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CO oxidation on perovskite-type LaCoO₃ synthesized using ethylene glycol and citric acid

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Abstract

In order to synthesize perovskite-type LaCoO_3 with good surface crystallinity, the gel prepared by adding both ethylene glycol (EG) and citric acid (CA) to the aqueous solution of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was fired at 600°C in air for 3 hours. The transmission electron microscopy (TEM) observation indicated that the particles of LaCoO_3 tended to have a uniform shape at $\text{EG}/\text{CA} = 4$. Although the specific surface area of LaCoO_3 synthesized using both EG and CA was slightly smaller than that of LaCoO_3 synthesized using only CA, the catalytic activity of CO oxidation became higher by adding EG.

Keywords: LaCoO_3 ; perovskite; sol-gel preparation; CO oxidation

1. Introduction

There has been some interest in examining the oxidation of carbon monoxide (CO) and hydrocarbons (C_nH_{2n+2}) on perovskite-type oxides [1–7]. Because oxidation occurs on the outmost surface, perovskite-type oxides must be synthesized with good surface crystallinity (regularity of ions) and/or a large specific surface area. Perovskite-type $LaCoO_3$ has been known to show high catalytic activity of CO oxidation [1, 3, 8]. When metal acetates or metal nitrates are used as starting materials, it is necessary to fire them above $850^\circ C$ and the specific surface area of $LaCoO_3$ is less than $5\text{ m}^2/\text{g}$ [2].

$LaMO_3$ ($M = Mn$ and Co) has been synthesized at a low temperature using poly(acrylic acid) (PAA) [9–11]. Although the specific surface area of $LaMnO_3$ was $15\text{--}28\text{ m}^2/\text{g}$, $LaMnO_3$ had many cracks due to the rapid combustion of PAA [12, 13]. In order to reduce the cracks in $LaMO_3$ ($M = Mn$ and Co), the gel was prepared by adding citric acid to the aqueous solution of metal nitrates and was then fired at low temperature [14]. Taguchi et al. reported that citric acid improved the surface crystallinity of $LaMO_3$ ($M = Mn$ and Co) from the catalytic activity of CO oxidation [14, 15]. However, because a lot of powder overflowed from the crucible when the gel was fired, we could not obtain $LaMO_3$ ($M = Mn$ and Co) in a high yield.

Pyrochlore-type $Y_2Ti_2O_7$ was synthesized using a polymerized complex technique [16]. Transparent gel was prepared by heating a mixed solution of citric acid, ethylene glycol, and yttrium and titanium ions. $Y_2Ti_2O_7$ was obtained by firing the gel at $750^\circ C$. In the present study, we made an attempt to decrease the amount of $LaCoO_3$ overflowing from the crucible and to improve the surface crystallinity (regularity of ions) of $LaCoO_3$. In order to prepare the gel, ethylene glycol and citric acid were weighed in a variety of molar ratios and were added to a solution of lanthanum and cobalt nitrates. Then $LaCoO_3$ was obtained by firing the gel at $600^\circ C$ in air. We characterized $LaCoO_3$ by examining the crystal structure, oxygen content,

crystallite size, specific surface area, average particle size, and catalytic activity of CO oxidation.

2. Experimental

Powders of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were weighed in equimolar amounts (0.0035 mol) and dissolved in a small amount of distilled water. Ethylene glycol (EG: 0.0035–0.021 mol) and citric acid (CA: 0.0035 mol) were used to make the gel. The molar ratio (EG/CA) was set from 2 to 5. The gel was obtained by keeping the solution at 100°C for several hours. Then the gel was fired above 500°C in air for 3 hours. The heating rate was 10°C/min.

The crystal phase of the sample was identified by powder X-ray diffraction (XRD) using monochromatic $\text{CuK}\alpha$ radiation. The oxygen content of the sample was determined by an oxidation-reduction method [17]. After a sodium oxalate solution and perchloric acid had been added to dissolve the sample in a flask, the solution was titrated with a standard potassium permanganate solution. The crystallite size (D_{024}) of the sample was calculated from the half-width of an X-ray diffraction peak (024) using Scherrer's formula [18]. The specific surface area of the sample was measured by the BET method for nitrogen adsorption. The average particle size of the sample was measured by transmission electron microscopy (TEM). The catalytic activity of CO oxidation was measured as follows. The sample (0.20 g) was preheated at 200°C in a flow of pure oxygen gas. A mixed gas of CO (1.0%), O_2 (4.0%), and He (balance) was fed in a flow reactor at a flow rate of $1.00 \times 10^{-4} \text{ m}^3/\text{min}$. The product was analyzed by gas chromatography using a column (molecular sieve 13X) kept at 50°C during the measurement.

3. Results and Discussion

Gel formation was possible in the range of $2 \leq \text{EG/CA} \leq 5$. Below 100°C , brown smoke from the decomposition of the nitrate ion was given off by the gel. The gel was fired at 500°C or 600°C in air for 3 hours. By adding EG, the amount of sample overflowing from the crucible decreased and the yield of the sample increased. Figure 1 shows the XRD patterns of the sample fired at 500°C or 600°C in air for 3 hours; the EG/CA of the gel was set to 4. All peaks of the sample fired at 600°C were completely indexed as the perovskite-type structure [19], but the peaks of the sample fired at 500°C were indexed as a mixture of perovskite-type LaCoO_3 and La_2O_3 . From the XRD measurement, we elucidated that the synthesis of LaCoO_3 was possible at 600°C in the range of $2 \leq \text{EG/CA} \leq 5$. The oxygen content of LaCoO_3 was determined to be 2.99–3.01 and independent of EG/CA.

