Sodium Hydrogencarbonate

Nobuyoshi Koga,<sup>\*,†</sup> Shuya Maruta,<sup>†</sup> Tomoyasu Kimura,<sup>†</sup> and Shuto Yamada<sup>‡</sup>

<sup>†</sup>Chemistry Laboratory, Department of Science Education, Graduate School of Education, Hiroshima University, 1-1-1 Kagamiyama, Higashi-Hiroshima 739-8524, Japan

<sup>‡</sup>Center for Research and Advancement in Higher Education, Kyushu University, 744 Motooka, Fukuoka 819-0395, Japan

#### Supporting Information

**ABSTRACT:** Aiming to find rigorous understanding and novel features for their potential applications, the physico-geometrical kinetics of the thermal decomposition of sodium hydrogencarbonate (SHC) was investigated by focusing on the phenomenological events taking place on a single crystalline particle during the course of the reaction. The overall kinetics evaluated by systematic measurements of the kinetic rate data by thermogravimetry under carefully controlled conditions were interpreted in association with the morphological studies on the precursory reaction, mechanism of surface reaction, structure of the



surface product layer, diffusion path of evolved gases, crystal growth of the solid product, and so on. The precursory reaction was identified as the decomposition of impurity, taking place at the boundary between the surface of the SHC crystal and the adhesive small SHC particles deposited on the surface. In flowing dry N<sub>2</sub>, the thermal decomposition of SHC proceeds by two-dimensional shrinkage of the reaction interface controlled by chemical reaction with the apparent activation energy of about 100 kJ mol<sup>-1</sup>, after rapid completion of the surface reaction and formation of porous surface product layer. Atmospheric CO<sub>2</sub> and water vapor influence differently on the overall kinetics of the thermal decomposition of SHC. Added gas phase of CO<sub>2</sub> slightly inhibits the overall rate because of the increasing contribution of the surface reaction. Under higher water vapor pressure, the physico-geometrical mechanism of the surface reaction changes drastically, indicating the preliminary reformation of reactant surface and the formation of needle crystals of solid product on the surface. The mechanistic change and extended contribution of the surface reaction result in the deceleration of the surface reaction and acceleration of the established reaction.

# **1. INTRODUCTION**

Thermal decomposition of sodium hydrogencarbonate (SHC: NaHCO<sub>3</sub>) is one of the most common reactions utilized even in our daily life. For the detailed understanding on the kinetics and mechanisms of the reaction, large efforts have been paid by a number of specialists of the solid-state reaction for more than two centuries. The experimental findings have contributed notably not only toward the provision of fundamental knowledge for the theoretical foundation of the thermal decomposition of solids,<sup>1,2</sup> but also toward the development and refinement of the applications of the thermal decomposition process of SHC. In addition to relevant industrial importance in the Solvay process, the thermal decomposition process has the potential for various applications as is seen in the recently published articles of utilizing the reversibility of the thermal decomposition of SHC for the  $CO_2$  separation technology.<sup>3,4</sup> On the basis of the findings accumulated, the thermal decomposition of SHC has also been applied as a kind of test process for developing the new experimental techniques of thermal analyses,<sup>5,6</sup> for testing the techniques and conditions of measuring the kinetic rate data of the

solid-state reaction,<sup>7,8</sup> and for evaluating the calculation methods of kinetic analysis.<sup>9–11</sup>

The overall process of the thermal decomposition of SHC is characterized by the simultaneous evolutions of CO<sub>2</sub> and water vapor to produce sodium carbonate (SC): 2NaHCO<sub>3</sub> (s)  $\rightarrow$ Na<sub>2</sub>CO<sub>3</sub> (s) + CO<sub>2</sub> (g) + H<sub>2</sub>O (g).<sup>12</sup> The overall kinetics has extensively been studied by thermoanalytical measurements, where the largely distributed values of apparent activation energy  $E_a$ , about 32–139 kJ mol<sup>-1</sup>, have been reported.<sup>3–11,13–15</sup> The distribution indicates that the overall rate behavior depends largely on the procedural factors such as sample preparations, experimental techniques, measuring conditions, calculation methods, and so on. By applying an instrument of controlled rate evolved gas analysis coupled with thermogravimetry (CREGA-TG),<sup>16</sup> we revealed that the rate behavior of the thermal decomposition of SHC is influenced sensitively by the very small change in the atmospheric CO<sub>2</sub> and water vapor concentrations in the level of self-generated

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gaseous atmosphere during the course of reaction,<sup>6</sup> where opposite behaviors of deceleration and acceleration of the overall reaction rate were confirmed by the respective effects of atmospheric CO<sub>2</sub> and water vapor. This indicates that careful control of the measuring conditions for recording the kinetic rate data is essential to the reliable kinetic analysis. This is also true for the estimation of the kinetic model function, which describes the physico-geometrical characteristics of the rate behavior. The rate behavior of the present reaction has been described in many cases by the simple first order model:  $f(\alpha) = 1 - \alpha$ .<sup>3,4,6-11</sup> However, the contracting geometry type model was also reported by some authors.<sup>8,13</sup> Although the fractional reaction  $\alpha$  is considered theoretically on the basis of a certain reactant body and matrix,<sup>17</sup> the practical determination of the value is, in many cases of the thermal decomposition reactions, due to the overall mass-loss with respect to the total mass-loss of the subjected reaction step. Accordingly, the degree of consistency between the kinetic model derived theoretically on the basis of the physico-geometrical characteristics of the single step reaction of a certain reactant body and that estimated by the empirical curve fitting of the thermoanalytical curves may change depending on the sample property, sampling, and measuring conditions for the thermoanalytical measurements.18,19

Detailed understanding on the physico-geometrical characteristics of the reaction, as is formalized in the kinetic model, is required for describing the physicochemical significance of the kinetic parameters evaluated by the macroscopic measurements of thermal analysis and for applying the kinetic information to the development and refinement of the practical applications. Microscopic observations of the morphological changes of the reactant solids during the course of reaction are the useful techniques for revealing the physico-geometrical characteristics of the reaction and the special events of solid-state reaction,<sup>20</sup> as has been demonstrated for the thermal dehydration of lithium sulfate monohydrate.<sup>21–23</sup> For the present reaction, Ball et al.<sup>13</sup> reported the drastic change of the surface texture at the very beginning of the decomposition reaction through examining the scanning electron microscopic views of the partially reacted particles. Several special textures of solid-state reaction, such as the reaction front, porous surface product layer, effluorescent growths of the product solid on the surface, formations of cracks and holes on the surface, and so on, were clearly presented. In contradiction, Guarini et al. reported<sup>15</sup> that the reaction is not accompanied by the significant change of surface textures through the optical microscopic observations on heating the sample.

The present study was undertaken to reveal the physicogeometrical kinetics of the reaction by focusing on a single crystalline particle of SHC. The overall kinetics was evaluated by systematic measurements of the kinetic rate data under well-controlled reaction conditions. The kinetic results were interpreted in association with the microscopic observations of the reaction morphology. Influences of atmospheric  $CO_2$  and water vapor on the physico-geometrical characteristics and the overall kinetics of the reaction were also demonstrated. The consensus between the theory of physico-geometrical kinetics of the thermal decomposition of solids and the experimentally resolved phenomenological features of the present reaction was carefully evaluated. It is hoped that the present very fundamental research contributes largely to the further development and refinement of the experimental approaches to the kinetics of the thermal decomposition of solids, together with the further detailed understanding on the kinetics of the thermal decomposition of SHC.

