Carbon oxidation activity of complex oxides (Part 2) — Characteristics of La$_{0.9}$Ag$_{0.1}$FeO$_x$ synthesized at low temperature using co-precipitation method —

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The perovskite oxide, LaFeO$_3$, was synthesized by different preparation methods, i.e., the calcination of co-precipitated precursors [La(Ag)Fe(CO)$_3$ and La–Fe(CO)$_3$] and a mixture of La$_2$O$_3$ and Fe$_2$O$_3$ (La–Fe–O). By using the solution of Ag, the formation temperature (600°C) of the LaFeO$_3$ single phase obtained by the calcining of La(Ag)Fe(CO)$_3$ was about 500°C lower than that of La–Fe–O. The formation temperature of the LaFeO$_3$ single phase of La–Fe–O was 1100°C as well as that of La–Fe–CO$_3$. Their carbon oxidations were investigated by DSC (differential scanning calorimetry) measurements. The DSC exothermic peak of La$_{0.9}$Ag$_{0.1}$FeO$_3$ obtained by the calcining of La(Ag)–Fe–CO$_3$ at 700°C occurred at 409°C and showed a higher carbon oxidation activity when compared to LaFeO$_3$ (477 and 562°C) obtained by the calcining of La–Fe–CO$_3$ and La–Fe–O at 1100°C. The carbon oxidation activation energies observed for the non-catalyzed and catalyzed reactions (mixture of La$_{0.9}$Ag$_{0.1}$FeO$_3$) were 160 and 130 kJ·mol$^{-1}$, respectively.

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Key-words : Perovskite oxide, LaFeO$_3$, Precursor, Oxide-mixing, Activation energy

[Received July 16, 2012; Accepted November 6, 2012]

1. Introduction

The perovskite oxides, ABO$_3$, have been used in many applications, such as gas sensors, solid oxide fuel cells, sorbents for air separation and oxidation catalysts.$^{1-4}$ A solid state reaction method or chemical processing methods have been widely adopted for the preparation of such perovskite oxides. Perovskite oxides are conventionally prepared by a solid-state reaction of the corresponding single oxides at high temperatures. By using these methods, it is difficult to obtain single phase materials, since residual amounts of the starting oxides are likely to remain in the final product, unless the repeated cycling of milling and heating are performed. Moreover, because the synthesis occurs at high temperatures, the obtained powders have a low specific surface area. The synthesis using chemical processing methods, such as a co-precipitation method, sol–gel method, glycothermal method and heteronuclear complex method, is performed at considerably lower temperatures than that through the solid-state reaction methods, and finer perovskite oxides are obtained.$^{5-7}$ Besides these studies, it was reported that the Ag-doped perovskite oxides, La$_{1-x}$Ag$_x$FeO$_x$ (0.0 < x < 0.3), were synthesized at 400°C by a glycinothermal method.$^9$ Recently, we proposed the development of catalysts which promote the combustion (oxidation) of soot (carbon), a principal ingredient of particulate matter emitted from diesel engines, at low temperature. It was reported that La$_2$CuO$_4$ and Pr$_2$CuO$_4$ showed higher carbon oxidation activities of the rare-earth cop-
La(Fe)–Fe–CO₃, respectively. A co-precipitate of La–Fe–CO₃ and La(Fe)–Fe–CO₃ was obtained by the titration of an ammonium hydrogen carbonate aqueous solution into a 1:1 solution of La and Fe and a 0.9:0.1:1 solution of La, Ag and Fe in which La(NO₃)₃·6H₂O, AgNO₃ and Fe(NO₃)₃·9H₂O were dissolved in deionized water. The precursors of LaFeO₃ prepared by the oxide-mixing method (SS) were labeled La–Fe–O, and the 1:1 mixture of La₂O₃ and Fe₂O₃ was prepared by ball-milling for 24 h. The precursors were dried at 100°C and calcined in the temperature range of 400 to 1100°C in air for 2 h.

