Preparation of perovskite-type oxides from heterometal coordination polymer precursors linked by oxalate ligands, \(\{\text{Sm}[M(\text{ox})_3] \cdot n\text{H}_2\text{O}\}_x\) (\(M = \text{Fe or Co}\))

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Two kinds of heterometal coordination polymer precursors, \(\{\text{Sm}[M(\text{ox})_3] \cdot n\text{H}_2\text{O}\}_x\) (\(M = \text{Fe and Co}\)), were prepared by the reaction of \(K_3[M(\text{ox})_3] \cdot 3\text{H}_2\text{O}\) with \(\text{Sm(NO}_3)_3 \cdot n\text{H}_2\text{O}\) in methanol solvent. These compounds were found to have oxalato-bridged network structure. On the other hand, the desired heterometal coordination polymer precursors could not be obtained by the present preparation method using water solvent. The thermal decomposition behaviors of these d-f heterometal coordination polymer precursors were investigated under air atmosphere. The perovskite-type oxides, \(\text{SmMO}_3\) (\(M = \text{Fe and Co}\)), were found to form in the temperature range of \(>600^\circ\text{C}\). The specific surface area of \(\text{SmFeO}_3\) powder increased with decreasing calcination temperature of Fe-containing heterometal coordination polymer precursor.

Key-words : Heterometal coordination polymer precursor, Oxalate ligand, Perovskite-type oxide, Specific surface area

1. Introduction

Perovskite-type oxide with general formula, \(\text{ABO}_3\), in which \(A\) is usually an alkaline earth metal ion or a lanthanoid ion and \(B\) is a transition metal ion, is one of the compounds used in the environmentally-friendly catalytic systems. The perovskite-type oxides have been reported to exhibit high catalytic activity for oxidations of hydrocarbon1-3 and chlorinated volatile organic compounds4,5) have been reported to exhibit high catalytic activity for oxidations of hydrocarbon1-3 and chlorinated volatile organic compounds4,5) and decomposition of \(\text{NO}\).6) In addition, some perovskite-type oxides have been investigated to be employed as electrode materials for solid oxide fuel cells7) and oxygen sensors8-10) and as sensing materials for the detection of humidity,11,12) alcohol,13) oxygen,14,15) \(\text{CO}\),16) \(\text{NO}_2\),19,20) and other gases.21)

The preparation method of perovskite-type oxide catalyst has progressively improved. Traditionally, perovskite-type oxides were prepared by solid state reaction of oxides or carbonates.22-24) However, the traditional method possesses the disadvantages of long processing time, low surface area, large particle size, and limited degree of chemical homogeneity. Wet-chemical methods are available to prepare finer and more homogeneous powders at low temperature. Up to date, numerous efforts of low temperature wet-chemical method have been undertaken to increase the surface area of perovskite-type oxide. For example, sol-gel25-27) co-precipitation,25,28) citrate route22,23) reverse micelle29,30) reverse homogeneous precipitation,31) and polymeric precursor methods,32,33) and flame hydrolysis of aqueous solution of precursor salts4) have been developed and designed to prepare nano-sized perovskite-type oxides. However, the development of simple and low-cost procedures for obtaining single-phase perovskite-type oxide nanoparticles with a homogeneous chemical composition under mild condition is still needed.

Sadaoka and co-workers34,42) reported the new preparation route of perovskite-type oxide via the thermal decomposition of heteronuclear cyano complex, \(\text{Ln}[\text{M(CN)}_6] \cdot n\text{H}_2\text{O}\) (abbreviated as CN method). Recently, we have prepared \(\text{SmFe}_x\text{Co}_{1-x}\text{O}_3\) catalyst by CN method and found that this catalyst exhibited the highest \(\text{CO}\) conversion among a series of \(\text{SmFe}_x\text{Co}_{1-x}\text{O}_3\) catalysts due to high homogeneity in composition.43) Thus, CN method possesses advantages for preparing perovskite-type oxide active for catalytic \(\text{CO}\) oxidation; however, there is a serious problem that CN” group with highly toxic property is containing in starting materials, \(\text{K}_3[\text{M(CN)}_6]\) complexes. Sakamoto and co-workers44,45) have succeeded the preparation of perovskite-type oxide using heteronuclear oxalato complex precursors, \(\text{La}[	ext{Cr(ox)}_3] \cdot 10\text{H}_2\text{O}\) \((\text{Ln} = \text{La, Pr or Nd})\) and \(\text{La}[	ext{Co(ox)}_3] \cdot 8.5\text{H}_2\text{O}\) (abbreviated as Ox method). However there is little information about the preparation method of lanthanoid(III)-transition metal(III) coordination polymer linked by oxalate ligands, \(\text{Ln}[\text{M(ox)}_3] \cdot n\text{H}_2\text{O}\). In this report, the heterometal coordination polymer precursor, \(\{\text{Sm}[\text{Fe(ox)}_3] \cdot 3\text{H}_2\text{O}\}_x\), was prepared by the reaction of \(\text{K}_3[\text{Fe(ox)}_3] \cdot 3\text{H}_2\text{O}\) with \(\text{Sm(NO}_3)_3 \cdot n\text{H}_2\text{O}\) in water or methanol as a solvent, and was characterized by several methods. The obtained \(\{\text{Sm}[\text{Fe(ox)}_3] \cdot 3\text{H}_2\text{O}\}_x\) precursor was calcined to yield perovskite-type oxide, \(\text{SmFeO}_3\). In a similar manner, \(\{\text{Sm}[\text{Co(ox)}_3] \cdot 3\text{H}_2\text{O}\}_x\) precursor was also prepared.

