate law of the linear advancement from the idealized rate law is also expected from the complicated interfacial chemical behavior at the reaction interface as was revealed by the mechanistic studies of the solid-state reactions. Such possible deviations of an apparent rate law of the reaction interface advancement from an ideal linear or parabolic law also support the extension of the kinetic exponents in the conventional kinetic model functions to non-integral values [93,94]. The well-known Sestak–Berggren model [95] composed of three kinetic terms with non-integral kinetic exponents can accommodate diverse

Table 3
Typical physico-geometric kinetic model functions for the solid-state reactions

Model	Symbol	$f(\alpha)$	$g(\alpha) = \int_0^\alpha (d\alpha/f(\alpha))$
Nucleation and growth (Avrami–Erofeev)	A_m ($m = 0.5, 1, 1.5, 2, 2.5, 3,$ and 4)	$m(1-\alpha)[-\ln(1-\alpha)]^{1-1/m}$	$[-\ln(1-\alpha)]^{1/m}$
Phase boundary controlled reaction	R_n ($n = 1, 2,$ and 3)	$n(1-\alpha)^{1-1/n}$	$1-(1-\alpha)^{1/n}$
One-dimensional diffusion	D_1	$1/2\alpha$	α^2
Two-dimensional diffusion	D_2	$-(1/\ln(1-\alpha))$	$\alpha+(1-\alpha)\ln(1-\alpha)$
Three-dimensional diffusion (Jander)	D_3	$3(1-\alpha)^{2/3}/2[1-(1-\alpha)^{1/3}]$	$[1-(1-\alpha)^{1/3}]^2$
Three-dimensional diffusion (Ginstring–Brounshtein)	D_4	$3/(2[(1-\alpha)^{-1/3}-1])$	$1-(2\alpha/3)-(1-\alpha)^{2/3}$

kinetic characteristics [91], although it is generally difficult to evaluate the meaning of the kinetic model in the practical kinetic study.

Several problems can also be pointed out in relation to the fact that the conventional kinetic models were derived on the basis of the reaction mechanism of a single reactant body. In the measurement of kinetic data for an assemblage of small reactant particles, an apparent rate behavior cumulated over all the reactant particles is recorded. If the measurement is performed for an assemblage of uniformly sized and shaped reactant particles, it is expected ideally that the apparent kinetic data can directly correspond to the kinetic data of a single reactant particle in the assemblage, because the kinetic behavior of all the reactant particles is the same. In practice, however, distribution in the fractional reaction, α, among the respective reactant particles may exist probably due to the effects of mass and heat transfer phenomena [96,97]. Although the distribution in α during the course of reaction is difficult to identify experimentally, the similar situation can be simulated by assuming the size distribution of the reactant particles in the sample assemblage [87]. It has been shown mathematically [88,98] that, with increasing the degree of particle size distribution, the apparent kinetic data deviate gradually from the ideal kinetic data for a single reactant particle.

7. Methodology of kinetic analysis

7.1. Fundamental kinetic equation and accommodation function

Irrespective of the temperature conditions during the course of reaction, the following kinetic equation of the Arrhenius type has been utilized for the kinetic analysis of the solid-state reactions [87].

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\exp\left(-\frac{E}{RT}\right)f(\alpha)a(\alpha, T, P, \ldots) \qquad (1)$$

where α, $f(\alpha)$ and $a(\alpha, T, P, \ldots)$ are, respectively, the fractional reaction, the conventional kinetic model function listed in Table 3 and the accommodation function. Other symbols have their standard meanings in kinetics. When the actual rate data for kinetic analysis are influenced by a certain kinetic factor other than those involved in the fundamental kinetic equation composed of the temperature dependence of the Arrhenius type and the kinetic model function, the function $a(\alpha, T, P, \ldots)$ is introduced in order to accommodate the actual reaction process in the kinetic equation [87,89,91]. For an ideal case, the accommodation function can be set equal to unity. In many cases, however, the actual kinetic behavior seems to deviate, more or less, from the ideal case, where a certain form of the accommodation function should be considered. In practice, the exact mathematical solution for the accommodation function taking account of all the possible parameters is not always successful, because of the complexity of the physico-chemical features of the solid-state reactions and of the averaged character of the measured kinetic data. For the purpose of simplifying the required accommodation function, it is important to control quantitatively some possible kinetic factors in the kinetic measurement. Examples of such simplified accommodation functions expressed in terms of one of the possible factors, e.g. α [88,99], temperature T [100], or partial pressure of evolved gas P [101,102], can be seen in the previous works.