2.2 Measurement

The precursors and samples calcined at several temperatures were characterized by powder X-ray diffraction (XRD, Rigaku MiniFlex II) measurements using Cu Kα radiation in the 2θ range of 20 to 80°. The morphology of the powder was examined using a scanning electron microscope (SEM-EDX, JEOL 6510LA) fitted with an energy dispersive X-ray analyzer (EDX). Three-point BET method by N₂ gas adsorption (Quantachrome NOVA3200) was used for the determination of the specific surface area after each sample was desorbed at 200°C. The samples and carbon black (Tokai Carbon Co., Ltd., #8500/F), as a model soot, were well mixed in the powder/carbon weight ratio of 19:1, and the mixture was then subjected to the evaluation of the carbon oxidation activity. The oxidation (combustion) experiments were carried out by heating the mixture (10 mg) from room temperature to 700°C at 10°C·min⁻¹ in a 20 ml·min⁻¹ air flow using a differential scanning calorimeter (DSC, Rigaku DSC8230) and thermo-gravimetric and differential thermal analyzer (TG–DTA, Rigaku TG8120).

The apparent activation energy of the carbon oxidation was determined by the Ozawa method using the following expression:13)

$$\frac{d \log(\Phi)}{d(1/T_x)} = \frac{0.4567 \cdot E_a}{R}$$

where $\Phi$ is the heating rate, $T_x$ is the temperature corresponding to the $x$ % carbon conversion, and $E_a$ is the apparent activation energy in kJ·mol⁻¹. $E_a$ can be estimated from the slope of the least squares straight line fit of $\log(\Phi)$ versus $1/T_x$ plot. The apparent activation energy experiments of the carbon oxidation were carried out by heating the mixture (10 mg) from room temperature to 700°C at 2, 5, 10 and 20°C·min⁻¹ in a 200 ml·min⁻¹ air flow by TG.

3. Results and discussion

3.1 Analysis of La₀.₉Ag₀.₁FeO₃ and LaFeO₃ powders by XRD and SEM-EDX

The XRD results of the products of La(Fe)–Fe–CO₃, La–Fe–CO₃ and La–Fe–O calcined at several temperatures for 2 h are shown in Figs. 1, 2 and 3, respectively. As seen in Fig. 1, some peaks attributed to the LaFeO₃ perovskite oxide were observed together with a broad band centered at about 30° in 2θ for the XRD pattern of La(Fe)–Fe–CO₃ calcined at 500°C. When La(Fe)–Fe–CO₃ was calcined at temperatures higher than 600°C, the XRD analysis showed only the pattern corresponding to the LaFeO₃ perovskite oxide and no peaks attributable to La₂O₃, Fe₂O₃, Ag₂O or Ag were observed. The synthesis of samples with $x \geq 0.2$ was tried, but an impurity, Fe₂O₃, was observed in the LaFeO₃ phase. On the other hand, weak peaks attributed to LaFeO₃ and La₂O₃ were observed for La–Fe–CO₃ calcined at 400°C as shown in Fig. 2. The formation of the LaFeO₃ perovskite oxide was clearly recognized at the calcining temperatures above 800°C. The peaks of La₂O₃ become smaller as the calcining temperature increased and then disappeared at 1100°C.

