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PHYSICO-GEOMETRIC KINETICS OF SOLID-STATE REACTIONS BY THERMAL ANALYSES

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Abstract

The physico-geometric kinetics for the solid-state reactions by thermoanalytical (TA) measurements were reexamined by focusing some fundamental aspects: (1) the fundamental kinetic equation, (2) the kinetic model function, (3) the fractional reaction α, and (4) the apparent kinetic parameters. It was pointed out that some pitfalls in the practical kinetic study are originated by the disagreement between the kinetic information from the TA measurements and the theory of the physico-geometric kinetics. In order to increase the degree of coordination between the theory and practice, several attempts were made from both the theoretical and experimental points of views. The significance of the apparent kinetic parameters was discussed with a possible orientation for obtaining the reliable kinetic parameters.

Keywords: accommodation function, fractional reaction, kinetics, solid-state reaction, thermal analysis

Introduction

Although thermoanalytical (TA) data for the solid-state reactions are of macroscopic nature averaged over the assemblage of sample, the experimentally resolved shape of the TA curves has widely been used as a possible source for the kinetic understanding of solid-state reactions [1, 2]. On the other hand, the kinetic analysis is in many cases performed by assuming the physico-geometric model functions, derived on the basis of a formal description for the geometrically well defined sample bodies [1–3]. Some difficulties have been found in providing a satisfactory kinetic description by the linkage of the macroscopically averaged TA data and the mathematically oversimplified physico-geometric kinetics [4]. The problem in the conventional TA kinetics is well recognized by comparing with the kinetic analysis by the Langmuir method [5], in which the linear advancement rate of the reaction interface along the selected crystallographic direction is subjected to the kinetic study. A collaboration for the kinetic analysis of the thermal dehydration of lithium sulfate monohydrate organized by the ICTAC kinetic committee [6] was actually initiated to evaluate the reliability of the physico-geometric kinetics by the conventional TA measurements [7, 8] with reference to the kinetic results by the Langmuir method [9]. Although many interesting findings concerning the dehydration kinetics

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of the crystalline hydrate have been clarified through the program, pitfalls in the physico-geometric kinetics by thermal analyses, which have long been discussed [10–12], were again emphasized. It seems very important here to discuss the influence of such disagreement between the measured rate data and the practical theory of the physico-geometric kinetics on the apparent kinetic results.

In the present paper, the physico-geometric kinetic analysis of the solid-state reactions by thermal analyses are reexamined by selecting some fundamental aspects. By introducing an accommodation function [4], properties of the fundamental kinetic equation with regard to the nature of the TA curves are discussed firstly. Practical meaning of the reaction geometry formalized in the physico-geometric kinetics is investigated by comparing with the typical microscopic views of the reaction interface advancement. Reality of the most fundamental concept in the physico-geometric kinetics, i.e., the fractional reaction α, is discussed in connection with the mass and heat transfer phenomena during the TA measurements. On the basis of the reexaminations at the most fundamental levels, possible orientation for obtaining the reliable kinetic results and/or for interpreting the apparent kinetic parameters are discussed as the concluding remarks.

Fundamental kinetic equation

Irrespective of the temperature conditions during the course of reaction, the kinetic equation for the solid-state reactions is generally expressed by

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

where α, $f(\alpha)$ and $a(\alpha, T, P, \ldots)$ are the fractional reaction, physico-geometric kinetic model function and accommodation function [4], respectively. Other symbols have their standardized meanings. Table 1 lists the typical kinetic model functions derived on the basis of simple physico-geometric assumptions on the reaction interface movement.

The function $a(\alpha, T, P, \ldots)$ is understood as is accommodating the actual reaction kinetics in the fundamental kinetic equation of the Arrhenius type. In the conventional kinetic analysis, the a function is usually setting equal to unity, assuming the highly idealized reaction behavior under strictly controlled conditions. If the kinetic data were really satisfying the idealized situation, the reliable kinetic results can be obtained irrespective of the calculation methods derived from the idealized kinetic equation, as is easily demonstrated through the kinetic analysis for the theoretically drawn kinetic curves.

