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INFLUENCES OF EVOLVED GASES ON THE THERMAL DECOMPOSITION OF ZINC CARBONATE HYDROXIDE EVALUATED BY CONTROLLED RATE EVOLVED GAS ANALYSIS COUPLED WITH TG

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The influences of atmospheric CO_2 and H_2O on the kinetics of the thermal decomposition of zinc carbonate hydroxide, $Zn_5(CO_3)_2(OH)_6$, were investigated by means of controlled rate evolved gas analysis (CREGA) coupled with TG. Although CO_2 and H_2O were evolved simultaneously in a single mass-loss step of the thermal decomposition, different effects of those evolved gases on the kinetic rate behavior were observed. No distinguished effect of atmospheric CO_2 was detected within the possible range of self-generated CO_2 concentration. On the other hand, apparent acceleration effect by the increase in the concentration of atmospheric H_2O was observed as the reduction of reaction temperature during the course of constant rate thermal decomposition. The catalytic effect was characterized by the decrease in the apparent activation energy for the established reaction with increasing the concentration of atmospheric H_2O, accompanied by the partially compensating decrease in the pre-exponential factor.

Keywords: *controlled rate evolved gas analysis (CREGA), kinetics, sample controlled thermal analysis (SCTA), thermal decomposition, zinc carbonate hydroxide*

Introduction

It is apparent in the kinetic analysis of the thermal decomposition of solids that the measurements of reliable kinetic rate data are essential as the major premise for the better kinetic calculation and interpretation of the kinetic results [1]. The reliability of the kinetic rate data depends not only on the measurement accuracy, but also on the appropriate control of the measuring condition during the course of reaction, because the actual reaction conditions are influenced largely by those generated by the reaction itself. The self-cooling effect due to the endothermic change [2] and the mass-transfer phenomena due to the diffusion of evolved gases [3] are typical examples of such self-generated conditions. Application of controlled transformation rate thermal analysis (CRTA) [4–6] to the kinetic measurements is highly suitable, because the overall rate of reaction is kept to a lower constant value during the course of reaction. Further, by controlling the reaction rate by monitoring a signal of the selected evolved gas in evolved gas analysis (EGA), it is expected to utilize CRTA as a sophisticated technique to evaluate the influence of the evolved gas on the kinetics of the thermal decomposition of solids.

The kinetic modeling for the thermal decomposition of metal carbonate hydroxides is one of our recent subjects [7–11]. We have encountered an abnormal effect of the evolved gases on the thermal decomposition of synthetic malachite $Cu_2CO_3(OH)_2$ [7], where the decomposition temperature shifts systematically to the lower temperature region with increasing the effect of evolved gases. By applying CRTA, especially controlled rate evolved gas analysis (CREGA), the rate behavior was revealed as the catalytic effect by the evolved H_2O [8, 9]. The similar catalytic effect of evolved H_2O during the thermal decomposition has been observed for the thermal decomposition of sodium hydrogencarbonate [12]. In the present study, the thermal decomposition of zinc carbonate hydroxide (ZCH), $Zn_5(CO_3)_2(OH)_6$, was subjected to the kinetic study as an alternative example of the reaction which produces CO_2 and H_2O simultaneously [10]. By applying the CREGA-TG, the respective effects of CO_2 and H_2O in the reaction atmosphere on the kinetic rate behavior of the thermal decomposition of ZCH are investigated.

Experimental

The same batch of ZCH prepared and identified in our previous study [10] was utilized in the present study. The sample of ca. 10.0 mg was weighed into a platinum cell (5 mm in diameter and 5 mm in height).

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TG/DTA-EGA measurement was carried out using an instrument (ULVAC TGD5000) at a heating rate β of 10 K min^{-1} under flowing dry N_2 (200 cm^3 min^{-1}), where the concentrations of CO_2 and H_2O, $c(CO_2)$ and $c(H_2O)$, in the outflow gas from the reaction chamber were monitored continuously by an infrared CO_2 meter (IIJIMA LX-720: sensitivity $1\cdot10^{-3}$ g m^{-3}) and a hygrometer (NTK HT20: sensitivity $1\cdot10^{-2}$ g m^{-3}), respectively.