As seen in Fig. 3, the XRD pattern of La–Fe–O calcined at 900°C showed many peaks attributed to La₂O₃ and Fe₂O₃ as the minor products, together with some peaks attributed to the perovskite oxide, LaFeO₃, as the major product. The intensity of the La₂O₃ and Fe₂O₃ peaks decreased with the increasing calcining temperature and some peaks attributed to La₂O₃ and Fe₂O₃ were not detected for La–Fe–O calcined at 1100°C. When the synthesis of La₀.₉Ag₀.₁FeO₃ using La₂O₃, Ag₂O and Fe₂O₃ by the oxide-mixing method was examined, the mixtures of LaFeO₃, La₂O₃, Fe₂O₃ and Ag₂O were observed below 800°C. At temperatures above 900°C, weak peaks attributed to LaFeO₃, La₂O₃, Fe₂O₃ and Ag were detected and the single phase of LaFeO₃ was still observed at even 1100°C. It is assumed that the low formation temperature with La₀.₉Ag₀.₁FeO₃ depends on the high oxygen diffusion ability of Ag.14) In order to investigate the
due to the combustion of the carbon black. On the other hand, it
with the literature data (ICDD No. 37-1493, orthorhombic), the
et al.8) the La, Ag and Fe species was very homogeneous.
(0.24001 and 0.24000 nm³) of LaFeO₃ obtained by the calcining
by the calcining of La(Ag)
350 to 450°C and an exothermic DTA peak with a maximum at
3.2 Carbon oxidation performance evaluated by TG–DTA and DSC
more details, it is necessary to progress the oxygen diffusion
measurements in La₉₀Ag₉₀FeO₉₀ and LaFeO₃. In agreement
the crystallographic data for the LaFeO₃ perovskite oxide obtained
by the calcining of La(Ag)–Fe–CO₃, La–Fe–CO₃ and La–Fe–O
were evaluated as shown in Table 1. The cell volumes of LaFeO₃ obtained
by the calcining of La(Ag)–Fe–CO₃ decreased with an increase in the calcining temperature. On the other hand, the
volume (0.24323 nm³) of La₉₀Ag₉₀FeO₉₀ obtained by the calcining of La(Ag)–Fe–CO₃ at 1100°C is larger than those
(0.24001 and 0.24000 nm³) of LaFeO₃ obtained by the calcining of La–Fe–CO₃ and La–Fe–O, probably due to the larger ionic size (0.115 nm) of Ag⁺ than that (0.1061 nm) of La³⁺.15) However, this result was not consistent with that reported by Bellakki et al.9) Figure 4 shows the elemental analysis results by SEM-
EDX for La₉₀Ag₉₀FeO₉₀ calcined at 700°C. The distribution of the La, Ag and Fe species was very homogeneous.

<table>
<thead>
<tr>
<th>Calcination temperature/°C</th>
<th>a/nm</th>
<th>b/nm</th>
<th>c/nm</th>
<th>V/nm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>0.56092</td>
<td>0.78429</td>
<td>0.55423</td>
<td>0.24382</td>
</tr>
<tr>
<td>700</td>
<td>0.55910</td>
<td>0.78454</td>
<td>0.55497</td>
<td>0.24343</td>
</tr>
<tr>
<td>La₉₀Ag₉₀FeO₉₀</td>
<td>800</td>
<td>0.55670</td>
<td>0.78600</td>
<td>0.56607</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>0.55633</td>
<td>0.78631</td>
<td>0.56618</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>0.55623</td>
<td>0.78628</td>
<td>0.56615</td>
</tr>
<tr>
<td>LaFeO₃(CP)</td>
<td>1100</td>
<td>0.55399</td>
<td>0.78294</td>
<td>0.55336</td>
</tr>
<tr>
<td>LaFeO₃(SS)</td>
<td>1100</td>
<td>0.55393</td>
<td>0.78300</td>
<td>0.55336</td>
</tr>
</tbody>
</table>

Table 2. Specific surface areas (SA), DSC peak temperatures corresponding to combustion of carbon back (T_DSC), and apparent activation energies of the carbon oxidation (E_a) of La₉₀Ag₉₀FeO₉₀ and LaFeO₃

