ELSEVIER
Thermochimica Acta 352–353 (2000) 53–60
thermochimica acta
www.elsevier.com/locate/tca

TG-DTA-MS of chromium(III) formate☆

Tadashi Arii[a], Yutaka Sawada[b,*], Kiyokata Iizumi[b], Katsuya Kudaka[b], Shigeyuki Seki[b]

[a]*Thermal Analysis Division, Rigaku Corporation, 3-9-12 Matsubara-cho, Akishima-shi, Tokyo 196-8666, Japan*
[b]*Department of Applied Chemistry, Faculty of Engineering, Tokyo Institute of Polytechnics, 1583 Iiyama, Atsugi-shi, Kanagawa 243-0297, Japan*

Received 2 June 1999; received in revised form 20 August 1999; accepted 6 September 1999

Abstract

The thermal decomposition of chromium(III) formate pentahydrate, $Cr_3(OH)_2(HCO_2)_7{\cdot}5H_2O$, in helium atmosphere and 20% O_2 in helium atmosphere has been successfully studied by means of TG-DTA-MS, i.e., thermogravimetry-differential thermal analysis (TG-DTA) coupled with evolved gas analysis (EGA) using mass spectrometry (MS). The TG-DTA-MS is useful to interpret the complicated successive reactions and to determine the mechanism of the thermal decomposition. The thermal process in He atmosphere proceeded by four steps, while in 20% O_2–He atmosphere it proceeded by three steps. The decomposition scheme of $Cr_3(OH)_2(HCO_2)_7{\cdot}5H_2O$ in He atmosphere was proposed by the following decomposition mechanism via formation of three intermediates:

$$Cr_3(OH)_2(HCO_2)_7 \cdot 5H_3O \rightarrow Cr_3(OH)_2(HCO_2)_7 \cdot 2H_2O + 3H_2O$$

$$Cr_3(OH)_2(HCO_2)_7 \cdot 2H_2O \rightarrow Cr_3(OH)_2(HCO_2)_7 + 2H_2O$$

$$Cr_3(OH)_2(HCO_2)_7 \rightarrow Cr_2O_3 + Cr(HCO_2)_3 + CO + 3CO_2 + 3H_2$$

$$2Cr(HCO_2)_3 \rightarrow Cr_2O_3 + 3CO + 3CO_2 + 3H_2.$$

After the decomposition, a slight mass loss was observed with a sharp exothermic crystallization of Cr_2O_3 due to evolution of H_2. In 20% O_2–He atmosphere, a drastic exothermic mass loss accompanying evolution of CO_2, H_2O and H_2 was explicable by one step combustion of the dehydrated formate, and a small amount of mass loss observed with a crystallization of Cr_2O_3 was attributed to evolution of O_2. The decomposition process without an intermediate was indicated by the temperature increase of the specimen produced by combustion heat.

Keywords: Simultaneous thermogravimetry; Differential thermal analysis and mass spectrometry (TG-DTA-MS); Thermal decomposition; Chromium(III) oxide (Cr_2O_3); Decomposition mechanism

1. Introduction

Chromium(III) formate consists of complex salt structures and is known as the structures of $Cr(HCO_2)_3{\cdot}6H_2O$, $Cr_3(OH)_2(HCO_2)_7{\cdot}5H_2O$ and

---

☆ A paper presented at the 2nd International and the 4th Japan–China Joint Symposium on Calorimetry and Thermal Analysis, 1–3 June 1999, Tsukuba, Japan (CATS 99)

* Corresponding author. Fax: +81-46-242-9532.
E-mail address: sawada@chem.t-kougei.ac.jp (Y. Sawada)

PII: S0040-6031(99)00437-2

$Cr_3(HCO_2)_9{\cdot}6H_2O$. Chromium(III) formate pentahydrate, $Cr_3(OH)_2(HCO_2)_7{\cdot}5H_2O$, is one of the preferable raw materials to obtain fine powdered chromium(III) oxide Cr_2O_3, which are highly reactive and sinterable during the solid-state reaction and the densification, for the production of the chromia ceramics such refractories, humidity sensors, varisters etc. Iizumi et al. reported that the decomposition in air proceeds via a dehydrated phase and terminated with a sharp exothermic phenomenon [1]. It has been established that the four water molecules in the sample dehydrate at 100–105°C [2].