Using the same instrument, CREGA-TG measurements were performed by applying a feedback control for the sample temperature by monitoring $c(CO_2)$ in the outflow gas from the reaction chamber. The details of instrumental configuration and controlling system have been reported previously [9, 13]. Under various controlled atmospheric conditions of introducing mixed gases of dry N_2, wet N_2 and dry air at a total amount of 200 cm^3 min^{-1}, the measurements were carried out at β=2 K min^{-1}, where the feedback control of the sample temperature was applied so as to maintain $c(CO_2)$ at a constant value during the course of reaction by regulating the increase in $c(CO_2)$ to be 0.05 g m^{-3} from the base concentration.

Results and discussion

Influences of atmospheric CO_2 and H_2O

Figure 1 shows typical TG/DTA-EGA traces for the thermal decomposition of ZCH. As has been reported previously [10], ZCH decomposes quantitatively to ZnO by showing a smooth mass loss curve with an endothermic DTA peak. During the course of the thermal decomposition, CO_2 and H_2O evolve simultaneously indicating peak maxima at the same temperature with the endothermic DTA peak.

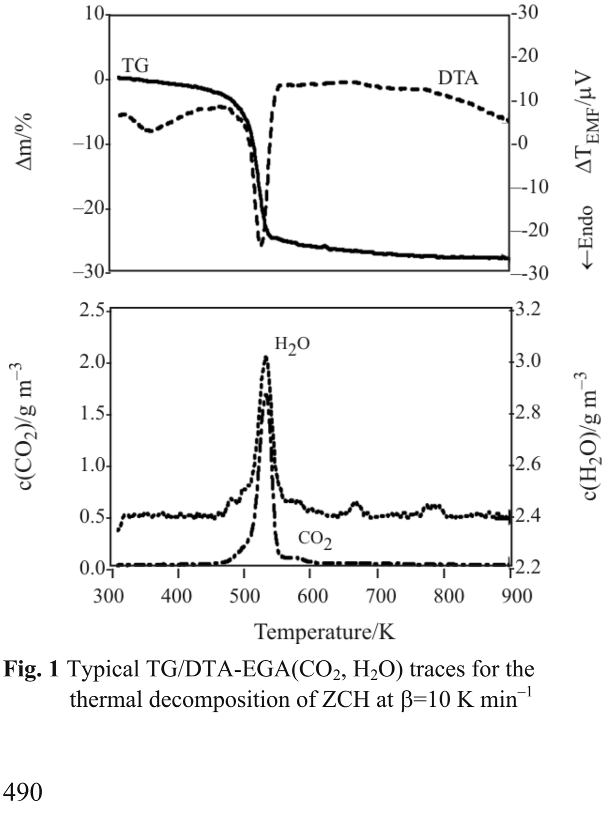

Fig. 1 Typical TG/DTA-EGA(CO_2, H_2O) traces for the thermal decomposition of ZCH at β=10 K min^{-1}

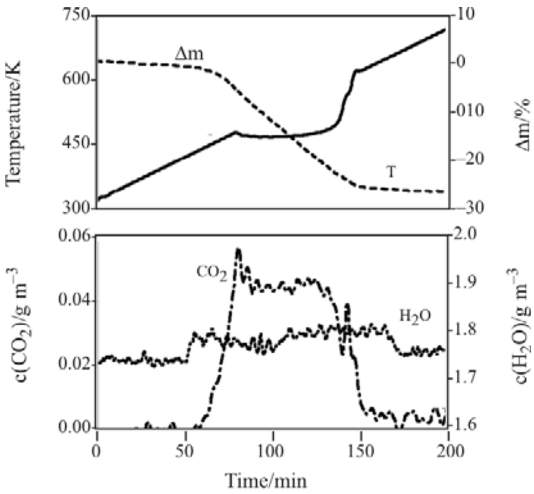

Fig. 2 Typical CREGA-TG traces for the thermal decomposition of ZCH

Figure 2 shows typical CREGA-TG traces recorded by regulating the increase of $c(CO_2)$ during the course of the reaction at a constant value of 0.05 g m^{-3}. Under such measuring conditions, the mass loss due to the thermal decomposition took place at a constant mass loss rate of 28.7±0.9 μg min^{-1}, irrespective of base $c(CO_2)$ and $c(H_2O)$ applied. The increase in $c(H_2O)$ is also nearly constant during the course of reaction as well as the controlled increase in $c(CO_2)$.