2. Experimental

2.1 Materials and instruments

All chemicals, \(\text{Sm(NO}_3)_3 \cdot 6\text{H}_2\text{O}\) (Wako, 99.5%), 18-crown-6 (Wako, 98.0%), methanol (Wako, 99.8%), and diethyl ether (Wako, 99.5%), were used as received. Transition metal oxalate potassium salts, such as \(\text{K}_3[\text{Fe(ox)}_3] \cdot 3\text{H}_2\text{O}\) and \(\text{K}_3[\text{Co(ox)}_3] \cdot 3\text{H}_2\text{O}\), were synthesized as starting materials according to reported method.46)

The powder XRD patterns of the catalysts were collected on a Rigaku MiniFlex II diffractometer using Cu Kα radiation. UV-visor spectra were recorded on a Hitachi U-4000 spectrometer. The thermal decomposition process of complex was studied by
thermogravimetry and differential thermal analysis (TG–DTA; DTG-60E, Shimadzu), performed at a heating rate of 10°C·min⁻¹ in air. FT-IR spectra of samples with KBr powder were recorded with a PerkinElmer Spectrum One spectrometer. The specific surface area was determined with the BET analysis (Belsorp-mini, BEL Japan) for the adsorption–desorption property measurements using N₂ adsorbent at −196°C.

### 2.2 Preparation of complexes

Sm[Fe(ox)₃]·nH₂O was prepared by the similar method reported for La[Co(ox)₃]·8.5H₂O preparation.⁴⁵) In the present study, two different solvents, water and methanol, were used. (i) A yellow-green aqueous solution (10 mL) containing K₃[Fe(ox)₃]·3H₂O (5.0 mmol) under stirring at room temperature. Immediately, white precipitates were formed. After the mixture was further stirred for 4 h, the white precipitates were corrected by suction filtration, washed with water and diethyl ether, and dried in the open air to yield sample (i). (ii) A yellow-green methanol solution (100 mL) containing both K₃[Fe(ox)₃]·3H₂O (5.0 mmol) and 18-crown-6 (22.7 mmol) was added to a methanol solution (10 mL) of Sm(NO₃)₃·6H₂O (5.0 mmol) under stirring at room temperature. Immediately, white precipitates were formed. After the mixture was further stirred for 4 h, the white precipitates were corrected by suction filtration, washed with water and diethyl ether, and dried in the open air to yield sample (iii).

Sm[Co(ox)₃]·nH₂O was prepared by as-described method of Sm[Fe(ox)₃]·nH₂O. In the case of water solvent, the white precipitates were immediately formed. After the mixture was further stirred for 4 h, the precipitates were corrected by suction filtration, washed with water and diethyl ether and dried in vacuum to yield sample (ii). Sm[Co(ox)₃]·nH₂O was prepared by as-described method of Sm[Fe(ox)₃]·nH₂O. In the case of water solvent, the white precipitates were immediately formed. After the mixture was further stirred for 4 h, the precipitates were corrected by suction filtration, washed with water and diethyl ether and dried in the open air to yield sample (ii).

The results of elemental analysis for samples (i–iv) are summarized in Table 1 as well as color of samples.

