Synthesis of perovskite-type oxide, LaFeO$_3$, from coordination polymer precursor, La[Fe(CN)$_6$]·5H$_2$O

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Perovskite-type oxide, LaFeO$_3$, was prepared from coordination polymer precursor, La[Fe(CN)$_6$]·5H$_2$O by calcination with the different two systems. In a muffle furnace system, the perovskite-type oxide was given by calcination at $>500^\circ$C. The specific surface area of LaFeO$_3$ powder calcined at 500°C for 24 h was 18 m$^2$·g$^{-1}$, which was the largest among single phase perovskite-type oxides calcined in a muffle furnace. In a gas-flow system, the perovskite-type oxide was given by calcination at significantly low temperature ($>250^\circ$C). The specific surface area of LaFeO$_3$ powder calcined at 300°C for 1 h in a gas-flow system was dependent on O$_2$ partial pressure.

Key-words : Perovskite-type oxide, Low temperature preparation, Coordination polymer precursor, Cyano ligand

Received August 31, 2015; Accepted November 5, 2015

1. Introduction

Perovskite-type oxide (ABO$_3$) has been reported to be active for some catalytic reactions such as oxidations of hydrocarbon$^{[1,2]}$, and chlorinated volatile organic compounds$^{[3]}$, and decomposition of NO$^{[4]}$. Up to date, the perovskite-type oxides were prepared by several methods as listed in Table 1. The solid state reaction of oxides and/or carbonates$^{[7,8,13]}$ is very simple method for yielding perovskite-type oxide; however, the calcination at more than 1000°C is required to obtain perovskite-type oxide. The wet-chemical methods such as evaporation-to-dryness$^{[12]}$, co-precipitation$^{[7,10,13-15]}$, sol-gel$^{[8,13,16-18]}$, and citrate route$^{[7,8,12,19,20]}$ are available to prepare finer and more homogeneous powders at relatively low temperature (650–1000°C). 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.

Recently, we have reported that the perovskite-type oxide was prepared via the thermal decomposition of heteronuclear cyano complex, Ln[M(CN)$_6$]$\cdot$nH$_2$O (abbreviated as CN method) and the resulting perovskite-type oxide catalysts exhibited the high catalytic activity for CO oxidation$^{[21]}$ and cyanosilylation$^{[22,23]}$. From the viewpoints of saving energy for preparation and improving surface area of catalysts, the low temperature synthesis of perovskite-type oxide is desirable. More recently, we demonstrated that LaFeO$_3$ and LaCoO$_3$ were prepared from the corresponding coordination polymer precursors, La[Fe(CN)$_6$]$\cdot$SH$_2$O, and La[Co(CN)$_6$]$\cdot$SH$_2$O, by the self-propagating high temperature synthesis (SHS) method that most of the heat required for the synthesis of perovskite-type oxide is provided by the reaction itself without an additional heating.$^{[24]}$ In this study, the preparation of perovskite-type oxide, LaFeO$_3$, from coordination polymer precursor, La[Fe(CN)$_6$]$\cdot$SH$_2$O, by two different calcination systems: a muffle furnace system and a gas-flow system, was investigated as functions of calcination temperature, calcination time, and atmosphere. The results obtained in this study are of preliminary ones for understanding SHS method for perovskite-type oxide synthesis.

2. Experimental

2.1 Materials and instruments

All chemicals, La(NO$_3$)$_3$·6H$_2$O (Wako, 99.5%), and K$_3$Fe(CN)$_6$ (Hayashi, 99%), were used without any purification. The heteronuclear cyano complex, La[Fe(CN)$_6$]$\cdot$5H$_2$O, as a coordination polymer precursor of perovskite-type oxide was synthesized by the method reported elsewhere.$^{[25]}$ The aqueous mixed solutions of La(NO$_3$)$_3$·6H$_2$O and K$_3$Fe(CN)$_6$ with appropriate amounts were continuously stirred at room temperature to obtain the precipitate of La[Fe(CN)$_6$]$\cdot$5H$_2$O. The resulting precipitate was collected by suction filtration, washed with deionized water, ethanol, and diethyl ether, and then dried in air at 50°C. As references, the other precursors were prepared by decomposition method of polymer precursor (abbreviated as PP method)$^{[26,27]}$, citrate route$^{[19,20]}$, and reverse homogenous precipitation method (RHP method)$^{[28]}$.

