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Kinetics of the thermal decomposition of sodium hydrogencarbonate evaluated by controlled rate evolved gas analysis coupled with thermogravimetry

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Abstract

Influences of the product gases on the kinetics of the thermal decomposition of sodium hydrogencarbonate, $NaHCO_3$, were investigated by means of controlled rate evolved gas analysis coupled with TG (CREGA-TG). From a series of CREGA-TG measurements carried out under controlled gaseous concentrations of CO_2 and H_2O by considering the self-generated CO_2 and H_2O during the course of reaction, anomalous effects of CO_2 and H_2O on the kinetic rate behavior of the thermal decomposition of $NaHCO_3$ were revealed, that the reaction is decelerated and accelerated by the effects of atmospheric CO_2 and H_2O, respectively. The kinetic rate behavior under controlled atmospheric condition of $CO_2 = 0.1\ \mathrm{g\,m^{-3}}$ and $H_2O = 1.2\ \mathrm{g\,m^{-3}}$ was characterized by the apparent fitting to a kinetic equation of Avrami–Erofeev type with the apparent activation energy of $E_a = 111.5 \pm 4.8\ \mathrm{kJ\,mol^{-1}}$ and pre-exponential factor of $A = (1.29 \pm 0.01) \times 10^{11}\ \mathrm{s^{-1}}$. The effects of atmospheric CO_2 and H_2O on the apparent kinetic parameters were appeared as the decreases in both the values of E_a and A and the increase in the value of A, respectively.

Keywords: Thermal decomposition; Sodium hydrogencarbonate; Controlled rate evolved gas analysis; Kinetics

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1. Introduction

It is generally accepted that kinetic rate behavior of the thermal decomposition of solids is influenced more or less by the gaseous concentration and/or partial pressure of the product gases in the reaction atmosphere, because the reactions are in many cases reversible. For more complicated cases which produce more than one product gases in a single decomposition step, it is also supposed such cases that the rate behavior is influenced differently by the respective product gases. It has been revealed in our previous studies [1–3] that the kinetic rate behavior of thermal decomposition of synthetic malachite which produces CO_2 and H_2O simultaneously as the product gases is influenced sensitively by the atmospheric concentrations of CO_2 and H_2O, where the respective effects of CO_2 and H_2O were characterized differently as the deceleration by CO_2 and acceleration by H_2O [1,2]. In order to measure the reliable kinetic rate data for such complicated decomposition reaction, the reaction atmosphere should be controlled strictly even including the self-generated reaction atmosphere. By adopting the concept of sample controlled thermal analysis (SCTA) [4–6], we have constructed an instrument of controlled rate evolved gas analysis coupled with TG (CREGA-TG) for the specialized purpose for the kinetic analysis of the thermal decomposition of solids which evolves more than one product gases [3]. The practical usefulness of the CREGA-TG for the kinetic analysis of such complicated reactions has been clarified as exemplified by the application to the thermal decomposition of synthetic malachite [3].

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In the present study, the thermal decomposition of sodium hydrogencarbonate, $NaHCO_3$, was subjected to the kinetic study as an alternative example of the reaction which produces CO_2 and H_2O simultaneously. By applying the CREGA-TG, the respective effects of CO_2 and H_2O concentrations in the reaction atmosphere on the kinetic rate behavior of the thermal decomposition of $NaHCO_3$ are investigated separately. The importance of the quantitative control of the reaction atmosphere including the self-generated atmosphere for the reliable kinetic analysis is demonstrated through the present study.

2. Experimental

Regent grade sodium hydrogencarbonate (Sigma–Aldrich, Japan, Special Grade) was sieved to various fractions of particle size. The sample with a sieve fraction of $-170+200$ mesh was subjected to thermoanalytical measurements.

The sample of ca. 15.0 mg was weighed into a platinum crucible (5 mm in diameter and 5 mm in height). Conventional TG-DTA measurement was carried out using an instrument of ULVAC TGD5000 under flowing dry nitrogen ($200\,cm^3\,min^{-1}$) at a heating rate of $10\,K\,min^{-1}$, where the concentrations of CO_2 and H_2O in the outflow gas from the reaction chamber were monitored by an infrared CO_2 meter (IIJIMA LX-720) and a hygrometer (NTK HT20), respectively.

