

THERMAL DECOMPOSITION OF COPPER(II) AND ZINC CARBONATE HYDROXIDES BY MEANS OF TG-MS

Quantitative analyses of evolved gases

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For the quantitative analyses of evolved CO₂ and H₂O during the thermal decomposition of solids, calibration curves, i.e. the amounts of evolved gases vs. the corresponding peak areas of mass chromatograms measured by TG-MS, were plotted as referenced by the reaction stoichiometry of the thermal decomposition of sodium hydrogencarbonate NaHCO₃. The accuracy and reliability of the quantitative analyses of the evolved CO₂ and H₂O based on the calibration curves were evaluated by applying the calibration curves to the mass chromatograms for the thermal decompositions of copper(II) and zinc carbonate hydroxides. It was indicated from the observed ratio of evolved CO₂ and H₂O that the compositions of copper(II) and zinc carbonate hydroxides examined in this study correspond to mineral malachite, Cu₂CO₃(OH)₂, and hydrozincate, Zn₅(CO₃)₂(OH)₆, respectively. Reliability of the present analytical procedure was confirmed by the fairly good agreement of the mass fraction of the evolved gases calculated from the analytical values with the total mass-loss during the thermal decompositions measured by TG.

Keywords: copper(II) carbonate hydroxide, evolved gas, quantitative analysis, TG-MS, thermal decomposition, zinc carbonate hydroxide

Introduction

Transition metal carbonate hydroxides have widely been utilized as precursors for the various inorganic syntheses, because reactive and/or catalytic active fine particles of the metal oxides can be obtained through their thermal decompositions. Characterizations of the mechanisms and kinetic behaviors of the thermal decomposition are very important to obtain the fundamental information about controlling the morphology and physico-chemical properties of the product oxides [1]. In many cases, the thermal decompositions of transition metal carbonate hydroxides proceed through simultaneous decarbonation and dehydroxylation [2–5]. The separated characterization of the decarbonation and dehydroxylation processes can be performed by measuring the evolution rates and amounts of CO₂ and H₂O evolved during the thermal decomposition using an instrument of evolved gas analysis (EGA). A coupled technique of thermogravimetry (TG) and mass spectrometry (MS) is useful for this purpose, as has been applied for variety of systems [6, 7]. Because, in many TG-MS systems, only a portion of the evolved gases is transferred to the mass spectrometer and various fragment ions are produced by the ionization of the gaseous molecules, the evolved amount of a specific gas is related to the peak

area of the mass chromatogram for the corresponding fragment ion via a calibration constant [8].

In the present study, quantitative analyses of the evolved CO₂ and H₂O during the thermal decomposition of copper(II) carbonate hydroxide (CCH) and zinc carbonate hydroxide (ZCH) were made by means of TG-MS. Calibration curves between the amounts of evolved gases and the peak areas of the mass chromatograms for various fragment ions were constructed by using the TG-MS data for the thermal decomposition of NaHCO₃. Through the determination of the amounts of evolved CO₂ and H₂O during the thermal decomposition of CCH and ZCH using the calibration curves, the reliability of the present analytical procedure was evaluated.

Experimental

Materials

Reagent grade sodium hydrogencarbonate (Sigma Aldrich Japan, SG grade) was sieved to various fractions of particle size. The sample of a sieve fraction of 100~170 mesh was used as the reference sample for establishing the calibration curves for the quantitative analyses of evolved CO₂ and H₂O.

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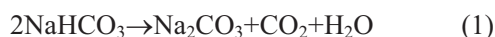
CCH and ZCH were prepared by titrating 1M CuSO₄ and 1M Zn(NO₃)₂ solutions by 1M Na₂CO₃ solution, respectively [2, 3, 9]. With mechanical stirring, the precipitates were aged in the mother liquor for 12 h. The precipitates were filtered off, washed with water and ethanol, and dried in air at 100°C.