### 2.3 Preparation of perovskite-type oxides with thermal decomposition of precursors

Perovskite-type oxides were prepared by calcining the prepared precursors at desired temperature; the prepared precursors was preheated at 300°C for 1 h and then calcined at 550–1000°C for 24 h in air.

### 3. Results and discussion

#### 3.1 Preparation and characterization of coordination polymer precursors

Preparation of coordination polymer precursors linked by oxalate ligands, Sm[M(ox)₃]·nH₂O, were carried out in water or methanol solvent.

#### 3.1.1 Water solvent

Nakayama et al.⁴⁵) reported that La[Co(ox)₃]·8.5H₂O could be prepared in water solvent. Therefore, we attempted to prepare Sm[Fe(ox)₃]·nH₂O and Sm[Co(ox)₃]·nH₂O precursors in water solvent [samples (i) and (iii)]. UV–vis. spectra of samples (i) and (iii) exhibited no absorption band of d-d transition or ligand-to-metal charge transfers (LMCT) characteristic for [M(ox)₃]¹⁺ frameworks [M = Fe(III) and Co(III)]. The IR spectra of samples (i) and (iii) exhibited the antisymmetric [s(CO)] and symmetric [υ(CO)] vibrations at 1640 and 1363 cm⁻¹, respectively, being in good agreement with those of Ln[Ln(ox)₃]·12H₂O (Ln = La–Yb, except for Prn) with the respective vibrations at 1686–1560 and 1370 cm⁻¹.⁴⁵) Furthermore, the analytical results of samples (i) and (iii), shown in Table 1, demonstrated that the compositions of samples (i) and (iii) were clearly different from those of desired coordination polymer precursors, Sm[Fe(ox)₃]·nH₂O and Sm[Co(ox)₃]·nH₂O; the amounts of Fe and Co were below detectable levels for samples (i) and (iii), respectively, and that the compositions of samples (i) and (iii) were roughly consistent with that of Sm[Sm(ox)₃]·12H₂O. Therefore, the samples (i) and (iii) was assigned to Sm[Sm(ox)₃]·12H₂O. These assignments were supported by the following experimental result; when samples (i) and (iii) were calcined at 700°C for 24 h, only XRD peaks assigned to SmO₃ were observed. Thus, the present method with water solvent did not give our desired heterometal coordination polymer precursors linked by oxalate ligands.

#### 3.1.2 Methanol solvent

The starting materials, such as K₃[M(ox)₃]·3H₂O (M = Fe and Co), are highly soluble in water, but are hardly soluble in methanol. When crown ether, 18-crown-6, was added to methanol solvent, such starting materials became soluble in methanol because the {18-crown-6}⁺ species soluble in methanol may be generated.⁴⁸)

Figure 1 shows the diffuse reflectance UV–vis. spectra of sample (ii) and the corresponding starting material (K₃[Fe(ox)₃]·3H₂O). In the UV vis. spectrum of sample (ii), the LMCT band characteristic of [Fe(ox)₃]¹⁺ was observed at 300–400 nm, suggesting that the structure of the chromophore, [Fe(ox)₃]¹⁺, was maintained in sample (ii). The IR spectrum of sample (ii) exhibited υ(CO) and υ(CO) vibrations at 1624 and 1384 cm⁻¹, respectively, whereas in K₃[Fe(ox)₃]·3H₂O, the respective vibrations were observed at 1675 and 1399 cm⁻¹. From these results, it is presumed for sample (ii) that the networks are constructed by Sm(III)–ox–Fe(III) linkages as reported for [NBu₄][CuCr(ox)₃]].⁴⁹) Furthermore, in contrast to water solvent, the

<table>
<thead>
<tr>
<th>Sample</th>
<th>Color</th>
<th>Found/wt % (Calcd/wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
<td>White</td>
<td>C 9.50  Sm 34.3</td>
</tr>
<tr>
<td>(ii)</td>
<td>Yellow green</td>
<td>Co 29.6</td>
</tr>
<tr>
<td>(iii)</td>
<td>Yellow green</td>
<td>Fe 31.7</td>
</tr>
<tr>
<td>(iv)</td>
<td>Green</td>
<td>N. D.</td>
</tr>
</tbody>
</table>

a) ICP and CHN elemental analysis results.