CREGA-TG measurements were also performed using the same instrumental configuration with the above conventional TG–DTA–EGA. A feedback control for the constant rate thermal analysis (CRTA) was performed using two independent PID controllers [7]. The analogue output signal from the CO_2 meter was interfaced to a PID controller, programmed to maintain the concentration of CO_2 constant during the course of decomposition reaction. A thermocouple, placed in contact to the bottom of sample pan in the TG–DTA instrument, was interfaced to another PID controller with the temperature program of linear heating. The lower output signal from two different PID controllers was selected suitably for heating the sample via an infrared image furnace. The details of CREGA-TG instrument have already been reported previously [3]. Some 20 of CREGA-TG runs were carried out under systematically changed reaction atmosphere by introducing mixed gases of dry N_2, wet N_2, dry air and wet air at a total amount of $200\,cm^3\,min^{-1}$, where the heating rate of $2\,K\,min^{-1}$ was applied and the increase in the concentration of CO_2 was regulated to be $0.10\,g\,m^{-3}$ during the course of reaction.

3. Results and discussion

3.1. Reaction behavior

Fig. 1 shows typical conventional TG–DTA–EGA traces for the thermal decomposition of $NaHCO_3$ at a heating rate of $10\,K\,min^{-1}$ under flowing dry N_2 ($200\,cm^3\,min^{-1}$). The reaction takes place showing a smooth mass-loss curve with an endothermic DTA peak, where the observed value of total mass-loss, 36.8 ± 0.6%, was in good agreement with the value calculated by assuming the reaction:

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O.$$

During the thermal decomposition, CO_2 and H_2O evolve simultaneously indicating peak maximums at the same temperature with the endothermic DTA peak. These typical features of the thermoanalytical curves for the thermal decomposition of solids expose apparent drawbacks for the kinetic use of the conventional thermoanalytical measurements carried out under linearly increasing temperature [8–10]. The well shaped endothermic DTA peak indicates that the sample temperature

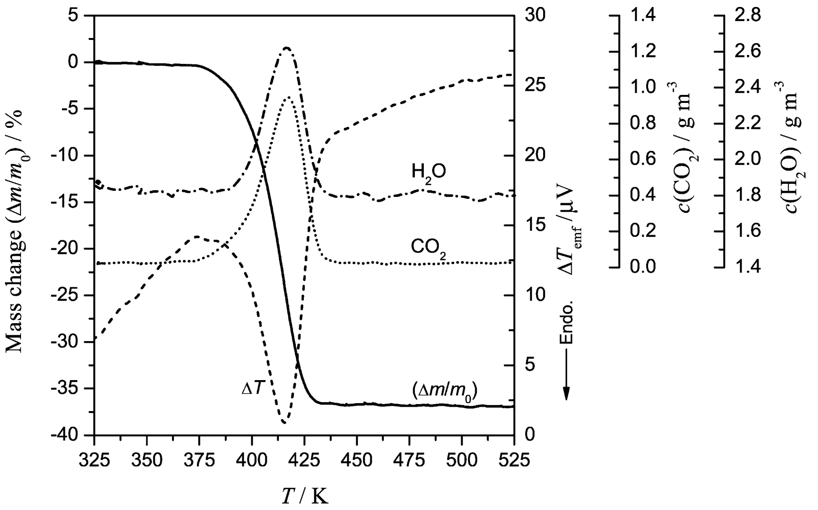

Fig. 1. Typical TG–DTA–EGA (CO_2, H_2O) traces for the thermal decomposition of $NaHCO_3$ (15.0 mg) at a heating rate of $10\,K\,min^{-1}$ under flowing dry N_2 ($200\,cm^3\,min^{-1}$).