Both thermogravimetry (TG) and differential thermal analysis (DTA) are widely used to study the thermal decomposition of various materials. Since such major thermal analysis techniques provide physical information, ancillary data is required for chemical interpretation of the observed thermal events. Moreover, it has been recognized by many researchers using thermal analysis that the experimental conditions will considerably affect results of thermoanalytical methods. To uncover the underlying mechanisms in such decomposition process it is highly advantageous to employ complementary experimental techniques in an in-situ manner, and so ambiguities in data interpretation are generally much reduced. For this reason, there is increased interest in hyphenated techniques such as themogravimetric-fourier transform infrared spectroscopy (TG-FTIR) and TG-mass spectrometry (TG-MS), where the experimental results are displayed in three dimensions such as the temperature, the mass number and the abundance [3–7]. In other words, this means that it is essential to determine simultaneously chemical species of the evolving gas products. TG-MS is most effective method to sensitively identify the volatile products formed during thermal decomposition and makes it possible to determine the mechanism kind of decomposition process more exactly.

First of all we focus on the interpretation of the actual decomposition mechanism of $Cr_3(OH)_2(HCO_2)_7{\cdot}5H_2O$. In the present work, we analyze the thermal decomposition process in more detail by TG-DTA-MS (simultaneous measurement of thermogravimetry, differential thermal analysis and mass spectrometry) in helium atmosphere and 20% oxygen in helium mixture (20% O_2–He) atmosphere. Then, we demonstrate the effectiveness of this simultaneous measuring method, and discuss the difference of the decomposition mechanisms with atmosphere.

2. Experimental

$Cr_3(OH)_2(HCO_2)_7{\cdot}5H_2O$ (Nakarai Tesque, regent grade) was used as received. The results of the compositional analysis for chromium, carbon and hydrogen (25.8, 14.2 and 3.0 mass%, respectively) agreed approximately with the value expected from the formula (26.2, 14.1 and 3.2 mass%, respectively).

Thermal properties of the sample was determined by a Rigaku Thermo Plus TG-DTA 8120 apparatus at the following conditions: starting temperature; 25°C, sample crucible; platinum, sample weight; ca. 10 mg, heating rate; 10°C min^{-1}, atmosphere; dry He and 20% O_2–He mixture, flow rate; 300 ml min^{-1}.

Evolved gas analysis was performed by set up consisting of the TG-DTA connected to a Rigaku Thermo Mass M-QA200TS system. The carrier gas from the furnace of the thermobalance was led to MS through a 1 m long fussed silica capillary with the internal diameter of 0.075 mm. Capillary was heated to 250°C to prevent condensation. Ion source of the quadrupole mass spectrometer (Q-MS) consists of a thoria-coated iridium filament to prevent oxidation-deterioration. This Q-MS was operated in the electron-bombardment ionization (70 eV) mode and the m/z ranging from 1 to 50 which enabled the detection of hydrogen ions (H^+) and molecules ($H_2{}^+$) evolved from the sample. Low background pressure of nitrogen (m/z 28) and water vapor was achieved so that carbon monoxide (m/z 28) and water vapor evolved from the sample was successfully evaluated. NIST/EPA/NIH chemical and structural database was used to assign the mass spectrum of an evolved unknown compound. Additionally, X-ray diffraction (XRD) analysis was performed to identify the crystalline phases and to determine the crystallinity. The specimens were quenched quickly from the TG-DTA apparatus at the predetermined temperatures.

The XRD spectra of the samples were obtained using a Rigaku/RINT2500 X-ray diffractometer. Cu Ka radiation (λ=1.5405 Å) with a graphite monochromator was used for the measurements. A line shape X-ray source was operated at 60 kV and 300 mA, and the data were collected in the range of

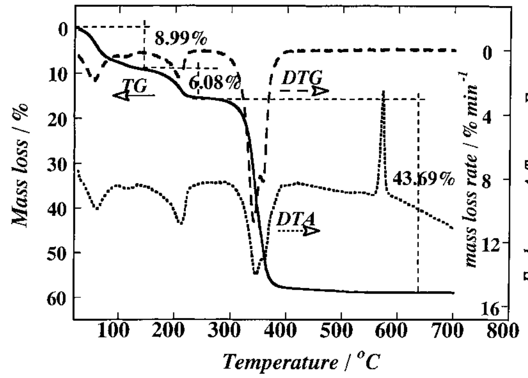

Fig. 1. TG-(DTG)-DTA for thermal decomposition of $Cr_3(OH)_2(HCO_3)_7{\cdot}5H_2O$ in He.