## 2. EXPERIMENTAL SECTION

**2.1. Sample Characterization**. Reagent grade sodium hydrogencarbonate (SHC: Sigma-Aldrich Japan, special grade) was sieved to various fractions of particle size and supplied as the sample without any further purification. Before subjecting to the kinetic study of the thermal decomposition process, the sample was characterized by powder X-ray diffraction (XRD: RINT 2200 V, Rigaku Co., monochrome Cu K $\alpha$ , 40 kV, 20 mA), Fourier transfer infrared spectroscopy (FT-IR: Shimadzu FTIR8400S, diffuse reflectance method), and thermogravimetry-differential thermal analysis (TG-DTA: Shimadzu DTG-50). The morphology of the sample particles was observed by scanning electron microscopy (SEM: JSM-6510, Jeol) after coating the sample with Pt by sputtering (JFC-1600, Jeol, 20 mA, 60 s).

2.2. Characterization of the Thermal Decomposition Process. The thermal decomposition process was characterized initially by TG/DTA-mass spectroscopy (MS) and high temperature powder XRD measurements. Using an instrument of TG/DTA-MS constructed by connecting TG-DTA (TG8120, Rigaku Co.) to a quadrupole mass spectrometer (M-200QA, Anelva Co.), the sample of 2.0 mg, weighed into platinum cell (5 mm of and 2.5 mm in height), was heated at a heating rate  $\beta$  = 5 K min<sup>-1</sup> in flowing He (200 cm<sup>3</sup> min<sup>-1</sup>, >99.99%, Japan Helium Center, introduced after passing through the moisture absorbent column of silica gel) for recording TG-DTA curves, where the mass spectra of evolved gases were recorded simultaneously in the range from 10 to 50 amu (EMSN, 1.0 A; SEM, 1000 V). In flowing N<sub>2</sub> (100 cm<sup>3</sup> min<sup>-1</sup>, >99.9%, Iwatani Gas, introduced after passing through the moisture absorbent column of silica gel), phase change of the sample, pressfitted on a platinum plate, during stepwise isothermal heating up to 393 K at  $\beta$  = 10 K min<sup>-1</sup> was traced by XRD using the above instrument by equipping with a programmable heating chamber (PTC-20, Rigaku Co.), where the sample temperature was kept constant during the respective diffraction measurements for 15 min. Subsequently, the sample was heated isothermally at 398 K and the XRD measurements were started repeatedly at every 15 min.

2.3. Measurements for the Precursory Reaction. For tracing the precursory endothermic phenomena accompanied with detectable mass-loss, differential scanning calorimetry (DSC: DSC-50, Shimadzu Co.) was applied for the samples (10.00  $\pm$ 0.05 mg) of different sieve fractions of particle size, weighed into an aluminum cell (5 mm of and 2.5 mm in height), and covered with an aluminum lid without sealing. The DSC measurements were carried out at a heating rate  $\beta = 5 \text{ K min}^{-1}$  in flowing N<sub>2</sub>.  $(50 \text{ cm}^3 \text{ min}^{-1})$ , introduced after passing through the moisture absorbent column of silica gel). Temperature and enthalpy calibrations of the instrument were performed preliminary by the melting point measurements for the pure metals (>99.99%) of Ga, In, Sn, Pb, and Zn. For the sample of 280 mesh passed fraction (<53  $\mu$ m in aperture), DSC curves for the precursory endothermic phenomena were recorded at different heating rates  $1 \le \beta \le 10$  K min<sup>-1</sup> for the kinetic analysis. The sample heated to the end of precursory endothermic phenomena was cooled down to room temperature and observed by SEM.

2.4. Measurements for the Thermal Decomposition Process. The samples (100-170 mesh sieve fraction: ca.  $90-150 \,\mu m$  in aperture) of 5.00  $\pm$  0.01 mg, weighed into a platinum cell (6 mm $\phi$  and 3 mm in height), were used for the measurements of kinetic rate data of the thermal decomposition process using a hanging-type thermobalance (TGA-50, Shimadzu Co.). In this



Figure 1. Typical SEM images of the reactant particles (100–170 mesh).

sampling condition, the sample particles spread on the bottom of the platinum cell without forming significant layer. The measured temperature of the instrument was calibrated preliminary by using the melting point of pure metal wires (>99.99%) of In, Sn, Pb, and Zn and a series of magnetic standards of Ni-Co compounds.<sup>24</sup> The measurements were carried out by three different modes of temperature program, that is, isothermal, linear nonisothermal, and controlled transformation rate (CRTG)<sup>25</sup> modes, in flowing N<sub>2</sub> or N<sub>2</sub>-CO<sub>2</sub> (5% N2-95% CO<sub>2</sub>, CO<sub>2</sub> purity: >99.9%, Nakamura Sanso) at a rate of 100 cm<sup>3</sup> min<sup>-</sup> (introduced after passing through the moisture absorbent column of silica gel). Isothermal mass-loss traces were recorded at different constant temperatures after heating up to the programmed temperature at  $\beta = 10$  K min<sup>-1</sup>. The linear nonisothermal measurements were performed at different  $\beta$  from 1 to 5 K min<sup>-1</sup>. By equipping with a self-constructed controller of sample controlled thermal analysis<sup>26,27</sup> to the above thermobalance, the sample was heated at  $\beta = 2 \text{ K min}^{-1}$ , where the massloss rate during the thermal decomposition was regulated at different constant rates C from 7.5 to 15  $\mu$ g min<sup>-1</sup>

Influence of the atmospheric water vapor on the thermal decomposition process was evaluated by TG-DTA measurements under controlled water vapor pressure,  $p(H_2O)$ . By keeping the sample of  $5.00 \pm 0.02$  mg, weighed into platinum cell (5 mm $\phi$  and 2.5 mm in height), at 340 K in an instrument of TG-DTA (TG8120, Rigaku Co.), a mixed gas of N<sub>2</sub>-H<sub>2</sub>O with a controlled  $p(H_2O)$  was introduced into the reaction tube at a rate of about 400 cm<sup>3</sup> min<sup>-1</sup> from a programmable humidity controller (HUM-1, Rigaku Co.). After stabilizing the reaction system for 30 min, the sample was heated at  $\beta = 5$  K min<sup>-1</sup> under different  $p(H_2O)$  from 0.8 to 10.3 kPa for recording TG-DTA curves. By selecting two different  $p(H_2O)$ , that is, 0.8 and 10.3 kPa, TG-DTA curves under those  $p(H_2O)$  were recorded at different  $\beta$  from 1 to 5 K min<sup>-1</sup>.

The sample particles reacted to different fractional reaction  $\alpha$  under different conditions of temperature program and reaction



**Figure 2.** Typical TG-DTA curves for the thermal decomposition of SHC (170–200 mesh) at  $\beta = 5 \text{ K min}^{-1}$  in flowing N<sub>2</sub> (100 cm<sup>3</sup> min<sup>-1</sup>).



Figure 3. Mass chromatograms of m/z 18 and 44 for the evolved gas during the thermal decomposition of SHC (280 mesh passed).

atmosphere were observed by SEM after cooling down to room temperature.