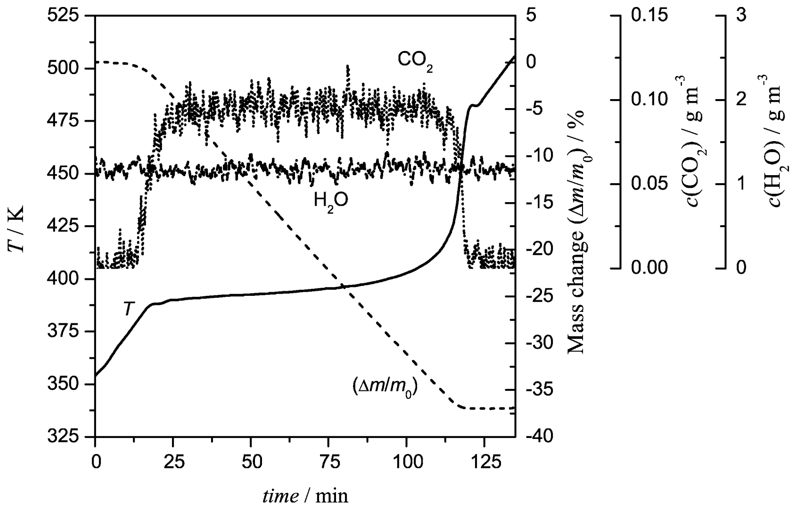

Fig. 2. Typical CREGA-TG traces for the thermal decomposition of $NaHCO_3$ (15.0 mg), recorded by regulating the increase of CO_2 concentration during the course of reaction at $0.1\,g\,m^{-3}$, under flowing dry N_2 ($200\,cm^3\,min^{-1}$).

deviates more or less from the programmed linear heating and a possible temperature distribution within the assemblage of sample particles is caused, called sometimes as the self-cooling effect [11]. The rate of reaction is directly influenced by the temperature deviation and distribution result from the self-cooling effect. Similarly, the changes in the reaction atmosphere during the course of reaction due to self-generated gaseous products are also the possible factors affecting the experimentally resolved shape of TG and DTG curves [10].

It has been expected from the time of development [4–6] that CRTA as one of the modes of sample controlled thermal analysis can be a possible solution of the problems inherent in the kinetic use of the conventional thermal analysis. Fig. 2 shows typical CREGA-TG traces recorded by regulating the increase of CO_2 concentration during the course of reaction at a constant value of $0.1\,g\,m^{-3}$. Although the concentration of H_2O should be increased by $0.1\,g\,m^{-3}$ during the course of reaction as is with CO_2, the expected change in the H_2O concentration could not be detected due to lower sensitivity of the present hygrometer. Because the reaction advances at a very slow constant rate, the undesirable influence of self-cooling effect on the precise control of sample temperature and on the rate behavior can be restrained largely in the CREGA-TG measurement. Evolution rates of the product gases are also kept constant during the course of reaction so that the influence of the self-generated reaction atmosphere on the rate behavior is also under control. The feedback temperature control by referring EGA signal employed in the present study as CREGA-TG enable us to control quantitatively the concentration of a specific gaseous product in the reaction atmosphere even for the complicated decomposition reaction where more than one gases are produced at different rate behaviors. Thus the influence of a specific product gas in the reaction atmosphere on the apparent kinetics of the thermal decomposition of solids can be examined by considering the increase in the concentration of a specific product gas during the course of reaction, in addition to the applied reaction atmosphere for the measurement.

In order to evaluate the respective influences of atmospheric CO_2 and H_2O on the kinetics of the thermal decomposition of $NaHCO_3$, CREGA-TG measurements were carried out under various concentrations of CO_2 and H_2O in the inflow gas by regulating the increase in the concentration of CO_2 in the outflow gas at $0.1\,g\,m^{-3}$. Irrespective of the applied concentrations of CO_2 and H_2O in the inflow gas, the mass-loss proceeded at a constant mass-loss rate of $(-5.48 \pm 0.08) \times 10^{-2}\,mg\,min^{-1}$. Fig. 3 shows the temperature profiles of the CREGA-TG measurements carried out under various concentrations of CO_2 and a restricted H_2O concentration of $1.2\,g\,m^{-3}$. The reaction temperature