Characterization of the precipitates

Contents of Cu²⁺ and Zn²⁺ in the precipitates of CCH and ZCH were determined by iodometry and chelatometry, respectively. Powder X-ray diffraction (XRD) measurements were carried out using a Rigaku RINT2200V diffractometer (Monochromed Cu-K_α, 40 kV, 20 mA). Infrared spectra of the precipitates were recorded on a Shimadzu FTIR-8100M spectrophotometer by the diffuse reflectance method.

Measurements of TG-MS

Various amounts of NaHCO₃ ranging from 1.0 to 5.0 mg were weighed onto a platinum cell (5 mm φ and 2.5 mm in height). Using a TG-MS instrument constructed by coupling a TG-DTA (Rigaku TG8120) with a quadrupole mass spectrometer (Anelva M-200QA), TG-DTA curves were recorded on heating at 10 K min⁻¹ under flowing He (200 mL min⁻¹), accompanied by continuous measurements of the mass spectra of the evolved gases (mass range: 10~50 amu, EMSN: 1.0 A, SEM: 1000 V). The recorded mass spectra were converted to mass chromatograms of the respective mass numbers. Calibration curves between the evolved amounts of CO₂ and H₂O determined by TG and the peak areas of the mass chromatograms for the respective fragment ions due to CO₂ and H₂O were drawn by assuming the following decomposition reaction of NaHCO₃.



TG-MS measurements for CCH and ZCH were also performed using ca. 5 mg of samples under the condition identical to that for the thermal decomposition of NaHCO₃. By measuring the peak areas of the mass chromatograms for the respective fragment ions, the evolved amounts of CO₂ and H₂O were determined using the calibration curves drawn for the thermal decomposition of NaHCO₃.

Results and discussion

Characterization of the samples

Prior to the quantitative analyses of evolved CO₂ and H₂O by TG-MS, CCH and ZCH were characterized

by chemical analyses for Cu²⁺ and Zn²⁺, XRD and FTIR. Figure 1 shows typical FTIR spectra for CCH and ZCH. The characteristic O–H stretching band centered at about 3300 cm⁻¹ and ν₃ mode of carbonate at around 1500 and 1390 cm⁻¹ [10] were observed for both the samples, indicating that the prepared samples are the basic carbonates.

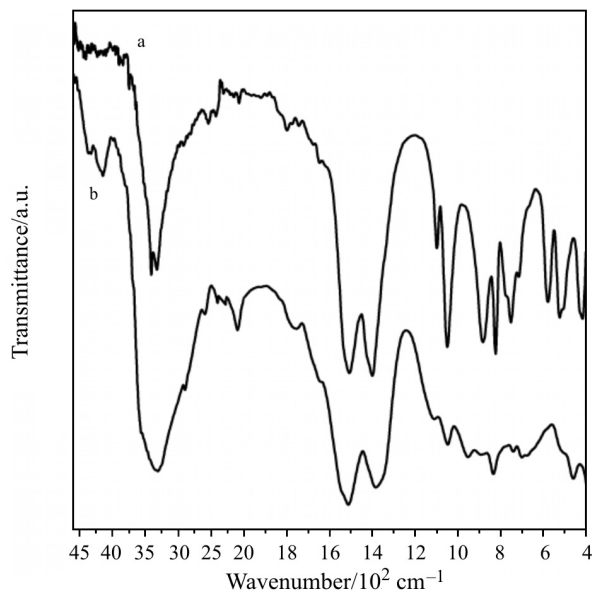


Fig. 1 Typical FTIR spectra for a – CCH and b – ZCH

Figure 2 shows typical XRD patterns for CCH and ZCH. The XRD pattern for CCH corresponding to mineral malachite, Cu₂CO₃(OH)₂ [11]. The content of Cu²⁺ determined by chemical analysis was 57.2±0.1%, which is in good agreement with the value calculated by assuming Cu₂CO₃(OH)₂, 57.5%. As for ZCH, all the major diffraction peaks correspond to either Zn₅(CO₃)₂(OH)₆ or Zn₄CO₃(OH)₆·H₂O phases [5, 12]. The content of Zn²⁺, 60.3±0.4%, shows a fairly good correspondence to the calculated values for Zn₅(CO₃)₂(OH)₆, 59.6%, and Zn₄CO₃(OH)₆·H₂O, 59.2%. The composition of ZCH prepared in the present study can not be determined only from the above results.