## 3. RESULTS AND DISCUSSION

**3.1.** Characterizations of Sample and Its Thermal Decomposition Process. Figure 1 shows typical SEM images of the sample particles (100-170 mesh). The sample particles are columnar crystals grown along to *b*-axis as usual,<sup>15</sup> Figure 1a. Many small particles in a size of several  $\mu$ m are deposited on the surfaces of columnar crystal, Figure 1b. The same feature of the adhesive particles deposited on the main crystal body have been seen in the previously reported SEM images of SHC.<sup>4,28</sup> The growth front of the columnar crystals are not smooth surfaces, which are covered with a crystalline layer, Figure 1c, and aggregates of crystalline particles, Figure 1d. As was shown in Figures S1 and S2 in the Supporting Information, the powder XRD pattern and FT-IR spectra of the sample are in good agreement with those of SHC.<sup>3,29,30</sup>

Figure 2 shows typical TG-DTA curves for the sample (170–200 mesh: ca. 75–90  $\mu$ m in aperture). The thermal decomposition proceeds in a smooth mass-loss process, where the measured mass-loss value of 37.0  $\pm$  0.2% averaged over the samples of different sieve fractions is comparable with the value, 36.9%, calculated by assuming the reaction: 2NaHCO<sub>3</sub> (s)  $\rightarrow$  Na<sub>2</sub>CO<sub>3</sub> (s) + CO<sub>2</sub> (g) + H<sub>2</sub>O (g). It should be noted here that a small but detectable endothermic peak is observed, at around 355–365 K,



Figure 4. DSC traces for the precursory reaction of the thermal decomposition of SHC. (a) Comparison among the samples of different sieve fractions of particle sizes. (b) For the sample particles of 280 mesh passed at different  $\beta$ .

before the main reaction process of the thermal decomposition. The area of endothermic peak increased with decreasing the particle size of the sample. The endothermic peak is accompanying a detectable mass-loss in TG, that is, 0.07% for the sample of 100– 170 mesh and 0.15% for the sample of 280 mesh passed. The similar precursory reaction can be seen in many reported thermoanalytical curves for the thermal decomposition of SHC.<sup>5,7,11,15,28</sup>

Figure 3 shows the mass chromatograms of m/z 18 and 44 of the evolved gases during the thermal decomposition of SHC. As has been reported previously,<sup>5,6,12</sup> the main part of the thermal decomposition is characterized by the simultaneous evolutions of CO2 and H2O. During the precursory reaction, evolutions of  $\mathrm{CO}_2$  and  $\mathrm{H}_2\mathrm{O}$  are confirmed, where the excess amount of  $\mathrm{H}_2\mathrm{O}$ with respect to CO<sub>2</sub> are evolved. The observed profiles of mass chromatograms of CO<sub>2</sub> and H<sub>2</sub>O for the precursory reaction is in coincident with those reported by Tiernan et al.<sup>5</sup> As a possible reaction at this stage, Dei and Guarini<sup>28</sup> proposed the thermal decomposition of sodium sesquicarbonate dihydrate (SSC:  $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ ), produced on the surface of SHC formed during prolonged aging. Under the reaction conditions comparable with the above thermoanalytical measurements, the thermal decomposition of SSC initiates at the temperature corresponding to that of the precursory reaction of the present SHC.<sup>31,32</sup> The thermal decomposition of SSC is described by:  $2(\text{Na}_2\text{CO}_3 \cdot \text{Na}\text{HCO}_3 \cdot 2\text{H}_2\text{O}) \xrightarrow{\sim} 3\text{Na}_2\text{CO}_3 + \text{CO}_2 + 5\text{H}_2\text{O}_2^{31,32}$ where an excess amount of  $H_2O$  with respect to  $CO_2$  is evolved. Although identifications of SSC and product SC were not successful in the present study, the findings on the reaction temperature





Figure 5. Typical SEM images of the surface textures of the sample particles (280 mesh passed) heated to the end of precursory reaction.

and evolved gases of the precursory reaction support circumstantially the above-mentioned proposal by Dei and Guarini.<sup>28</sup>

Change in the XRD pattern of the sample during stepwise isothermal heating up to 393 K and subsequent isothermal heating at 393 K in flowing  $N_2$  was shown in Figure S3 in the Supporting Information. It was confirmed from the monotonous attenuation of the XRD peaks of SHC and the compensative growth of those of SC that the main reaction is exclusively the thermal decomposition of SHC to produce SC without forming any crystalline intermediate compounds.

3.2. Precursory Reaction. The precursory reaction was traced by DSC, as shown in Figure 4. The area of DSC endothermic peak increases with decreasing the particle size of the sample, where no detectable change of the reaction temperature is observed, Figure 4a. This behavior indicates that the precursory reaction is associated with the reaction of surface groups, and the rate behavior is not influenced by the size and geometry of the main body of sample particle. Although Dei and Guarini detected the formation of SC by FT-IR spectrum during the precursory reaction for the sample, which indicates a remarkable DSC endothermic peak,<sup>28</sup> the clear evidence of the formation of SC during the precursory reaction could not be detected in the present study by the changes of FT-IR spectra and powder XRD. This may be due to the smaller portion of the sample participated in the precursory reaction. As was listed in Table S1 in the Supporting Information, the apparent enthalpy changes  $\Delta H$  observed for the present samples are smaller by  $10 \times$  than that reported by Dei and Guarini.28

Figure 5 shows typical SEM images of the sample particles (280 mesh passed) heated to the end of the precursory reaction. The reaction sites of the precursory reaction can be identified at the boundaries between the surface of reactant crystals and the adhesive particles, Figure 5c,d, where no distinguished textural change can be found on the surfaces of reactant crystals, Figure 5a,b. The product solid of the precursory reaction is needle-like crystal-lites irradiating in parallel to the surface of reactant crystal, stal, but the surface of reactant crystal, but the surface of reactant crystal,

Table 1.	Summary	v of the	Kinetic	Results for	r the	Precursory	7 Reaction
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method	range of $\beta$	range of $a$	$E_{\rm a}/{\rm kJ}~{\rm mol}^{-1}$	$\gamma_1^{a}$	$f(\alpha)$	kinetic exponents	$A/s^{-1}$	$\gamma_2^2, d$
Kissinger Freidman	$1 \le \beta \le 10$ $1 \le \beta \le 5$	peak max. $0.1 \le \alpha \le 0.9$	$114.1 \pm 8.4$ $124.8 \pm 7.0$	-0.9999 -0.9978 ± 0.0035	$JMA(m)^{b}$ $SB(m, n, p)^{c}$	$m = 2.30 \pm 0.08$ $m = -0.21 \pm 0.22$ $n = 1.66 \pm 0.09$ $p = 1.13 \pm 1.13$	$\begin{array}{l} (3.57\pm0.10)\times10^{16}\\ (1.47\pm0.03)\times10^{15} \end{array}$	0.9014 0.9992

<sup>*a*</sup> Correlation coefficient of the linear regression analysis for the Kissinger and Friedman plots.  ${}^{b}f(\alpha) = m(1-\alpha)[-\ln(1-\alpha)]^{1-1/m}$ .  ${}^{c}f(\alpha) = \alpha^{m}(1-\alpha)^{n}[-\ln(1-\alpha)]^{p}$ . <sup>*d*</sup> Square of the correlation coefficient of the nonlinear regression analysis for the fitting of experimental master plot.

Figure 5c, and some of those are penetrating to the reactant crystal, Figure 5d.

