

Carbon oxidation activity of complex oxides (Part 2) —Characteristics of $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_\alpha$ 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 $[\text{La}(\text{Ag})\text{-Fe-CO}_3$ and $\text{La-Fe-CO}_3]$ and a mixture of La_2O_3 and Fe_2O_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 $\text{La}(\text{Ag})\text{-Fe-CO}_3$ was about 500°C lower than that of La-Fe-CO_3 . 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 $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_\alpha$ obtained by the calcining of $\text{La}(\text{Ag})\text{-Fe-CO}_3$ 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 $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_\alpha$) were 160 and 130 $\text{kJ}\cdot\text{mol}^{-1}$, respectively.

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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, $\text{La}_{1-x}\text{Ag}_x\text{FeO}_\alpha$ ($0.0 < x < 0.3$), were synthesized at 400°C by a glycinothermal method.⁸⁾ 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_2CuO_4 and Pr_2CuO_4 showed higher carbon oxidation activities of the rare-earth cop-

per oxides.⁹⁾ The combustion temperature of the carbon black decreased to 465°C by mixing the La_2CuO_4 and Pr_2CuO_4 , whereas the carbon black itself was oxidized at 665°C. Similarly, perovskite oxides are good candidate catalysts for diesel soot combustion, because of their good redox properties, thermochemical stability and tunable catalytic performances.¹⁰⁾ The oxidation activity of the perovskite oxide catalysts can be comparable to that of the noble metal catalysts under suitable conditions. Fino et al. have related the reactivity of perovskite oxide for soot combustion with the abundance of α -oxygen (O^- species) that is weakly chemisorbed on the surface of perovskite oxide and able to enrich the surface of soot particles with oxygenated species.^{11),12)} To improve the carbon oxidation activity of the perovskite oxide, it is thought that the larger supply of oxygen from the perovskite oxide lattice and/or the larger surface area influences the activation of soot combustion. Therefore, it is assumed that the addition of the large ionic size metal (e.g. Ag) in the perovskite oxide and the synthesis of perovskite oxide at lower temperature are effective. In the present study, we examined the synthesis of the Ag-doped perovskite oxides, $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_\alpha$, at low temperature using a co-precipitation method and the carbon oxidation activity of the perovskite oxide prepared by the calcination of co-precipitated precursors, $(\text{La}_2(\text{CO}_3)_3)_{0.9}(\text{Ag}_2\text{CO}_3)_{0.1}\cdot\text{Fe}_2(\text{CO}_3)_3$ and $\text{La}_2(\text{CO}_3)_3\cdot\text{Fe}_2(\text{CO}_3)_3$, and a mixture of La_2O_3 and Fe_2O_3 .

2. Experimental

2.1 Sample preparation

The precursors of LaFeO_3 and $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_\alpha$ prepared by the co-precipitation method (CP) were labeled La-Fe-CO_3 and

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$\text{La}(\text{Ag})\text{-Fe-CO}_3$, respectively. A co-precipitate of La-Fe-CO_3 and $\text{La}(\text{Ag})\text{-Fe-CO}_3$ 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 $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, AgNO_3 and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in deionized water. The precursors of LaFeO_3 prepared by the oxide-mixing method (SS) were labeled La-Fe-O , and the 1:1 mixture of La_2O_3 and Fe_2O_3 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 $\text{Cu K}\alpha$ 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 N_2 gas adsorption (Quantachrome NOVA3200) was used for the determination of the specific surface area after each sample was deaerated 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 $10^\circ\text{C}\cdot\text{min}^{-1}$ in a $20\text{ ml}\cdot\text{min}^{-1}$ 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⁾

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

where Φ is the heating rate, T_x is the temperature corresponding to the x % carbon conversion, and E_a is the apparent activation energy in $\text{kJ}\cdot\text{mol}^{-1}$. 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 $20^\circ\text{C}\cdot\text{min}^{-1}$ in a $200\text{ ml}\cdot\text{min}^{-1}$ air flow by TG.

