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Synthesis of perovskite-type $(La_{1-x}Ca_x)CoO_3$ at low temperature using ethylene glycol and citric acid

**Hideki Taguchi · Satoshi Yamasaki · Mahiko Nagao ·
Yumi Sato · Ken Hirota · Osamu Yamaguchi**

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Abstract To synthesize perovskite-type $(La_{1-x}Ca_x)CoO_3$ with good crystallinity (regularity of ions), a gel was prepared by adding ethylene glycol and citric acid to an aqueous solution of $La(NO_3)_3 \cdot 6H_2O$, $CaCO_3$, and $Co(CH_3COO)_2 \cdot 4H_2O$. Perovskite-type $(La_{1-x}Ca_x)CoO_3$ ($0.0 \le x \le 0.3$) was obtained by firing the gel above 600 °C in air for 3 h. Samples were examined for oxygen content, crystallite size, specific surface area, and the catalytic activity of CH_4 oxidation. The samples were also investigated by transmission electron microscopy (TEM). Based on the variation in crystallite size and in the average particle size, the $(La_{1-x}Ca_x)CoO_3$ particle became finer as x increased. In all samples, CH_4 oxidation occurred above 300°C. The catalytic activity of $(La_{1-x}Ca_x)CoO_3$ fired at 700 °C monotonously increased as x increased.

Introduction

There has been an interest in examining the catalytic oxidation of hydrocarbon (C_nH_{2n+2}) or the direct decomposition of nitric oxide on perovskite-type $LaMO_3$ (M = Cr, Mn, Fe, Co, and Ni) [1–6]. Since catalytic decomposition occurs on the outermost surface, $LaMO_3$ must be synthesized with good crystallinity (regularity of ions) and/or a large specific surface area. $LaCoO_3$ has a rhombohedral perovskite-type structure and shows the high catalytic activity of CO oxidation [1, 3, 7]. $LaCoO_3$ is generally synthesized above 800 °C using a mixture of acetates or metal nitrates as starting materials, and the specific surface area of $LaCoO_3$ is less than 5 m^2/g [1–3].

Taguchi et al. reported the synthesis of $LaMnO_3$ and $LaCoO_3$ using poly(acrylic acid) [8–12]. Although $LaMnO_3$ was obtained at a low temperature, those authors noticed that the amount of poly(acrylic acid) strongly influenced both the crystal structure and the oxygen content [9]. Thereafter, they elucidated that the rapid combustion of poly(acrylic acid) caused large numbers of cracks [11, 12]. To decrease the cracking of $LaMnO_3$ and $LaCoO_3$, they prepared a gel by adding citric acid to the aqueous solution of metal nitrates and then fired the gel above 500 °C for $LaMnO_3$ and above 600 °C for $LaCoO_3$, respectively [13, 14]. Based on the catalytic activity of CO oxidation, they reported that citric acid improved the crystallinity of $LaMnO_3$ and $LaCoO_3$. However, when the gel with citric acid or poly(acrylic acid) was fired, a lot of powder blew out of the crucible.

Perovskite-type $(La_{1-x}Ca_x)CoO_3$ is semiconductive in the range of $0.0 \le x \le 0.15$ and metallic in the range of $0.2 \le x \le 0.5$ [15, 16]. Samoilov *et al.* reported that $(La_{1-x}Ca_x)CoO_3$ exhibits novel magnetoresistive behavior at $x = 0.2$ and a very large spontaneous Hall effect at $x \ge 0.2$ [17]. The Co^{4+} ion content of $(La_{1-x}Ca_x)CoO_3$ increases as x increases. Therefore, it is interesting to clarify the relationship between the

H. Taguchi (✉) · S. Yamasaki · M. Nagao
Research Laboratory for Surface Science,
Faculty of Science, Okayama University,
3-1-1 Tushima-naka, Okayama 700-8530, Japan
e-mail: htaguchi@cc.okayama-u.ac.jp