#### Table 1. Analytical results of all samples prepared in this work.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Color</th>
<th>Found/wt % (Calcd/wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sm[Sm(ox)₃]·12H₂O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sm[Fe(ox)₃]·3H₂O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sm[Co(ox)₃]·8H₂O</td>
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</table>

WN = 2.75, 5.48, 5.00, 3.10, 2.63, 2.47, 1.56, 1.38, 0.92, 0.71, 0.37, 0.24, 0.11, 0.08, 0.07, 0.05, 0.04, 0.03, 0.02, 0.01, 0.00.49) Furthermore, in contrast to water solvent, the
elemental analysis demonstrated that Sm:Fe:C elemental molar ratio (0.9:1.0:6.1) of sample (ii), calculated from Table 1, was in fair agreement with that of Sm[Fe(ox)3]·3H2O (1:1:6). These results lead us to conclude that Sm[Fe(ox)3]·nH2O was formed under the present condition with methanol solvent and that the addition of crown ether to methanol solution makes it possible to prepare the coordination polymer precursor with oxalate ligands, Sm[Fe(ox)3]·nH2O.

Similarly, sample (iv) was characterized by UV–vis., IR, and elemental analysis. Figure 2 shows the diffuse reflectance UV–vis. spectra of sample (iv) and K3[Co(ox)3]·3H2O. The d-d bands characteristic of [Co(ox)3]³⁺ were observed at 434 and 609 nm. In addition, the vibrations of \( \bar{\nu}_1(\text{CO}) \) and \( \bar{\nu}_2(\text{CO}) \) in IR spectrum of sample (iv) were observed at 1624 and 1384 cm⁻¹, respectively. The elemental analysis shown in Table 1 exhibited that Co/Sm weight ratio (Co/Sm molar ratio = 0.95) in sample (iv) agreed with that of the calculated value of Sm[Co(ox)3]·8H2O. Considering above experimental results, sample (iv) was assigned to Sm[Co(ox)3]·nH2O.

The sample (iv) gradually changed in color from green to pink under air atmosphere. This change may be due to the decomposition of oxalate ligands in Sm[Co(ox)3]·nH2O, accompanying with the reduction from Co(III) to Co(II). A similar change in color has been already reported for the reformation of La[Co(ox)3]·8.5H2O to \( 1/2 \text{La}_2(\text{C}_2\text{O}_4)_3 \) and CoC2O4.45) Thus, Sm[Co(ox)3]·nH2O was unstable under air, but comparatively stable under a vacuum condition.

### 3.2 Thermal decomposition of coordination polymer precursors with oxalate ligands

The thermal decomposition behaviors of samples (ii) and (iv), assigned to Sm[Fe(ox)3]·nH2O and Sm[Co(ox)3]·nH2O, respectively, in section 3.1, were investigated in order to prepare the perovskite-type oxides, SmFeO3 and SmCoO3, respectively.

TG–DTA curve of Sm[Fe(ox)3]·nH2O is shown in Fig. 3. The decomposition started at about 50°C to give the first plateau in the temperature range of 100 to 200°C. The weight loss percentage in this plateau range was about 12%, indicating the formation of anhydrate species, [Sm(Fe(ox)3)]x. This weight loss corresponds to that of about 3 crystallization water molecules; namely the n value in Sm[Fe(ox)3]·nH2O was found to be 3. With further increasing temperature, the abrupt weight loss accompanying with large exothermic DTA peak was observed at ca. 270°C to give the second plateau. It is suggested that this weight loss is attributable to the oxidation of oxalate ligands. After gradual decrease in weight, probably due to the desorption of CO2 from oxidative products formed on sample, and the third plateau appeared at above 650°C. The total weight loss percentage (ca. 59%) of sample (ii) was consistent with the calculated one (57%) by assuming the formation to SmFeO3 from Sm[Fe(ox)3]·3H2O.

The decompostion product of Sm[Fe(ox)3]·3H2O was characterized by measuring the powder X-ray diffraction spectrum of the product calcined at 550, 600, 700, 800, 900, and 1000°C for 24 h under air. The XRD results are shown in Fig. 4. The perovskite-type oxide, SmFeO3, was formed at >600°C and no peak attributable to Sm2O3 and Fe2O3 was observed. The crystal system and space group of sample calcined at 700°C were orthorhombic and \( Pbnm \), respectively, and the lattice constants (Å) were estimated as follows: \( a = 5.425, b = 5.609, c = 7.622 \). The average sizes of the SmFeO3 crystallites in the (110) direction, evaluated from XRD line broadening using Scherrer’s equation, are shown in Table 2. The evaluated values decreased with decreasing calcination temperature of a hetero-metal coordination polymer precursor. BET specific surface areas of the SmFeO3 samples calcined at each temperature are also shown in Table 2. The specific surface areas increased with decreasing calcination temperature. The specific surface area of

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Fig. 2. Diffuse reflectance UV–vis. spectra of sample (iv) (a), and K3[Co(ox)3]·3H2O (b).

