Journal of Thermal Analysis and Calorimetry, Vol. 92 (2008) 2, 391–394

DEDUCTION OF CHANNEL-LENGTH DISTRIBUTION FROM ISOTHERMAL THERMOGRAVIMETRY

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A possible deduction is proposed of channel length distribution in one-dimensional porous materials from the kinetic data obtained in isothermal thermogravimetry (TG). The method utilizes the absorption/desorption of small molecules into one-dimensional nano-channel. In the surface-controlled absorption/desorption, the second derivative with respect to time is directly proportional to the channel-length distribution function. Even in the diffusion-controlled case, the second derivative with respect to the square root of time gives rough information on the distribution function.

Keywords: *nano-channel, solid-state kinetics, thermogravimetry*

Introduction

The reaction kinetics in solid-state is affected not only by a basic reaction mechanism but also by a number of factors such as particle size distribution even if the environment where the reactants are placed remains the same. It is crucially important from the practical point of view such as industrial manufacturing of functional ceramics. Thermal analysis is one of the best methods to characterize reaction mechanisms in the solid state. A number of studies have been made in the field [1–5].

Recently, inorganic, organic and their hybrid porous materials attract growing interests because of their potential functions such as gas storage, catalytic activity and so on [6, 7]. There are four types of materials, which are basically different in shape of pore: materials with isolated voids (zero dimensional pore, 0D), those having one-dimensional (1D) channel, those having interlayer space (2D) and those having 3D-interconnected nano-pores. Besides, some peculiar materials have been discovered, where the shape of nano-pores changes in response to the environment, leading to the gate effect in gas absorption [8]. Hereafter, we focus our attention on the 1D nano-channel materials. The characterization of nano-channel is desired in both basic science and practical utilization. The radius of the channel and specific surface area are of the main interest from the basic point of view, whereas the channel length and its distribution is also important factor for application. The microscopic observation may afford direct information on the channel length for a single crystal. It is however not practical for real materials that are an ensemble of a vast number of particles. A method applicable to real materials is, therefore, desired. In this paper, a special aspect of solid-state reaction of highly-anisotropic materials is pointed out and a method utilizing isothermal thermogravimetry (TG) is proposed to give the information on channel-length distribution [7].

Solid-state reaction in one-dimension

There have been some attempts to incorporate the sample size distribution in analysis of solid-state reaction kinetics utilizing thermal analyses [9–14]. In general, the reaction kinetics depends upon shapes of the sample crystallite and its distribution. However, the situation becomes very simple if the reaction proceeds only in one-dimension due to structural anisotropy of the crystalline sample. The kinetics is solely governed by the length distribution of the sample along the direction in which the reaction proceeds as exemplified below while assuming the environment around the sample remains the same throughout the reaction.

Here we consider the absorption/desorption of gas molecules under the well-ventilated environment. This environment ensures that the partial pressure of the gas is kept constant during the reaction: the supply of the gas for absorption or the removal of the desorbed gas is sufficient. Then the reaction certainly start from the surface and proceeds along the channel, being irrespective of the basic reaction mechanism, diffusion-controlled or surface (interface)-controlled. If the shape of the material is infinitely long along the

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1388–6150/$20.00

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channel, a kinetic constant remains constant during the reaction. Real system usually consists of many particles having different length, i.e., channel-length. Each particle contributes to the reacted fraction by the common contribution per unit sectional area of the channel only before the reaction covers the whole particle. Thus the reaction rate defined appropriately is directly proportional to the total sectional area (normal to the channel) present at the moment. This is the basic principle of the present method to deduce the channel-length distribution from the isothermal absorption/desorption kinetics.

As for experimental techniques, any kind of isothermal techniques can be used to record the kinetics assuming the time lag intrinsic to the technique is sufficiently short in comparison with the characteristic time scale of the reaction. Isothermal gravimetry (TG) apparently fits for the purpose.

The above method assumes that the process of the absorption/desorption reaction is described by a single reaction mechanism. The assumption can be assessed by the comparison of the kinetic data at plural temperatures. If the data can be reduced to a single (master) curve by normalizing the time (such as $t/t_{1/2}$: $t_{1/2}$ is the time when the reacted fraction is the half of full), it is reasonable to conclude that the assumption is reasonable [15]. In this case, the activation energy for the governing reaction mechanism is readily obtained by plotting the logarithm of the times at the same reacted fraction *vs*. the inverse temperature.