On the basis of the above findings, the kinetic behavior of the precursory reaction was estimated by the formal kinetic analysis of the DSC curves recorded at different  $\beta$  shown in Figure 4b. The results of kinetic analysis were summarized in Table 1. The methodologies and course of the kinetic analysis for the precursory reaction were described in detail in the Supporting Information. The apparent activation energy  $E_{\rm a}$  for the precursory reaction was slightly higher than that for the thermal decomposition of SHC, which will be described below. The value of  $E_{\rm a}$  determined by the Kissinger method,<sup>33</sup> 114.1  $\pm$  8.4 kJ mol<sup>-1</sup>, is closely corresponding to the value reported for the thermal decomposition of SSC.<sup>34</sup> From the shape of the experimental master plot for the precursory reaction, one of the nucleation and growth type model was estimated as the possible physico-geometrical reaction model. Through the nonlinear fitting of the experimental master plot by Johnson-Mehl-Avrami model,<sup>35</sup> JMA(m):  $f(\alpha) =$  $m(1-\alpha)[-\ln(1-\alpha)]^{1-1/m}$ , of the nucleation and growth type reaction, the best value of the kinetic exponent was estimated as  $m = 2.30 \pm 0.08$ , which is also indicating the close correspondence to the reported rate behavior of the thermal decomposition of SSC.<sup>31</sup> However, in comparison with the nearly perfect fitting by an empirical kinetic model of Sestak-Berggren,  $^{36}$  SB(*m*,*n*,*p*):  $f(\alpha) = \alpha^m (1 - \alpha)^n [-\ln(1 - \alpha)]^p$ , the rate process cannot be described satisfactorily by JMA(m) model.

From the above findings, it is probable that the precursory reaction can be avoided by eliminating the adhesive particles on the surface of SHC crystal. Even if the precursory reaction took part in the thermal decomposition, the influence on the overall kinetic of the thermal decomposition of the main body of SHC crystal is very limited.

3.3. Thermal Decomposition of SHC. Figure 6 shows the mass-loss traces at different constant temperatures (Figure 6a) and under linear nonisothermal heating at different  $\beta$  (Figure 6b) for the main reaction of the thermal decomposition in flowing  $N_{2}$ , together with their time derivative curves. In the isothermal measurements, no distinguished behavior of induction period can be found. The reaction decelerates as reaction advances in a manner of the reaction controlled by the contracting geometry.<sup>37</sup> The reaction advances smoothly even under dynamic heating, where the fractional reaction  $\alpha$  at the maximum mass-loss rate varied systematically from  $\alpha_{\rm p}$  = 0.70 at  $\beta$  = 1.0 K min<sup>-1</sup> to  $\alpha_{\rm p}$  = 0.65 at  $\dot{\beta}$  = 5.0 K min<sup>-1</sup>. Figure 7 shows a typical record of the mass-loss data under the controlled constant mass-loss rate at  $C = 10.0 \,\mu g \,\mathrm{min}^{-1}$ (Figure 7a) and the temperature profiles of the reaction at different C (Figure 7b). The mass-loss rate was controlled successfully during the course of reaction. After reaching at the programmed C, the reaction temperature increases gradually as reaction advances and rapidly at the final stage of the reaction. The shape



**Figure 6.** Mass-loss traces and their time derivative curves for the main thermal decomposition of SHC (100–170 mesh,  $m_0 = 5.0$  mg) in flowing N<sub>2</sub>: (a) under isothermal heating at different *T* and (b) under linearly increasing temperature at different  $\beta$ .

of the temperature profile is also corresponding to a contracting geometry type reaction.<sup>38,39</sup>

For analyzing the overall kinetics of the main thermal decomposition of SHC, the following fundamental kinetic equation was assumed.

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A \exp\left(-\frac{E_{\mathrm{a}}}{RT}\right) f(\alpha) \tag{1}$$

where A,  $E_{\rm a}$ , and  $f(\alpha)$  are the Arrhenius pre-exponential factor, apparent activation energy, and kinetic model function, respectively. In the present study, all the kinetic rate data converted from the mass-loss data under different temperature program modes, that is, isothermal, linear nonisothermal, and CRTG modes, were applied universally to the kinetic calculations based on eq 1.<sup>37,40–43</sup>

The results of kinetic calculations are illustrated in Figure 8. An isoconversional relationship between the overall reaction rate,  $d\alpha/dt$ , and temperature, *T*, is derived by taking logarithms



**Figure 7.** Typical results of mass-loss measurements under controlled mass-loss rate, *C*, for the main thermal decomposition of SHC (100–170 mesh,  $m_0 = 5.0$  mg) in flowing N<sub>2</sub>. (a) A typical record at  $C = 10.0 \,\mu \text{g min}^{-1}$  and (b) the temperature profiles of the reaction at different *C*.

of eq 1.44

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = \ln[Af(\alpha)] - \frac{E_{\mathrm{a}}}{RT} \tag{2}$$

When the overall kinetic behavior is fully satisfied with eq 1, the plot of ln  $(d\alpha/dt)$  against  $T^{-1}$  for the data points at a restricted  $\alpha$ , that is so-called Friedman plot,<sup>44</sup> should be a straight line irrespective of the program modes for measuring the kinetic rate data. The plots of ln  $(d\alpha/dt)$  against  $T^{-1}$  at different  $\alpha$  in steps of 0.1 in the range  $0.1 \le \alpha \le 0.9$  were shown in Figure 8a. At the selected  $\alpha$ , all the data points recorded under different modes of temperature program line up on a straight line. Slopes of the plots at different  $\alpha$  are nearly constant, indicating the constant value of  $E_a$  in the wide range of  $\alpha$ , Figure 8b. The  $E_a$  value averaged over  $0.1 \le \alpha \le 0.9$  was  $101.8 \pm 1.6$  kJ mol<sup>-1</sup>, which is closely corresponding to some of those reported previously.<sup>5,7–9,11,15</sup>

The dependence of the rate behavior on  $\alpha$  was evaluated by drawing an experimental master plot, Figure 8c. The hypothetical reaction rate,  $d\alpha/d\theta$ , was calculated by extrapolating the rate data at the respective  $\alpha$  to infinite temperature, according to<sup>37,40,41,43</sup>

$$\frac{\mathrm{d}\alpha}{\mathrm{d}\theta} = \frac{\mathrm{d}\alpha}{\mathrm{d}t} \exp\left(\frac{E_{\mathrm{a}}}{RT}\right) \quad \text{with} \quad \theta = \int_{0}^{t} \exp\left(-\frac{E_{\mathrm{a}}}{RT}\right) \quad (3)$$

where  $\theta$  is Ozawa's generalized time.<sup>45,46</sup> The experimental master plot of  $d\alpha/d\theta$  against  $\alpha$  indicates the deceleration as reaction advances, which is corresponding to one of the contracting geometry type reaction.<sup>37</sup> The experimental master



**Figure 8.** Kinetic analysis for the thermal decomposition of SHC (100–170 mesh) in flowing N<sub>2</sub>. (a) The Friedman plots at different  $\alpha$  from 0.1 to 0.9 in steps of 0.1, (b) the values of  $E_a$  at various  $\alpha$ , and (c) comparisons of the experimental master plot with the theoretical curves of RO(*n*) and SB(*m*,*n*,*p*) models.

