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THERMAL ANALYSIS AND KINETICS OF SOLID-STATE REACTIONS
Its application to education in chemistry

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Abstract

In an attempt to show the importance of preparing extensively teaching materials for comprehensive education in thermal analysis at an undergraduate level, the significance of the teaching materials concerning the thermal analysis and kinetics of the solid-state reactions is discussed by reviewing our teaching activities at Hiroshima University. Application of the thermoanalytical techniques to thermal decomposition of basic copper(II) salts is appropriate for an introductory experiment to thermal analysis. Microscopic observations of the textural change during the thermal dehydration of inorganic salt hydrates are suitable for introducing the kinetics of solid-state reactions. A computer practice of drawing the experimental master plot enables students to understand the kinetic theory.

Keywords: education, kinetics, microscopy, solid-state reactions, teaching materials

Introduction

In light of the present situation in which the techniques of thermal analysis (TA) are widely used for a variety of purposes such as research, development, product control and so on, the importance of education in TA should be considered for the effective application of TA and reasonable data analysis. Such a problem has been discussed at every international conference on TA [1, 2].

Here, we consider education in TA at an undergraduate level, which introduces the techniques of TA and provides fundamental understanding on the theoretical basis. To cope with the present problem of rather poor student preparation in the field of TA, teaching materials should be extensively prepared for comprehensive education at this level. Several workers have suggested that the DTA technique is useful in teaching students in undergraduate physical or analytical chemistry laboratory courses [3–5], where the relevant DTA equipment could also be designed and constructed at a reasonable cost to university or college laboratories [3, 6, 7]. As an ideal introductory experiment, the thermal decomposition of urea has been examined by means of TG and DSC [5]. Thermal analyses of a nickel complex and a mixture of the oxalates of calcium, strontium, and barium have been suggested as advanced undergraduate TA experiments [8].

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Since 1985, we have examined the usefulness of various teaching materials for education in TA in our undergraduate chemical laboratory course at Hiroshima University [9–13]. As an introductory experiment to TA, TG-DTA measurements of the thermal decomposition of basic copper(II) compounds have been utilized as a teaching material compared to that of copper(II) hydroxide [9, 12]. Techniques of microscopic observation of textural change during thermal dehydration of inorganic salt hydrates have been used to introduce the kinetic characteristics of the solid-state reactions [10, 13]. In order to integrate the kinetic information from TA data and the theory of heterogeneous kinetics, a computer practice of drawing various kinds of experimental master curves [14, 15] seems to be suitable. In the present paper, we review briefly such educational activities concerning the TA at the undergraduate level.

Usefulness of thermal analysis in chemistry

Substances selected for an introductory experiment to TA are basic copper(II) compounds. Among others, basic copper(II) sulfate is suitable because the thermal decomposition proceeds through two distinguished reactions [12, 16–18], i.e., dehydroxylation and desulfation, as is shown in Fig. 1(a). It has long been known that the precipitate prepared by adding hydroxide solution to copper(II) sulfate solution is not simply copper(II) hydroxide, but basic copper(II) sulfate [19]. Most students are not familiar with the composition of basic copper(II) sulfate, because many chemistry textbooks at high school describe that copper(II) hydroxide is precipitated by the

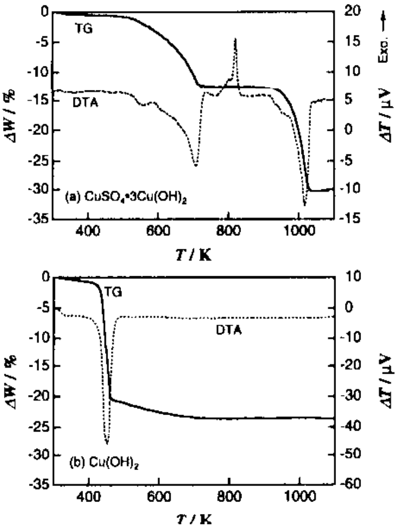

Fig. 1 Typical TG-DTA curves for the thermal decomposition of synthetic brochantite and copper(II) hydroxide at a heating rate of 10 K min^{-1} under flowing N_2 (50 ml min^{-1})

reaction. As shown in Fig. 1, the difference in the composition of the precipitate from that of $Cu(OH)_2$ can be easily recognized by comparing the TG-DTA traces for these compounds, where $Cu(OH)_2$ is prepared by adding hydroxide solution to tetraamminecopper(II) solution [20]. Utilizing the TG curve for the thermal decomposition of $Cu(OH)_2$, students learn that the stoichiometry of the decomposition reaction is easily estimated from the mass loss data [9].