$3<2\theta<100$ with an interval of 0.02° and a scan speed of 4 min^{-1}.

3. Results

3.1. In He atmosphere

Fig. 1 shows the TG, DTG and DTA curves for the thermal decomposition of $Cr_3(OH)_2(HCO_2)_7{\cdot}5H_2O$ in He atmosphere. The total mass loss at 700°C was 58.76%, and the thermal decomposition was roughly divided into the three steps. Fig. 2 shows the three-dimensional representation of TG-DTA-MS data. The change of fragment ions in the mass spectra for the evolved gasses was clearly observed during the several decomposition stages and suggested that the different species evolved simultaneously. The results of TG-DTA-MS and the mass spectra during the endothermic mass losses at 60.2 and 209.7°C (8.99 and 6.08%) are shown in Fig. 3. The total ion current (TIC) of *m/z* 1–50 was indicated in the figure after subtracting the background (the TIC before heating). The TG and DTA curves were in good correspondence with the TIC curve. The mass spectra observed at these peak-top temperatures were recognized to be similar to each other. Evolution of water vapor was indicated by the simultaneous detection of *m/z* 18 (H_2O^+), 17 (OH^+) and 1 (H^+), whose intensity (ion current) ratios are approximately constant. The *m/z* 1 is not cited in the NIST database[1]. In the present work, the intensity

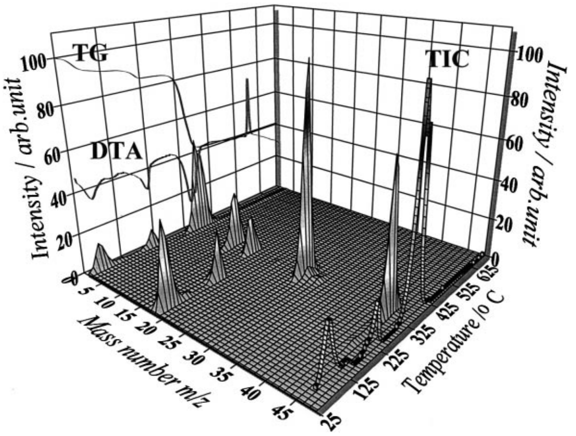

Fig. 2. Three-dimensional representation of TG-DTA-MS data for thermal decomposition of $Cr_3(OH)_2(HCO_3)_7{\cdot}5H_2O$ in He.

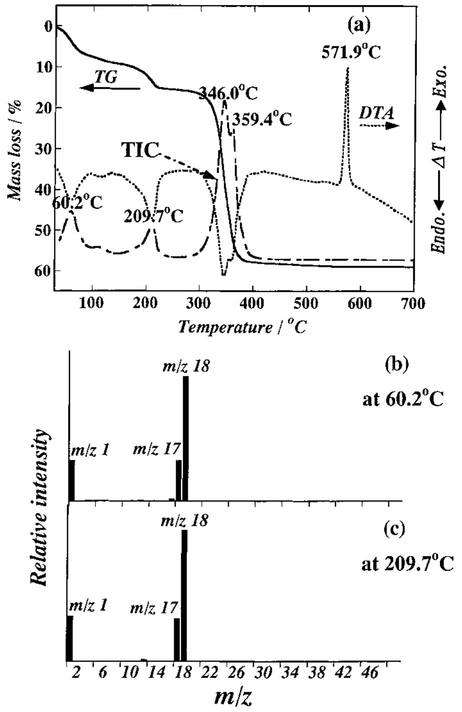

Fig. 3. Overall TG, DTG, DTA and TIC curves and mass spectra observed at 60.2 and 209.7°C corresponding to first two mass losses for thermal decomposition in He. (a) TG-DTA and TIC curves, (b) mass spectrum at 60.2°C, (c) mass spectrum at 209.7°C.