Calibration curves for the quantitative analyses of evolved CO₂ and H₂O

Figure 3 shows typical TG-DTA curves for the thermal decomposition of NaHCO₃, together with the mass chromatograms of various mass numbers. The total mass-loss due to the thermal decomposition was 36.8±0.1%, being in good agreement with the value of 36.9% calculated by assuming Eq. (1). During the thermal decomposition, the mass spectra indicated fragment ions at m/z=12, 16, 17, 18, 28, and 44. The

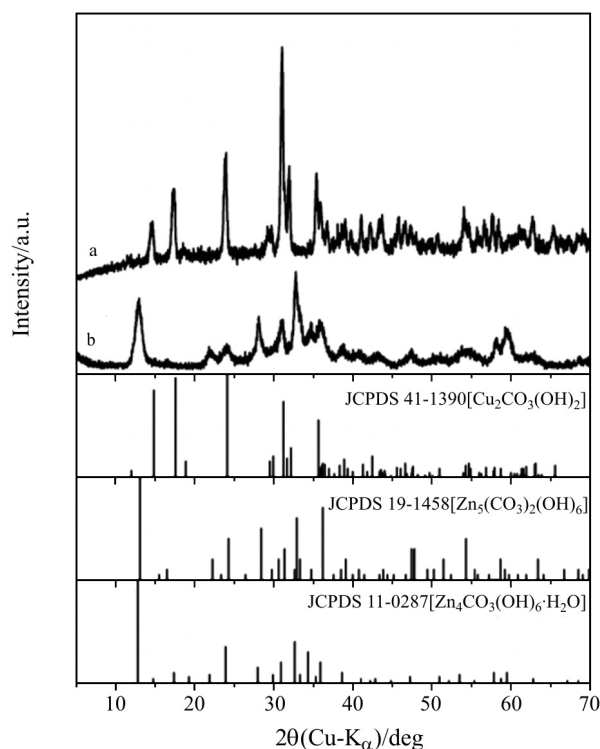


Fig. 2 Typical XRD patterns for a – CCH and b – ZCH

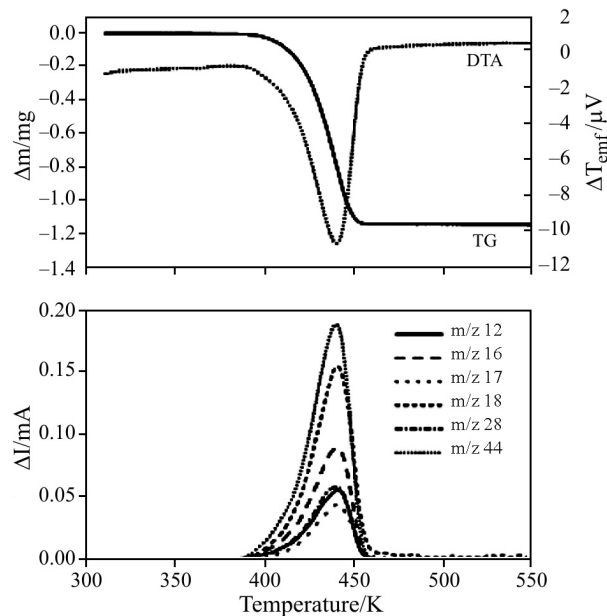


Fig. 3 Typical TG-DTA curves for the thermal decomposition of NaHCO_3 (3.10 mg), together with the mass chromatograms of various mass numbers

fragment ions at $m/z=12(\text{C}^+)$, $28(\text{CO}^+)$, and $44(\text{CO}_2^+)$ and at $m/z=17(\text{HO}^+)$ and $18(\text{H}_2\text{O}^+)$ can be ascribed to evolved CO_2 and H_2O , respectively. The fragment ion at $m/z=16(\text{O}^+)$ results from both the evolved CO_2 and H_2O . The peak maxima of the mass chromatograms of all the fragment ions correspond to the peak tempera-