<table>
<thead>
<tr>
<th>Calcination temperature/°C</th>
<th>SA/m²·g⁻¹</th>
<th>T_DSC/°C</th>
<th>E_a/kJ·mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>29.34</td>
<td>426</td>
<td>136</td>
</tr>
<tr>
<td>700</td>
<td>16.39</td>
<td>409</td>
<td>130</td>
</tr>
<tr>
<td>La₉₀Ag₉₀FeO₉₀</td>
<td>800</td>
<td>9.81</td>
<td>474</td>
</tr>
<tr>
<td>La₉₀Ag₉₀FeO₉₀</td>
<td>1000</td>
<td>2.60</td>
<td>525</td>
</tr>
<tr>
<td>LaFeO₃(CP)</td>
<td>1100</td>
<td>0.58</td>
<td>592</td>
</tr>
<tr>
<td>LaFeO₃(SS)</td>
<td>1100</td>
<td>3.04</td>
<td>477</td>
</tr>
<tr>
<td>Carbon back</td>
<td>—</td>
<td>6.06</td>
<td>562</td>
</tr>
</tbody>
</table>

The DSC peak temperature corresponding to the combustion of the carbon black was evaluated to be 665°C, and drastically decreased to 409°C when La₉₀Ag₉₀FeO₉₀ calcined at 700°C was mixed as a catalyst. The (carbon black + La₉₀Ag₉₀FeO₉₀ calcined at 700°C) mixture showed the DSC exothermic peak at 409°C, which was 256°C lower than that (665°C) of the carbon black itself. For the [carbon black + LaFeO₃ (CP) calcined at 1100°C] mixture and the [carbon black + LaFeO₃ (SS) calcined at 1100°C] mixture, the DSC exothermic peak temperatures were 477 and 562°C, respectively. The higher the calcination temperature, the lower its oxidation activity toward carbon black becomes. As seen in Table 2, the specific surface areas of La₉₀Ag₉₀FeO₉₀ calcined at 700°C, LaFeO₃ (CP) calcined at 1100°C and LaFeO₃ (SS) calcined at 1100°C were estimated to be 16.39, 3.04 and 0.96 m²·g⁻¹, respectively. These findings are consistent with the report that the surface area is one of the important factors controlling the catalytic performance for diesel particulate combustion.17) This tendency can be confirmed on La₉₀Ag₉₀FeO₉₀ calcined at several temperatures. On the other hand, the carbon oxidation activity of La₉₀Ag₉₀FeO₉₀ calcined at 600°C is low though the specific surface area is high. It is postulated that this is due to the poor mixing with the carbon black for the agglutination of the catalyst. Further researches on the mechanisms of oxidation activity for carbon black are in progress by several complex oxides.

By applying the different heating rates during the carbon oxidation in the TG, the Ozawa plots at the various carbon conversion levels were constructed (an example for La₉₀Ag₉₀FeO₉₀ calcined at 700°C is shown in Fig. 7). The plots of the logarithmic heating rates used versus the inverse temperatures at the various carbon conversion levels showed a good linear fit. Such experiments were carried out for all the samples. The carbon oxidation activation energies (E_a), estimated from the slopes of the linear fits, are given in Table 2. The activation energies for the non-catalyzed and catalyzed reactions were 160 and 130–141 kJ·mol⁻¹, respectively, and the presence of a catalyst significantly influenced this activation energy. The activation energy for the non-catalyzed one was consistent with that (163 kJ·mol⁻¹) reported by Dhakad et al.18) Such a difference may be caused by the evolution of active oxygen from the
catalyst. As seen in Table 2, the small changes observed in the activation energies for the catalyzed reaction are thought to be due to the difference in the specific surface areas. The activation energy of La$_{0.9}$Ag$_{0.1}$FeO$_x$ calcined at 600°C, is 6 kJ·mol$^{-1}$ is higher than that at 700°C. It is thought that this difference is due to the poor mixing state with the carbon black for the agglutination of the catalyst though the specific surface area is high, as described in section 3.2.