Fig. 3. TG–DTA curves of Sm[Fe(ox)3]·nH2O.

Fig. 4. XRD patterns of Sm[Fe(ox)3]·3H2O calcined at 550 (a), 600 (b), 650 (c), 700 (d), 800 (e), 900 (f), and 1000°C (g).
Sm[Co(ox)₃]·nH₂O is shown in SmCoO₃ through anhydrate species, by calcination at relatively low temperature (ligands, Sm[M(ox)₃]·nH₂O( M = heterometal coordination polymer complex linked by oxalate ligands, Sm[Fe(ox)₃]·nH₂O, three steps of weight losses were observed at 50°C, 200–380 (31%), and 380–600°C (3%), and the total weight loss percentage was 57%. These results suggest that the decomposition of Sm[Co(ox)₃]·8H₂O to SmCoO₃ through anhydrate species, (Sm[Co(ox)₃] ), successively occurred. Figure 6 shows the XRD pattern of Sm[Co(ox)₃]·8H₂O calcined at 700°C for 24 h. Clearly, the single phase SmCoO₃ was formed with crystal system: orthorhombic, space group: Pbnm, and the lattice constants: \( a = 5.307 \), \( b = 5.305 \), and \( c = 7.549 \) Å.

TG-DTA and XRD measurements demonstrated that the d-f heterometal coordination polymer complex linked by oxalate ligands, Sm[M(ox)₃]·nH₂O (M = Fe and Co), is a potential candidate of precursor to give the perovskite-type oxide, SmMO₃, by calcination at relatively low temperature (\( > 600°C \)).

4. Conclusion

The d-f heteronuclear oxalato complex, [Sm[M(ox)₃]·nH₂O]ₙ, (M = Fe and Co), with the network structures constructed by Sm(III)-ox-M(III) linkages was prepared as a precursor of perovskite-type oxide with high surface area. The thermal decomposition behavior of the resulting precursor was examined. The obtained results are summarized as follows.

### Table 2. Average sizes of crystallite and specific surface areas of products calcined at each temperature

<table>
<thead>
<tr>
<th>Sample</th>
<th>Calc. Temp. (^°C)</th>
<th>Crystallite size (\text{nm}^3)</th>
<th>Surface area (\text{m}^2\cdot\text{g}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
<td>550</td>
<td>25</td>
<td>7.9</td>
</tr>
<tr>
<td>(ii)</td>
<td>600</td>
<td>32</td>
<td>8.6</td>
</tr>
<tr>
<td>(iii)</td>
<td>650</td>
<td>33</td>
<td>7.9</td>
</tr>
<tr>
<td>(iv)</td>
<td>700</td>
<td>36</td>
<td>3.9</td>
</tr>
</tbody>
</table>

a) The average sizes of SmFeO₃ and SmCoO₃ crystallites in the (110) and (002) directions, respectively, were evaluated from XRD line broadening using Scherrer’s equation. b) No peaks. c) Not measured.

Fig. 6. XRD pattern of Sm[Co(ox)₃]·8H₂O calcined at 700°C.

(1) Two kinds of f-d heterometal coordination polymer precursors, Sm[M(ox)₃]·nH₂O (M = Fe and Co), were prepared by the reaction of K₃[M(ox)₃]·3H₂O with Sm(NO₃)₃·nH₂O in methanol solvent containing crown ether, 18-crown-6.

(2) Perovskite-type oxides were formed by calcining Sm-[M(ox)₃]·nH₂O precursors at 600°C.

(3) The average crystallite size and the specific surface area of perovskite-type oxide decreased with decreasing calcination temperature of a heterometal coordination polymer precursor. The specific surface area of SmFeO₃ powder prepared by Ox method (calcination temperature = 600°C) was 8.6 m²·g⁻¹, which was comparable to that of SmCoO₃ powder prepared by CN method at same temperature (ca. 9 m²·g⁻¹).

Acknowledgement This work was supported by JSPS KAKENHI Grant Number 21360397 and 24560948.

References

Yamaguchi et al.: Preparation of perovskite-type oxides from heterometal coordination polymer precursors linked by oxalate ligands, 

\[\text{[Sm[M(ox)\_3] \cdot nH}_2\text{O]} \ (M = \text{Fe or Co})\]