In many cases, however, the actual kinetic behavior seems to be deviated, more or less, from that idealized, where a certain form of the a function should be considered. In practice, the exact mathematical solution for the a function is not always possible, because of the complexity of the overall reaction kinetics. In this sense, the possible factors in the a function are required to control quantitatively during the course of reaction in the TA measurements, in order to simplify the functional

Table 1 Typical physico-geometric kinetic model functions for the solid-state reactions

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

form. Such simplified a functions are sometimes expressed by one of the possible factors, e.g., α [4, 13, 14], temperature T [15] or partial pressure of gas P [16, 17]. The function $a(\alpha)$ is the accommodation function for the $f(\alpha)$, expressing the difference between the idealized kinetic model function and the actual reaction process, $h(\alpha)=f(\alpha)a(\alpha)$. Temperature dependence of the preexponential factor A is sometimes described as $a(T)=T^n$. For the solid-state reactions including the gaseous reactant and/or product, the influence of the partial pressures of the gases P_i should be taken into account with respect to the equilibrium pressure P_0, such as $a(P_i)=1-P_i/P_0$. For further complication, formulation of the sophisticated accommodation function seems to be difficult due to the possible interactions of the influence of the respective factors on the reaction kinetics.

In many kinetic studies by TA measurements reported for various solid-state reactions, the a function has sometimes been ignored because of the diffculty to control and measure the factors affecting the kinetic behavior during the TA measurements. In this case, it should be bear in mind that the significance of the apparent kinetic results is influenced by the properties of the ignored accommodation function and the calculation method employed.

Kinetic model function

The physico-geometric characteristics of the solid-state reactions estimated from the experimentally resolved kinetic curves is one of the most important experimental results in the physico-geometric kinetics, as well as the apparent kinetic parameters. The function $f(\alpha)$ in Eq. (1) plays important roles both as a model function for estimating the physico-geometric characteristics of the reaction mechanism and as

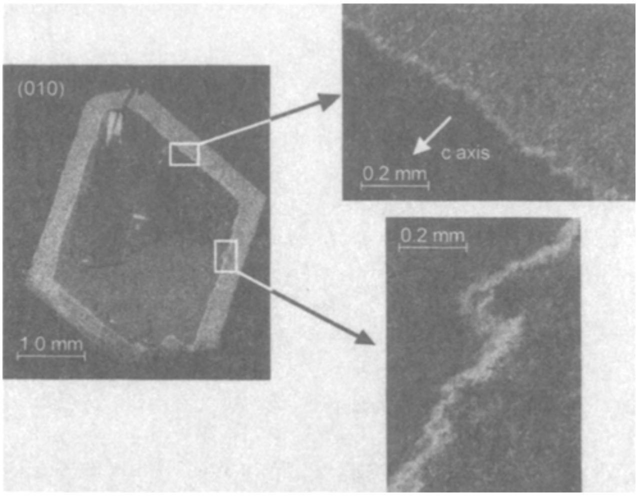

Fig. 1 Typical polarizing microscopic views of the internal (010) surfaces of the partially dehydrated single crystal of copper(II) acetate monohydrate

an accommodation function for evaluating the appropriate kinetic parameters. From the former point of view, the $f(\alpha)$ is conventionally derived by assuming the simple reaction geometry and overall kinetics of reaction interface advancement, see Table 1.

Figure 1 shows the typical polarizing microscopic views of the internal (010) surface of the partially dehydrated single crystal of copper(II) acetate monohydrate. Although the reaction behavior is well characterized by the interface shrinkage type model, the shrinkage dimension deviates from the sphere or cubic due to the original shape of the reactant. The reactivity of the interface advancement is influenced by the crystallographic direction as expected from the different morphologies of the reaction interfaces. From the isothermal kinetic analysis, the R_2 or R_3 model has been estimated for this reaction as the appropriate kinetic model function [18].