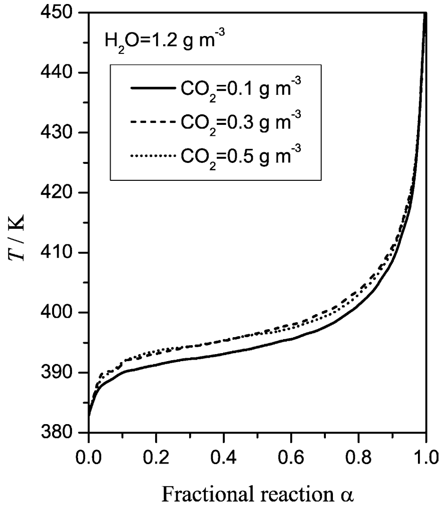

Fig. 3. Comparison of the temperature profiles of the CREGA-TG measurements carried out under various concentrations of CO_2 and a restricted H_2O concentration of $1.2\,g\,m^{-3}$.

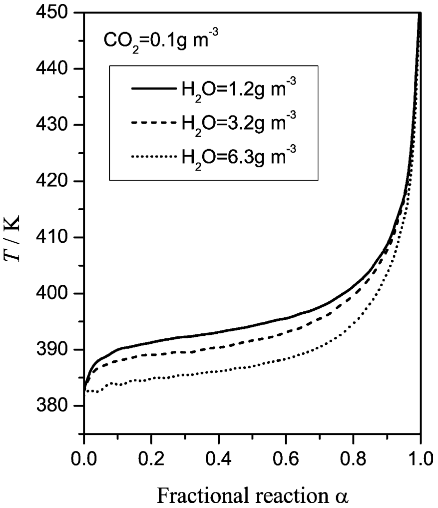

Fig. 4. Comparison of the temperature profiles of the CREGA-TG measurements carried out under various concentrations of H_2O and a restricted CO_2 concentration of 0.1 g m^{-3}.

shifts to higher temperature with increasing the concentration of CO_2 from 0.1 to 0.3 g m^{-3}. This is apparently the normal effect of atmospheric CO_2 from the view point of chemical equilibrium. Fig. 4 compares the temperature profiles of the CREGA-TG measurements carried out under various concentrations of H_2O and a restricted CO_2 concentration of 0.1 g m^{-3}. Unexpectedly, the reaction temperature decreases with increasing the atmospheric concentration of H_2O. It is indicated by the opposite effect of the atmospheric H_2O on the reaction temperature that the atmospheric H_2O promotes the reactivity. Comparing the shapes of the reaction temperature profiles, a trend of temperature increase observed at the initial part of the reaction ($\alpha < 0.1$) is restrained with increasing the atmospheric concentration of H_2O, which indicates possibly the acceleration of surface nucleation process by the existence of atmospheric H_2O. The similar behavior of the abnormal effect of atmospheric H_2O has been also observed for the thermal decomposition of synthetic malachite, $Cu_2(OH)_2CO_3$ [1–3].

3.2. Kinetic analyses

Because the reaction rate behavior of the thermal decomposition of $NaHCO_3$ is influenced sensitively by the atmospheric CO_2 and H_2O including the self-generated these gases, any changes of reaction atmosphere during the course of reaction and among a series of rate data for kinetic calculation are desired to be diminished for measuring the reliable kinetic rate data. As a possible method to record a series of kinetic rate data at different reaction rates without any practical changes of reaction atmosphere during the course of reaction and among the series of kinetic measurements, a simple method of measuring a pair of temperature profiles of CREGA-TG was employed in the present study [3]. One measurement was carried out as usually by setting single sample cell weighed 15.0 mg of sample to the sample holder (single sample). For alternating the constant reaction rate, another measurement was carried out using twin sample cells weighed every 15.0 mg of sample in the respective sample cells by setting one to the sample holder for the TG–DTA measurements and another to the holder for the reference material of DTA measurement (twin samples). Fig. 5 shows the CREGA-TG traces recorded for the measurements of single sample and twin samples under flowing dry N_2 (200 cm^3 min^{-1}) by controlling the increase of CO_2 concentration in the outflow gas at 0.1 g m^{-3}. In the case of the measurement of twin samples, the constant mass-loss rate decreases by half compared with that for the measurement of single sample, because both the samples contribute equally to the increase in the concentration of CO_2 during the course of reaction.