The powder X-ray diffraction (XRD) patterns of the samples were collected on a Rigaku MiniFlex II diffractometer using Cu Kα radiation. 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 O$_2$ and air. The specific surface area was determined with the BET analysis (Belsorp-mini, BEL Japan) for the adsorption–desorption property measurements using N$_2$ adsorbent at $-196^\circ$C.

2.2 Preparation of perovskite-type oxides with thermal decomposition of precursors

In the present study, two different calcination procedures were used. (i) Perovskite-type oxides were prepared by calcining the
prepared precursors in a muffle furnace [Fig. 1(a)]; the prepared precursor was preheated at 300°C for 1 h and then calcined at 450–700°C for 1–24 h in the air. The sample powder was spread over alumina boat because of easy diffusion of the air into the inside of sample (shallow bed). (ii) Perovskite-type oxides were prepared by calcining the prepared precursors in a gas-flow system [Fig. 1(b)]; the prepared precursor was calcined at 200–300°C for 1 h in several atmospheres, such as O2, synthetic air, N2, and CO2 (flow rate = 50 mL min⁻¹).

3. Results and discussion

3.1 TG measurement of coordination polymer precursor

TG–DTA curves of coordination polymer precursor, La[Fe(CN)₆] · nH₂O, under O₂ and synthetic air are shown in Fig. 2. In the case of O₂ atmosphere [Fig. 2(a)], the decomposition started at about 50°C to give the first plateau in the temperature range of 100 to 200°C. The percentage of weight loss until this plateau region was about 22%, suggesting the desorption of crystal water (n = 5) to form anhydrate species, [La[Fe(CN)₆]x]n, as reported previously.25) With further increasing temperature, the abrupt weight loss accompanying with large exothermic DTA peak was observed at ca. 358°C to give the second plateau. This weight loss can be attributable to the oxidation of cyano ligands.25) After gradual decrease in weight, probably due to the desorption of CO₂ from carbonate formed during CN oxidation,25) the third plateau appeared at 612°C. The percentage of total weight loss (ca. 48%) was consistent with the calculated one (45%) by assuming the formation of LaFeO₃ from La[Fe(CN)₆] · 5H₂O. A similar TG–DTA curve was obtained for synthetic air [Fig. 2(b)]. These TG–DTA results indicate that the oxidation of CN groups in precursor occurs at more than 300°C in an oxidizing atmosphere.

### Table 1. Reported methods for preparing perovskite-type oxide, LaFeO₃

<table>
<thead>
<tr>
<th>Preparation method</th>
<th>Calcination temperature /°C</th>
<th>Calcination time /h</th>
<th>Phase</th>
<th>Specific surface area /m² g⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid state reaction</td>
<td>1000</td>
<td>2</td>
<td>LaFeO₃</td>
<td>-a)</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>2</td>
<td>LaFeO₃ + La₂O₃ + Fe₂O₃</td>
<td>0.8</td>
<td>11</td>
</tr>
<tr>
<td>Evaporation to dryness</td>
<td>650</td>
<td>5</td>
<td>LaFeO₃</td>
<td>12.1</td>
<td>12</td>
</tr>
<tr>
<td>Co-precipitation</td>
<td>700</td>
<td>6</td>
<td>LaFeO₃</td>
<td>20.9</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>2</td>
<td>LaFeO₃ + La₂O₃ + TeO₂</td>
<td>-a)</td>
<td>10</td>
</tr>
<tr>
<td>Sol–gel</td>
<td>650</td>
<td>4</td>
<td>LaFeO₃</td>
<td>-a)</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>4</td>
<td>LaFeO₃</td>
<td>16.5</td>
<td>13</td>
</tr>
<tr>
<td>Citrate</td>
<td>700</td>
<td>2</td>
<td>LaFeO₃</td>
<td>18.5</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>5</td>
<td>LaFeO₃</td>
<td>3</td>
<td>19</td>
</tr>
</tbody>
</table>

a) Not reported.