7.2. Evaluation of kinetic parameters

If the measured kinetic data really satisfied the idealized situation, the reliable results of kinetic calculation can be obtained irrespective of the calculation methods based on the fundamental kinetic equation without considering the accommodation function, as is easily demonstrated through the kinetic analysis of the theoretically drawn kinetic curves [24–28,103]. In many kinetic studies reported for various solid-state reactions, the accommodation function has sometimes been ignored without discussing the necessity. In this case, the reliability of the evaluated kinetic parameters change depending on the properties of the ignored accommodation function and the calculation method employed.

As an example, are considered the reliabilities of the respective kinetic parameters, E and A, obtained by ignoring a required accommodation function of α, i.e. $a(\alpha)$. In the conventional isothermal analysis, a value of E nearly close to the true value can be obtained by the Arrhenius plot if the kinetic plots for determining the apparent rate constants give the acceptable linearity, whereas the value of A derived from the intercept of the Arrhenius plot deviates depending on the ignored $a(\alpha)$ [88,104]. When the apparent kinetic parameters were obtained by one of the non-isothermal methods based on a single kinetic measurement, both the values of E and A deviate from the true values due to the ignored $a(\alpha)$, even when the kinetic plot for determining the values showed a fairly linear correspondence [88]. The situation is the same with the case that a wrong kinetic model function is used for the kinetic calculations [105,106]. The degree of deviations of the apparent kinetic parameters, determined by using an inappropriate kinetic model function, has been analyzed mathematically [107–109]. Using peak and/or isoconversional methods applied for a series of kinetic data under different heating rates [110–113], the true value of E can be evaluated from the kinetic plots for the peak top and/or at various restricted α, because any simple α-dependent functions as expressed by $f(\alpha)$ and $a(\alpha)$ are canceled in the kinetic plots [88,110–119]. The Friedman method [111], known as the isoconversional method in differential forms, can be applied to a series of kinetic data measured under any temperature conditions [115, 120–122]. Application of the isoconversional methods to the further complicated α-dependent processes have been analyzed by Vyazovkin [123,124], and Vyazovkin and Sbirrazzuoli [99].

Owing to the developments of the computer aided data acquisition system and sophisticated software of mathematical calculations, the main stream of kinetic calculation of the solid-state reactions changed from the age of the integral method to that of the differential method in the past two decades [125]. It is further expected that any ambiguities of the calculated kinetic parameters due to mere mathematical problems in the kinetic calculations will be cleared in the near future. Even by using any sophisticated calculation methods, however, it is difficult to evaluate the physico-chemical meaningful kinetic parameters, so far as any required kinetic factors are missed in the kinetic equation [126]. The mechanistic investigations of the solid-state reaction play an important role in identifying and classifying the required kinetic factors for analyzing kinetically the reaction process under investigation. On the basis of such mechanistic considerations, the kinetic equations that introduced several physico-chemical factors have been proposed and utilized successfully for the kinetic analyses of the practical solid-state reactions [86,99,101,102,127,128].

8. Measurement of kinetic data

8.1. Sample and measuring conditions

The sample and measuring conditions for the thermal analysis of the solid-state reactions have been discussed by many workers [1–6,129,130]. The details of the appropriate sample and measuring conditions have been proposed to increase the reliability and reproducibility of the thermoanalytical data. In the measurement for obtaining the kinetic data, it is desired that the factors related to the possible accommodation function in Eq. (1) are controlled quantitatively during the course of reaction in order to simplify the kinetic calculation [130].