---

[1] Entry No. 4, NIST 107 (H_2O).

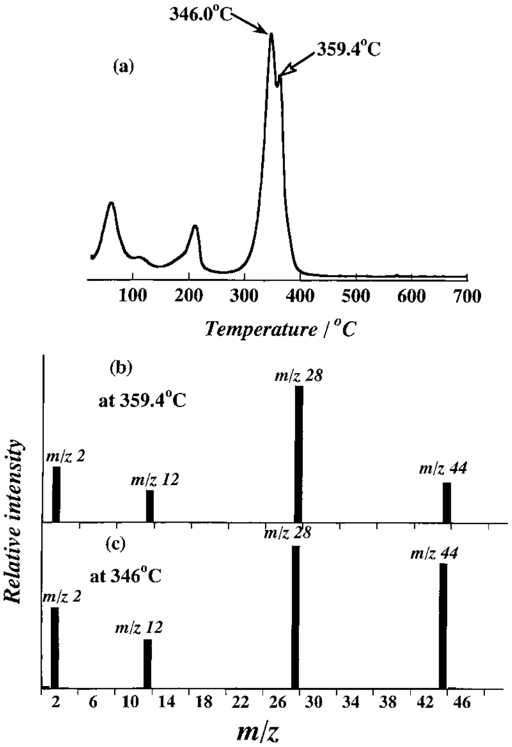

Fig. 4. Mass spectra at 346.0 and 359.4°C in the TIC for the evolved gases during the decomposition of chromium formate anhydrate. (a) TIC curve, (b) mass spectrum at 359.4°C, (c) mass spectrum at 346.0°C.

ratio of $[OH^+]/[H_2O^+]$ (approximately 30.2%) is higher than that of reference spectra (21.2%) reported in the NIST database. The difference should be attributed to the difference of instrument.

The results of mass spectra at each DTA peak temperatures (346.0°C and 359.4°C) during the endothermic mass losses (total amount; 43.69%) are shown in Fig. 4. Also, apparent two peaks were recognized in the TIC curve for this decomposition stage synchronizing with the TG-DTA curve. The mass spectra observed at these peak temperatures seem to be similar to each other, except that the ion ratio of *m/z* 28 (CO^+) to *m/z* 44 ($CO_2{}^+$) changed. Simultaneous evolution of carbon monoxide (*m/z* 12, 16 and 28)[2], carbon dioxide (*m/z* 16, 28 and 44)[3] and hydrogen (*m/z* 2) was clearly detected. Here, evolution of carbon monoxide was supported by the detection of *m/z* 12 and the intensity of the *m/z* 28 higher than that of the fragmentation of *m/z* 44. Evolution of water vapor (*m/z* 17 and 18) was not recognized during this stage.

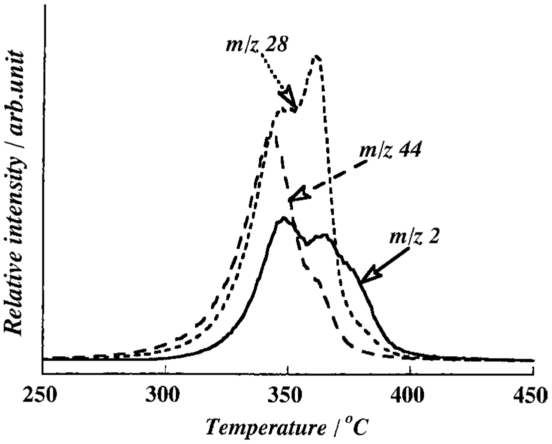

Fig. 5. Mass chromatogram curves of *m/z* 2(H_2), 28(CO), and 44(CO_2) ions depicted based on the mass spectra in Fig. 4.

Fig. 5 shows the mass chromatogram curves extracted from the mass spectra in Fig. 4. Evolution of hydrogen, carbon monoxide and carbon dioxide was approximately simultaneous but not synchronized completely. The peak-top temperatures for the evolved gases are as follows:

342°C: CO_2
347°C: H_2 and CO
360°C: CO
364°C: H_2.