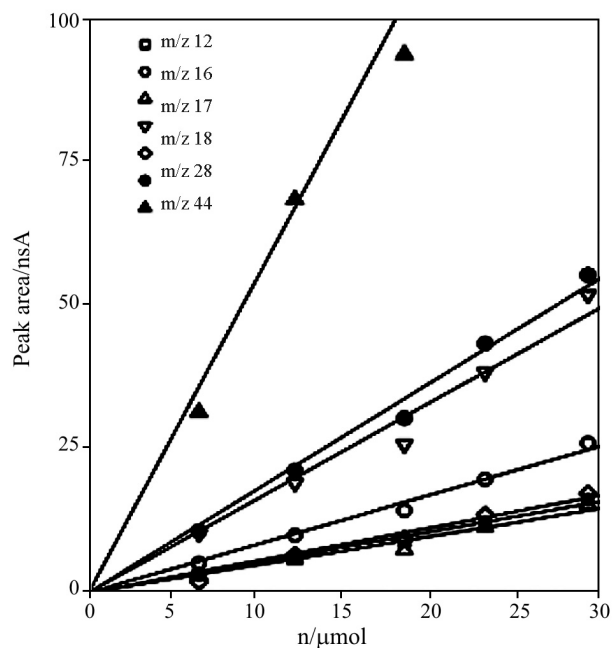


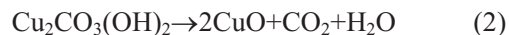
Fig. 4 Linear relationships between the evolved amounts of CO_2 and H_2O and the peak areas of mass chromatograms for various mass numbers, observed for the thermal decomposition of NaHCO_3

ture of DTA, indicating the simultaneous evolutions of CO_2 and H_2O .

By assuming Eq. (1), the amounts of evolved CO_2 and H_2O during the thermal decomposition of NaHCO_3 were calculated from the total mass-loss value observed by TG. Figure 4 shows the relations of peak area of mass chromatograms for the respective fragment ions to the evolved amount of CO_2 and H_2O during the thermal decomposition of NaHCO_3 . For all the fragment ions, linear relationships between the evolved amounts and the peak areas can be observed, which enable us to use the relationship as calibration curves for the quantitative analyses of evolved CO_2 and H_2O .

Quantitative analyses of evolved CO_2 and H_2O

Figure 5 shows typical TG-DTA curves for the thermal decomposition of CCH, together with the mass chromatograms of various mass numbers. The observed mass-loss due to the thermal decomposition, $28.7 \pm 0.3\%$, was in good agreement with the calculated value of 28.1% for the thermal decomposition of $\text{Cu}_2\text{CO}_3(\text{OH})_2$.



As is the case with the thermal decomposition of NaHCO_3 , all the mass chromatograms for the thermal decomposition of CCH indicated peak maxima at the peak temperature of DTA, indicating the simultaneous evolutions of CO_2 and H_2O .