plot is correlated to the kinetic model function by  $^{37,40,41,43}$ 

$$\frac{\mathrm{d}\alpha}{\mathrm{d}\theta} = Af(\alpha) \tag{4}$$

For describing the experimental master plot, the kinetic model function of reaction order model, RO(n):  $f(\alpha) = n(1 - \alpha)^{1-1/n}$ , was applied for evaluating the dimension of reaction interface shrinkage *n*. For a comparison, an empirical kinetic model of Sestak–Berggren, SB(m,n,p):  $f(\alpha) = \alpha^m(1 - \alpha)^n[-\ln(1 - \alpha)]^p$ , which fits to various physico-geometric types of reaction and those deviated cases with nonintegral or fractal dimension of reaction geometry, size distribution of reactant particles, and so on,<sup>43,47,48</sup> was also applied. The most appropriate kinetic exponents in these kinetic model functions and the value of *A* were estimated simultaneously through the nonlinear regression analysis

atmosphere	measurement	$E_{\rm a}/{\rm kJ}~{\rm mol}^{-1}$	$f(\alpha)$	kinetic exponents	$A/s^{-1}$	$\gamma^{2, d}$		
$N_2 (100 \text{ cm}^3 \text{ min}^{-1})$	controlled rate isothermal	$101.8 \pm 1.6$ (0.1 $\le \alpha \le 0.9$ )	$RO(n)^{a}$ $(0.1 \le \alpha \le 0.9)$	$n = 2.18 \pm 0.02$	$(2.59 \pm 0.02) \times 10^9$	0.9961		
	nonisothermal		$SB(m,n,p)^{b}$	$m = -2.69 \pm 0.25$	$(4.89 \pm 0.08) \times 10^{9}$	0.9988		
			$(0.1 \le \alpha \le 0.9)$	$n=1.61\pm0.10$				
				$p=2.63\pm0.25$				
$CO_2 (100 \text{ cm}^3 \text{ min}^{-1})$	controlled rate	$102.2\pm1.1$	$RO(n)^{a}$	$n=1.99\pm0.02$	$(2.47 \pm 0.03) \times 10^{9}$	0.9906		
	isothermal	$(0.1 \le \alpha \le 0.9)$	$(0.1 \le \alpha \le 0.9)$					
	nonisothermal		$SB(m,n,p)^{b}$	m=-3.35 ± 0.24	$(4.26 \pm 0.07) \times 10^{9}$	0.9989		
			$(0.1 \le \alpha \le 0.9)$	$n=1.86\pm0.09$				
				$p=3.31\pm0.23$				
$N_2 - H_2 O$ (ca. 400 cm <sup>3</sup> min <sup>-1</sup> )	nonisothermal	$103.4\pm0.5$	$SB(m,n,p)^{b}$	$m=-5.92\pm0.35$	$(1.59\pm 0.04)\times 10^{10}$	0.9985		
$p(\mathrm{H_2O}) = 0.8 \mathrm{kPa}$		$(0.1 \le \alpha \le 0.9)$	$(0.1 \le \alpha \le 0.9)$	$n=2.32\pm0.14$				
				$p=5.73\pm0.34$				
			$RO(n)^{a}$	$n=2.34\pm0.04$	$(1.03\pm 0.02)\times 10^{10}$	0.9921		
			$(0.2 \le \alpha \le 0.9)$					
			$JMA(m)^{c}$	$m=1.43\pm0.02$	$(2.67\pm 0.03)\times 10^{10}$	0.9814		
			$(0.2 \le \alpha \le 0.9)$					
$N_2 - H_2 O$ (ca. 400 cm <sup>3</sup> min <sup>-1</sup> )	nonisothermal	$109.7\pm5.4$	$SB(m,n,p)^{b}$	$m=-5.31\pm0.18$	$(2.30\pm 0.03)\times 10^{11}$	0.9985		
$p(\mathrm{H_2O}) = 10.3 \mathrm{kPa}$		$(0.1 \le \alpha \le 0.9)$	$(0.1 \le \alpha \le 0.9)$	$n=2.60\pm0.07$				
				$p=5.23\pm0.18$				
			$\mathrm{RO}(n)^{a} (0.35 \le \alpha \le 0.9)$	$n=2.08\pm0.05$	$(1.52\pm 0.02)\times 10^{11}$	0.9826		
			$JMA(m)^{c} (0.35 \le \alpha \le 0.9)$	$m=1.88\pm0.02$	$(2.84\pm 0.03)\times 10^{11}$	0.9950		
$f(\alpha) = n(1-\alpha)^{1-1/n}$ . ${}^{b}f(\alpha) = \alpha^{m}(1-\alpha)^{n}[-\ln(1-\alpha)]^{p}$ . ${}^{c}f(\alpha) = m(1-\alpha)[-\ln(1-\alpha)]^{1-1/m}$ . ${}^{d}$ Square of the correlation coefficient of the								

### Table 2. Summary of the Kinetic Results for the Main Reaction of the Thermal Decomposition of SHC (100-170 Mesh)

nonlinear regression analysis for the fitting of experimental master plot.

by applying the Levenberg-Marquardt optimization algorithm.<sup>49</sup> As was shown in Figure 8c, the experimental master plot was fitted satisfactorily by RO(n) model with  $n = 2.18 \pm 0.02$  and  $A = (2.59 \pm 0.02) \times 10^9 \text{ s}^{-1} (\gamma^2 = 0.9961)$ , indicating twodimensional shrinkage of reaction interface controlled by chemical reaction.<sup>18,37,50</sup> In addition, the fitting curve by RO(2.18) is very close to that by the empirical SB(-2.69, 1.61, 2.63) with  $A = (4.89 \pm 0.08) \times 10^9 \text{ s}^{-1} (\gamma^2 = 0.9988)$ . Although the physico-geometrical meanings of the kinetic exponents in SB-(-2.69, 1.61, 2.63) are difficult to evaluate at present, the comparable good fitting by the empirical SB(-2.69, 1.61, 2.63) and physico-geometrical RO(2.18) models supports the validity of RO(2.18) for describing the physico-geometrical characteristics of the reaction. The results of above formal kinetic analyses are summarized in Table 2.

Figure 9 shows typical SEM images of the sample at the initial stage of the thermal decomposition in flowing N2. The reaction initiates at the surface of the sample particles. Formation of whiskers on the surfaces can be found as the special event of the surface reaction, Figure 9a. In addition to the side surface of the columnar crystals, the whiskers are formed on the base surfaces and on the adhesive particles deposited on the surfaces of the columnar crystals, Figure 9b. The reaction front of the surface reaction is seen in Figure 9b,c. Erosion of the original surface in the depth of submicrometer order can be observed, where the whiskers are formed in the eroded area. Length of the whiskers is 0.5-1.0  $\mu$ m, Figure 9d. Possible participation of liquid phase on the surface reaction is expected from the erosion of original reactant surface in the considerable depth and formation of whiskers in the eroded area. The liquid phase may be produced at the initial reaction sites as the aqueous solution of SHC and/or SC and

spread on the reactant surface by eroding the original reactant surface. Vaporization of water and evolution of CO<sub>2</sub> from the intermediate liquid phase promote the growth of solid product, SC, in the form of whisker. The SC whiskers formed on the side surfaces of columnar crystal disappear before  $\alpha$  = 0.1 by the crystal growth of SC, forming the surface product layer of aggregates of SC particles in the size of several hundred nanometers, Figure 9e. The surface product layer maintains interstices to be possible channels for the diffusional removal of the gaseous products evolved at the internal reaction zone during the subsequent established reaction. The whiskers produced on the base surfaces of columnar crystals, growing in parallel to the long axis of the sample crystal, tend to have the lifetime slightly longer than those formed on the side surfaces, Figure 9f.