TG-DTA curves and the mass chromatogram curve of hydrogen ion (*m/z* 2) around a sharp exothermic DTA phenomenon (571.9°C) are indicated in Fig. 6. A small amount of mass loss (0.04%) was observed and also evolution of hydrogen (*m/z* 2) was clearly detected.

3.2. In 20% O_2 in He atmosphere

Fig. 7 shows the TG, DTG and DTA curves in 20% O_2–He flow for the thermal decomposition of $Cr_3(OH)_2(HCO_2)_7{\cdot}5H_2O$. The thermal decomposition was terminated at 500°C and the total mass loss was calculated as 57.27%. First two endothermic mass

---

[2] Entry No. 8, NIST 107 (CO).

[3] Entry No. 36, NIST 107 (CO_2).

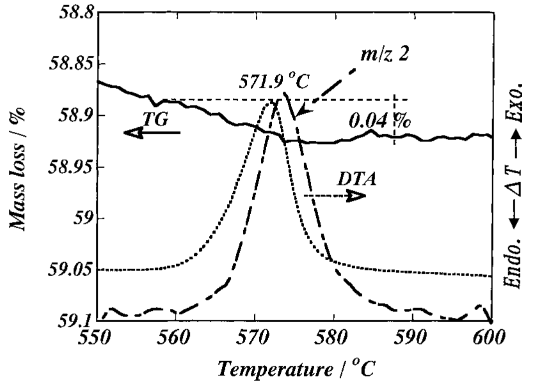

Fig. 6. Enlargement of TG-DTA and mass chromatogram of hydrogen (m/z 2) around a crystallization of Cr_2O_3 (570°C).

losses were approximately identical to those obtained in He atmosphere, i.e., evolution of water vapor. However, a small amount of carbon dioxide was detected during the second endothermic mass loss as shown in Fig. 8. The each dehydration was shifted to higher temperatures than that in He atmosphere.

A steep mass loss (43.92%) accompanied with a remarkable exothermic DTA peak (310°C) was observed. The specimen temperature increased by 50°C. The results of TG-DTA-MS and the mass spectrum for the evolved gas during the exothermic mass loss are shown in Fig. 9: here, detection of m/z 16(O^+) and 32(O_2^+) ions evolved from the sample were virtually impossible, because these ions were saturated in the ionization chamber by high partial pressure of O_2 in the atmosphere. Hydrogen, water vapor and carbon dioxide were detected simultaneously. The existence of carbon monoxide seems to be predictable, because the intensity ratio of $[CO^+]/[CO_2^+]$ was apparently higher than that of individual carbon dioxide.

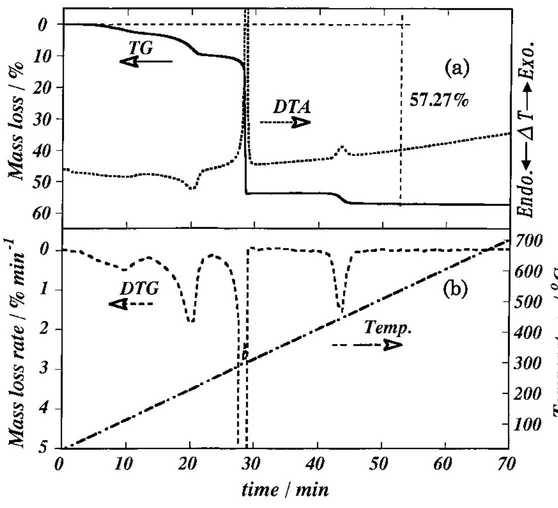

Fig. 7. TG-(DTG)-DTA for thermal decomposition of $Cr_3(OH)_2(HCO_3)_7{\cdot}5H_2O$ in 20% O_2–He. (a) TG-DTA curves, (b) temperature and DTG curves.