As was described above, the particle size distribution of the reactant particles should be minimized, because the conventional kinetic models were derived on the basis of the reaction mechanism of a single reactant body. If the particle size distribution of the reactant particle is not negligible, the form of distribution function and degree of the distribution have to be identified quantitatively for the mathematical treatment during the kinetic calculations [88]. Even for a uniformly sized reactant particles, some distribution in α among the reactant particles may result, during the course of reaction, by the effects of a temperature gradient in the reactant system due to the self-cooling or self-heating by the reaction itself and of a gradient of partial pressure of the evolved gases due to the mass transfer phenomena [87]. Because the distribution in α during the course of reaction cannot be identified experimentally, influences of the mass and heat transfer phenomena on the measured kinetic data should be diminished by selecting the appropriate sample and measuring conditions [130]. The experimental conditions to be considered to diminish the influences of the mass and heat transfer phenomena are the sample mass, heating rate, reaction atmosphere, reaction rate, and so on.

8.2. Usefulness of the controlled rate thermal analysis

A higher suitability of the controlled rate thermal analysis (CRTA) for applying the kinetic measurements has been emphasized from the time of development [131,132]. In the measurement of CRTA, the

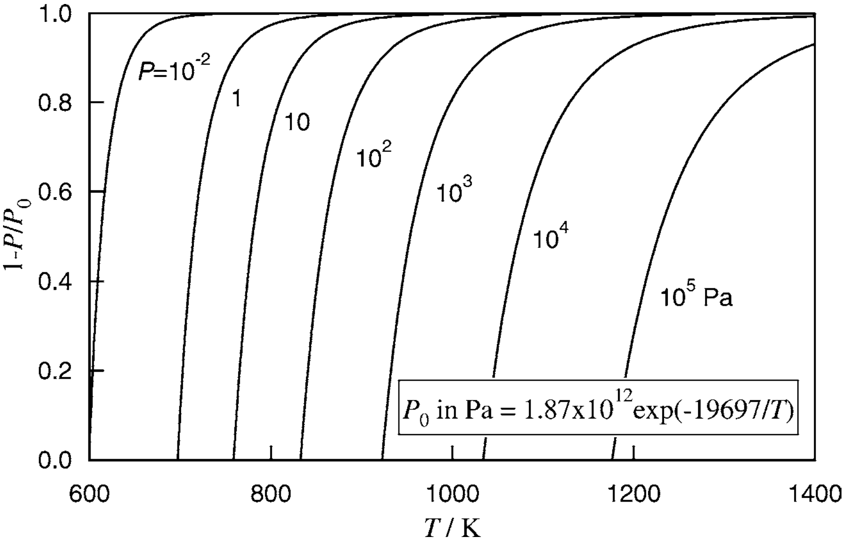

Fig. 11. Influence of partial pressure of CO_2 and temperature on the accommodation function $(1 - P/P_0)$ for the thermal decomposition of calcium carbonate.

influences of the mass and heat transfer phenomena can be restrained in comparison with conventional isothermal and non-isothermal measurements [131–137], because the overall rate of the reaction is kept to a lower constant value during the course of reaction. In addition, the variation in the self-generated atmospheric conditions during the course of the reaction can be diminished because of the constant evolution rate of gaseous products. Such characteristics of the CRTA are useful to the measurement of kinetic processes for the reactions influenced largely by the partial pressure of the evolved gases.

For example, for the thermal decomposition of calcium carbonate, the following rate equation has been proposed by considering the influence of the partial pressure of carbon dioxide, P [101,102].

