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Complete oxidation of methane and CO at low temperature over $LaCoO_3$ prepared by spray-freezing/freeze-drying method

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Abstract

Perovskite-type $LaCoO_3$ oxides were prepared by spray-freezing/freeze-drying method using citrate precursor. The calcination temperature for a single phase of $LaCoO_3$ could be lowered to 500 °C without formation of any other oxides and the product had the highest surface area of 23.7 m^2/g. Below 500 °C, this catalyst with the perovskite structure and the high surface area showed higher activity for complete oxidation of low concentration methane (2000 ppm) and CO (1%) compared to Pt/Al_2O_3 catalyst.

Keywords: Perovskite; Methane; Complete oxidation; CO; $LaCoO_3$

1. Introduction

ABO_3 perovskite-type oxides are considered of great interest as the environmentally friendly and cheap catalyst. Especially, the perovskite catalysts including Co or Mn as B-site atom showed high activity for the complete oxidation of CO and hydrocarbon. Therefore, they are very suitable materials for the replacement of noble catalysts being used in the catalytic combustion of methane as well as for the air electrode of fuel cell [1–4]. However, since the generally high calcination temperature (at least 700 °C [5]) of the catalysts during the preparation inevitably leads to large grain size and reduces the specific surface area of the catalysts to less than 5 m^2/g [6], the potential applications of these materials as catalysts are limited. Therefore, in order to increase the specific surface area of the perovskite-type catalysts, the synthesis at a lower temperature would be required.

Many studies have been conducted to increase the specific surface area via the various preparation methods such as evaporation drying method using citrate precursor [7], firing method using polyacrylate precursor [8], drip pyrolysis method [9], and spray-freezing/freeze-drying method using nitrate precursor [10] as shown in Table 1. According to these papers, the specific surface area of catalysts was increased to some extent around 19 m^2/g. Even though several recent researches insist higher surface area of perovskite up to 40 m^2/g, those results did not show the crystalline data of perovskite.

In our recent paper [11], we could prepare perovskite-type $LaCoO_3$ oxides with the surface area of 23.7 m^2/g by combining two advanced techniques of the citrate precursor [7] and the spray-freezing/freeze-drying method [10]. This coupled method led to the decrease of the calcination temperature for the formation of perovskite structure to 500 °C. The obtained catalyst in this work was the single phase of $LaCoO_3$ free of any other by-product. These results were confirmed by the analysis through the BET, XRD and IR.

However, even though the perovskite catalyst with high surface area is prepared, if it is used at higher temperature than the calcination temperature, it will lose the high surface area quickly during the reaction. Therefore, the catalyst should be applied for the reaction at relatively low temperature, below 500 °C in this case, in order to utilize the high surface area successfully.

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Table 1
Several methods for preparation of perovskite-type oxides with high surface area

Precursor	Drying	Calcination	BET surface area of $LaCoO_3$(m^2/g)	Ref.
Citrate	Evaporation	600 °C (5 h)	11	[7]
Polyacrylate	–	Firing	12	[8]
Nitrate + glucose	–	Drip pyrolysis	19 (mixed oxides)	[9]
Nitrate	Spray-freeze /freeze-drying	580 °C (22 h)	18.5 ($La_{0.8}Sr_{0.2}CoO_3$)	[10]
Citrate	Spray-freeze /freeze-drying	500 °C (5 h)	23.7	[11]

Recently the abatement of methane emissions from natural gas or methane combustion devices such as lean-burn natural gas vehicles (NGVs) is becoming important [12]. Natural gas engines can operate under lean conditions and the fuel efficiency is high. Since less CO, NOx, SOx, and particulates are produced compared to diesel, the number of NGVs is currently being increased very rapidly worldwide (3,317,036 vehicles on April, 2004). However, without any after-treatment, the total hydrocarbon (HC) emission from a lean-burn NGV is 3–4 g/kWh, which values are much higher than the limit value of 1.6 or 1.7 g/kWh in Euro III and US standards, respectively. Since the HC emission from a lean-burn NGV contains 90–95% methane, at least 60% methane conversion is required in order to adjust it to the regulations. However, since the methane concentration is very low (500–1000 ppm) and the temperature at which the catalyst must operate is relatively low (typically less than 500–550 °C), to reduce the methane emission is not an easy task.