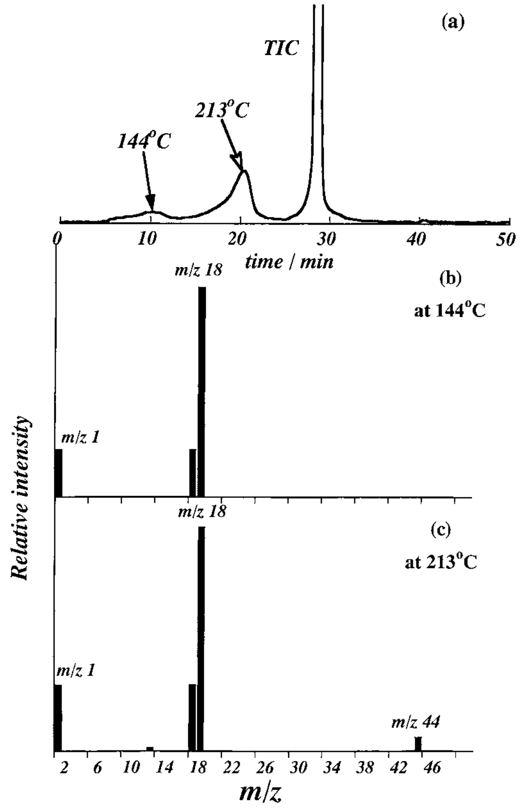

Fig. 8. Mass spectra at 114 and 213°C in TIC corresponding to first two mass losses for thermal decomposition in 20% O_2–He. (a) TIC curve, (b) mass spectrum at 114.0°C, (c) mass spectrum at 213.0°C.

An exothermic mass loss (3.25%) at 442.3°C occurred at lower temperature than that (571.9°C) in He atmosphere and with more mass loss than that (0.04%) in He atmosphere. As shown in Fig. 9, however, ions of the evolution gas components that should be corresponding to this exothermic mass loss could not be detected in the TIC.

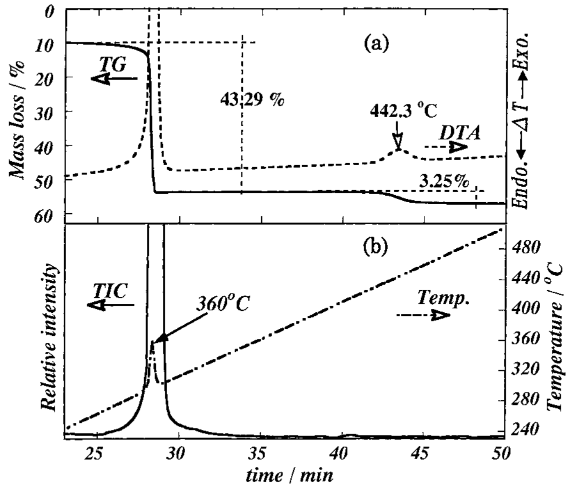

Fig. 9. Results of TG-DTA-MS and mass spectrum at 360°C in TIC during thermal decomposition of chromium formate anhydrate in 20% O_2–He. (a) TG-DTA curves, (b) temperature and TIC curves.

4. Discussions

4.1. Decomposition in He atmosphere

In order to clarify the decomposition mechanism, the mass loss during each decomposition process should be characterized by the identified evolution components. In the first two stages, the mass losses accompanying the DTA peaks (60.2 and 209.7°C) were estimated to 8.99 and 6.08%. These experimental values agreed closely with the theoretical values corresponding three (9.08%) and two water molecules (6.06%), respectively, and thus the dehydration products of each stage will be $Cr_3(OH)_2(HCO_2)_7{\cdot}2H_2O$ and $Cr_3(OH)_2(HCO_2)_7$, respectively. The most probable thermal decomposition scheme is:

$$Cr_3(OH)_2(HCO_2)_7 \cdot 5H_2O \rightarrow Cr_3(OH)_2(HCO_2)_7 \cdot 2H_2O + 3H_2O \quad (1)$$

$$Cr_3(OH)_2(HCO_2)_7 \cdot 5H_2O \rightarrow Cr_3(OH)_2(HCO_2)_7 \cdot 2H_2O \quad (2)$$

From the TG curve on the third mass loss, the thermal decomposition of the chromium formate anhydrate will be corresponded to a single decomposition stage, and the following reaction was derived from evolution of hydrogen, carbon monoxide and carbon dioxide.

$$2Cr_3(OH)_2(HCO_2)_7 \rightarrow 3Cr_2O_3 + 5CO + 9CO_2 + 9H_2 \quad (3)$$

The following reaction is impossible because water vapor was not detected;

$$2Cr_3(OH)_2(HCO_2)_7 \rightarrow 3Cr_2O_3 + nH_2O + 5CO + (9-n)CO_2 + (9-n)H_2 \quad (n = 1-4) \quad (4)$$

The total mass loss (43.69%) in this stage was smaller than that of the theoretical mass loss (46.57%) calculated from the evolved components, i.e., carbon monoxide, carbon dioxide and hydrogen. The difference may be attributed to the proportion of carbonized residue that remained in Cr_2O_3 by carbonization.