3. Results and discussion

3.1 Analysis of $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_x$ and LaFeO_3 powders by XRD and SEM-EDX

The XRD results of the products of $\text{La}(\text{Ag})\text{-Fe-CO}_3$, La-Fe-CO_3 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 LaFeO_3 perovskite oxide were observed together with a broad band centered at about 30° in 2θ for the XRD pattern of $\text{La}(\text{Ag})\text{-Fe-CO}_3$ calcined at 500°C . When $\text{La}(\text{Ag})\text{-Fe-CO}_3$ was calcined at temperatures higher than 600°C , the XRD analysis showed only the pattern corresponding to the LaFeO_3 perovskite oxide and no peaks attributable to La_2O_3 , Fe_2O_3 , Ag_2O or Ag were observed. The synthesis of samples with $x \geq 0.2$ was tried, but an impurity, Fe_2O_3 , was observed in the LaFeO_3 phase. On the other hand, weak peaks attributed to LaFeO_3 and La_2O_3 were observed for La-Fe-CO_3 calcined at 400°C as shown in Fig. 2. The formation of the LaFeO_3 perovskite oxide was clearly recognized at the calcining temperatures above 800°C . The peaks of La_2O_3 become smaller as the

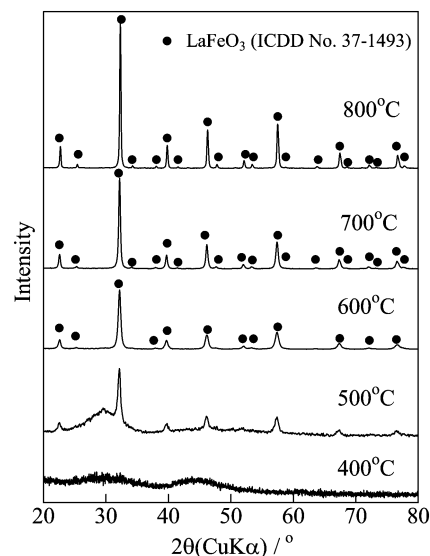


Fig. 1. XRD results of $\text{La}(\text{Ag})\text{-Fe-CO}_3$ calcined at several temperatures.

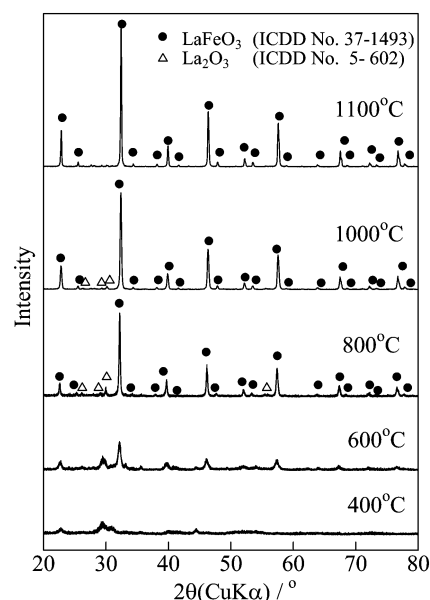


Fig. 2. XRD results of La-Fe-CO_3 calcined at several temperatures.

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 La_2O_3 and Fe_2O_3 as the minor products, together with some peaks attributed to the perovskite oxide, LaFeO_3 , as the major product. The intensity of the La_2O_3 and Fe_2O_3 peaks decreased with the increasing calcining temperature and some peaks attributed to La_2O_3 and Fe_2O_3 were not detected for La-Fe-O calcined at 1100°C . When the synthesis of $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_x$ using La_2O_3 , Ag_2O and Fe_2O_3 by the oxide-mixing method was examined, the mixtures of LaFeO_3 , La_2O_3 , Fe_2O_3 and Ag_2O were observed below 800°C . At temperatures above 900°C , weak peaks attributed to LaFeO_3 , La_2O_3 , Fe_2O_3 and Ag were detected and the single phase of LaFeO_3 was still observed at even 1100°C . It is assumed that the low formation temperature with $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_x$ depends on the high oxygen diffusion ability of Ag.¹⁴⁾ In order to investigate the

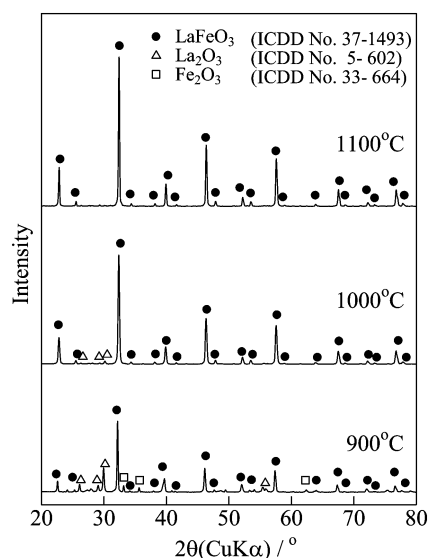


Fig. 3. XRD results of La-Fe-O calcined at several temperatures.