In order to evaluate the influences of small changes in atmospheric $c(CO_2)$ and $c(H_2O)$ on the rate behavior of the thermal decomposition of ZCH, CREGA-TG measurements were carried out under various $c(CO_2)$ and $c(H_2O)$ in the inflow gas by regulating the increase in $c(CO_2)$ in the outflow gas at 0.05 g m^{-3}. Figure 3 shows the temperature profiles of

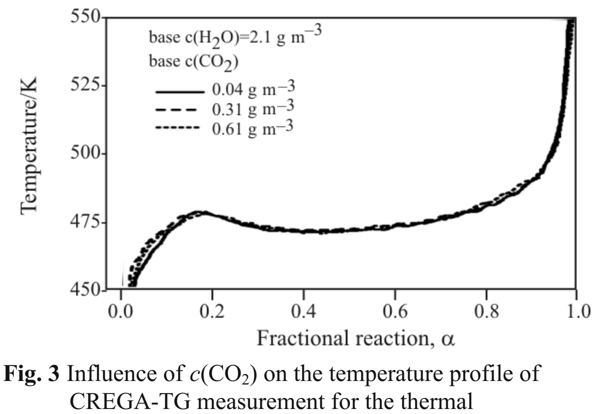

Fig. 3 Influence of $c(CO_2)$ on the temperature profile of CREGA-TG measurement for the thermal decomposition of ZCH

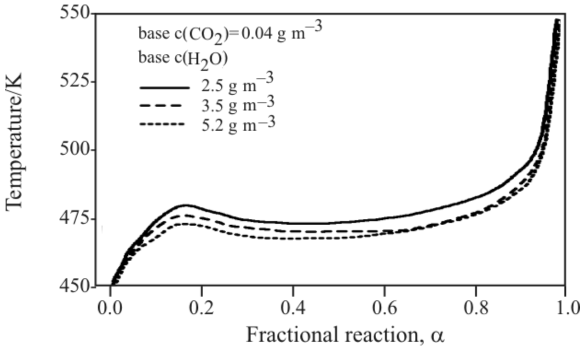

Fig. 4 Influence of $c(H_2O)$ on the temperature profile of CREGA-TG measurement for the thermal decomposition of ZCH

the CREGA-TG recorded under different base $c(CO_2)$ and at a restricted $c(H_2O)$ of 2.1 g m^{-3}. The reaction temperature and the shape of the temperature profile do not change largely by the change of the base $c(CO_2)$. Figure 4 compares the temperature profiles of the CREGA-TG recorded under different base $c(H_2O)$ and at a restricted base $c(CO_2)$ of 0.04 g m^{-3}. With increasing the base $c(H_2O)$, the reaction temperature during the constant rate thermal decomposition shifts to lower temperature region, indicating the inverse effect from the view point of chemical equilibrium. Although the catalytic effect of atmospheric H_2O is known as Smith-Topley effect for the thermal dehydration of inorganic hydrates [14–17], the similar behavior has been observed for the thermal decomposition of synthetic malachite, $Cu_2(OH)_2CO_3$ [7–9] and sodium hydrogencarbonate [12] which evolve CO_2 and H_2O simultaneously in a single decomposition step as in the case of the present reaction.