In this research, the prepared $LaCoO_3$ catalyst with high surface area was applied to the complete oxidation of methane and CO at low temperature below 500 °C. Very severe reaction conditions such as low methane (or CO) and oxygen concentrations and short contact time were adopted considering a commercial application such as a catalytic system for the abatement of methane emissions from NGVs.

2. Experimental

2.1. Catalyst preparation

The perovskite-type $LaCoO_3$ oxides were prepared according to the following three steps.

2.1.1. Precursor preparation

About 250 ml of 0.25 M lanthanum nitrate (Aldrich, 99.99%) aqueous solution and 250 ml of 0.25 M cobalt nitrate (Aldrich, 99%) aqueous solution were mixed and 0.122 mol of citric acid ($(CH_2COOH)_2C(OH)(COOH)$, Aldrich, 99.5%) was added to the mixed solution. The amount of citric acid added plays an important role in the homogeneity of precursor and in this study, the moles of citric acid were determined to be the same with those of total metal ions [13]. For the pH control, ammonia water (Yakuri, extra pure reagent, 28%) was dropped into the precursors. The pH before pH adjustment and precipitation were 1.4 and 2.1, respectively. To examine the effect of pH, the mixed solutions with pH of 1.4, 1.7, and 2.1 were used as the precursors. In case of pH 2.1 of the solution, it was filtered three times with filter paper (Advantec, 5A) to eliminate the effect of precipitates, if any, on the product.

2.1.2. Drying of precursor

The precursors were dried with two different ways: evaporation drying and spray-freezing/freeze-drying. In case of evaporation drying, the precursor was dried for 6 h at 80 °C by rotary vacuum evaporator (EYELA, Japan, aspirator: 19 l/min). Spray-freezing/freeze-drying was carried out as follows; (a) *Spray-freezing*: the precursor was sprayed into the evacuation flask filled by half with liquid nitrogen using a sprayer with nozzle tip diameter of 0.3 mm. The resulting frozen products were immediately transferred to a freeze dryer. Nitrogen was used as a carrier gas in spraying and the spraying pressure was 5.5 bar. (b) *Freeze-drying*: the resulting ice powder from the spray-freezing was dried for 72 h by freeze

Table 2
The results of XRD and surface properties of $LaCoO_3$ prepared by various methods [11]

Precursor	Drying method	pH	XRD results and BET surface area (m^2/g)			
			500[a]	550[a]	600[a]	650[a]
Nitrates (citric acid was added)	Evaporation-drying	1.4[b]	Am[c]	M[d]	P[e](12.3)[f]	–
		1.7	Am	M	M	P(6.7)
		2.1[g]	Am	M	P(10.2)	–
	Spray-freezing/freeze-drying	1.4	P(23.7)	P(15.3)	P(7.3)	–
		1.7	M	P(18.4)	P(12.4)	–
		2.1	M	P(17.2)	P(12.0)	–

[a] Calcination temperature (°C).

[b] pH unadjusted.

[c] Amorphous.

[d] Mixed oxides (La_2O_3, Co_3O_4, etc.).

[e] Single phase perovskite.

[f] BET surface area.

[g] pH just before precipitation.