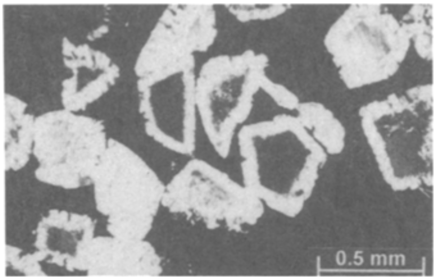

Fig. 2 A typical polarizing microscopic view of the internal surfaces of the partially dehydrated crushed crystals of α-nickel sulfate hexahydrate (–32+48 mesh)

A typical polarizing microscopic view of the partially dehydrated crushed crystals (–32+48 mesh) of nickel sulfate hexahydrate to dihydrate are shown in Fig. 2, as an example of the reaction in an assemblage of the reactant particles. In addition to the geometric deviation from the idealized kinetic model, it is also expected that the experimentally resolved TA curves are influenced by the distributions in the size and shape of the reactant particles in the sample assemblage. The R_2 model estimated by the isothermal kinetic analysis for the reaction [19] can be interpreted as a certain averaged physico-geometric information over the reactant particles.

From the above microscopic views, it is likely that the conventional physico-geometric kinetic model functions listed in Table 1 are suitable for describing the characteristics of the reactions as the model function. As the accommodation function, however, these are not always directly applicable for the kinetic calculation, because the apparent kinetic parameters are distorted by the disagreement between the actual reaction process and the model function [20, 21]. For such reaction processes with slight deviations from that idealized, the empirical kinetic model functions with a nonintegral kinetic exponent are applied in order to satisfy the two differently orientated roles of the kinetic model function in the fundamental kinetic equation [14, 22]. Table 2 lists the typical empirical kinetic model functions with a nonintegral kinetic exponent, derived by applying the nonintegral kinetic exponent

Table 2 Typical empirical kinetic model functions $h(\alpha)$ with nonintegral exponents, expressed by multiplying the physico-geometric kinetic model function $f(\alpha)$ with the accommodation function $a(\alpha)$

$f(\alpha)$	Exponent for interface kinetics	Dimension	$h(\alpha)$	$a(\alpha)^{*1}$
A_m	nonintegral	fractal	$M(1-\alpha)[-\ln(1-\alpha)]^{1-1/M}$	$\frac{M}{m}[-\ln(1-\alpha)]^{(M-m)/mM}$
R_n	nonintegral p	fractal N	$\frac{N(1-\alpha)^{1-1/N}}{p\left[1-(1-\alpha)^{1/N}\right]^{p-1}}$	$\frac{N(1-\alpha)^{(N-n)/nN}}{np\left[1-(1-\alpha)^{1/N}\right]^{p-1}}$
D_1	2	$1 \leq N < 2$	$\left[1-(1-\alpha)^{2/N-1}\right]^{-1}$	$2\alpha\left[1-(1-\alpha)^{2/N-1}\right]^{-1}$
D_4	2	$2 < N \leq 3$	$\left[(1-\alpha)^{2/N-1}-1\right]^{-1}$	$\frac{2\left[(1-\alpha)^{-1/3}-1\right]}{3\left[(1-\alpha)^{2/N-1}-1\right]}$

[*1] Exponents m and n are the kinetic exponents in the conventional $f(\alpha)$, see Table 1.

of the rate equation for the interface advancement and the nonintegral dimension. According to Eq. (1), the empirical kinetic model function $h(\alpha)$ is expresses by multiplying the physico-geometric model function $f(\alpha)$ with an accommodation function $a(\alpha)$, $h(\alpha)=f(\alpha)a(\alpha)$ [4, 13, 14, 22].