The discrimination of the basic mechanism of the reaction is necessary to proceed. If a single-crystalline particle is used as a sample for experiments, the reacted fraction grows in proportion to time ($\propto k_s t$) in the case of surface-controlled reaction throughout the reaction whereas it is proportional to square root of time ($\propto k_d t^{1/2}$) in diffusion-controlled reactions by virtue of the property of diffusion equation in one-dimension. Unless some special material having no characteristic size (geometrically fractal material) is considered, there will be a characteristic size (length) in real material as an ensemble of particles. The early stage of the kinetic data is therefore expected to show either of the diffusion-controlled (linear in time) or surface-controlled character (proportional to the square root of the time).

It is noted that the proposed method cannot give the information of the absolute length scale. This should be determined separately by other methods such as X-ray diffractometry or, optical or electron microscopic observation. On the contrary, needless to say, there is a possibility that the method is used to determine the 'rate constant' such as diffusion constant if the length scale and the its distribution are known previously.

Surface-controlled absorption/desorption

For the surface-controlled absorption/desorption, the discussion given in the preceding section directly applies. The apparent kinetic constant, which is obtained from the experimental kinetic data is related to the kinetic constant for infinitely long sample (k) by

$$k^{\mathrm{app}}(t) = k\int_{\mathrm{L(t)}}^{\infty}\rho(l)\mathrm{d}l = k\int_{\mathrm{t}}^{\infty}\rho[l(t)]\frac{\mathrm{d}l}{\mathrm{d}t}\mathrm{d}t$$

where $\rho(l)$ is the channel length distribution function.

Some materials lose their crystallinity upon desorption of small molecules. Since the reaction front is the fresh surface at any moment, the surface-controlled mechanism is reasonable for this type of materials. Application of the method was intended to an inorganic coordination polymeric complex with a brief description of the principle [7].

Diffusion-controlled absorption/desorption

The diffusion equation for a rod (in X-direction) is given by

$$\frac{\partial C(T,X)}{\partial T} = D\frac{\partial^2 C(T,X)}{\partial X^2}$$

where C, T, X and D are concentration, time, space coordinate and diffusion constant, respectively. The solution under the boundary condition $C(T, 0)=0$ and the initial condition $C(0, X)=1$ is given by $C(T, X)=\mathrm{erf}(\mathrm{X}/2\sqrt{T})$. Here, erf(•) denotes the (normalized) error function. The total amount of diffused into the rod is calculated as $A(T)=\int_0^{\infty}[1-C(T,X)]\mathrm{d}X = 2\sqrt{DT/\pi}$, proportional to the square root of time. This suggests that the relevant 'rate' in the diffusion-controlled case be the derivative of the total amount diffused with respective to the square root of time, i.e., $[\mathrm{d}A(t)/\mathrm{d}\sqrt{T} = (1/2\sqrt{T})(\mathrm{d}A(T)/dT)]$. That is, the length distribution function is possibly obtained as the second derivative of the total amount diffused with respect to the square root of the time, which is obtained as

$$\mathrm{d}^2A(T)/\mathrm{d}\sqrt{T})^2 = (1/4T)(\mathrm{d}^2A(T)/\mathrm{d}T^2 - 2\mathrm{d}A(T)/\mathrm{d}T)$$

The diffusion equation for a rod with the length L can be rewritten as

$$\frac{\partial c(t,x)}{\partial t} = \frac{\partial^2 c(t,x)}{\partial x^2}$$

using reduced variables, $x=X/L$ and $t=T/(L^2/D)$. The boundary condition is modified to $c(t, 0)=c(t, 1)=0$. At the beginning of the reaction, the