Table 1. Cell constants and cell volumes of $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_x$ and LaFeO_3

	Calcination temperature/°C	a/nm	b/nm	c/nm	V/nm ³
$\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_x$	600	0.56092	0.78429	0.55423	0.24382
	700	0.55910	0.78454	0.55497	0.24343
	800	0.55670	0.78600	0.55607	0.24332
	1000	0.55633	0.78631	0.55618	0.24330
	1100	0.55623	0.78628	0.55615	0.24323
$\text{LaFeO}_3(\text{CP})$	1100	0.55399	0.78294	0.55336	0.24001
$\text{LaFeO}_3(\text{SS})$	1100	0.55393	0.78300	0.55336	0.24000

more details, it is necessary to progress the oxygen diffusion measurements in $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_x$ and LaFeO_3 . In agreement with the literature data (ICDD No. 37-1493, orthorhombic), the crystallographic data for the LaFeO_3 perovskite oxide obtained by the calcining of $\text{La}(\text{Ag})\text{-Fe-CO}_3$, La-Fe-CO_3 and La-Fe-O were evaluated as shown in Table 1. The cell volumes of LaFeO_3 obtained by the calcining of $\text{La}(\text{Ag})\text{-Fe-CO}_3$ decreased with an increase in the calcining temperature. On the other hand, the cell volume (0.24323 nm³) of $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_x$ obtained by the calcining of $\text{La}(\text{Ag})\text{-Fe-CO}_3$ at 1100°C is larger than those (0.24001 and 0.24000 nm³) of LaFeO_3 obtained by the calcining of La-Fe-CO_3 and La-Fe-O , probably due to the larger ionic size (0.115 nm) of Ag^+ than that (0.1061 nm) of La^{3+} .¹⁵⁾ However, this result was not consistent with that reported by Bellakki et al.⁸⁾ Figure 4 shows the elemental analysis results by SEM-EDX for $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_x$ calcined at 700°C. The distribution of the La, Ag and Fe species was very homogeneous.

3.2 Carbon oxidation performance evaluated by TG-DTA and DSC

Figure 5 shows the TG-DTA curves of the (carbon black + $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_x$ calcined at 700°C) mixture, in which the amount of carbon black was 5 wt %. The weight gradually decreased from room temperature. An abrupt weight loss occurred in the range of 350 to 450°C and an exothermic DTA peak with a maximum at 409°C was observed. The weight loss above 300°C, ca. 5 wt %, is due to the combustion of the carbon black. On the other hand, it is thought that the weight loss below 300°C is due to the release

Table 2. Specific surface areas (SA), DSC peak temperatures corresponding to combustion of carbon black (T_{DSC}) and apparent activation energies of the carbon oxidation (E_a) of $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_x$ and LaFeO_3

	Calcination temperature/°C	SA/m ² ·g ⁻¹	$T_{\text{DSC}}/^\circ\text{C}$	$E_a/\text{kJ}\cdot\text{mol}^{-1}$
$\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_x$	600	29.34	426	136
	700	16.39	409	130
	800	9.81	474	134
	1000	2.60	525	140
	1100	0.58	592	141
$\text{LaFeO}_3(\text{CP})$	1100	3.04	477	140
$\text{LaFeO}_3(\text{SS})$	1100	0.96	562	139
Carbon black	—	—	665	160

of CO_2 which $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_x$ had absorbed. The CO_2 absorptivity of the perovskite oxide is known¹⁶⁾ and the abrupt weight loss (release of CO_2) around 350°C from the TG measurement is observed for $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_x$ that has been left in the open atmosphere. Figure 6 shows DSC curves of the carbon black itself, (carbon black + $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_x$ calcined at 700°C) mixture, [carbon black + LaFeO_3 (CP) calcined at 1100°C] mixture and [carbon black + LaFeO_3 (SS) calcined at 1100°C] mixture. 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 $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_x$ calcined at 700°C was mixed as a catalyst. The (carbon black + $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_x$ 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 + LaFeO_3 (CP) calcined at 1100°C] mixture and the [carbon black + LaFeO_3 (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 $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_x$ calcined at 700°C, LaFeO_3 (CP) calcined at 1100°C and LaFeO_3 (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 $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_x$ calcined at several temperatures. On the other hand, the carbon oxidation activity of $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_x$ 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 agglomeration 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 $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_x$ 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 did significantly influence 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