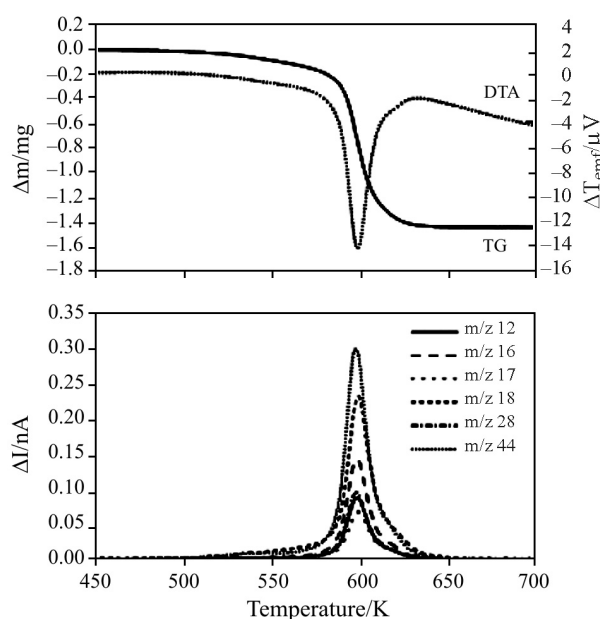
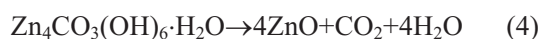


Fig. 5 Typical TG-DTA curves for the thermal decomposition of CCH (5.01 mg), together with the mass chromatograms of various mass numbers

Typical TG-DTA curves for the thermal decomposition of ZCH were shown in Fig. 6, together with the mass chromatograms of various mass numbers. The mass-loss due to the thermal decomposition of ZCH observed by TG, $26.4 \pm 0.4\%$, corresponds to either the case of assuming the following two reactions, i.e. 25.9 and 26.3%, respectively.



Although all the mass chromatograms of different fragment ions indicated maxima at the same temperature with the DTA peak, the water vapor tends to be evolved at a larger relative rate to that of CO_2 evolution at the early stage and the final stage of the de-

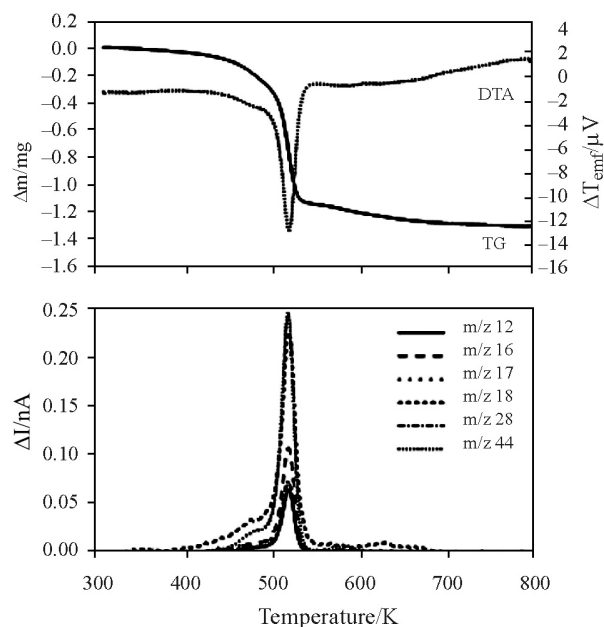


Fig. 6 Typical TG-DTA curves for the thermal decomposition of ZCH (4.95 mg), together with the mass chromatograms of various mass numbers

composition, which may imply a more complicated kinetic behavior of the thermal decomposition of ZCH than that of CCH.

Table 1 lists the results of quantitative analyses of evolved CO_2 and H_2O during the thermal decompositions of CCH and ZCH, determined by assuming the calibration curves shown in Fig. 4. As for the thermal decomposition of CCH, the ratio of evolved CO_2 and H_2O was determined as $n(\text{CO}_2)/n(\text{H}_2\text{O})=1.01$, being in good agreement with the reaction stoichiometry of Eq.(2). The total mass fraction of evolved CO_2 and H_2O vs. the reactant mass determined from the quantitative analyses was 28.3%, which corresponds to the total mass-loss fraction observed by TG, $28.7 \pm 0.3\%$, and that calculated for Eq. (2), 28.1%.