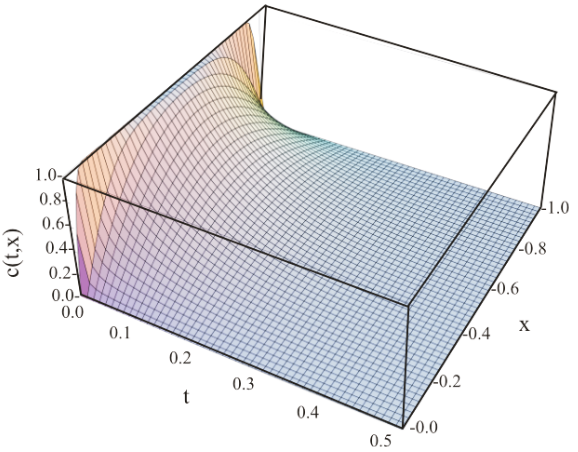

Fig. 1 Numerical solution of the diffusion equation in one-dimension for a rod having a unit length

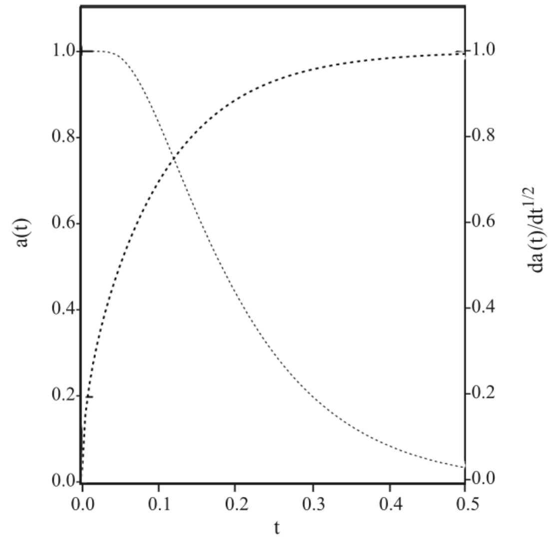

Fig. 2 Total amount of --- – diffused $a(t)$ and ··· – its first derivative with respect to the square root of time for the numerical solution shown in Fig. 1

solution is well represented by the superposition of two error functions: $c(t, x)\approx\mathrm{erf}(x/2\sqrt{t})+\mathrm{erf}[(1-x)/2\sqrt{t}]$ ($t<<1$). This implies that the initial ‘rate’ be governed solely by the diffusion constant and the total number of the channel. If the diffusion constant in the channel is known prior to the experiments, the total number of the channel is readily determined from the initial ‘rate’.

The exact solution can be constructed using a function $f(x)$ representing the initial condition as

$$c(t,x)=(4\pi t)^{-1/2}\int_0^1 f(y)\left[\sum_{n=-\infty}^{\infty}\left\{\exp\left(-\frac{(x-y+n)^2}{4t}\right)-\right.\right.$$
$$\left.\left.-\exp\left(-\frac{(x+y+n)^2}{4t}\right)\right\}\right]dy$$

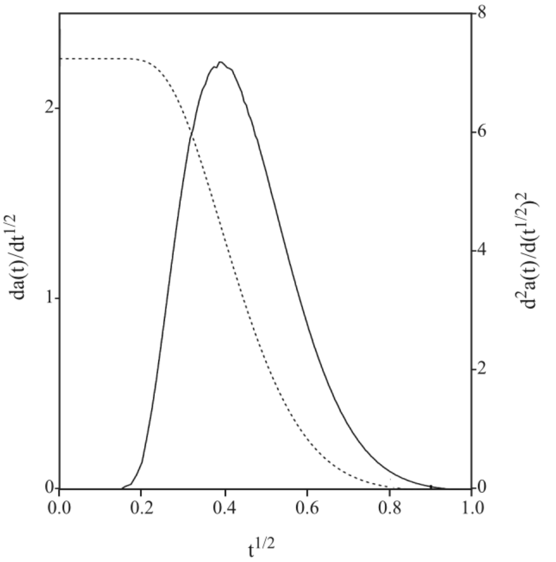

Fig. 3 --- – First and — – second derivatives of $a(t)$ with respect to the square root of time for the numerical solution shown in Fig. 1

Unfortunately, the construction by this way does not give a physically feasible formula. Numerical solution was therefore performed as shown in Figs 1 and 2. Figure 2 shows that the proportionality of the total amount diffused $a(t)$ (defined similarly to $A(T)$ using t and x as variables) to the square root of time holds before $c>0.5$ covers the total length. This corresponds to $t\approx0.05$ in this normalized notation.

