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Preparation, microstructure and electrical property of (Co + CoO) mixture by thermal decomposition of $[Co(NH_3)_6](C_2O_4)_2{\cdot}4H_2O$

Susumu Nakayama [a,*], Masatomi Sakamoto [b]

[a] *Department of Applied Chemistry and Biotechnology, Niihama National College of Technology, Niihama 792-8580, Japan*
[b] *Department of Material and Biological Chemistry, Faculty of Science, Yamagata University, Yamagata 990-8560, Japan*

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Abstract

The thermal decomposition of hexaamminecobalt(III) oxalate tetrahydrate, $[Co(NH_3)_6](C_2O_4)_2{\cdot}4H_2O$, was investigated in a helium stream. The decomposition occurs in three steps. TG, IR and XRD analyses revealed that the anhydrate, the cobalt (II) oxalate, CoC_2O_4, and the (Co + CoO) mixture are formed in the range of 165 to 175°C, 250 to 270°C and above 330°C, respectively. SEM photographs and XRD results of the final (Co + CoO) mixture showed that the Co-component is rich near the upper part and the CoO-component is rich in the lower part. Specific surface areas and electrical resistivities of decomposition products are also reported.

Keywords: Hexaamminecobalt(III) oxalate; Thermal decomposition; Metallic cobalt; Cobalt(II) oxide

1. Introduction

A mixture of metallic cobalt and cobalt (II) oxide is known to form by the thermal decomposition of cobalt(II) oxalate under anaerobic condition. In fact, we have confirmed that the thermal decomposition of $CoC_2O_4{\cdot}2H_2O$ in a helium atmosphere gives a (1 + 1) mixture of Co and CoO as a final product above 300°C, where the formation of metallic Co is owing to the presence of oxalate groups as a reducing agent. We previously reported also that the {2Co + 2CoO + 3(Zr,Hf)O_2} mixture and the {Co + CoO + (Zr,Hf)O_2} mixture can be obtained as the final products when double complex salts, $[Co(NH_3)_{6-n}(H_2O)_n]_4[(Zr,Hf)(C_2O_4)]_3{\cdot}mH_2O$ ($n = 0$, 1 or 2) and $[CoX(NH_3)_5]_2[(Zr,Hf)(C_2O_4)_4]{\cdot}mH_2O$ (X = NO_3, NO_2 or NCS), are thermally decomposed in a helium stream, respectively [1,2]. Such (metal + metal oxide) mixtures are very interesting to the development of functional materials such as the Ni-YSZ (Y_2O_3 stabilized ZrO_2) cermet fuel-electrode of SOFC (solid oxide fuel cell) [3,4].

In the present work, the thermal decomposition of $[Co(NH_3)_6]_2(C_2O_4)_3{\cdot}4H_2O$ was undertaken in a helium stream, in order to investigate whether the (Co + CoO) mixture can be prepared from the more simple complex or not.

2. Experimental

$[Co(NH_3)_6](C_2O_4)_2{\cdot}4H_2O$ was synthesized according to the conventional method [5]. Thermo gravimetric analysis (TG) was carried out using a Cahn 2000 recording electrobalance. Sample was heated at a rate of 5°C min^{-1} in a constant flow (50 ml min^{-1}) of helium gas. Analyses of evolved gases (EGA) were carried out with a Hitachi 163 Gas-chromatograph. Infrared spectra (IR) and powder X-ray diffraction patterns (XRD) were measured with a Hitachi 270-50 spectrophotometer and a Rigaku Rint-2500V diffractometer using CuK_α(10 kW) radiation, respectively. Scanning electron micrographs (SEM) were taken with a Nihon Denshi JSM-6400. Specific surface areas were determined by the BET method with nitrogen gas as a sorbate. The resistivity of sample powder was measured as follows: After the sample powder was ground in an agate mortar, a disc of 20 mm diameter and 3 mm thickness was prepared by

* Corresponding author. Tel.: +81-897-37-7786; fax: +81-897-37-1245.
E-mail address: nakayama@chem.niihama-nct.ac.jp (S. Nakayama).