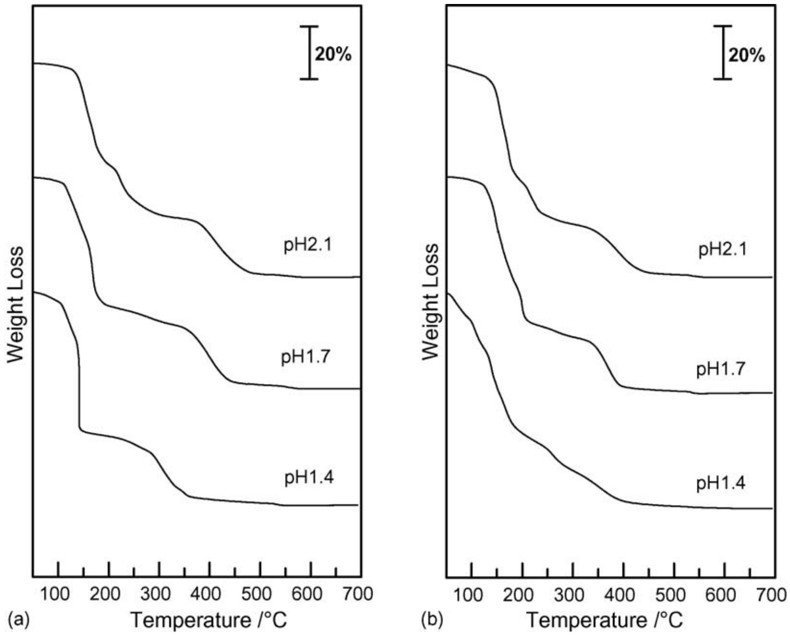

Fig. 1. Weight loss of the dried precursors prepared by the evaporation method (a), and spray-freezing/freeze-drying method (b).

dryer (TAITEC, Japan, trap temperature: –75 °C, vacuum: 0.05 Torr).

2.1.3. Decomposition and calcinations of precursor

Based on the results from the TGA analysis, the dried precursor was previously decomposed at 300 °C for an hour in air to prevent the abrupt expansion during calcination and then, it was ground to fine powder in mortar. The powder was calcined at different temperatures of 500, 550 and 600 °C for 5 h in air.

2.1.4. Performance of the prepared catalyst

The reactions are performed using a flow-type packed bed reactor under the following reaction conditions. In case of the complete oxidation of methane, 2000 ppm of methane was used. O_2 concentration was 1.8% and He was used as a