However, from DTG, DTA and TIC curves during this stage implied that the decomposition consists of two overlapping reactions, i.e., the thermal decomposition progressed through the formation of intermediate. The mass spectra obtained at two overlapping reaction (346.0 and 359.4°C) are shown in Fig. 4. As the intensity of m/z 28 (CO) ions obtained at 359.4°C is compared with that at 346.0°C, an increase of CO amounts in later reaction (359.4°C) is remarkable. Additionally, the mass losses could be approximately divided to the proportion of 6:4. Consequently, we can deduce from these data that a different type of dehydrated chromium(III) formate $Cr(HCO_2)_3$ as the intermediate formed in the course of decomposition process.

From this finding, the most probable decomposition scheme of $Cr_3(OH)_2(HCO_2)_7$ was suggested as follows:

$$Cr_3(OH)_2(HCO_2)_7 \rightarrow Cr_2O_3 + Cr(HCO_2)_3 + CO + 3CO_2 + 3H_2 \quad (5)$$

$$2Cr(HCO_2)_3 \rightarrow Cr_2O_3 + 3CO + 3CO_2 + 3H_2 \quad (6)$$

the theoretical mass losses at steps (5) and (6) are 27.90 and 18.66%, respectively, and agreed approximately with the proportions of the divided mass losses (6:4) above-mentioned, and also evolution amount of CO (m/z 28) increased by step (6).

The last evolution of hydrogen (peak top temperature 571.9°C) occurred at higher temperature than the other gases, which indicated that hydrogen element existed as some inorganic condensed matter, discussed in Section 4.2.

4.2. A sharp exothermic phenomenon at 571.9°C in He atmosphere

Crystallization Cr_2O_3 from the amorphous phase is interpreted to be the sharp exothermic phenomenon by which hydrogen incorporated in the amorphous phase seemed to evolve. This crystallization phenomenon was supported by the unambiguous change of XRD spectra for the samples quenched before and after the temperatures of the sharp exothermic phenomenon. A water vapor from oxidation of hydrogen was not detected, so this implied that the amount of residual oxygen in the atmosphere is extremely small.

4.3. Decomposition in 20% O_2 in He atmosphere

A part of the evolved hydrogen was expected to be oxidized in the 20% O_2–He flow to cause water vapor, which was not detected in He atmosphere. Carbon monoxide should be partly oxidized to increase the amount of carbon dioxide. The temperature jump (correspond to exothermic peak at 310°C) was explained by the heat of oxidation (combustion) by which the decomposition was accelerated.

A crystallization phenomenon (443.3°C) occurred at lower temperature than that (571.9°C) in He atmosphere. Since the evolution gases correspond to the mass loss (3.25%) at 442.3°C could not be detected, undetected gas species, i.e., concealed oxygen into the atmosphere was suggested. Conceivably, the amorphous product formed by the vigorous combustion contained oxygen with the supersaturated conditions by incorporating oxygen element, and the observed mass loss seemed to correspond to release with the crystallization. In order to clarify this conjecture, the sample quenched after the third decomposition stage in 20% O_2–He atmosphere was re-heated in He atmosphere. TG-DTA-MS data are shown in Fig. 10. The mass loss of 3.25% caused by the crystallization was attributed to evolution of oxygen (*m*/*z* 16 and 32) and a small amount of water vapor, so the results have substantiated above hypothesis.