The above thermal dehydration processes presented as the polarizing microscopic views are taken as the examples of the reactions with the rather simple physico-geometric characteristics. We sometimes encounter the more complicated reaction processes in the practical kinetic studies [4, 19, 23]. Although the kinetic modeling is required for the respective complicated processes, it is in many cases difficult to express by a simple function. In such cases, it is recommended to employ a really empirical function which gives the best mathematical fitting to the shape of the kinetic curve, in order to accomplish the role of the kinetic model function as the accommodation function. For this purpose, any kinds of mathematical expression can be applied as the empirical kinetic model function. The typical example is the well-known Šesták-Berggren model [24].

$$h(\alpha) = \alpha^m(1-\alpha)^n[-\ln(1-\alpha)]^p \tag{2}$$

The empirical kinetic model function plays an important role to cancel the influence of the nonexponential term on the exponential term in the fundamental kinetic equation, as is the case of the *a* function in Eq. (1). Accordingly, the distortion of the evaluated Arrhenius parameters by the inappropriate kinetic model function is avoided by the use of an appropriate empirical kinetic model function. In the practical kinetic study, type of the kinetic model functions, physico-geometric or empirical, have to be selected depending on the characteristics of the kinetic process under investigation and the purpose of the kinetic study.

Fractional reaction α

In the physico-geometric kinetics, the fractional reaction α is introduced instead of the concentration in the homogeneous kinetics, expressed by the volume fraction

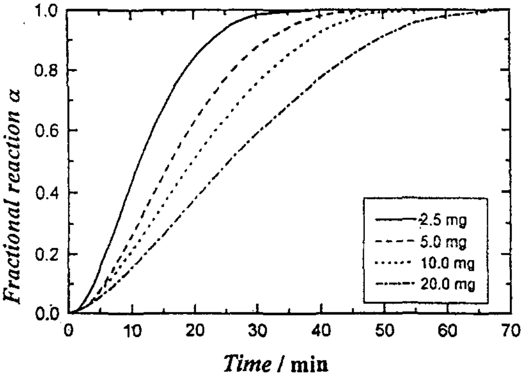

Fig. 3 Influence of the sample mass on the experimentally resolved kinetic curves for the isothermal dehydration of crushed crystals of lithium sulfate monohydrate at 364 K

of the product layer to the original reactant in a geometrically well defined single particle. When the sample composed of the uniformly sized particles was subjected to the TA measurements, the kinetic curves obtained is ideally not influenced by the sample mass [25, 26]. On the other hand, the practical fractional reaction is determined from the experimentally resolved TA curves as the ratio of the change in a particular physical property to the total change. Figure 3 shows the sample mass dependence of the isothermal kinetic curves for the thermal dehydration of lithium sulfate monohydrate (–100+170 mesh), obtained from the isothermal mass change traces at 364 K under flowing N_2 at a rate of 30 ml min^{-1}. The shape and position of the kinetic curves change systematically with the sample mass. This seems to be due to the mass transfer phenomena [27] which have long been discussed as a possible cause of the unreliable kinetic results from the TA methods, as well as the heat transfer phenomena [28].

Recently, we tried to find out the region of the experimental conditions to give the reliable kinetic data free from the mass transfer phenomena [29], as exemplified by the thermal decomposition of calcium carbonate by the CRTA under reduced pressure of 4.0×10^{-3} Pa using an instrument of Rouquerol type [30]. In the CRTA, the generalized transformation rate, $d\alpha/dt$, can be varied by changing only the sample mass in remaining the other measuring conditions constant. The kinetic curves obtained from the series of the CRTA curves with different sample masses were subjected to the Friedman plots [31] for determining the activation energy at a given α. The typical Friedman plots for the thermal decomposition of calcium carbonate at various α were shown in Fig. 4. It is clearly seen that the data points of the sample mass more than 10.0 mg deviate from the linear regression line drawn for the sample mass less than 10.0 mg. The E values calculated from the Friedman plots within the range of the sample mass less than 10.0 mg were at around 220 kJ mol^{-1} irrespective of α, being in good agreement with that estimated by the Langmuir method [5]. This result implies that the mass transfer phenomena is negligible only