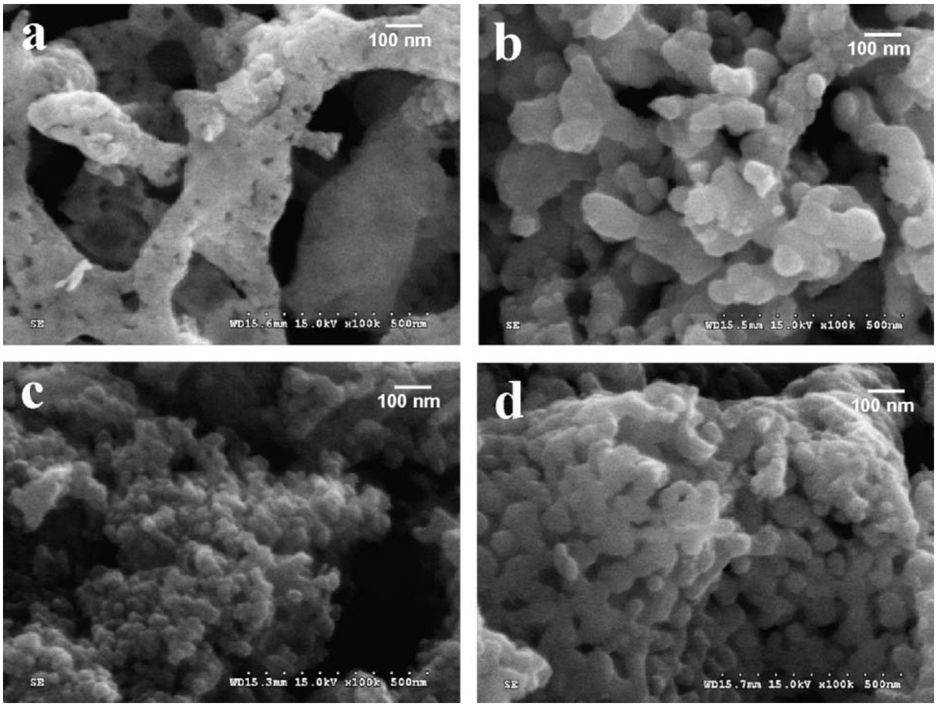

Fig. 2. SEM images of the catalysts: (a and b) $LaCoO_3$ prepared by evaporation method and calcined at 500 and 600 °C, respectively; (c and d) $LaCoO_3$ prepared by spray-freezing/freeze-drying method and calcined at 500 and 600 °C, respectively.

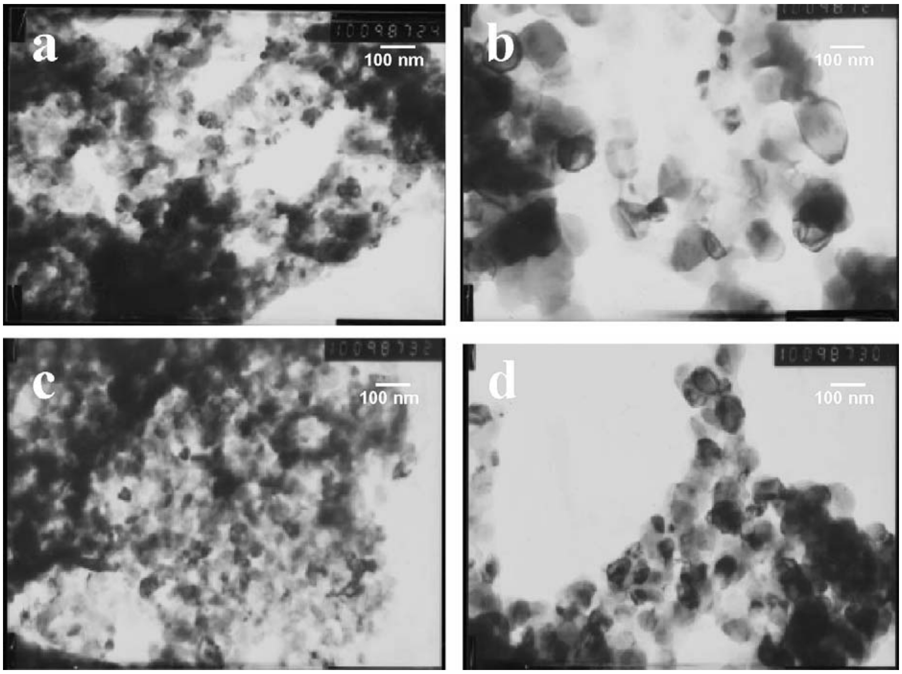

Fig. 3. TEM images of the catalysts: (a and b) $LaCoO_3$ prepared by evaporation method and calcined at 500 and 600 °C, respectively; (c and d) $LaCoO_3$ prepared by spray-freezing/freeze-drying method and calcined at 500 and 600 °C, respectively.

balance gas. Total flow rate was 27.5 ml/min and 0.025 g of the prepared perovskite catalyst was used. For comparison, 0.05 g of 1.5 wt.% Pt/Al_2O_3 prepared by a conventional impregnation method was used. CO oxidation was also performed similarly. 1% of CO was used. O_2 concentration was 1% and He was used as a balance gas. Total flow rate was 100 ml/min and 0.01 g of the prepared perovskite catalyst was used. 0.05 g of 1.5 wt.% Pt/Al_2O_3 was used for comparison as well.

3. Results and discussion

3.1. Thermal gravimetric analysis and morphology of the catalysts

We have reported in the previous paper, the structure and the surface area of the perovskite catalysts were very different depending on drying method and pH of precursors as shown in Table 2 [11]. Especially, the more remarkable difference is shown according to drying method. In case of the spray-freezing/freeze-drying and pH 1.4, the highest surface area, 23.7 m^2/g was obtained. The crystal size of $LaCoO_3$ prepared by spray-freezing/freeze-drying method at 500 °C was calculated about 16 nm using Scherrer's equation.