Y. Sato · K. Hirota · O. Yamaguchi
Department of Molecular Science and Technology,
Faculty of Engineering, Doshisha University,
1-3 Tatara-miyakotani, Kyo-tanabe, Kyoto 610-0321, Japan

catalytic activity of CH_4 decomposition and the Co^{4+} ion content of $(La_{1-x}Ca_x)CoO_3$. Merino *et al.*, prepared the gel of $(La_{1-x}Ca_x)CoO_3$ by adding the aqueous solution of citric acid to that of the metal nitrates, and the gel was calcined in air at 600 °C [18]. The specific surface area increased from 7.3 m^2/g for $LaCoO_3$ to 19.1 m^2/g for $(La_{0.5}Ca_{0.5})CoO_3$. For the measurement of electrocatalytic activity and stability of $(La_{1-x}Ca_x)CoO_3$, Kahoul et al. prepared the gel by dissolving the metal nitrates and citric acid in 1–propanol, and the gel was calcined in air at 700 °C [19]. Weidenkaff reported the microemulsion and polynuclear polymeric syntheses of nanostructured perovskite-type oxides [20]. In the microemulsion synthesis, the precipitation was prepared by titrating the specific amount of nonylphenyl-polyethylene glycol and *n*-octane with the solution of the metal nitrates. Then, precipitation was separated by centrifugation and calcined in air at 700 °C. On the other hand, in the polynuclear polymeric syntheses, the precursor was prepared by adding citric acid and the polymer additives to the solution of the metal nitrates. The solution was treated in an aerosol process to dry and decompose the precursor droplets and to form the metal oxides at 700 °C.

In the present study, we synthesized perovskite-type $(La_{1-x}Ca_x)CoO_3$ with good crystallinity (regularity of ions) using Pechini-type polymerized complex route [21]. To prepare the gel, both ethylene glycol and citric acid were added to a solution of $La(NO_3)_3 \cdot 6H_2O$, $CaCO_3$, and $Co(CH_3COO)_2 \cdot 4H_2O$. Perovskite-type $(La_{1-x}Ca_x)CoO_3$ $(0.0 \le x \le 0.3)$ was obtained by firing the gel above 600 °C in air. We characterized $(La_{1-x}Ca_x)CoO_3$ samples by examining oxygen content, crystallite size, specific surface area, and the catalytic activity of CH_4 oxidation. We also examined the samples using transmission electron microscopy (TEM).

Experimental

To prepare the $(La_{1-x}Ca_x)CoO_3$ samples (0.0035 mol), high-purity powders of $La(NO_3)_3 \cdot 6H_2O$, $CaCO_3$, and $Co(CH_3COO)_2 \cdot 4H_2O$ were weighed to the desired proportions. Small amounts of distilled water and nitric acid were added to dissolve the powders. Then, citric acid (0.0035 mol) and ethylene glycol (0.014 mol) were added to make the gel. The solution was left to sit for 6 h at 100 °C until it had gelled, and the gel was fired at 600 °C, 700 °C, or 800 °C in air for 3 h. The heating rate was 10°C/min.

The oxygen content of each sample was determined by the oxidation-reduction method [22]. After sodium oxalate and perchloric acid were added to the sample, the dissolved solution was titrated with a standard potassium permanganate solution. The crystal structure of the powder sample was identified by powder X-ray diffractometry (XRD) with monochromatic CuKα radiation. The crystallite size (D_{024}) of the sample was calculated from the half-width of a diffraction peak (024) using the Scherrer formula [23].

The specific surface area of the particle was estimated using the BET method for nitrogen adsorption. The particle size was measured using TEM. The catalytic activity of CH_4 oxidation was measured by gas chromatography [14]. Each sample (0.20 g) was preheated at 300 °C in a flow of pure oxygen gas. A gas mixture of CH_4 (1.0%), O_2 (4.0%), and He (balance) was fed into a flow reactor at a flow rate of 1.00×10^{-4} m^3/min. The product was analyzed by gas chromatography using a column (molecular sieve 13×) kept at 50 °C during measurement.