Fig. 1. The apparatus of calcination of coordination polymer precursor: (a) a muffle furnace system and (b) a gas-flow system.

Fig. 2. TG–DTA curves of La[Fe(CN)₆] · 5H₂O under O₂ (a) and synthetic air (b).
The XRD peaks due to the hexagonal structure disappeared completely at 500°C of the calcination temperature for 1 h and the very broad XRD peak derived from amorphous phase newly appeared at ca. 30 degree [Fig. 3(a)]. When the sample was heated for 5 h, the XRD peaks assigned to LaFeO$_3$ perovskite-type oxide (JCPDS file No. 37-1493, orthorhombic structure) appeared at 22.5, 32.2, 39.7, and 46.2 degrees [Fig. 3(b)]. The overlapped broad XRD peak due to the amorphous phase disappeared completely for 24 h and the XRD peaks assignable to LaFeO$_3$ perovskite-type oxide became sharper [Fig. 3(c)].

The XRD patterns of the decomposition product of La[Fe(CN)$_6$]·5H$_2$O calcined at 500, 550, 600 and 700°C for 1 h in the air are shown in Fig. 4. As mentioned previously, the sample heated at 500°C for 1 h exhibited only a broad XRD peak due to amorphous phase at ca. 30 degree [Fig. 4(a)]. When the coordination polymer precursor was heated at 550°C for 1 h, the XRD peaks assigned to LaFeO$_3$ perovskite-type oxide were observed at 22.7, 32.2, 39.7, and 46.1 degrees [Fig. 4(b)]. With increasing decomposition temperature, the XRD peaks of LaFeO$_3$ perovskite-type oxide increased in intensity. On the other hand, the XRD peak due to the amorphous phase disappeared completely at 600 and 700°C [Figs. 4(c) and 4(d)]. Based on the XRD results, the decomposition products of La[Fe(CN)$_6$]·5H$_2$O calcined at 450–700°C for 1–24 h are listed in Table 2 as well as the specific surface areas of each samples. As can be seen in Table 2, the single phase LaFeO$_3$ was obtained by calcining La[Fe(CN)$_6$]·5H$_2$O at 500°C for 24 h, 550°C for 5 h, and >600°C for 1 h and their temperatures were lower than those of the other methods shown in Table 1. Among the LaFeO$_3$ samples with single phase, LaFeO$_3$ obtained by the calcination at 500°C for 24 h exhibited the highest specific surface area. Figure 5 shows the specific surface area of products as a function of calcination temperature of La[Fe(CN)$_6$]·5H$_2$O. The specific surface area of products tends to increase with decreasing calcination temperature of a cyano complex precursor.

### 3.3 Thermal decomposition of coordination polymer precursors in a gas-flow system

The XRD results of the La[Fe(CN)$_6$]·5H$_2$O calcined at 200, 250, and 300°C for 1 h in flowing O$_2$ are shown in Fig. 6. The XRD peaks due to the hexagonal structure derived from coordination polymer precursor were maintained at 200°C [Fig. 6(a)]. These XRD peaks disappeared at >250°C and the sharp XRD peaks assignable to LaFeO$_3$ perovskite-type oxide were observed [Figs. 6(b) and 6(c)].

Figure 7 shows the XRD results of the La[Fe(CN)$_6$]·5H$_2$O calcined at 300°C for 1 h in different atmospheres: O$_2$, synthetic air, N$_2$, and CO$_2$. As mentioned previously, the sharp XRD peaks assignable to LaFeO$_3$ perovskite-type oxide were observed under O$_2$ atmosphere [Fig. 7(a)]. In the case of synthetic air, the XRD peaks due to coordination polymer precursor disappeared completely; however, no distinct XRD peaks due to perovskite-type oxide were observed [Fig. 7(b)]. N$_2$ and CO$_2$ atmospheres gave no XRD peaks due to perovskite-type oxide [Figs. 7(c) and 7(d)] and the XRD peaks due to the coordination polymer precursor still remained because of no oxygen source enough to oxidize cyano complex in precursor. From these results, it was