4. Conclusions

The perovskite oxides, La$_{0.9}$Ag$_{0.1}$FeO$_x$ and LaFeO$_x$, synthesized by the calcination of the co-precipitated precursors (La$_2$-(CO$_3$)$_3$)$_{0.9}$·(Ag$_2$CO$_3$)$_{0.1}$·Fe$_2$(CO$_3$)$_3$ (La(Ag)-Fe-CO$_3$) and La$_2$-(CO$_3$)$_3$·Fe$_2$(CO$_3$)$_3$ (La-Fe-CO$_3$)) and a mixture of La$_2$O$_3$ and Fe$_2$O$_3$ (La-Fe-O) and their oxidation activities for carbon black were examined using a differential scanning calorimeter (DSC) and a thermo-gravimetric analyzer (TG).

(1) The formation of the single phase perovskite oxides is clearly recognized for La(Ag)-Fe-CO$_3$, La-Fe-CO$_3$ and La-Fe-O at calcining temperatures above 600, 1100 and 1100°C, respectively. The effect of the Ag solution was confirmed for the low temperature synthesis of the perovskite oxide.
The DSC peak temperature corresponding to the combustion of the carbon black decreased to 409°C by mixing La$_{0.9}$Ag$_{0.1}$FeO$_3$ obtained by the calcining of La(Ag)$_3$Fe$_2$CO$_3$ at 700°C, whereas the carbon black itself was oxidized at 665°C. On the other hand, when the carbon black was mixed with LaFeO$_3$ obtained by the calcining of LaFe$_2$CO$_3$ and LaFe$_2$O$_3$ at 1100°C, the combustion temperatures of the carbon blacks were 477 and 562°C, respectively. The specific surface areas of La$_{0.9}$Ag$_{0.1}$FeO$_3$, LaFeO$_3$ (LaFe$_2$CO$_3$) and LaFeO$_3$ (LaFe$_2$O$_3$) were estimated to be 16.39, 3.04 and 0.96 m$^2$·g$^{-1}$, respectively, and the combustion temperature decreased with the increasing specific surface area of the catalyst.

(3) The activation energies for the non-catalyzed and catalyzed reactions were 160 and 130–141 kJ·mol$^{-1}$, respectively. The activation energies of La$_{0.9}$Ag$_{0.1}$FeO$_3$, LaFeO$_3$ (LaFe$_2$CO$_3$) and LaFeO$_3$ (LaFe$_2$O$_3$) were estimated to be 16.39, 3.04 and 0.96 m$^2$·g$^{-1}$, respectively, and the combustion temperature decreased with the increasing specific surface area of the catalyst.

Based on these results, it was found that the La$_{0.9}$Ag$_{0.1}$FeO$_3$ synthesized by the calcination of the co-precipitated precursors (La$_2$(CO$_3$)$_3$)$_{0.9}$(Ag$_2$CO$_3$)$_{0.1}$Fe$_2$(CO$_3$)$_3$ is pure and a very fine perovskite oxide powder was obtained at low temperatures. This synthesis method is rather simple and the obtained La$_{0.9}$Ag$_{0.1}$FeO$_3$ is expected for application on a catalyst which promotes the low temperature combustion of soot as the principal ingredient of particulate matter emitted from diesel engines.

The activation energies for the non-catalyzed and catalyzed reactions were 160 and 130–141 kJ·mol$^{-1}$, respectively. The activation energies of La$_{0.9}$Ag$_{0.1}$FeO$_3$, LaFeO$_3$ (LaFe$_2$CO$_3$) and LaFeO$_3$ (LaFe$_2$O$_3$) were estimated to be 130, 140 and 139 kJ·mol$^{-1}$, respectively.

Based on these results, it was found that the La$_{0.9}$Ag$_{0.1}$FeO$_3$ synthesized by the calcination of the co-precipitated precursors (La$_2$(CO$_3$)$_3$)$_{0.9}$(Ag$_2$CO$_3$)$_{0.1}$Fe$_2$(CO$_3$)$_3$ is pure and a very fine perovskite oxide powder was obtained at low temperatures. This synthesis method is rather simple and the obtained La$_{0.9}$Ag$_{0.1}$FeO$_3$ is expected for application on a catalyst which promotes the low temperature combustion of soot as the principal ingredient of particulate matter emitted from diesel engines.

References