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pressing the sample powder at 100 MPa. Four Pt wires were connected with the distance of 5 mm on one side of the disc by an Ag paste and the disc was dried at 150°C. The dc-resistivity was measured with a 1V DC power supply at room temperature by the four-probe method using a multi-meter.

3. Results and discussion

3.1. Thermal decomposition

The TG curve of complex is shown in Fig. 1. The decomposition begins at about 120°C to give the first plateau in the range of 165 to 175°C. The weight loss percentage in this plateau range is about 11.2%, which is in good agreement with the value, 10.95%, calculated by assuming the formation of anhydrate, $[Co(NH_3)_6]_2(C_2O_4)_3$. The abrupt weight loss occurs at about 220°C and the second plateau is observed in the range of 250 to 270°C. The weight loss percentage, 55.0%, in the second plateau range agrees very well with that, 55.36%, calculated by assuming the formation of CoC_2O_4. Finally, the last plateau is observed about 310°C, after the decomposition at about 310°C. The weight loss percentage, 79.5%, in the last plateau agrees with that, 79.67%, calculated by assuming the formation of Co + CoO.

Decomposition products in each plateau was characterized by measuring IR spectra and XRD patterns. IR spectrum of the product in the second plateau is very similar to that of $CoC_2O_4{\cdot}2H_2O$. XRD patterns shown in Fig. 2 suggests the formation of Co and CoO in the last plateau range, being consistent with the TG result [6].

EGA results revealed that H_2O, NH_3 and CO_2, and CO_2 and CO molecules are evolved by the decomposition around 140, 220 and 310°C, respectively. The metallic Co may be formed by the reaction between oxalate group as a reducing agent and cobalt ion.

From the above results and discussion, the decomposition of $[Co(NH_3)_6]_2(C_2O_4)_3{\cdot}4H_2O$ in a He atmosphere seems to proceed in the following steps:

$$[Co(NH_3)_6]_2(C_2O_4)_3{\cdot}4H_2O \underset{4H_2O}{\rightarrow} [Co(NH_3)_6]_2 \times (C_2O_4)_3,\ 165-175^{\circ}C$$

$$\underset{12NH_3+2CO_2}{\rightarrow} 2CoC_2O_4,\ 250-270^{\circ}C \underset{3CO_2+2CO}{\rightarrow} Co + CoO,\ > 330^{\circ}C$$

The formation of (Co + CoO) mixture was also confirmed in the thermal decomposition of $[Co(NH_3)_5H_2O]_2(C_2O_4)_3 4H_2O$.

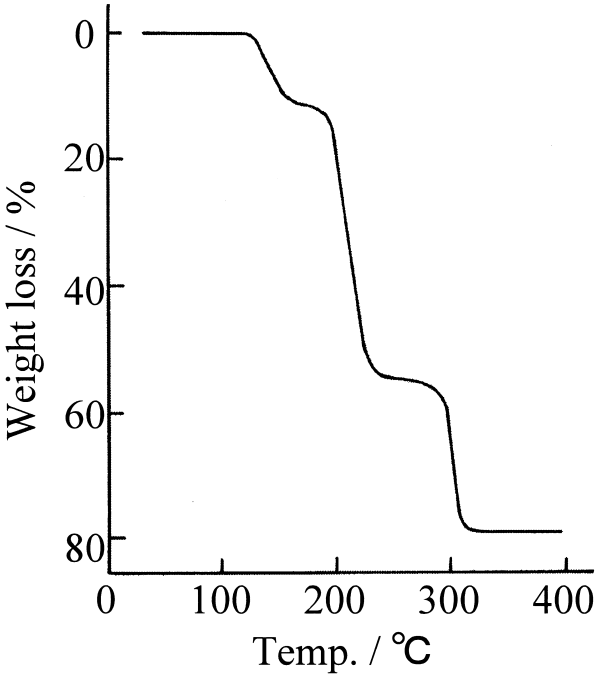

Fig. 1. TG curve of $[Co(NH_3)_6]_2(C_2O_4)_3{\cdot}4H_2O$ in a stream of helium.