Results and discussion

A homogeneous gel was obtained by adding citric acid and ethylene glycol to a solution of $La(NO_3)_3 \cdot 6H_2O$, $CaCO_3$, and $Co(CH_3COO)_2 \cdot 4H_2O$. The gel was fired at 600 °C, 700 °C, or 800 °C in air for 3 h. By adding citric acid and ethylene glycol, the amount of powder blew out of the crucible decreased. The XRD pattern of $(La_{1-x}Ca_x)CoO_3$ $(0.0 \le x \le 0.3)$ was completely indexed as a rhombohedral perovskite-type structure. Extra peaks in the XRD pattern of $(La_{0.6}Ca_{0.4})CoO_3$ $(x = 0.4)$ were assigned to cobalt oxides. Although Merino et al. or Kahoul et al. synthesized perovskite-type $(La_{1-x}Ca_x)CoO_3$ at 700 °C by firing the gel, we could lower the synthetic temperature by using citric acid and ethylene glycol [18, 19]. In the present study, therefore, we characterized $(La_{1-x}Ca_x)CoO_3$ in the range of $0.0 \le x \le 0.3$. The oxygen content ($3\text{-}\delta$) and the Co^{4+} ion content of $(La_{1-x}Ca_x)CoO_3$ are shown in Table 1. The Co^{4+} ion content of $(La_{0.8}Ca_{0.2})CoO_3$ $(x = 0.2)$ fired at 600 °C was somewhat low relative to the other samples. The Co^{4+} ion content of $(La_{1-x}Ca_x)CoO_3$ fired at 700 °C or 800 °C monotonously increased from 0% $(x = 0)$ to 22% $(x = 0.3)$.

The crystallite size (D_{024}) and the specific surface area of $(La_{1-x}Ca_x)CoO_3$ $(0.0 \le x \le 0.3)$ are shown in Table 2. At all firing temperatures, D_{024} monotonously decreased as x increased. In fixed composition, D_{024} increased as the firing temperature increased. Although the specific surface area of the samples fired at 700 °C is nearly equal to that reported by Merino et al. [18], the specific area of the samples fired at

Table 1 Relationships among firing temperature, oxygen content (3-δ), and Co^{4+} ion content of $(La_{1-x}Ca_x)CoO_3$

Firing temperature (°C)	x	3-δ	Co^{4+} ion content (%)
600	0.0	3.00	0
	0.1	3.00	10
	0.2	2.93	6
	0.3	2.93	16
700	0.0	3.00	0
	0.1	3.00	10
	0.2	2.96	12
	0.3	2.96	22
800	0.0	3.00	0
	0.1	3.00	10
	0.2	3.00	20
	0.3	2.96	22

Table 2 Relationships among crystallite size (D_{024}), specific surface area (S), average particle size (P_s), temperature corresponding to 50% conversion ($T_{1/2}$) from CH_4 to CO_2 and H_2O of $(La_{1-x}Ca_x)CoO_3$

Firing temperature (°C)	x	D_{024} (nm)	S (m^2/g)	P_s (nm)	$T_{1/2}$ (°C)
600	0.0	21.1	13.0	44	515
	0.1	14.4	15.7	22	484
	0.2	11.6	18.2	20	487
	0.3	10.5	20.8	16	484
700	0.0	24.8	9.9	56	555
	0.1	20.2	11.2	—	500
	0.2	16.5	12.4	—	495
	0.3	15.7	15.2	—	480
800	0.0	29.4	4.6	60	590
	0.1	24.8	4.5	—	554
	0.2	20.7	4.9	—	556
	0.3	18.8	4.6	—	552

600 °C is larger by 1.3–1.5 times than that fired at 700 °C. The specific surface area of the samples fired at 600 °C or 700 °C increased as x increased. On the other hand, the specific surface area of the sample fired at 800 °C was ca. 4.6 m^2/g and independent of x. Figure 1 shows the TEM photographs of $(La_{1-x}Ca_x)CoO_3$ (x = 0.0 and 0.2) fired at 600 °C. The particles did not show a distinctive shape, and their average size as determined from the TEM observation decreased from ca. 44 nm (x = 0.0) to ca. 16 nm (x = 0.3) as x increased (Table 2). This decrease corresponded to the variation in crystallite size (D_{024}). As the firing temperature increased, the average particle size of $LaCoO_3$ increased from ca. 44 nm to ca. 60 nm.