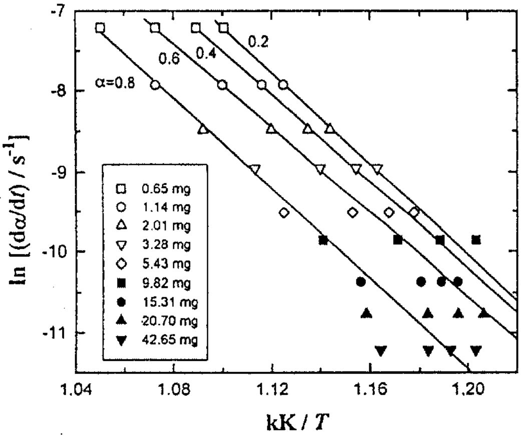

Fig. 4 The typical Friedman plots for the thermal decomposition of calcium carbonate measured by the CRTA with different sample masses under reduced pressure of 4.0×10^{-3} Pa

within the range of sample mass less than 10.0 mg even for the reaction process at a moderate reaction rate under high vacuum. It is expected that the mass transfer phenomena is possibly producing a certain distribution in α of the respective particles in the sample assemblage.

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 particles in the sample assemblage [32]. The theoretical kinetic curves with a particular particle size distribution (PSD) were drawn by assuming the log-normal distribution with the averaged particle size of 10 μm and the Arrhenius parameters, $E=100$ kJ mol^{-1} and $\ln A=20$ μm s^{-1}. The Friedman plots were applied for the series of kinetic curves with a particular PSD. Figure 5 shows the Friedman plots at $\alpha=0.5$ for the isothermal and nonisothermal kinetic curves drawn by assuming the R_3 law. It is clearly demonstrated that the slope of the Friedman plot is not influenced by the PSD and thus by the possible distribution in α, if the distribution at a given α remains constant among the series of the kinetic curves. Similarly, it was proved mathematically [32] that the E values determined by an isoconversion method [33] and the conventional isothermal method are independent of such distributions. In order to evaluate the kinetic model for a single particle and physico-geometrically meaningful A value, however, it is necessary to identify the distribution function [32]. In the practical kinetic study, the influence of the mass transfer phenomena should be, at least, kept constant among the series of kinetic curves for the kinetic calculation, by controlling the reaction conditions and by selecting the appropriate range of the experimental conditions.

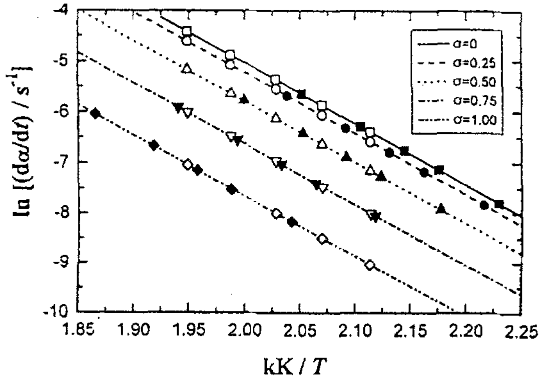

Fig. 5 The Friedman plots at $\alpha=0.5$ for the R_3 reaction with the log-normal particle size distribution of various logarithmic standard deviation σ. Open and solid symbols correspond to the isothermal and nonisothermal kinetic data, respectively

Apparent kinetic parameters

Form the present discussions, it is understood that the practical kinetic study is the trying task, searching the physico-geometrically meaningful kinetic parameters both by controlling the reaction conditions during the TA measurements and by se-