Figure 10 shows typical SEM images of sample particles at the final stage of the reaction. No distinguished change of the surface morphology of the reacting particles can be found during the course of the established reaction. At  $\alpha$  = 0.8, the surface product layer is still maintaining the interstices in the aggregates of product SC particles, Figure 10a. Whiskers of several micrometers in the length, radiating from the interstices of the solid product layer, are sometimes observed during the course of the established reaction, Figure 10b. The whiskers seem to be the tracks of spouting of liquid phase produced by the condensation of water vapor and dissolution of product SC during the course of diffusion through the solid product layer. Self-cooling due to the endotherm by reaction itself<sup>51</sup> and the local increase in the partial pressure of evolved gases by the possible impedance of the diffusion through the solid product layer<sup>52</sup> can be possible causes of the formation of the liquid phase. Comparing the surface morphologies of the final products under isothermal and nonisothermal



**Figure 9.** Typical SEM images of the surface textures of the sample (100–170 mesh) at the initial stage of the thermal decomposition in flowing N<sub>2</sub>: (a–d) decomposed to  $\alpha = 0.04$  by heating isothermally at 378 K for 5 min and (e, f) decomposed to  $\alpha = 0.10$  by heating isothermally at 383 K for 5 min.

conditions, Figure 10c,d, the larger particles of product SC are observed for the product under nonisothermal condition due to the heating to the higher temperature to complete the reaction. Because the interstices of the surface product layer is maintaining in both the product solids under isothermal and nonisothermal conditions, the difference in the degree of crystal growth of product SC may not influence largely on the overall kinetics under the respective conditions.

From the above findings of the formal kinetic analysis and reaction morphology for the reaction in flowing N<sub>2</sub>, the physicogeometrical mechanism of the thermal decomposition is characterized by the surface reaction and subsequent advancement of the reaction interface, formed between the original reactant crystal and the surface product layer, inward the reactant particle. The possible existence of the intermediate liquid phase during the surface reaction indicates that the kinetics of the surface reaction depends largely on the reaction atmosphere applied and self-generated by the reaction itself. In flowing N<sub>2</sub>, the surface reaction completes in the early stage of the thermal decomposition before  $\alpha = 0.1$ , so that the overall kinetics evaluated from the thermoanalytical measurements in  $0.1 \le \alpha \le 0.9$  is corresponding



**Figure 10.** Typical SEM images of the surface textures of the sample (100–170 mesh) at the final stage of the thermal decomposition in flowing N<sub>2</sub>: (a, b) decomposed to  $\alpha$  = 0.80 by heating isothermally at 393 K for 50 min, (c) decomposed to  $\alpha$  = 1.00 by heating isothermally at 403 K for 150 min, and (d) decomposed to  $\alpha$  = 1.00 by heating non-isothermally at  $\beta$  = 5.0 K min<sup>-1</sup> to 473 K.

to that for the established reaction of the shrinkage of reaction interface. The two-dimensional shrinkage of the reaction interface controlled by the chemical reaction at the reaction interface estimated by the curve fitting of the experimental master plot is supported by the SEM observation of the reaction morphology, where the interstices of the product layer on the side faces of columnar reactant particle maintaining during the course of established reaction is to be the diffusion channels of the gaseous products produced at the reaction zone inside the particle. The contribution of the surface reaction on the overall reaction may increase with decreasing particle size of SHC crystal. The present physico-geometrical description of the overall kinetics based on a single reactant particle is not applicable when a distinguished size distribution of the reactant crystals exists and when a large amount of sample particles were applied for the measurements of the kinetic rate data. The former directly causes the distribution of  $\alpha$  among the reacting particles. <sup>53,54</sup> Similarly, the distribution of  $\alpha$  among the reacting particles also results from the possible gradients of temperature and partial pressure of the evolved gases within the sample bed.<sup>18</sup> When such a distribution of  $\alpha$  among the reacting particles exists during the course of reaction, the shape of the kinetic rate data tends to indicate superficially that similar to the nucleation and subsequent growth as is described by Johnson-Mehl-Avrami model, JMA(m).<sup>53,54</sup> The differences in the sampling and measuring conditions can be the possible causes of the discrepancy of the most appropriate kinetic model function reported previously, that is, RO(n) or JMA(*m*). Even in such cases of distribution of  $\alpha$  among the reacting particles, the apparent value of  $E_a$  evaluated by one of the isoconversional methods is nearly constant, indicating the apparent value for the advancement of the reaction interface. 53,54

**3.4. Influence of Atmospheric CO<sub>2</sub>.** Figure 11 compares the mass-loss traces and those derivative curves for the thermal



**Figure 11.** Comparisons of the mass-loss traces and those derivative curves for the thermal decomposition of SHC (100–170 mesh,  $m_0 = 5.0 \text{ mg}$ ) recorded in flowing N<sub>2</sub> and CO<sub>2</sub>: (a) under isothermal condition at T = 403 K and (b) under linear nonisothermal condition at  $\beta = 5$  K min<sup>-1</sup>.

decomposition of SHC (100–170 mesh) under isothermal and nonisothermal conditions recorded in flowing N<sub>2</sub> and CO<sub>2</sub>. Deceleration effect by atmospheric CO<sub>2</sub> can be detected by the slight decrease in the mass-loss rate in the isothermal mass-loss data and slight increase in the reaction temperature in the nonisothermal mass-loss data in comparison with those in flowing N<sub>2</sub>. When the mass-loss rate was controlled to be constant, the reaction temperature increased slightly in flowing CO<sub>2</sub>. Although we have reported that the rate of the thermal decomposition is decelerated sensitively by atmospheric CO<sub>2</sub> in the order of 10 ppm,<sup>6</sup> the present results indicate that the deceleration effect by atmospheric CO<sub>2</sub> observed in the region of very low concentration is not continuous and is saturated in the higher CO<sub>2</sub> concentrations.

The same kinetic calculation, as is the above for the reaction in flowing  $N_2$ , was applied for the mass-loss data in flowing  $CO_2$ under three different modes of temperature program. The typical kinetic rate data and detailed results of kinetic calculation for the reaction in flowing CO<sub>2</sub> were described in the Supporting Information, together with typical figures in Figures S6, S7, and S8. All the data points recorded under isothermal, nonisothermal, and CRTG modes of temperature program satisfied the isoconversional relationship based on eq 2, representing the straight line of the plots of  $\ln(d\alpha/dt)$  against  $T^{-1}$  at the selected  $\alpha$ . The values of  $E_{\rm a}$  calculated from the Friedman plots were nearly constant irrespective of  $\alpha$ . The  $E_a$  value averaged over 0.1  $\leq \alpha \leq 0.9$  was 102.2  $\pm 1.1$  kJ mol<sup>-1</sup>, which is substantially the same value with that for the reaction in flowing N<sub>2</sub>. The experimental master plot of  $d\alpha/d\theta$  against  $\alpha$  was fitted satisfactorily by RO(*n*) model with *n* = 1.99  $\pm$  0.02 and *A* = (2.47  $\pm$  0.02)  $\times$  $10^9 \text{ s}^{-1}$  ( $\gamma^2 = 0.9906$ ), where the validity of RO(1.99)



**Figure 12.** Typical SEM images of the surface textures of the sample (100–170 mesh) decomposed in flowing CO<sub>2</sub>: (a) decomposed to  $\alpha = 0.15$  by heating isothermally at 398 K for 5 min and (b) decomposed to  $\alpha = 1.00$  by heating nonisothermally at  $\beta = 5.0$  K min<sup>-1</sup> to 473 K.

was supported by the comparable good fitting by SB(-3.35, 1.86. 3.31) with  $A = (4.26 \pm 0.07) \times 10^9 \text{ s}^{-1} (\gamma^2 = 0.9989)$ . The physico-geometrical mechanism estimated by the kinetic calculation is unchanged by the effect of atmospheric CO<sub>2</sub>. The deceleration effect by atmospheric CO<sub>2</sub> is detected by the slight decrease in the value of A. The results of kinetic analysis were also summarized in Table 2.