For determining the composition of basic copper(II) sulfate, various chemical techniques can be used, together with TA measurements [12]. Reaction ratio of OH^-/Cu^{2+} during the precipitation reaction is determined by the pH titration curve. From the ratio of $OH^-/Cu^{2+}\approx 1.5$, it is possible to estimate the composition of the precipitate, $Cu_4(OH)_6SO_4$, following the procedure of King and Cooper [21]. IR spectrum of the precipitate indicates the absorption bands due to OH^- and SO_4^{2-} [12]. Contents of Cu^{2+} and SO_4^{2-} in the sample precipitate can be determined quantitatively by means of the iodometric analysis and gravimetric analysis as $BaSO_4$, respectively. X-ray diffractometry (XRD) reveals that the crystal structure of the precipitate corresponds to mineral brochantite [16, 19].

On the basis of the estimated composition, the TG-DTA curve in Fig. 1(a) can be explained by assuming that the thermal decomposition proceeds according to the following two separated steps [12, 16–19].

$$Cu_4(OH)_6SO_4 \rightarrow Cu_4O_3SO_4 + 3H_2O$$

$$Cu_4O_3SO_4 \rightarrow 4CuO + SO_3$$

The above reaction steps are confirmed by identifying the intermediate and end products through the combination of chemical analyses, IR spectroscopy and XRD [12, 16]. Using XRD, an exothermic peak observed around 815 K is identified as the crystallization of amorphous dehydroxylated product to CuO and $CuO{\cdot}CuSO_4$ [18].

The experimental procedure makes students feel that they are participating in a small research program. The experiment can be offered to students in various ways depending on the level of class and the laboratory session from a simple TA to integrated analytical chemistry.

Reaction mechanism of solid-state processes

The shape of TA traces during a reaction is closely related to the kinetics and physico-geometric characteristics of the reaction. Direct observations of the textural changes during the thermal dehydration of crystalline hydrates of inorganic salts enable students to understand typical patterns of kinetic behavior that is characteristic of the solid-state reactions [10, 13]. A variety of the microscopic techniques can be used depending on the level of class.

In many cases, the dehydration reaction initiates by the nucleation and growth mechanisms at preferable sites on the surface of the single crystal. The superficial textural change during the surface processes can be observed directly using a simple optical microscope to examine partly dehydrated single crystals. It has been shown that the surface processes of the single crystals of $CuSO_4{\cdot}5H_2O$ [10, 13, 22], $NiSO_4{\cdot}6H_2O$ [13, 23] and $KCr(SO_4)_2{\cdot}12H_2O$ [13, 24] are suitable for such observations. Using an apparatus of thermomicroscopy with a programmable heating stage for a microscope, the nucleation and growth processes on the surface of the single crystals can be observed continuously, representing dramatic changes of the surface texture that accompany dehydration reaction. For example, by heating the single crystal of $CuSO_4 \cdot 5H_2O$ at a constant temperature of 330 K, nucleus formation of trihydrate is observed on the (010) surface within 5 min [10, 13]. Each nucleus has crater-like surface irregularity with cracks radiating from the center that act as water escape channels. The escape process of water vapor from the center of the nuclei can also be observed under microscopy. The shape and alignment of the crystallites, which construct the nuclei, can be observed by scanning electron microscopy (SEM).

More detailed examinations of the internuclear crack structure are possible by using a replication technique [13, 25]. Replication of the crystal surface of partly dehydrated sample is performed by placing a drop of 2% solution of formvar in chloroform. A replica retaining the detailed surface texture is obtained as a hardened plastic after dissolving the single crystal into water. The dried replica can be examined by SEM. It has been reported by the technique that the intranuclear crack structure of an individual nucleus is clearly observed for the thermal dehydration of $KCr(SO_4)_2 \cdot 12H_2O$ [24].

Once a surface of the single crystal was covered with the product layer, a coherent active reaction interface is generated just beneath the original reactant surface. Subsequent advance of the reaction interface is regulated by the geometry of volume contraction. Observation of the reaction interface advancing inward toward the center of the single crystal is possible using a thin section technique [10, 13, 26]. A crystal face of partially dehydrated single crystal is rubbed with abrasive cloth and paper (ACP) of grit 500–2000, and the rubbed face is then mounted on a glass slide with an adhesive resin and dried in air. The top is rubbed with the ACP to ca. 0.03 mm thickness, covered with a thin glass slide that is fixed in position by an adhesive resin, and dried in air. The thin section is then examined through a polarizing microscope. Single crystals of the hydrates, which dehydrate in a well-defined single step reaction, are preferable for the observations of the established reaction. The reaction interfaces of the thermal dehydration of single crystalline $Li_2SO_4 \cdot H_2O$ [26], $Cu(CH_3COO)_2 \cdot H_2O$ [27] and $Zn(CH_3COO)_2 \cdot 2H_2O$ [28] have been successfully observed using the thin section technique, representing characteristic shape and structure of the interface depending on the material and crystallographic direction.

Using the above microscopic techniques, the course of dehydration reaction can be followed by microscopic views of the textural changes. For a complicated reaction process, such microscopic observations provide a basis to interpret the kinetic behavior [23, 29, 30]. Figure 2 shows the TG-DTG curves for the thermal dehydration of single crystalline $NiSO_4 \cdot 6H_2O$, together with typical microscopic views of the sample at selected reaction steps. It was revealed by comparing the TG-DTG curves with the microscopic views [23] that the non-isothermal dehydration proceeds in two stages: (1) surface nucleation and growth of nuclei at the surface, followed by advance of reaction front inward; (2) random nucleation and growth near the reaction front as well as in the bulk, accompanied by the rapid escape of the product water vapor though the crack formed on the surface layer created in stage (1).