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E}{RT}\right)f(\alpha)\left(1-\frac{P}{P_0}\right) \tag{2}$$

where P_0 is the equilibrium partial pressure of carbon dioxide. By considering the temperature dependence of P_0, the value of the accommodation function $(1 - P/P_0)$ introduced in Eq. (2) varies as the function of T and P as is shown in Fig. 11 [137]. Two possible kinetic approaches to such a system can be designed. One is to measure the kinetic data within the conditions of T and P, so that the accommodation function in Eq. (2) is equal to unity [138]. Another approach requires the precise measurement of P including the self-generated atmosphere during the course of reaction. The precise measurement of P in the vicinity of the sample is very difficult during the course of reaction. In this sense, it is recommended that we should use CRTA for keeping the evolution rate of carbon dioxide constant during the course of reaction.

9. Conclusions

Through the present review of the mechanistic investigation on the solid-state reaction, the kinetic treatment of the overall reaction and the measurement of kinetic data, the present status and problems that now confront us are summarized as follows.

9.1. Mechanistic investigations

On the basis of traditional investigations on the crystallographic relations between the reactant and product solids and on the reaction geometry, mechanistic investigations on the solid-state reactions have progressed to the level of discussing microscopically the structure of the localized kinetic events at the nucleation site, reaction interface and solid-product layer to evaluate the physico-chemical roles of the respective kinetic events on the overall kinetics. It is expected that an advanced classification of the type of solid-state reactions will be established by clarifying the physico-chemical and interfacial chemical features for the heterogeneous and complicated processes of our interest. The models and classifications for the thermal dehydration of solids, proposed by Brown et al. [5], and Galwey and co-workers [7–12], are highly valued as a basis for the advanced kinetic modeling of the solid-state reactions.

9.2. Kinetic treatment of the overall reaction

It is easily recognized that the conventional kinetic equation does not always express satisfactorily the heterogeneous and complicated chemical features of the solid-state reactions. Lack of such required physico-chemical features in the conventional kinetic equation is one of the problems related to the ambiguous physico-chemical meaning of the apparent kinetic parameters evaluated by the formal kinetic calculation. In order to break away the formal kinetic analysis of empirical curve fittings, steady efforts to incorporate the missing physico-chemical features in the advanced kinetic equation should be made on the basis of the mechanistic investigations.

9.3. Measurement of kinetic data

Thermal analysis is a very convenient technique of measuring the kinetic data for the solid-state reaction, which provide us with all the required data for the formal kinetic calculation. At the same time, some coupled techniques, which make the simultaneous measurements of the conventional thermoanalytical data with other physico-chemical factor possible, are required to evaluate influences of factors affecting the overall kinetics. Various new and/or improved techniques are now available for the measurements of kinetic data, such as thermoanalytical techniques coupled with microscopy, mass spectroscopy, X-ray diffractometry, and so on. Systematic use of such newly developed techniques of simultaneous measurements will make it possible to understand quantitatively various physico-chemical factors affecting the kinetics of the solid-state reactions. The strict control of the reaction condition including the self-generated reaction condition, as is achieved by the CRTA, is another important future task in the measurement of the kinetic data. Not only controlling the overall rate of the reaction, but also other physico-chemical factors related to the reaction rate, such as the evolution rate of a gaseous product, can be controlled to realize a required condition for the measurement of kinetic data and to perform a specific kinetic analysis related to a certain physico-chemical feature of the reaction.

9.4. Physico-geometric kinetics of solid-state reaction

It has been pointed out frequently by many workers [139–142] that kinetic parameters for a certain solid-state reaction evaluated by different workers widely deviate from one another and a physico-chemical meaningful pattern of this dispersion cannot be identified at present. In such a situation, it is dangerous to recognize the apparent kinetic parameters as the physico-chemical parameters related to the kinetic model and the rate-limiting step assumed in the formal kinetic analysis without any other detailed examinations. A further comprehensive approach, through extension of the mechanistic investigations, further detailed kinetic modeling by considering chemical features, progress in the thermoanalytical techniques for the measurement of kinetic data, and so on, are required to ensure an advanced physico-chemical kinetics of solid-state reactions.

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