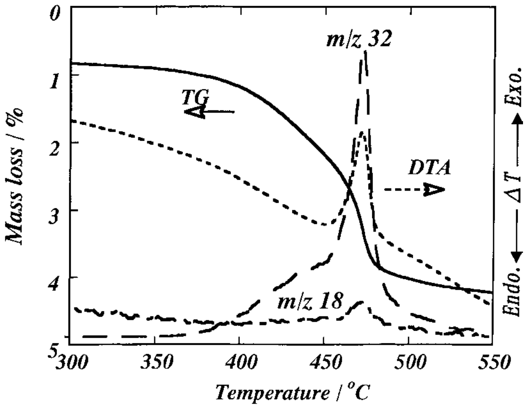

Fig. 10. Overall TG, DTA and extracted mass chromatogram of *m*/*z* 32 and mass spectra at TIC peak during the mass loss with the crystallization in He. The quenched intermediate specimen after the thermal decomposition of chromium formate anhydrate in 20% O_2–He was used.

The total experimental mass loss of 47.17% (43.92+3.25%) from $Cr_3(OH)_2(HCO_2)_7$ to crystal Cr_2O_3 agreed excellently with the theoretical mass loss (46.57%).

5. Conclusions

The thermal decomposition of $Cr_3(OH)_2(HCO_2)_7{\cdot}5H_2O$ to form Cr_2O_3 was investigated in both atmospheres of He and 20% O_2–He by means of TG-DTA-MS.

In He atmosphere, the thermal process consisted of apparent four steps. First, two endothermic mass losses with evolution of water vapor occurred at 60.2 and 210.7°C. The decomposition of the chromium(III) formate anhydrate in the third stage occurred by the endothermic mass losses at 346.0 and 359.4°C accompanying evolution of hydrogen, carbon monoxide and carbon dioxide. Since the close-lying reactions in this stage took place successively, it was virtually difficult to elucidate the decomposition mechanism by simple TG-DTA. The analysis of simultaneous evolved gases using MS was effective to determine the intermediate product that existed in the course of such complicated decomposition. The formula for the present intermediate formed during the overlapping reactions was estimated to be $Cr(HCO_2)_3$

by which the following reaction mechanism was formulated satisfactorily:

$$\mathrm{Cr_3(OH)_2(HCO_2)_7\cdot 5H_2O} \rightarrow \mathrm{Cr_3(OH)_2(HCO_2)_7\cdot 2H_2O + 3H_2O}$$

$$\mathrm{Cr_3(OH)_2(HCO_2)_7\cdot 2H_2O} \rightarrow \mathrm{Cr_3(OH)_2(HCO_2)_7 + 2H_2O}$$

$$\mathrm{Cr_3(OH)_2(HCO_2)_7} \rightarrow \mathrm{Cr_2O_3 + Cr(HCO_2)_3 + CO + 3CO_2 + 3H_2}$$

$$\mathrm{2Cr_3(OH)_2(HCO_2)_3} \rightarrow \mathrm{Cr_2O_3 + 3CO + 3CO_2 + 3H_2}$$

The mass loss of 0.04% with the rapid exothermic crystallization at 571.9°C after the decomposition was attributed to evolution of hydrogen.

In 20% O_2–He atmosphere, the decomposition of the anhydrous formate occurred by the exothermic (combustion) mass loss at 300°C accompanying evolution of hydrogen, water vapor, carbon monoxide and carbon dioxide. It was demonstrated that the mass loss of 3.25% with the exothermic crystallization occurred accompanied by evolution of oxygen.

References

[1] K. Iizumi, Y. Hukuchi, K. Kudaka, M. Ogawa, S. Okada, in: Proceedings of the 35th IUPAC Congress, Abs. II, Istanbul, 1995, pp. 143.

[2] Encylopaedia Chimica 2, Kyoristu Shuppan, 1965, pp. 706–707.

[3] E.K. Gibson Jr, S.M. Jonson, Thermochimca Acta 4 (1972) 49.

[4] J. Chiu, A.J. Battie, Thermochimica Acta 50 (1981) 49.

[5] T. Arii, T. Senda, N. Fujii, Thermochimica Acta 267 (1995) 209.

[6] M. Mittleman, Thermochimica Acta 166 (1990) 301.

[7] R. Kinoshita, Y. Teramoto, T. Nakano, H. Yoshida, J. Thermal Anal. 38 (1992) 1891.