### Table 2. Products prepared by calcination under air in muffle furnace

<table>
<thead>
<tr>
<th>Calcination temp./°C</th>
<th>Calcination time/h</th>
<th>Phase</th>
<th>Specific surface area/m$^2$ g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>24</td>
<td>Amorphous + LaFeO$_3$</td>
<td>25</td>
</tr>
<tr>
<td>500</td>
<td>1</td>
<td>Amorphous</td>
<td>18</td>
</tr>
<tr>
<td>500</td>
<td>5</td>
<td>Amorphous + LaFeO$_3$</td>
<td>22</td>
</tr>
<tr>
<td>550</td>
<td>1</td>
<td>Amorphous + LaFeO$_3$</td>
<td>29</td>
</tr>
<tr>
<td>550</td>
<td>5</td>
<td>LaFeO$_3$</td>
<td>18</td>
</tr>
<tr>
<td>600</td>
<td>1</td>
<td>LaFeO$_3$</td>
<td>14</td>
</tr>
<tr>
<td>700</td>
<td>1</td>
<td>LaFeO$_3$</td>
<td>9</td>
</tr>
</tbody>
</table>
found that the preparation at 300°C in a gas-flow system needs the relatively high concentration of oxygen source to obtain perovskite-type oxide.

In order to investigate the influence of O₂ partial pressure on the product, the precursor was calcined with different O₂ partial pressure at 300°C in a gas-flow system. The XRD results of the La[Fe(CN)]₆·5H₂O calcined at 300°C for 1 h with different O₂ partial pressures are shown in Fig. 8. More than 50% O₂ partial pressure provided the single phase of LaFeO₃ [Figs. 8(a)–8(c)], while 21% O₂ partial pressure (synthetic air) provided an amorphous phase [Fig. 8(d)]. Thus the formation of perovskite-type oxide prepared by CN method was found to be strongly influenced by the O₂ partial pressure in a flowing gas.

The products obtained by calcining La[Fe(CN)]₆·5H₂O at 200–300°C for 1 h in the different atmospheres (different O₂ partial pressures) are summarized in Table 3 as well as their specific surface areas and crystalline sizes. The minimum calcination temperature giving single phase LaFeO₃ perovskite-type oxide in a gas-flow system were 250 and 550°C for O₂ and synthetic air, respectively, being much lower than those in a muffle furnace.

In a similar way, the precursors prepared by the other methods, PP, citrate, and RHP, were calcined in a gas-flow system. The XRD results of the precursors calcined at 300°C for 1 h under O₂ atmosphere are shown in Fig. 9. The sample by CN method provided the single phase of LaFeO₃ [Fig. 9(a)]. On the other hand, the samples by PP and citrate methods provided the mixed phases of amorphous and LaFeO₃ [Figs. 9(b) and 9(c)] and that by RHP method provided an amorphous phase [Fig. 9(d)]. It is likely that the precursors containing organic compounds give the perovskite-type oxide by calcining at relatively low temperature under O₂ rich atmosphere. This may be due to the increase in sample temperature accompanying with the oxidation of organic compound in precursor, as mentioned later.

### 3.4 Temperature monitoring in a gas-flow system

As mentioned in 3.1, the precursor prepared by CN method gave large exothermic DTA peak when it was oxidized. This fact

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**Table 3.** Products prepared by calcination for 1 h in gas-flow system

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>Calcination temp./°C</th>
<th>Phase</th>
<th>Specific surface area /m² g⁻¹</th>
<th>Crystallite size /nm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂ (100%)</td>
<td>200</td>
<td>La[Fe(CN)]₆</td>
<td>—a</td>
<td>—a</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>LaFeO₃</td>
<td>15</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>LaFeO₃</td>
<td>17</td>
<td>35</td>
</tr>
<tr>
<td>O₂ (75%), N₂ (25%)</td>
<td>300</td>
<td>LaFeO₃</td>
<td>19</td>
<td>32</td>
</tr>
<tr>
<td>O₂ (50%), N₂ (50%)</td>
<td>300</td>
<td>LaFeO₃</td>
<td>30</td>
<td>28</td>
</tr>
<tr>
<td>Synthetic air [O₂ (21%)</td>
<td>300</td>
<td>Amorphous</td>
<td>43</td>
<td>—c</td>
</tr>
<tr>
<td>N₂ [O₂ (0%)]</td>
<td>550</td>
<td>LaFeO₃</td>
<td>22</td>
<td>24</td>
</tr>
<tr>
<td>CO₂</td>
<td>300</td>
<td>La[Fe(CN)]₆</td>
<td>7</td>
<td>—c</td>
</tr>
</tbody>
</table>