Typical SEM images of the sample surface at the initial stage of the reaction and of final product decomposed in flowing CO2 are shown in Figure 12. At the initial stage of the reaction, the larger numbers of whiskers are radiating on the surface of the reacting particles in comparison with those in flowing  $N_{2}$ , Figure 12a. The size and thickness of the whiskers are also larger than those in flowing N<sub>2</sub>, where largely grown bars of solid product can be found in several places. The growth of whisker seems to be due to the diffusion and release of gaseous product, possibly intermediated by liquid phase, along with the surfaces of the whiskers and to the slower release rate of CO2 and H2O by the effect of chemical equilibrium with respect to CO<sub>2</sub>. Formation of the surface product layer of sintered SC particles as was observed for the reaction in flowing N<sub>2</sub> is retarded until about  $\alpha = 0.2-0.3$ . Because the surface product layer with interstices provides the channels for diffusion of gaseous products, retardation of the formation may have an influence on the overall reaction rate to be decelerated. Once the surface product layer was established, it maintains the interstices during the latter course of reaction as in flowing N<sub>2</sub>. Figure 12b shows the surface morphology of the product solid produced by the thermal decomposition under linear heating in flowing CO<sub>2</sub>. In comparison with those produced in flowing N2 under otherwise identical reaction conditions, see Figure 10d, sintering of the constituent product particles of the surface product layer is more extensive, reducing slightly the interstices of the surface product layer.

From the above observations, it is apparent that the atmospheric CO<sub>2</sub> influences mainly on the reaction behavior of the surface reaction at the initial part of the thermal decomposition by retarding the establishment of the surface product layer. In spite of such influences of atmospheric CO<sub>2</sub> in heterogeneous characteristics, the overall rate behavior of the established reaction, characterized by two-dimensional shrinkage of the reaction interface controlled by chemical reaction with  $E_a = \sim 100 \text{ kJ mol}^{-1}$ , is not influenced largely.

**3.5. Influence of Atmospheric Water Vapor.** Figure 13 shows the influence of  $p(H_2O)$  on the mass-loss data and those derivative curves for the thermal decomposition of SHC (100–170 mesh)



**Figure 13.** Influence of  $p(H_2O)$  on the mass-loss traces and those derivative curves for the thermal decomposition of SHC (100–170 mesh) recorded under linearly increasing temperature at  $\beta$  = 5 K min<sup>-1</sup>.

recorded under linearly increasing temperature at  $\beta = 5$  K min<sup>-1</sup>. Even under the higher  $p(H_2O)$ , the precursory reaction was detected as the endothermic process with detectable mass-loss. The mass-loss data for the main thermal decomposition of SHC indicate a complex behavior by the effect of atmospheric water vapor. With increasing  $p(H_2O)$ , the onset temperature of the derivative curve shifts to higher temperature, whereas the peak top temperature shifts to lower temperature. From the observations, it is expected that the influences of  $p(H_2O)$  on the surface reaction and the subsequent established reaction are different. The apparent acceleration effect of  $p(H_2O)$  on the overall kinetics of the established reaction is in coincident with that of our previous result.<sup>6</sup> The enhancement of the overall decomposition rate with increasing  $p(H_2O)$  has been observed for the thermal decomposition process of several metal hydroxides.<sup>16,55-57</sup>

Selecting two different  $p(H_2O)$ , 0.8 and 10.3 kPa, the overall kinetics under the respective  $p(H_2O)$  were evaluated by using a series of the mass-loss data recorded under linearly increasing temperature at different  $\beta$ ,  $1 \le \beta \le 5$  K min<sup>-1</sup>. The typical kinetic rate data under the respective measuring conditions were shown in Figure S9 in the Supporting Information. The results of kinetic calculation are illustrated in Figure 14. The Friedman plots at selected  $\alpha$  indicate fairly good linearity irrespective of  $\alpha$  and of  $p(H_2O)$  applied, as was shown in Figure 14a for the reaction under  $p(H_2O) = 10.3$  kPa. However, the slopes of the Friedman plot change among different  $\alpha$ , where the change is more extensive for the reaction under higher  $p(H_2O)$ . The variation of  $E_a$  with  $\alpha$  was shown in Figure 14b. In the initial part of the reaction, the higher value of  $E_{a}$ , ~140 kJ mol<sup>-1</sup>, and its rapid decrease to  $\sim 100 \text{ kJ mol}^{-1}$  are observed as the characteristic behavior by the effect of atmospheric water vapor. The shift of the onset temperature of the reaction to the higher temperature with increasing  $p(H_2O)$  can be correlated to the change of  $E_a$  during the initial part of the reaction. After the values of  $E_a$  were stabilized at around  $\alpha = 0.10$ , the  $E_a$  values for the reaction under  $p(H_2O) = 0.8$  kPa remain the nearly constant values during the later course of the reaction, giving the value of  $E_a$  =  $103.4 \pm 0.5$  kJ mol<sup>-1</sup> averaged over  $0.1 \le \alpha \le 0.9$ . Under  $p(H_2O) = 10.3$  kPa, the values of  $E_a$  change during the later course of the reaction, indicating a convex shape with the maximum value of 116.4  $\pm$  1.1 kJ mol<sup>-1</sup> at  $\alpha$  = 0.40. The value of  $E_a$  averaged over  $0.1 \le \alpha \le 0.9$  was  $109.7 \pm 5.4$  kJ mol<sup>-1</sup>, indicating the larger standard deviation due to the variation during the course of reaction.



**Figure 14.** Kinetic analysis for the thermal decomposition of SHC (100-170 mesh) under controlled  $p(H_2O)$ . (a) The Friedman plots at different  $\alpha$  from 0.1 to 0.9 in steps of 0.1 for the reaction under  $p(H_2O) = 10.3 \text{ kPa}$ , (b) the values of  $E_a$  at various  $\alpha$ , and (c) comparisons of the experimental master plot with the theoretical curves of RO(n) and SB(m,n,p) models.

Figure 14c shows the experimental master plots for the reactions under  $p(H_2O) = 0.8$  and 10.3 kPa. The plots indicate the bends at  $\alpha = 0.20$  and 0.35 for the reactions under  $p(H_2O) = 0.8$  and 10.3 kPa, respectively. The bends indicate the possible change of the reaction mechanism. In the part before the bend, the surface reaction is likely contributing largely on the overall rate behavior, where the region is extending with increasing  $p(H_2O)$ . In addition to the above RO(n) model, a nucleation and growth type model of JMA(m) was applied for fitting the experimental master plots in the part after the bend, because JMA(m) model has been estimated as one of the most appropriate kinetic model functions for the present reaction.<sup>3,4,6-11</sup> The fitting curves of RO(n) and JMA(m) were compared in Figure 14c in the respective ranges of  $0.2 \le \alpha \le 0.9$  and  $0.35 \le \alpha \le 0.9$  for the reactions under

![](_page_10_Figure_2.jpeg)

**Figure 15.** Typical SEM images of the surface textures of the sample (100–170) decomposed under controlled  $p(H_2O) = 10.3 \text{ kPa: } (a-d)$  decomposed to  $\alpha = 0.05$  by heating nonisothermally at  $\beta = 5.0 \text{ K min}^{-1}$  to 373 K and (e, f) decomposed to  $\alpha = 1.00$  by heating nonisothermally at  $\beta = 5.0 \text{ K min}^{-1}$  to 473 K.