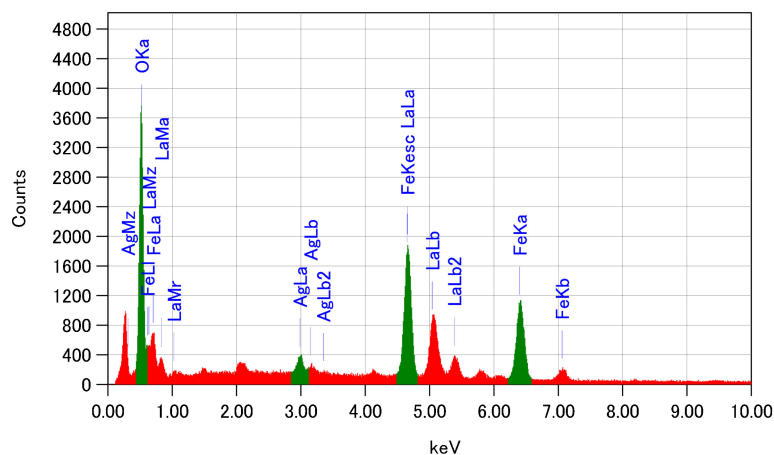
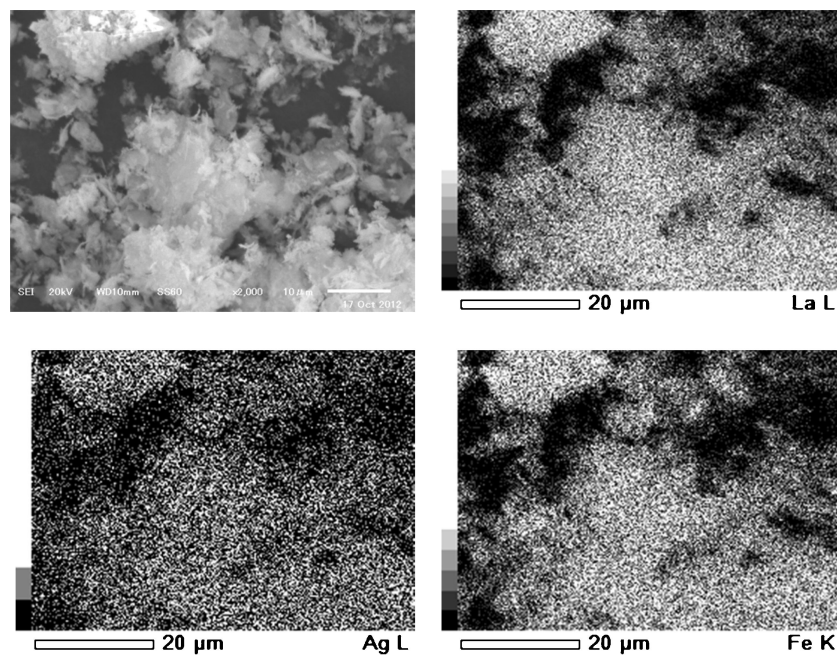


Fig. 4. (Color online) SEM-EDX analysis for $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_x$ calcined at 700°C .

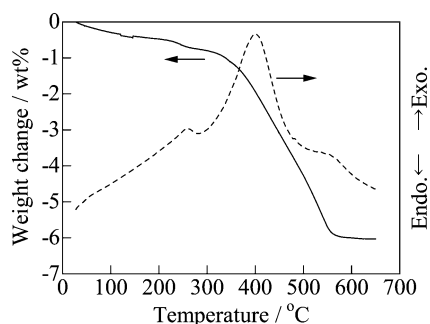


Fig. 5. TG-DTA curves of (carbon black + $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_x$ calcined at 700°C) mixture.