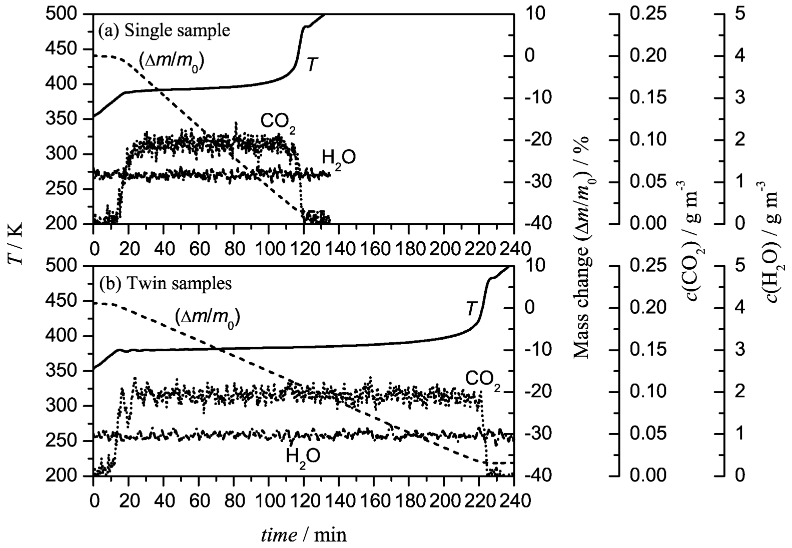

Fig. 5. Comparison of CREGA-TG traces recorded using single sample and twin samples.

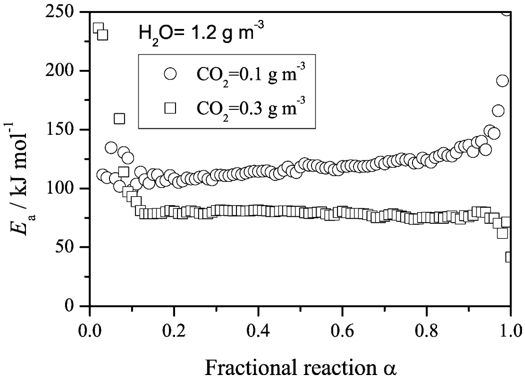

Fig. 6. Influence of atmospheric CO_2 on the α-dependence of E_a under atmospheric H_2O at 1.2 g m^{-3}.

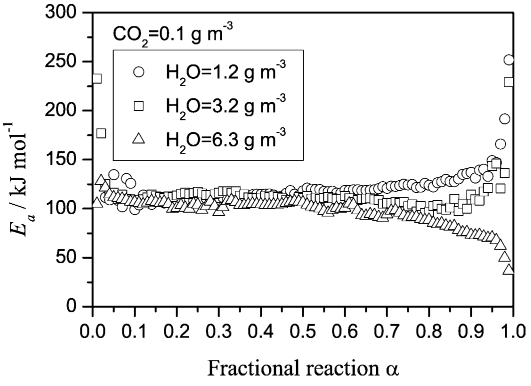

Fig. 7. Influence of atmospheric H_2O on the α-dependence of E_a under controlled atmospheric CO_2 at 0.1 g m^{-3}.