Kinetic analysis

Avoiding the possible influence of the atmospheric H_2O on the measured rate data, a pair of kinetic rate data at different controlled decomposition rates was recorded as follows. One CREGA-TG measurement was carried out as usually by setting single sample cell with 10.0 mg of sample to the sample holder (single sample). In the alternative CREGA-TG measurement, two sample cells with every 10.0 mg of sample were set one to the sample holder and another to the holder for the reference material of DTA (double samples). Figure 5 compares the CREGA-TG curves recorded using single sample and double samples. Because the reference material holder for the DTA measurement is configured independently to the balance system, TG trace reflects only the mass change of the sample placed at the sample holder. On the other hand, when using double samples the evolved gases from both the samples are reflected as the increase of $c(CO_2)$ and $c(H_2O)$ in the outflow gas. Accordingly, by remaining $c(CO_2)$ and $c(H_2O)$ during the course of the reaction unchanged between the pair of measurements, the reaction time takes twice and the reaction rate reduces by half in the measurement for the double samples in comparison with that for the single sample.

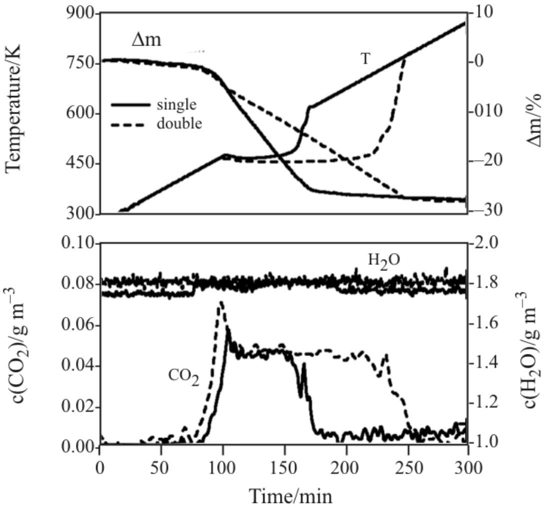

Fig. 5 Comparison of CREGA-TG traces for the thermal decomposition of ZCH recorded using single sample and double samples

The following kinetic rate equation of the Arrhenius type was applied for the present thermal decomposition:

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

where A, E_a, and $f(\alpha)$ are the pre-exponential factor, apparent activation energy, and kinetic model function in differential forms, respectively. The 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 for the rate jump method [9, 12, 18].

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

where T_i and $(\mathrm{d}\alpha/\mathrm{d}t)_i$ (i=1, 2) are the data points on the respective kinetic rate curves at a selected α. Figure 6 compares the α-dependence of E_a calculated for the reactions under different base $c(H_2O)$ of 2.5 and 5.2 g m^{-3} and at the restricted base $c(CO_2)$ of 0.04 g m^{-3}. In both cases, the apparent E_a decreases steeply in the initial part of the reaction ($\alpha \le 0.2$) and maintains the respective constant values during the subsequent established reaction ($\alpha \ge 0.8$). As is listed in Table 1, the value of E_a for the established reaction tends to decrease largely by the increase of $c(H_2O)$.

For further kinetic characterization, the measured kinetic rate data in the α range of the estab-

Table 1 Comparison of the kinetics parameters evaluated for the thermal decomposition of ZHC under different controlled $c(H_2O)$ ($c(CO_2)_{base}$=0.04 g m^{-3}, $0.2\leq\alpha\leq0.8$)

$c(H_2O)$/g m^{-3}	E_a/kJ mol^{-1}	$f(\alpha)$	γ^2	A/min^{-1}
2.5	110.3±4.5	JMA(2.54)	0.9152	$(1.65\pm0.03)\cdot10^{10}$
5.2	82.4±1.0	JMA(2.56)	0.9859	$(1.90\pm0.02)\cdot10^{7}$