a) The average crystallite size in the (110) direction of LaFeO₃ was evaluated from XRD line broadening using Scherrer’s equation. b) Not measured. c) Peaks derived from LaFeO₃ were not observed.
implied that the sample temperature increase by oxidation of CN group. Therefore, we attempted to monitor sample temperatures at different positions during calcination. The schematic view of the system is depicted in Fig. 10(a). Three thermocouple detectors were set at the different positions, (i), (ii), and (iii). The length of sample bed was 20 mm and the furnace temperature was kept at 250°C. As expected, all the temperatures monitored by thermocouple detectors suddenly increased from 250°C under O2 atmosphere [Fig. 10(b)]. The temperatures at the entrance (i), middle (ii) and exit (iii) sides reached the maximum values at 600, 700 and 450°C, respectively. This result suggests that a part of the heat required for the synthesis of perovskite-type oxide is provided by the oxidation of the CN group in coordination polymer precursor.

Figure 11 shows the change in actual temperature of the La[Fe(CN)6]·5H2O calcined at 300°C for 1 h under several gases with different O2 partial pressure in a gas-flow system. When nitrogen (0% O2) was used as a flowing gas, the sample temperature closely followed the furnace temperature during the whole treatment [Fig. 11(a)]. Under oxygen atmosphere [21% O2 [Fig. 11(b)], 50% O2 [Fig. 11(c)], and 100% O2 [Fig. 11(d)], a local overheating was observed at each positions. The maximum temperature and time showing exothermic nature were dependent on O2 partial pressure. The maximum sample temperatures at positions (i), (ii), and (iii) were 348, 400, and 370°C, respectively, at 21% O2 partial pressure and they increased with increasing O2 partial pressure. Under oxygen atmosphere [Figs. 11(b)-11(d)], the maximum temperature at position (ii) was higher than those at positions (i) and (iii), suggesting that the heat propagates effectively to the middle side of sample bed. On the other hand, the time showing exothermic nature was more than 60 min at 21% O2 partial pressure and that became shorter with increasing O2 partial pressure. The oxidation of CN groups in coordination polymer precursor is considered to be kinetically slow at lower O2 partial pressure, resulting in the thermal transfer to the surroundings preferentially. As shown in Fig. 8, the crystallinity of LaFeO3 perovskite-type oxide increased with increasing O2 partial pressure. This is reasonable because, in general, higher calcination temperature provides higher crystallinity of perovskite-type oxide.

4. Conclusion

The heteronuclear cyano complex, La[Fe(CN)6]·5H2O, was prepared as a coordination polymer precursor to obtain perovskite-type oxide, LaFeO3, with high surface area. The thermal decomposition behavior of La[Fe(CN)6]·5H2O precursor was examined using two different calcination systems. The results obtained in the present study are summarized as follows.

(1) LaFeO3 perovskite-type oxide with single phase was obtained by calcining La[Fe(CN)6]·5H2O at 500°C for 24 h under the air in a muffle furnace and the resulting sample exhibited the highest specific surface area among the samples prepared under several calcination conditions.

(2) LaFeO3 perovskite-type oxide with single phase was obtained by calcining La[Fe(CN)6]·5H2O at low temperature (250°C) under O2 atmosphere in a gas-flow system.
(3) The relatively high concentration of oxygen source was required to obtain perovskite-type oxide in a gas-flow system.

(4) It was found that a part of the heat required for the synthesis of perovskite-type oxide was provided by the oxidation of the CN group in coordination polymer precursor.

Acknowledgement This work was supported by JSPS KAKENHI Grant Numbers 21360397, 24560948 and 15K06569.

References