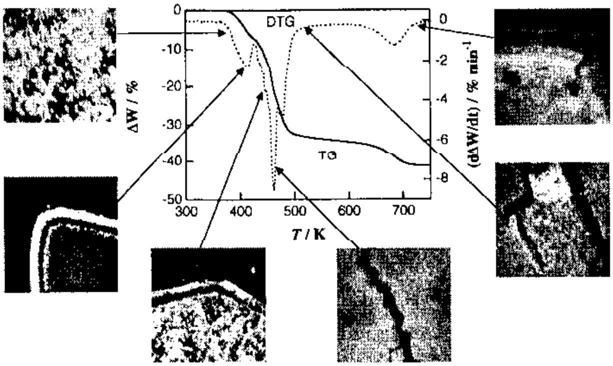

Fig. 2 TG-DTG curves for the thermal dehydration of single crystalline α-$NiSO_4{\cdot}6H_2O$ at a heating rate of 10 K min^{-1} under flowing N_2 (50 ml min^{-1}), together with typical microscopic views of the sample at selected reaction steps

Such microscopic observations enable students to appreciate the fundamental concepts of the interface reactions that underlie the kinetic characteristics of solid-state reaction. Typical kinetic model functions of the solid-state reactions are successfully introduced to students on the basis of the visual experiences [10, 13].

A computer practice of drawing experimental master curves

Through the above experiments, students can understand that the shape of the TA curves during a reaction is determined by the kinetics and physico-geometric characteristics of the reaction. A computer practice of drawing theoretical TA curves seems to be useful to illustrate the relation between the shape of TA curves and the kinetics of the reaction.

An integral kinetic equation for the solid-state reaction is expressed as follows.

$$g(\alpha)=A\theta \qquad \text{with} \qquad \theta=\int_0^t \exp\left(-\frac{E}{RT}\right)\mathrm{d}t \tag{1}$$

where θ is the generalized time introduced by Ozawa [31]. Other symbols are in standardized meanings. Under the condition of linearly increasing temperature at a rate of φ, θ can be expressed by

$$\theta\approx\frac{E}{\varphi R}\frac{\exp(-x)}{x}\pi(x) \qquad \text{with} \qquad x=\frac{E}{RT} \tag{2}$$

where $\pi(x)$ is a function to approximate the exponential integral. Using a simple approximate function $\pi(x)=1/x$, the theoretical TA curves can be drawn by a simple spread sheet program by assuming $g(\alpha)$, A, E and φ. Figure 3 shows theoretical TA

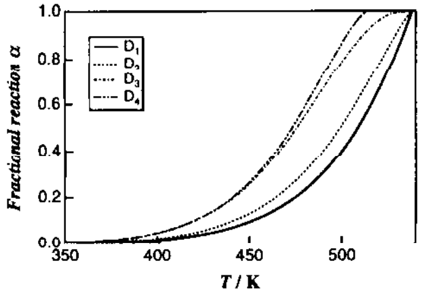

Fig. 3 Theroretical TA curves for the diffusion controlled reactions with E=100 kJ mol^{-1}, ln$A$=22 s^{-1} and φ=5 K min^{-1}

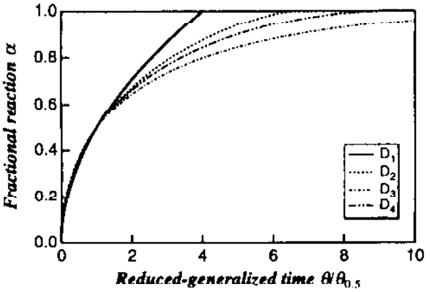

Fig. 4 Plots of α *vs.* $\theta/\theta_{0.5}$ for the diffusion controlled reactions

curves for the diffusion controlled reactions drawn by assuming E=100 kJ mol^{-1}, ln A=22 s^{-1} and φ=5 K min^{-1}.

From the theoretical TA curves, the experimental master curves, only depending on the kinetic model function, can be drawn by calculating the value of θ at various α, according to Eq. (2). The values of θ at various α are then divided by the value at α=0.5, to obtain the reduced-generalized time $\theta/\theta_{0.5}$. The plot of α *vs.* $\theta/\theta_{0.5}$ is utilized as the experimental mater curve for the kinetic model. Figure 4 shows such curves for the diffusion controlled reactions. The experimental master curves drawn can be used universally for the reaction under isothermal and non-isothermal conditions [14, 15], because these are precisely identical with those for the isothermal reactions, *i.e.*, the plot of α *vs.* $t/t_{0.5}$. The relation of the isothermal and non-isothermal kinetics is also illustrated through drawing the experimental master curves.

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