The fundamental kinetic rate equation of the Arrhenius type was applied for analyzing the kinetic analysis of the present thermal decomposition:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \qquad (1)$$

where A, E_a, and $f(\alpha)$ are the pre-exponential factor, apparent activation energy, and kinetic model function in differential forms, respectively. The other symbols have their usual meanings. The values of E_a at selected α were determined from a pair of kinetic rate data using a simple isoconversional method which has been utilized as the rate jump method [7].

$$E_a = -\frac{RT_1T_2}{T_2 - T_1} \ln \frac{(d\alpha/dt)_1}{(d\alpha/dt)_2} \qquad (2)$$

where the data point (T_i, $(d\alpha/dt)_i$) are on the respective kinetic rate curves at a restricted α. Fig. 6 shows the values of E_a evaluated at various α for the reactions under different CO_2 concentrations, 0.1 and 0.3 g m^{-3}, and a restricted H_2O concentration of 1.2 g m^{-3}. Although the values of E_a at various α indicated acceptable constant values in the wide range of $0.1 \leq \alpha \leq 0.9$ irrespective of CO_2 concentrations applied, the averaged value of E_a decreased about 30 kJ mol^{-1} by increasing the CO_2 concentration from 0.1 to 0.3 g m^{-3}, i.e., 111.5 ± 4.8 and 78.5 ± 3.0 kJ mol^{-1} in the range of $0.1 \leq \alpha \leq 0.9$. Fig. 7 compares the α-dependence of E_a calculated for the reactions at a controlled CO_2 concentration of 0.1 g m^{-3} and various H_2O concentrations. Irrespective of the H_2O concentrations controlled, the values of E_a for the first half of the reaction remain unchanged. For the second half ($\alpha > 0.5$), the values of E_a tend to deviate gradually to the lower values from the constant value with increasing the atmospheric concentration of H_2O. This trend is clearly observed for the reaction under controlled concentrations of CO_2 = 0.1 g m^{-3} and H_2O = 6.3 g m^{-3}. For the reactions under the lower H_2O concentrations, 1.2 and 3.2 g m^{-3}, the values of E_a averaged over $0.1 \leq \alpha \leq 0.9$ were determined as 111.5 ± 4.8 and 109.6 ± 5.2 kJ mol^{-1}, respectively.Further kinetic characterization was made for the processes under three selected atmospheric conditions which indicated the constant E_a values in the whole course of reaction, i.e. for the reactions under controlled concentrations of (CO_2, H_2O) = (0.1, 1.2), (0.3, 1.2) and (0.1, 3.2) g m^{-3}. Using the averaged values of E_a for the respective processes, the measured rate data were extrapolated to infinite temperature according to the following equation [12,13].

$$\frac{d\alpha}{d\theta} = \frac{d\alpha}{dt} \exp\left(\frac{E_a}{RT}\right) \qquad (3)$$

where θ is the generalized time and/or reduced time proposed by Ozawa [12,13] and indicates the simulated reaction time at infinite temperature. Fig. 8 compares the shapes of the simulated kinetic rate data at infinite temperature as the plots of $(d\alpha/d\theta)$ normalized by dividing the value at $\alpha = 0.5$, i.e., $(d\alpha/d\theta)/(d\alpha/d\theta)_{0.5}$, against α [14]. The simulated rate data under three different atmospheric conditions indicated the similar rate behavior of decelerate process with slightly convex. As referenced by the reaction under the lowest CO_2 and H_2O concentrations examined, the values of $(d\alpha/d\theta)/(d\alpha/d\theta)_{0.5}$ for the higher CO_2 concentration deviate to the higher values at $\alpha > 0.5$. Oppositely, deviation of $(d\alpha/d\theta)/(d\alpha/d\theta)_{0.5}$ to the lower values was observed at $\alpha > 0.5$ for the reaction under the higher H_2O concentration.

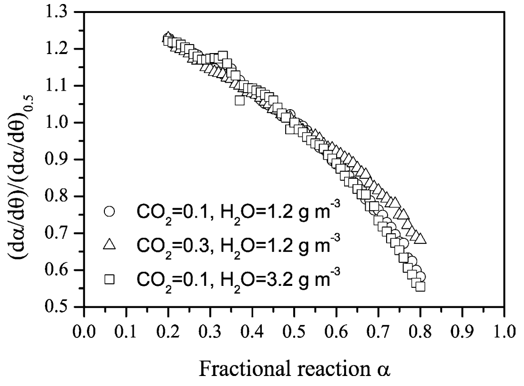

Fig. 8. Comparison of the simulated kinetic rate data at infinite temperature for the reactions under three selected atmospheric conditions.