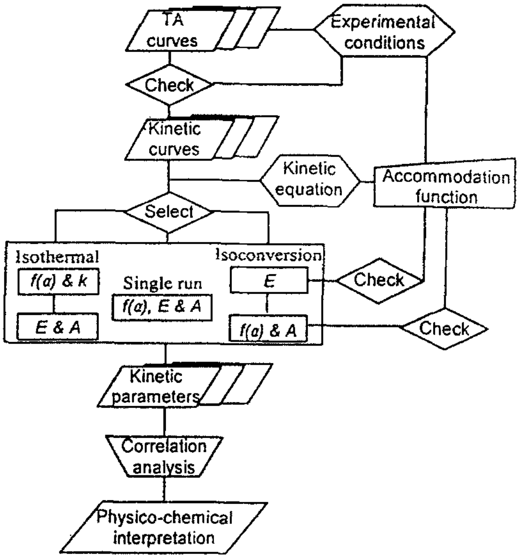

Fig. 6 A flow chart of the kinetic procedure including the possible check system for the reliable kinetic determination

lecting or modifying the theory of the kinetic calculation. Figure 6 shows a typical flow chart of the kinetic calculation. The reliability of the TA curves as the source of the kinetic curves has to be checked as is demonstrated for the mass transfer phenomena during the thermal decomposition of calcium carbonate, which in turn provides the appropriate range of the experimental conditions for the TA measurements. The method of kinetic calculation is selected on the basis of the reliability of the TA curves examined in drawing the kinetic curves, in the light of the limitation and characteristics of the respective calculation methods. Applicability of the kinetic procedure for the reactions under investigation has to be checked on the respective steps of the kinetic calculation. If necessary, an appropriate accommodation function should be introduced in the fundamental kinetic equation. For example, the kinetic model function is extended from the conventional physico-geometric kinetic models to the more sophisticated empirical models.

The kinetic parameters thus determined will be used for the comparative study of a series of reactions, classified into the correlation analysis [34]. In a strict sense, only the physico-chemically meaningful kinetic parameters can be applied for the correlation analysis. The well-known kinetic compensation effect (KCE) [35] is one of the typical examples of the correlation analysis. Although the linear dependence of the series of apparent Arrhenius parameters has widely been observed in the practical kinetic studies, it is very difficult to obtain the physico-chemically meaningful preexponential factor by the present TA kinetics. On the other hand, the linear dependence of the Arrhenius parameters itself can be easily demonstrated as a simple mathematical consequence of the exponential form of the kinetic equation [36]. Sophistication of our kinetic procedure is required for the further detailed discussions about the KCE.

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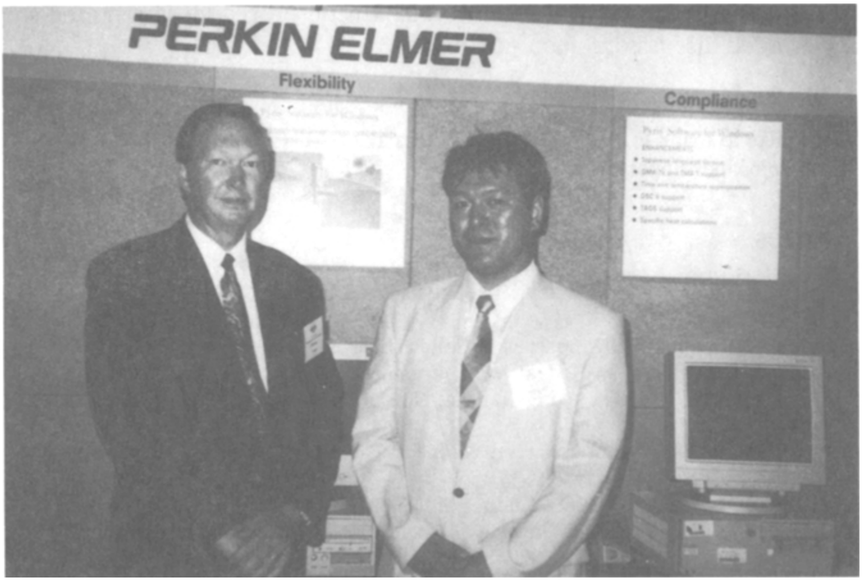

Presentation of ICTAC-Perkin Elmer Young Scientist Award. The recipient was Professor Nobuyoshi Koga.The award was presented by Mr. Richard Fyans of Perkin-Elmer. Congratulations!