Table 1 The amounts of evolved CO_2 and H_2O during the thermal decompositions of CCH and ZCH

| (a) copper(II) carbonate hydroxide (CCH) | | | |
|--|---|------------|--|
| <i>m/z</i> | $n(\text{CO}_2) / \text{mol (g sample)}^{-1}$ | <i>m/z</i> | $n(\text{H}_2\text{O}) / \text{mol (g sample)}^{-1}$ |
| 12 | $(4.50 \pm 0.15) \times 10^{-3}$ | 17 | $(4.50 \pm 0.12) \times 10^{-3}$ |
| 28 | $(4.65 \pm 0.23) \times 10^{-3}$ | 18 | $(4.57 \pm 0.28) \times 10^{-3}$ |
| 44 | $(4.57 \pm 0.34) \times 10^{-3}$ | | |
| average | $(4.57 \pm 0.23) \times 10^{-3}$ | average | $(4.53 \pm 0.20) \times 10^{-3}$ |
| (b) zinc carbonate hydroxide (ZCH) | | | |
| <i>m/z</i> | $n(\text{CO}_2) / \text{mol (g sample)}^{-1}$ | <i>m/z</i> | $n(\text{H}_2\text{O}) / \text{mol (g sample)}^{-1}$ |
| 12 | $(3.72 \pm 0.07) \times 10^{-3}$ | 17 | $(5.52 \pm 0.17) \times 10^{-3}$ |
| 28 | $(3.75 \pm 0.10) \times 10^{-3}$ | 18 | $(5.70 \pm 0.07) \times 10^{-3}$ |
| 44 | $(3.70 \pm 0.16) \times 10^{-3}$ | | |
| average | $(3.72 \pm 0.10) \times 10^{-3}$ | average | $(5.61 \pm 0.15) \times 10^{-3}$ |

The ratio of evolved CO₂ and H₂O during the thermal decomposition of ZCH was determined to be $n(\text{CO}_2)/n(\text{H}_2\text{O})=0.664$, supporting the reactant composition of hydrozincate, Zn₅(CO₃)₂(OH)₆, and the decomposition reaction of Eq. (3). Finally, the composition of ZCH synthesized in the present work was determined as Zn₅(CO₃)₂(OH)₆ from the results of quantitative analyses of evolved CO₂ and H₂O. The total mass fraction of evolved CO₂ and H₂O with reference to the reactant mass was calculated from the analytical values as 26.5%. The fairly good correspondence to both the observed mass-loss by TG, 26.4±0.4%, and the calculated mass-loss for Eq. (3), 25.9%, indicate a strictly quantitative relationship of the present analytical procedure for determining evolved CO₂ and H₂O during the thermal decomposition.

Conclusions

The linear relationships between the evolved amounts of CO₂ and H₂O and the peak areas of mass chromatograms for the corresponding fragment ions were obtained by TG-MS measurements for the thermal decomposition of NaHCO₃, which can be utilized as calibration curves for the quantitative analyses of evolved CO₂ and H₂O during the thermal decomposition of basic metal carbonates. By applying the calibration curve method to the determination of the amounts of evolved CO₂ and H₂O during the thermal decompositions of CCH and ZCH prepared in the present study, the ratios of evolved amounts, $n(\text{CO}_2)/n(\text{H}_2\text{O})$, were determined as 1.01 and 0.664 for the copper(II) and zinc salts, respectively. The ratios support the expected compositions of CCH and ZCH which correspond to mineral malachite, Cu₂CO₃(OH)₂, and hydrozincate, Zn₅(CO₃)₂(OH)₆, respectively. For both the samples, the analytical value of total mass fraction of evolved CO₂ and H₂O vs. the sample mass was in good agreement with the mass-loss fraction observed on TG and the calculated values by assuming the respective com-

positions, which implies strictly quantitative relationship of the present analytical procedure for determining the amounts of evolved CO₂ and H₂O during the thermal decomposition of solids.

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