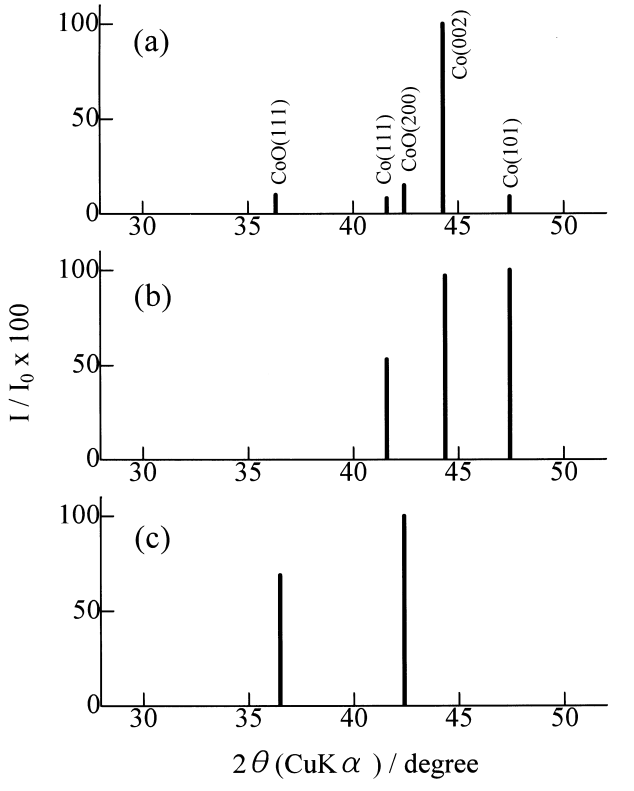

Fig. 2. XRD results of (a) product in the last plateau (400°C), (b) metallic Co and (c) oxide of cobalt (CoO).