The crystallite size (D_{024}) and specific surface area of LaCoO_3 are shown in Table 1. D_{024} had a minimum value (20.7 nm) at EG/CA = 4, and the specific surface area had a maximum value ($14.2 \text{ m}^2/\text{g}$) at EG/CA = 3. Compared with LaCoO_3 synthesized using only CA, the present LaCoO_3 had a slightly smaller specific surface area and slightly larger D_{024} [15]. Since LaCoO_3 was synthesized at low temperature by this preparation method, we could obtain homogeneous fine particles of LaCoO_3 . Therefore, LaCoO_3 had good surface area. Figure 2 shows the TEM photographs of LaCoO_3 fired at 600°C in air for 3 hours, with the EG/CA of the gel being set from 2 to 5. The particles did not show a distinct shape, and their average particle sizes (P_S) determined from the TEM observation were $63 \pm 8 \text{ nm}$ (EG/CA = 2), $68 \pm 12 \text{ nm}$ (EG/CA = 3), $52 \pm 6 \text{ nm}$ (EG/CA = 4), and $61 \pm 11 \text{ nm}$ (EG/CA = 5). Because P_S and the standard deviation had minimum values at EG/CA = 4, it was considered that the particles of LaCoO_3 tended to have a uniform shape at EG/CA = 4.

Figure 3 shows the conversion from CO to CO_2 on LaCoO_3 . CO oxidation started above 70°C and finished below 200°C . The catalytic activity of a given catalyst is usually expressed in terms of the temperature corresponding to the 50% conversion ($T_{1/2}$) of CO to CO_2 , which

can be obtained from the conversion-versus-temperature curve [20]. As shown in Table 1, $T_{1/2}$ had a minimum value (124°C) at EG/CA = 4 and was lower by ca. 15°C than the $T_{1/2}$ of LaCoO₃ synthesized using only CA [15].

Voorhoeve et al. reported that CO oxidation occurs at the metal ion of the surface [21]. Both the metal ion content and surface crystallinity (regularity of ions) play an important role in the catalytic activity of CO oxidation. CO₂ is produced by the reaction of CO with oxygen adsorbed on the metal ions of the outmost surface, and the amount of adsorbed oxygen depends on the surface crystallinity [14]. It is considered that Co ions in LaCoO₃ coordinate adsorbed oxygen and become 3+ on the surface. Because the carbon monoxide removes oxygen from Co ions, some Co ions become 2+. However, Co ions adsorb oxygen at once and become 3+. According to Kakihana [22], many metal ions form a very stable chelate complex with CA. Such a chelate complex can be further stabilized in EG, allowing successive ester reactions between CA and EG occur. In the present study, the decrease in the amount of powder overflowing from the crucible indicated that the rapid combustion of the gel was depressed by adding EG. Although the specific surface area decreased slightly by adding EG, LaCoO₃ synthesized using both EG and CA had high catalytic activity of CO oxidation at EG/CA = 4. Therefore, it is considered that the LaCoO₃ synthesized using both EG and CA had sufficiently good surface crystallinity in the vicinity of EG/CA = 4. In order to improve the catalytic activity of CO oxidation on LaCoO₃, it is necessary to add an adequate amount of EG.

4. Conclusion

The gel was prepared by adding both EG and CA to the aqueous solution of La(NO₃)₃·6H₂O and Co(NO₃)₂·6H₂O. Perovskite-type LaCoO₃ was obtained by firing the gel at 600°C in air for 3 hours, and the amount of powder overflowing from the crucible was

decreased by adding EG. The TEM observation indicates that particles of LaCoO_3 tended to have a uniform shape at $\text{EG/CA} = 4$. Although the specific surface area of LaCoO_3 synthesized using both EG and CA was slightly smaller than that of LaCoO_3 synthesized using only CA, the catalytic activity of CO oxidation was high at $\text{EG/CA} = 4$. These results indicate that the surface crystallinity of LaCoO_3 was improved by adding EG.

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Table 1. Relationship among synthetic condition, crystallite size (D_{024}), specific surface area (S), average particle size (P_S), and temperature corresponding to the 50% conversion ($T_{1/2}$) from CO to CO₂ of LaCoO₃.

Synthetic condition		D_{024}	S	P_S	$T_{1/2}$
EG/CA	Temperature (°C)	(nm)	(m ² /g)	(nm)	(°C)
2	600	24.8	8.4	63	134
3	600	21.7	14.2	68	130
4	600	20.7	13.0	52	124
5	600	24.1	8.4	61	132

Figure Captions

Fig. 1 XRD patterns of the sample fired at 500°C or 600°C in air for 3 hours. The gel was prepared using both ethylene glycol (EG) and citric acid (CA), and the molar ratio EG/CA was set to 4.

Fig. 2 TEM micrographs of LaCoO₃. The gel was prepared using both ethylene glycol (EG) and citric acid (CA), and was fired at 600°C in air for 3 hours. (A): EG/CA = 2, (B): EG/CA = 3, (C): EG/CA = 4, (D): EG/CA = 5.

Fig. 3 Conversion from CO to CO₂ on LaCoO₃. The gel was prepared using both ethylene glycol (EG) and citric acid (CA), and was fired at 600°C in air for 3 hours.