Fig. 1 shows thermal gravimetric analysis (TGA) results of dried precursors according to drying methods and pH of precursors. The trends of weight change according to drying methods seem to be similar except the dried precursor for pH 1.4. For pH 1.4, the dried precursor by spray-freezing/freeze-drying shows many steps in weight loss compared with others. On the other hand, dried precursor by evaporation drying shows the steep weight loss at 150 °C (Fig. 1a) which is due to combustion of citric acid without substitution by metal ion [7]. These results mean that for the precursor with pH 1.4, dried precursor by spray-freezing/freeze-drying has smaller amount of citric acid, and relatively larger amount of metal citrate than that by evaporation drying. For the preparation of the $LaMnO_3$, Taguchi et al. reported the similar results of TGA [8]. As reported from the IR results in the previous paper [11], in case of dried precursor with pH 1.4 by spray-freezing/freeze-drying, relative IR intensity of C=O stretching against C–O was stronger than that of evaporation drying. It means clearly that, in case of pH 1.4, the amount of citrate in dried precursor of spray-freeze/freeze-drying is larger than that of evaporation drying, which coincides with the TGA results. Considering the result that a single phase of perovskite was formed at the lowest calcination temperature by spray-freeze/freeze-drying with precursor of pH 1.4 [11], it can be concluded that the larger the amount of citrate in precursor is, the lower the calcination temperature for a single phase of perovskite is.

In general, the increase of pH enhances the deprotonation of organic acid in solution so that the metal carboxylate can be formed easily. However, it is concluded that ammonia water added to increase pH of solution made some by-products like ammonium citrate and nitrate, which affect the homogeneity of precursor negatively. Nevertheless, as shown in Table 2, in case of evaporation drying, the calcination temperature for a single phase of perovskite was lower for precursor with pH 2.1 than that with pH 1.7. Therefore, it is supposed that the homogeneity of the precursor with pH 2.1 was some improved by the increase of pH rather than that with pH 1.7, even though it cannot be examined by IR and TG analyses.

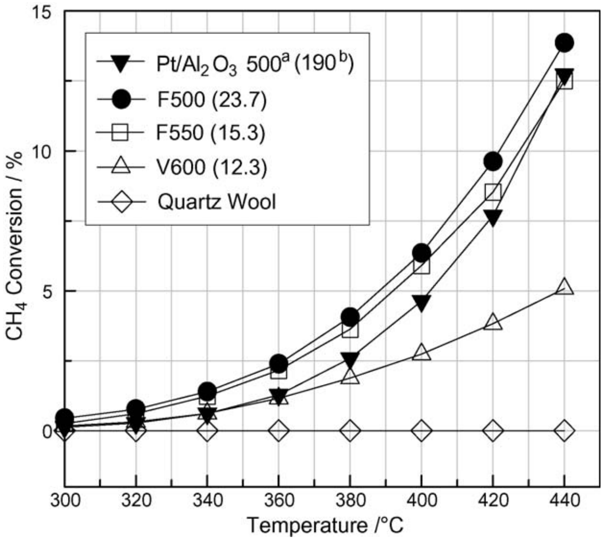

Fig. 4. Complete oxidation of methane. F, freeze-drying; V, evaporation-drying; a, calcination temperature; b, surface area.