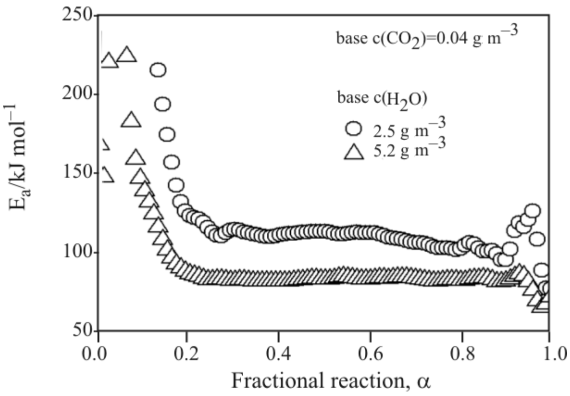

Fig. 6 Influence of $c(H_2O)$ on the α-dependence of E_a for the thermal decomposition of ZCH

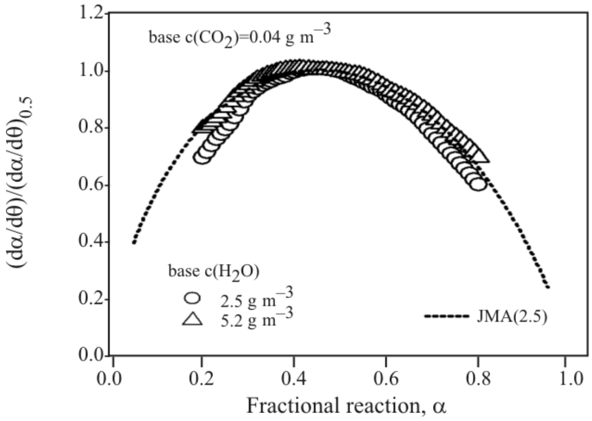

Fig. 7 Comparison of the experimental master plots for the thermal decomposition of ZCH under different $c(H_2O)$

lished reaction were converted to the simulated data at infinite temperature by the equation [19, 20]:

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

with

$$\theta = \int_0^t \exp\left(-\frac{E_a}{RT}\right)dt \qquad (3)$$

where θ is the generalized time proposed by Ozawa [21–23], which indicates the reaction time at infinite temperature. Figure 7 shows the rate behavior at infinite temperature as the experimental master plot of $(d\alpha/d\theta)/(d\alpha/d\theta)_{0.5}$ *vs.* α [24, 25]. The experimental master plots for the reactions under the base $c(H_2O)$ of 2.5 and 5.2 g m^{-3} are practically identical, indicating the maximum at around α=0.40~0.45. By combining Eq. (1) with Eq. (3), the value of dα/dθ is related to $f(\alpha)$ as follows [19, 20].

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

Through comparisons of the experimental master plots in Fig. 7 with the theoretical master plots of $f(\alpha)/f(0.5)$ *vs.* α with various $f(\alpha)$, the acceptable agreement was found for the nucleation and growth type model JMA(*m*), $f(\alpha)=m(1-\alpha)[-\ln(1-\alpha)]^{1-1/m}$ with m=2.5. On the basis of Eq. (4) with JMA(*m*) model as the appropriate $f(\alpha)$, the value of preexponential factor *A* and the best value of kinetic exponent in JMA(*m*) were determined simultaneously through the nonlinear least square fitting by the Lovenberg–Marquardt optimization algorithm [26, 27]. The values of *m* and *A* determined were listed in Table 1, together with the correlation coefficient of the nonlinear least square fitting. As was expected from the master plots in Fig. 7, the best value of *m* in JMA(*m*) function is around 2.5 irrespective of $c(H_2O)$ compared. On the other hand, the value of *A* decreases with the increase in $c(H_2O)$, compensating the effect of decrease in the value of E_a [28, 29]. Accordingly, the catalytic effect of atmospheric $c(H_2O)$ on the established part of the thermal decomposition of ZCH is characterized formally by the compensating decreases in the E_a and *A* values without any practical change in $f(\alpha)$.

For the physico-chemical interpretation on the catalytic effect of $c(H_2O)$, it is required to reveal the effect on the initial part of the reaction in the wider range of $c(H_2O)$. In parallel with the present study, we have performed an experimental approach to the problem using TG-DTA equipped with a programmable humidity controller. The result is reported separately with the integrated discussion on the mechanism of catalytic effect of atmospheric water vapor.