Table 1
Summary of the apparent kinetic parameters evaluated for the reactions under various controlled reaction atmosphere

Controlled reaction atmosphere		From Eq. (2) E_a (kJ mol^{-1})	From ($d\alpha/d\theta$) vs. $m(1-\alpha)[-\ln(1-\alpha)]^{1-1/m}$ plot		
CO_2 (g m^{-3})	H_2O (g m^{-3})		m	A (s^{-1})	γ[a]
0.1	1.2	111.5 ± 4.8	1.25	$(1.29 \pm 0.01) \times 10^{11}$	0.9981
0.3	1.2	78.5 ± 3.0	1.15	$(9.19 \pm 0.08) \times 10^{6}$	0.9977
0.1	3.2	109.6 ± 5.2	1.30	$(1.65 \pm 0.02) \times 10^{11}$	0.9971

[a] Correlation coefficient of the linear regression analysis.

Combining Eqs. (1) and (3), the following equation is derived [12,13–15].

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

By plotting $d\alpha/d\theta$ against $f(\alpha)$, a straight line with slope A is obtained when an appropriate function of $f(\alpha)$ was applied for the plot. Through plotting $d\alpha/d\theta$ against various $f(\alpha)$ for the reactions under three different controlled atmospheric conditions, Avrami–Erofeev model [16], i.e. $f(\alpha) = m(1-\alpha)[-\ln(1-\alpha)]^{1-1/m}$ with the values of m close to unity, was selected as the most appropriate kinetic model function. Although the apparent fit to the Avrami–Erofeev model derived originally for the nucleation and growth type reaction should be further investigated from the physico-geometrical view points [10], the empirical fitting to a particular kinetic model enable us to determine the apparent value of A and to compare the values among the series of reactions under investigation.

Table 1 summarizes the apparent kinetic parameters evaluated for the reactions under three different controlled atmosphere. The change in the rate behavior at the second half of the reaction depending on the atmospheric condition is reflected apparently by the change in the kinetic exponent m in the Avrami–Erofeev equation. The changes in the reaction temperature at a restricted reaction rate depending on the atmospheric condition observed as the changes in the temperature profiles of the CREGA-TG measurements, see Figs. 3 and 4, can be expressed by the changes in the value of A. Unexpected decrease in the reaction temperature with increasing the atmospheric H_2O concentration from 1.2 to 3.2 g m^{-3} appears as the increase in the value of A without any practical change in E_a. As for the increase in the reaction temperature with increasing the CO_2 concentration from 0.1 to 0.3 g m^{-3}, the value of A decreases drastically, but the effect of the large decrease in A on the reaction temperature is compensated partially by the decrease in E_a.

4. Conclusion

The reaction rate behavior of the thermal decomposition of $NaHCO_3$, which evolves CO_2 and H_2O simultaneously, is influenced sensitively by the atmospheric CO_2 and H_2O including the self-generated these gases. The respective product gases in the reaction atmosphere influence differently on the rate behavior of the thermal decomposition. As is expected from the chemical equilibrium of the reaction, the reaction rate of the forward reaction is decelerated apparently by the atmospheric CO_2. On the other hand, opposite effect was observed for the atmospheric H_2O which enhances the reaction rate within the range of H_2O concentration examined in the present study.

CREGA-TG was successfully applied for measuring the kinetic rate data under a quantitatively controlled condition of reaction atmosphere including the self-generated conditions. The rate behavior of the thermal decomposition was characterized apparently by a kinetic equation of Avrami–Erofeev type, where the appropriate kinetic exponent decreased and increased by the effects of atmospheric CO_2 and H_2O, respectively. The enhancement of the reactivity by the effect of atmospheric H_2O was expressed by the increase in the value of A without any practical change in the value of E_a. The normal effect of chemical equilibrium observed for the effect of atmospheric CO_2, i.e., the decrease in the reaction rate, appeared as the decreases in both the values of E_a and A.

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