To see what is the apparent distribution function from the diffused amount $a(t)$, the second derivative with respect to the square root of time was also estimated numerically for a single rod with a unit length as shown in Fig. 3. An unsymmetrical broad peak was obtained. This can be approximated by

$$g(\sqrt{t})=\frac{1}{1+\exp\left[-\dfrac{\sqrt{t}-0.26947}{0.03524}\right]}\cdot$$
$$\left\{1-\frac{1}{1+\exp-\left[\dfrac{\sqrt{t}-0.55064}{0.08123}\right]}\right\}$$

The result indicates that the peak around t=0.4 corresponds to the unit length in the reduced notation.

Since the result in Fig. 3 applies for *a* any combination of the length of the channel L and the diffusion constant D, the successful deconvolution of an experimental $a(t)$ (and its derivatives) should give the channel-length distribution function. For example, if the sample under study consists of two groups, each of which have the same sectional area but the length ratio being 2, the resulting first and second derivatives

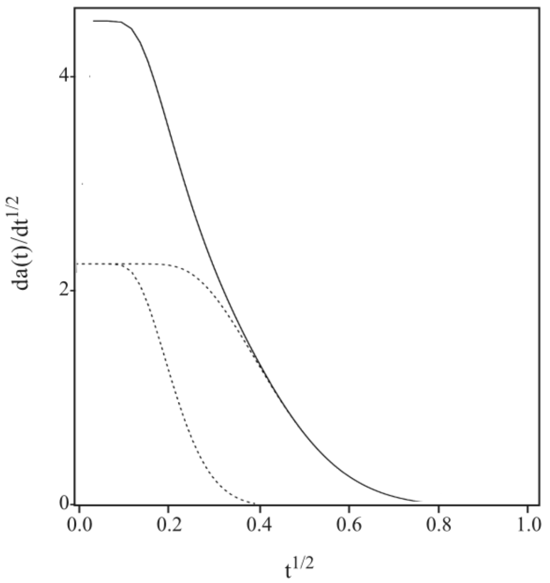

Fig. 4 First derivative of the total amount of — – diffused *a*(*t*) with respect to the square root of time for two rods having the same sectional area and length ratio 2. --- – contribution of each rod

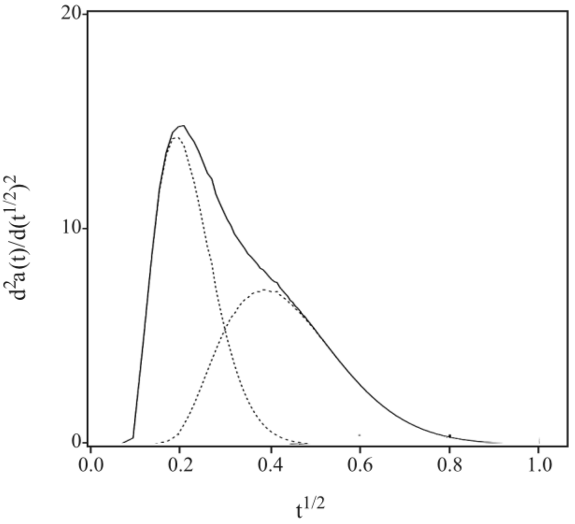

Fig. 5 Second derivative of the total amount of — – diffused *a*(*t*) with respect to the square root of time for two rods having the same sectional area and length ratio 2. --- – contribution of each rod

of *a*(t) behaves like the uppermost curves in Figs 4 and 5, respectively. Although the resolution is not excellent, recent improvement in computing power will open the possibility for a new way to utilize isothermal thermal analysis.

Conclusions

A special character of the kinetics of the one-dimensional reaction was pointed out. This property can be observed in highly anisotropic materials such as porous materials having one-dimensional nanochannels. Gas absorption/desorption kinetics monitored by isothermal TG can be utilized for possible deduction of channel length distribution. In the surface-controlled absorption/desorption, the second derivative with respect to time is directly proportional to the channel-length distribution function. Even in the diffusion-controlled case, the second derivative with respect to the square root of time gives rough information on the distribution function.

Acknowledgements

This work was supported by Grant-in-Aid for Priority Area ‘Chemistry of Coordination Space’ (No. 18033004) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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DOI: 10.1007/s10973-007-8957-z