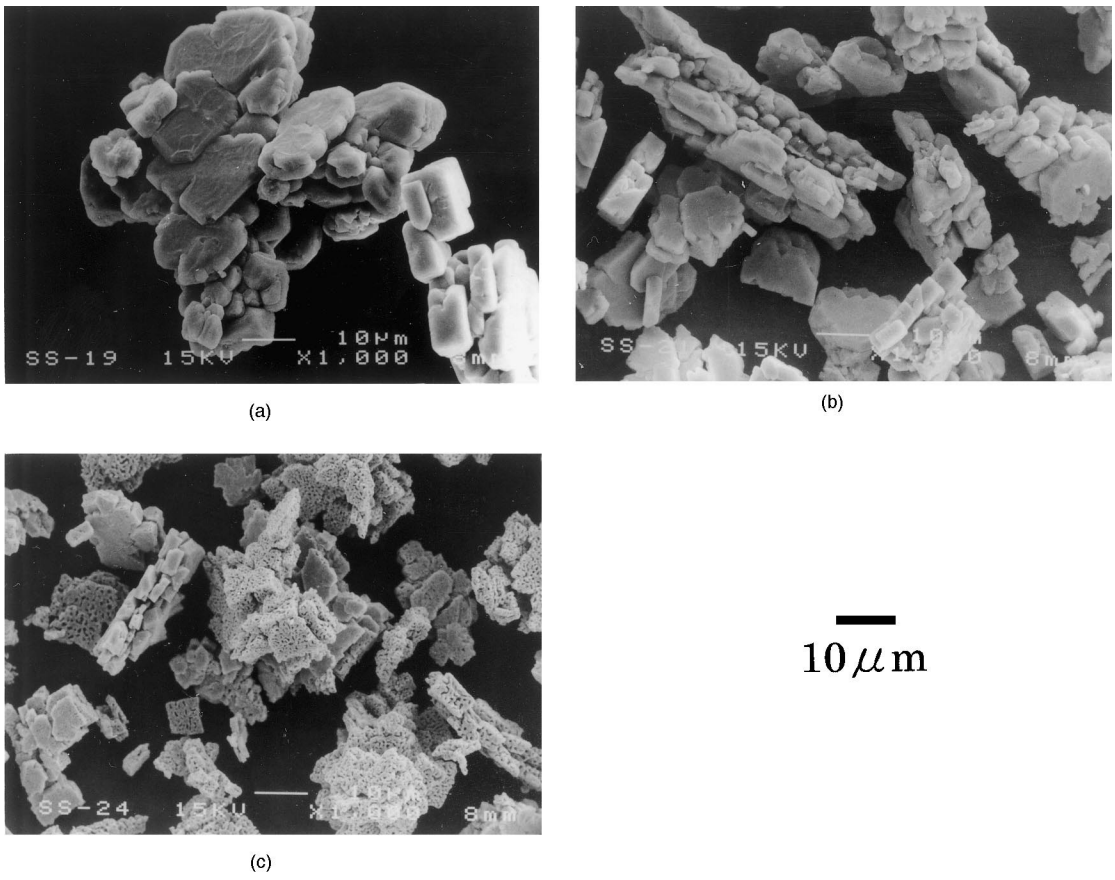

Fig. 3. SEM photographs of (a) starting complex, $[Co(NH_3)_6]_2(C_2O_4)\cdot 4H_2O$, (b) product in the second plateau (250°C) and (c) product in the last plateau (400°C).

3.2. Microstructure

Fig. 3 shows SEM photographs of the starting complex, $[Co(NH_3)_6]_2(C_2O_4)_3\cdot 4H_2O$, CoC_2O_4 in the second plateau range and (Co + CoO) mixture in the last plateau. Chunk-size of the starting complex is in the range of 10 to 30 μm. Each chunk is decomposed to give many finer grains, where the original chunk-shape of starting complex is essentially maintained with the contraction in size. Specific surface area of CoC_2O_4 obtained in the second plateau is the largest (Table 1).

The microstructure of the final product, (Co + CoO) mixture, was investigated in more detail. Fig. 4 shows the SEM photographs of the upper and lower parts of the product. The difference in the microstructure is clearly observed between these two parts. XRD results suggest that the metallic Co-component is rich in the upper part, whereas CoO-component is rich in the lower part (Fig. 5) [6]. Thus, the present complex was found to be suitable for the preparation of (Co + CoO) mixture which has the concentration gradients of each component from the upper to the lower part (Fig. 6), though the quantitative analysis is not carried out.

Table 1
Resistivities and specific surface areas

	Resisitivity (Ω cm)	Specific surface area ($m^2\ g^{-2}$)
Starting complex $[Co(NH_3)_6]_2(C_2O_4)_3\cdot 4H_2O$	–	0.8
Product in the second plateau CoC_2O_4	–	38.7
Product in the last plateau (Co + CoO) mixture	1.9×10^{-1}	4.2
Reagent grade		
Metallic Co	1.6×10^{-1}	1.9
Oxide CoO	$>10^{-7}$	0.5
(Co + CoO) mixture	7.7×10^{-1}	–

3.3. Electrical properties

Table 1 summarizes also the electrical resistivities of discs which were fabricated from the final (Co + CoO) mixture obtained in the last plateau, the metallic Co, the