 $p(H_2O) = 0.8$  and 10.3 kPa, together with those of SB(*m,n,p*) in the range  $0.1 \le \alpha \le 0.9$ . Under  $p(H_2O) = 0.8$  kPa, the experimental master plot is fitted satisfactorily by RO(2.34) with  $A = (1.03 \pm 0.02) \times 10^{10} \text{ s}^{-1}$  ( $\gamma^2 = 0.9921$ ) and JMA(1.43) with  $A = (2.67 \pm 0.03) \times 10^{10} \text{ s}^{-1}$  ( $\gamma^2 = 0.9811$ ). Similarly, RO(2.08) with  $A = (1.52 \pm 0.02) \times 10^{11} \text{ s}^{-1}$  ( $\gamma^2 = 0.9826$ ) and JMA(1.88) with  $A = (2.84 \pm 0.03) \times 10^{11} \text{ s}^{-1}$  ( $\gamma^2 = 0.9950$ ) were evaluated as the most appropriate kinetic model functions of the respective types for fitting the experimental master plot under  $p(H_2O) =$ 10.3 kPa. Under  $p(H_2O) = 0.8$  kPa, the RO(*n*) model is still indicating the better fitting than that by JMA(*m*), although the kinetic exponent n = 2.34 is slightly larger in comparison with that evaluated for the reaction in flowing N<sub>2</sub> and CO<sub>2</sub>. At the higher  $p(H_2O) = 10.3$  kPa, the fitting by JMA(*m*) model is more appropriate than that by RO(*n*). The apparent fitting to JMA(*m*) under  $p(H_2O) = 10.3$  kPa are likely due to the extended contribution from the surface reaction and the acceleration of the established reaction enhanced by the atmospheric water vapor.

Typical SEM images of the surface textures of the sample during the thermal decomposition under  $p(H_2O) = 10.3$  kPa were shown in Figure 15. Under a high  $p(H_2O)$ , the surface textures of the sample at the initial part of the reaction are quite

different from those observed in flowing N2 and CO2. Before initiating the reaction, the surfaces of the sample particles are reforming as is typically seen for the accommodation of the small deposited particles into the surface of the main crystal body, see Figure 15a. This indicates the interaction between the sample surface and atmospheric water vapor. The needle crystals of surface product growing in parallel to the direction of the long axis of the reactant crystal can be distinguished as the characteristics of the surface reaction under high  $p(H_2O)$ , Figure 15b,c. The needle crystals are platelet and construct the stacking structure, Figure 15d. Formation of the similar surface product at the beginning of the reaction has been reported by Ball et al. as "exfoliated layer".<sup>13</sup> The preliminary reformation of SHC crystal surface and formation of SC needle crystals during the surface reaction are likely to result from dissolution-recrystallization mechanisms. Formation of the surface product layer as was observed for the reaction in flowing  $N_2$  is retarded with increasing  $p(H_2O)$ , where the formation was confirmed at around  $\alpha = 0.3 - 0.4$  under  $p(H_2O) = 10.3$  kPa. Although the acceleration mechanism of the established reaction by the atmospheric water vapor could not be revealed in the present study, the structural change of the surface product layer can be suggested as one of the possible causes from the viewpoint of the reaction morphology. At the same time, the increasing contribution of the liquid phase during the course of reaction is also to be a possible cause. The surface texture of the completely reacted sample is comparable with those obtained by the reactions in flowing N2 and  $CO_2$ , Figure 15e. The constituent product particles in the surface product layer are smaller apparently than those produced under comparable heating conditions in flowing N<sub>2</sub>, compare Figure 10d and Figure 15f. This may be due to the retarded formation of the surface product layer. The above observations of surface textures during the reaction under  $p(H_2O) = 10.3$  kPa support the explanations of the characteristics of thermoanalytical curves and the interpretation of the kinetic results by the extended contribution of the surface reaction on the overall kinetics.

## 4. CONCLUSIONS

The overall kinetics of the thermal decomposition of SHC was investigated in view of the physico-geometrical characteristics of the reaction taking place on a single crystalline particle. The reaction is really heterogeneous in nature, exhibiting various characteristic behaviors of the solid-state reaction. The precursory reaction, which has been observed in many reported thermoanalytical data, is identified as taking place at the boundary between the surface of the SHC crystal and the adhesive small particles deposited on the surface. From several circumstantial evidence, the thermal decomposition of SSC is proposed as the possible origin of the precursory reaction. In flowing dry  $N_{2}$ , the thermal decomposition of SHC crystals initiates on the surface. Erosion of crystal surface and formation of whiskers are the characteristic events of the surface reaction, where possible existence of liquid phase in the process of surface reaction is expected from those textural observations. The surface reaction is completed in the early stage of the reaction,  $\alpha < 0.1$ , by the formation of surface product layer. The surface product layer is the sintered aggregates of the SC particles of several hundred nanometers, where the interstices are to be the possible channels of the diffusion of evolved gases. The established reaction proceeds by the advancement of reaction interface inward. The overall kinetics of the established reaction is described by the two-dimensional shrinkage of the reaction interface controlled by the chemical

reaction, that is, contracting cylinder model, with the apparent  $E_{\rm a}$  of ~100 kJ mol<sup>-1</sup>. Formation of whiskers of SC irradiating from the interstices of the surface product layer also indicates the possible existence of the liquid phase during the established reaction.

Atmospheric CO<sub>2</sub> and water vapor influence differently on the overall kinetics of the thermal decomposition of SHC. The atmospheric CO<sub>2</sub> decelerates slightly the overall kinetics due to the increasing contribution of the surface reaction on the overall reaction and to the retardation of the formation of surface product layer. However, the physico-geometrical mechanisms of surface reaction and established reaction do not change substantially by the effect of atmospheric  $CO_{2}$ , where the overall kinetics is described by the same kinetic features with that in flowing N<sub>2</sub> with slight decrease in the value of *A*. Under higher  $p(H_2O)$ , the physico-geometrical mechanism of the surface reaction changes drastically. The preliminary reformation of reactant surface and the formation of needle crystals of solid product on the surface are the characteristic events induced by the higher  $p(H_2O)$ . The mechanistic change of the surface reaction result in the deceleration of the surface reaction and acceleration of the established reaction. With increasing  $p(H_2O)$ , the apparent value of  $E_a$  and the apparent reaction model deviate from that estimated for the reaction in flowing dry N<sub>2</sub>.

### ASSOCIATED CONTENT

**Supporting Information.** Powder XRD pattern and FT-IR spectra of the sample. Changes of the powder XRD pattern during the thermal decomposition. The enthalpy change during the precursory reaction. Detailed descriptions of the kinetic analyses for the precursory reaction and the main decomposition reaction in flowing  $CO_2$ . The typical mass-loss traces for the reaction under controlled  $p(H_2O)$ . This material is available free of charge via the Internet at http://pubs.acs.org.

### AUTHOR INFORMATION

Corresponding Author

\*Tel\Fax: +81-82-424-7092. E-mail: nkoga@hiroshima-u.ac.jp.

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