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 $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_x$ calcined at 600°C , is $6\text{ kJ}\cdot\text{mol}^{-1}$ 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, $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_x$ and LaFeO_3 , synthesized by the calcination of the co-precipitated precursors ($\text{La}_2(\text{CO}_3)_3$) $_{0.9}$ (Ag_2CO_3) $_{0.1}$ $\cdot\text{Fe}_2(\text{CO}_3)_3$ ($\text{La}(\text{Ag})\text{-Fe-CO}_3$) and $\text{La}_2(\text{CO}_3)_3\cdot\text{Fe}_2(\text{CO}_3)_3$ (La-Fe-CO_3) and a mixture of La_2O_3 and Fe_2O_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 $\text{La}(\text{Ag})\text{-Fe-CO}_3$, 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.

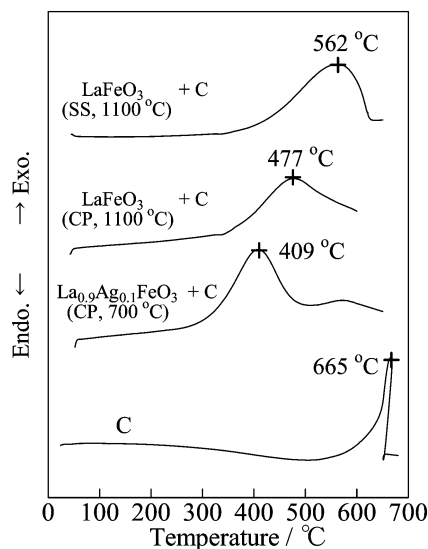


Fig. 6. DSC curves of carbon black, [carbon black + $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_\alpha$ calcined at 700°C] mixture, [carbon black + LaFeO_3 (CP) calcined at 1100°C] mixture and [carbon black + LaFeO_3 (SS) calcined at 1000°C] mixture.

- (2) The DSC peak temperature corresponding to the combustion of the carbon black decreased to 409°C by mixing $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_\alpha$ obtained by the calcining of $\text{La}(\text{Ag})\text{-Fe-CO}_3$ 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 La-Fe-CO_3 and La-Fe-O at 1100°C, the combustion temperatures of the carbon blacks were 477 and 562°C, respectively. The specific surface areas of $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_\alpha$, LaFeO_3 (La-Fe-CO_3) and LaFeO_3 (La-Fe-O) were estimated to be 16.39, 3.04 and 0.96 $\text{m}^2\cdot\text{g}^{-1}$, 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 $\text{kJ}\cdot\text{mol}^{-1}$, respectively. The activation energies of $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_\alpha$, LaFeO_3 (La-Fe-CO_3) and LaFeO_3 (La-Fe-O) were estimated to be 130, 140 and 139 $\text{kJ}\cdot\text{mol}^{-1}$, respectively.

Based on these results, it was found that the $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_\alpha$ synthesized by the calcination of the co-precipitated precursors $(\text{La}_2(\text{CO}_3)_3)_{0.9}(\text{Ag}_2\text{CO}_3)_{0.1}\cdot\text{Fe}_2(\text{CO}_3)_3$ is pure and a very fine perovskite oxide powder was obtained at low temperatures. This synthesis method is rather simple and the obtained $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_\alpha$ 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.

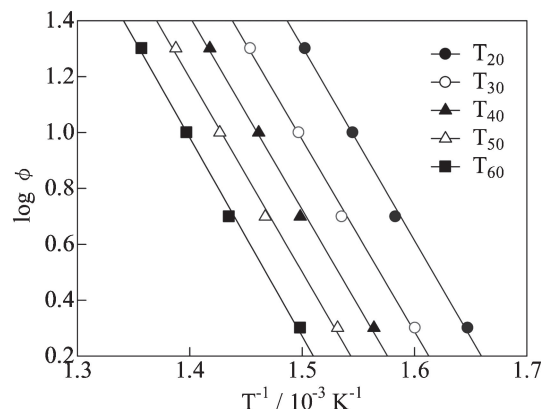


Fig. 7. Ozawa plots of $\text{La}_{0.9}\text{Ag}_{0.1}\text{FeO}_\alpha$ (700°C) at different carbon black conversion levels. Different heating rates (5, 10, 15 and 20°C·min⁻¹) were applied during the carbon black oxidation.

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