Conclusions

It was revealed from the measurements of CREGA-TG under controlled reaction atmosphere that the thermal decomposition of ZCH, which evolves CO_2 and H_2O simultaneously in a single mass-loss step, is accelerated by the increase in the atmospheric H_2O. By analyzing a pair of the kinetic curves recorded by avoiding the change in the reaction atmosphere between the respective measurements, the reaction was characterized by the initial part ($\alpha \leq 0.2$) accompanied by the steep decrease in E_a and the established part ($\alpha \geq 0.2$) described formally by the kinetic model function of JMA(2.5) with the constant E_a. As for the established part of the reaction, the acceleration of reaction by the effect of increasing base $c(H_2O)$ from 2.5 to 5.2 g m^{-3} was reflected by the decrease in E_a from 110.3 to 82.4 kJ mol^{-1}, together with the compensating decrease in A from $1.65 \cdot 10^{10}$ to $1.90 \cdot 10^{7}$ min^{-1}.

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References

1 N. Koga and H. Tanaka, Thermochim. Acta, 388 (2002) 41.
2 H. Tanaka and N. Koga, J. Thermal Anal., 36 (1990) 2601.
3 N. Koga and J. M. Criado, Int. J. Chem. Kinet., 30 (1998) 737.
4 J. Rouquerol, J. Thermal Anal., 2 (1970) 123.
5 J. Paulik and F. Paulik, Anal. Chim. Acta, 56 (1971) 328.
6 O. T. Sorensen and J. Rouquerol, Eds, Sample Controlled Thermal Analysis, Kluwer, Dordrecht 2003.
7 N. Koga, J. M. Criado and H. Tanaka, Thermochim. Acta, 340–341 (1999) 387.
8 N. Koga, J. M. Criado and H. Tanaka, J. Therm. Anal. Cal., 60 (2000) 943.
9 N. Koga and S. Yamada, Int. J. Chem. Kinet., 37 (2005) 346.
10 N. Koga and H. Tanaka, J. Therm. Anal. Cal., 82 (2005) 725.
11 N. Koga and Y. Yamane, J. Therm. Anal. Cal., 93 (2008) 963.
12 S. Yamada and N. Koga, Thermochim. Acta, 431 (2005) 38.
13 J. M. Criado, L. A. Perez-Maqueda, M. J. Dianez and P. E. Sanchez-Jimenez, J. Therm. Anal. Cal., 87 (2007) 297.
14 B. Topley and M. L. Smith, J. Chem. Soc., (1935) 321.
15 D. A. Young, Decomposition of Solids, Pergamon, Oxford 1966.
16 M. E. Brown, D. Dollimore and A. K. Galwey, Reactions in the Solid State, Elsevier, Amsterdam 1980.
17 A. K. Galwey and M. E. Brown, Thermal Decomposition of Ionic Solids, Elsevier, Amsterdam 1999.
18 M. Reading, D. Dollimore, J. Rouquerol and F. Rouquerol, J. Thermal Anal., 29 (1984) 775.
19 T. Ozawa, J. Thermal Anal., 31 (1986) 547.
20 N. Koga, Thermochim. Acta, 258 (1995) 145.
21 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.
22 T. Ozawa, J. Thermal Anal., 2 (1970) 301.
23 T. Ozawa, Thermochim. Acta, 100 (1986) 109.
24 F. J. Gotor, J. M. Criado, J. Malek and N. Koga, J. Phys. Chem. A, 104 (2000) 10777.
25 J. M. Criado, L. A. Perez-Maqueda, F. J. Gotor, J. Malek and N. Koga, J. Therm. Anal. Cal., 72 (2003) 901.
26 D. M. Bates and D. G. Watts, Nonlinear Regression and its Applications, Wiley, New York 1988.
27 N. Koga, A. Mako, T. Kimizu and Y. Tanaka, Thermochim. Acta, 467 (2008) 11.
28 N. Koga, Thermochim. Acta, 244 (1994) 1.
29 A. K. Galwey and M. Mortimer, Int. J. Chem. Kinet., 38 (2006) 464.

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