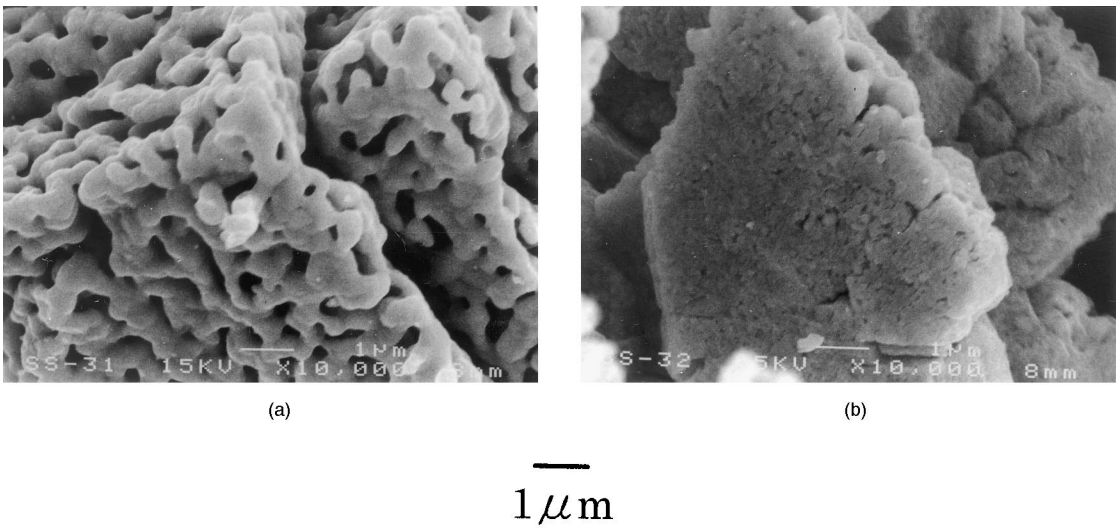

Fig. 4. SEM photographs of (a) upper part and (b) lower part of product in the last plateau (400°C).

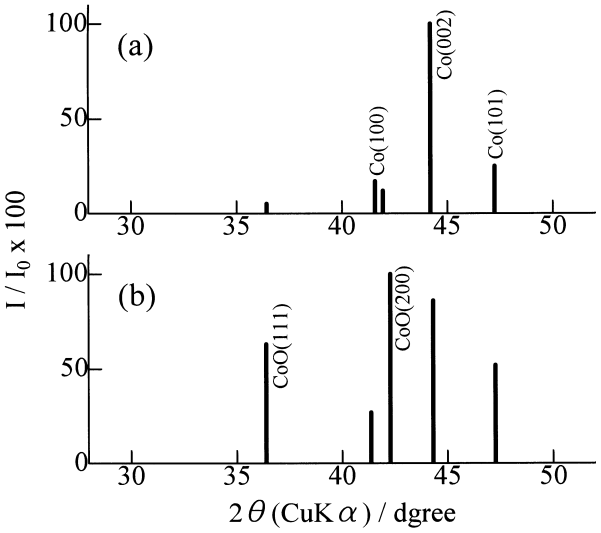

Fig. 5. XRD results of (a) upper part and (b) lower part of product in the last plateau (400°C).

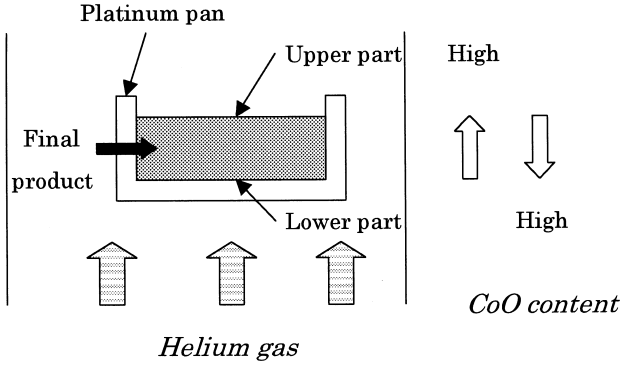

Fig. 6. Relative distribution of Co and CoO in the final product.

oxide CoO and the (Co + CoO) mixture prepared by mixing Co and CoO using a mortar. The resistivity of final (Co + CoO) mixture is closer to those of Co and (Co + CoO) prepared by mortar-mixing than that of CoO, suggesting the existence of metallic Co in the final product.

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