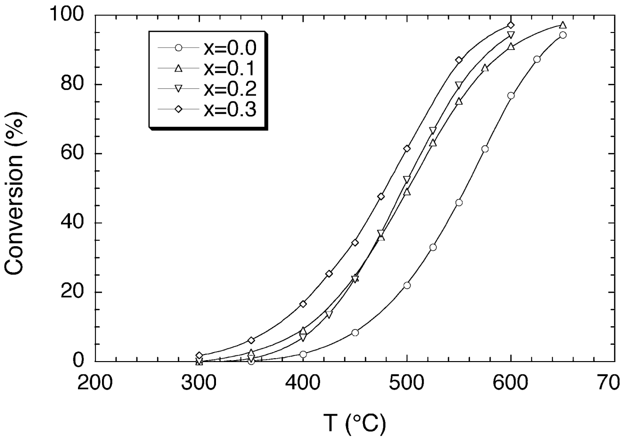

Fig. 2 The conversion from CH_4 to CO_2 and H_2O on $(La_{1-x}Ca_x)CoO_3$ fired at 700 °C in air for 3 h

Figure 2 shows the conversion from CH_4 to CO_2 and H_2O on $(La_{1-x}Ca_x)CoO_3$ ($0.0 \le x \le 0.3$) fired at 700 °C. In all of the samples, CH_4 oxidation occurred above 300 °C. The catalytic activity of a given catalyst is usually expressed in terms of temperature corresponding to 50% conversion ($T_{1/2}$) of CH_4 to CO_2 and H_2O, which can be obtained from the conversion-versus-temperature curve [24]. Table 2 shows the $T_{1/2}$ of each sample. That of $(La_{1-x}Ca_x)CoO_3$ fired at 600 °C or 800 °C fell in the range of $0.0 \le x \le 0.1$ and was independent of x in the range of $0.1 \le x \le 0.3$: ca. 485 °C for $(La_{1-x}Ca_x)CoO_3$ fired at 600 °C and ca. 555 °C for $(La_{1-x}Ca_x)CoO_3$ fired at 800 °C. On the other hand, the $T_{1/2}$ of $(La_{1-x}Ca_x)CoO_3$ fired at 700 °C fell monotonously as x increased. The $T_{1/2}$ of $LaFeO_3$

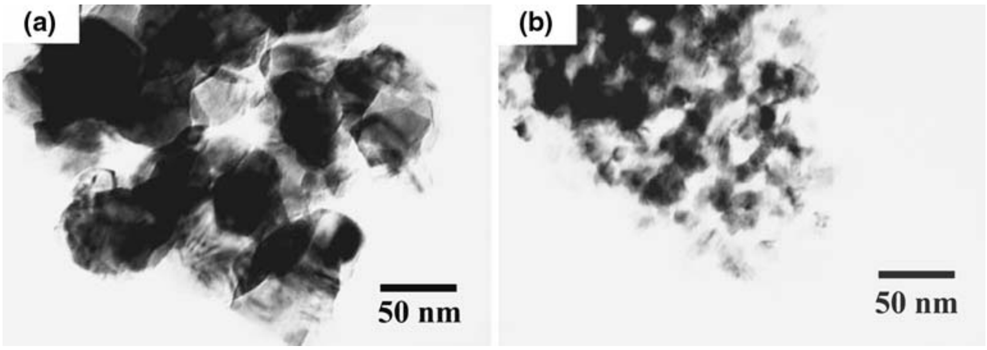

Fig. 1 TEM photographs of $(La_{1-x}Ca_x)CoO_3$ fired at 600 °C in air for 3 h: (**A**) x = 0.0 and (**B**) x = 0.2

and $(La_{0.8}Sr_{0.2})(Cu_{0.15}Fe_{0.85})O_3$ were reported at ca. 800 °C and ca. 780 °C, respectively [5, 6]. Since the $T_{1/2}$ of $(La_{1-x}Ca_x)CoO_3$ was 300 °C lower than that of $LaFeO_3$ or $(La_{0.8}Sr_{0.2})(Cu_{0.15}Fe_{0.85})O_3$, our results showed that $(La_{1-x}Ca_x)CoO_3$ synthesized from the gel with citric acid and ethylene glycol had greater catalytic activity of CH_4 oxidation than $LaFeO_3$ or $(La_{0.8}Sr_{0.2})(Cu_{0.15}Fe_{0.85})O_3$.

Voorhoeve et al. reported that CO oxidation occurs at the metal ions on the surface [25]. Both the metal ion content and crystallinity (regularity of ions) play important roles in the catalytic activity of CO oxidation. CO_2 is produced by the reaction of CO with oxygen adsorbed on the metal ions on the outermost surface, and the amount of adsorbed oxygen depends on the crystallinity and/or the specific surface area [11, 12]. In the case of CH_4 oxidation, both CO_2 and H_2O are produced by the reaction of CH_4 with oxygen adsorbed on the metal ions on the outermost surface. Merino et al. reported that the order of propane oxidation was $(La_{0.8}Ca_{0.2})CoO_3$ < $LaCoO_3$ < $(La_{0.6}Ca_{0.4})CoO_3$ < $(La_{0.5}Ca_{0.5})CoO_3$ [18]. The same tendency was observed for $(La_{1-x}Sr_x)CoO_3$ and $(La_{1-x}Ce_x)CoO_3$ systems [26, 27]. Although the specific surface area of $(La_{0.8}Ca_{0.2})CoO_3$ is almost double that of $LaCoO_3$, the catalytic activity of $(La_{0.8}Ca_{0.2})CoO_3$ is higher than that of $LaCoO_3$. They considered that other modification produced by the calcium was responsible for the change in the catalytic behavior, and that a greater oxygen mobility caused by the oxygen vacancies would be the cause. In the present study, the oxygen vacancy occurs at $(La_{0.8}Ca_{0.2})CoO_3$ fired at 600 °C, $(La_{0.8}Ca_{0.2})CoO_3$ fired at 700 °C, and $(La_{0.7}Ca_{0.3})CoO_3$ fired at 800°C, respectively. However, we could not observe the significant reversal of catalytic activity at $x = 0.2$. Although the crystallinity was improved as the firing temperature increased in the present $(La_{1-x}Ca_x)CoO_3$ system, the catalytic activity of $LaCoO_3$ fired at 600 °C was higher than that of $LaCoO_3$ fired at 700 °C or 800 °C. This indicated that the catalytic activity of $LaCoO_3$ was dominated not by the crystallinity but by the specific surface area. The variation in the crystallite size (D_{024}) and in the average particle size determined from the TEM observation indicated that the particle became finer as x increased. The large standard deviation of the a-axis also suggested that the particle was fine. However, we did not observe any variation in $T_{1/2}$ of $(La_{1-x}Ca_x)CoO_3$ fired at 600°C or 800°C. As for $(La_{1-x}Ca_x)CoO_3$ fired at 600 °C, the particle became finer as x increased and the Co^{4+} ion content was independent of x. It is assumed that the crystallinity became poorer and less oxygen was adsorbed. As for $(La_{1-x}Ca_x)CoO_3$ fired at 800 °C, it had good crystallinity and the Co^{4+} ion content increased linearly as x increased. Since it had a small specific surface area, the amount of adsorbed oxygen was low and independent of x. Consequently, $T_{1/2}$ of $(La_{1-x}Ca_x)CoO_3$ fired at 600 °C or 800 °C did not vary in the range of $0.1 \le x \le 0.3$. The monotonous fall in the $T_{1/2}$ of $(La_{1-x}Ca_x)CoO_3$ fired at 700 °C suggests an increase in the amount of adsorbed oxygen, because the specific surface area and the Co^{4+} ion content increased and the crystallinity improved. From these results, it is obvious that $(La_{1-x}Ca_x)CoO_3$ fired at 700 °C has the most suitable specific surface area, crystallinity, and Co^{4+} ion content for CH_4 oxidation. To obtain the good catalytic activity for CH_4 oxidation, it is important to control the specific surface area, the crystallinity, and the Co^{4+} ion content of $(La_{1-x}Ca_x)CoO_3$.

Conclusion

A gel was formed by adding ethylene glycol and citric acid to an aqueous solution of $La(NO_3)_3 \cdot 6H_2O$, $CaCO_3$, and $Co(CH_3COO)_2 \cdot 4H_2O$. The amount of powder blown from the crucible was decreased by adding ethylene glycol. A perovskite-type $(La_{1-x}Ca_x)CoO_3$ $(0.0 \le x \le 0.3)$ was obtained by firing the gel above 600 °C in air for 3 h. The variation in the crystallite size (D_{024}) and in the average particle size indicated that the $(La_{1-x}Ca_x)CoO_3$ particle became finer as x increased. $(La_{1-x}Ca_x)CoO_3$ fired at 700 °C had the most suitable specific surface area, crystallinity, and Co^{4+} ion content for CH_4 oxidation.

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