Fig. 2 shows SEM images of the catalysts. Fig. 2a and b are the images of $LaCoO_3$ prepared by evaporation method and calcined at 500 and 600 °C, respectively. Fig. 2c and d are $LaCoO_3$ prepared by spray-freezing/freeze-drying method and calcined at 500 and 600 °C, respectively. $LaCoO_3$ prepared by spray-freezing/freeze-drying method and calcined at 500 °C had small and uniform grain size around 20 nm. The size increased and sintered to around 50 nm particles after calcinations at 600 °C. As shown in Fig. 2a, the catalyst prepared by evaporation method and calcined at 500 °C shows the different morphology of particles from others. XRD of the catalyst represented that this catalyst is amorphous (Table 2). Fig. 3 shows TEM images of the same samples as Fig. 2. The small and uniform morphology of the catalysts prepared by the spray-freezing/freeze-drying method was clearly observed. The ratio of La to Co at the surface was measured by EDX. It was near 1 with ±5% error in the all samples measured.

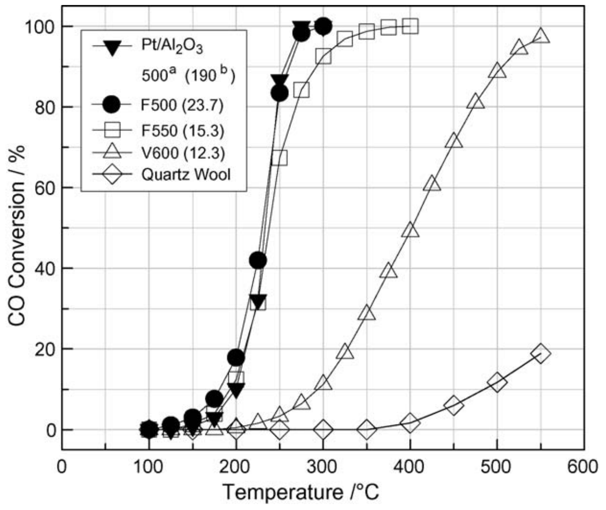

Fig. 5. Complete oxidation of CO. F, freeze-drying; V, evaporation-drying; a, calcination temperature; b, surface area.

3.2. Performance of the catalysts

Figs. 4 and 5 show the results of the complete oxidation of methane and CO over $LaCoO_3$ prepared by spray-freezing/freeze-drying method, respectively. Among the catalysts compared, $LaCoO_3$ catalyst after calcination at 500 °C with 23.7 m^2/g (F500) showed the highest catalytic activity for the both reaction. It is also notable that the catalyst revealed much higher catalytic activity than that of the Pt/Al_2O_3 catalyst.

In the complete oxidation of methane, the $LaCoO_3$ catalyst (0.025 g) showed higher catalytic activity compared to double amount of Pt/Al_2O_3 catalyst (0.05 g) at the same reaction condition. The $LaCoO_3$ prepared in this study showed ca. 85 kJ/mol of activation energy for CH_4 oxidation at low temperature region, which activation energy is the same as those of 2.2 wt.% Pd/Al_2O_3 and 1.9 wt.% Pt/Al_2O_3 according to a literature [14].

In case of CO oxidation, five times less amount of $LaCoO_3$ (0.01 g) showed similar catalytic activity to Pt/Al_2O_3 catalyst (0.05 g). The $LaCoO_3$ prepared in this study showed ca. 61 kJ/mol of activation energy for CO oxidation at low temperature region. The activation energy of $LaMnO_3$ for CO oxidation has been reported as 62.5 kJ/mol [15].

The activity difference between F550 and V600 is not accounted for with only surface area. Further study is necessary to elucidate it.

4. Conclusions

The conclusions of this study can be summarized as follows: the calcination temperature for a single phase of perovskite could be lowered using spray-freezing/freeze-drying more than evaporation-drying regardless of pH of precursor. The metal citrate could be produced more in the dried precursor using spray-freezing/freeze-drying than evaporation drying. Using citrate and spray-freezing/freeze-drying method, the calcination temperature for a single phase of perovskite, $LaCoO_3$ could be lowered to 500 °C and the product had high surface area, 23.7 m^2/g. The catalyst showed higher activity for complete oxidation of low concentration methane (2000 ppm) and CO (1%) compared to Pt/Al_2O_3 catalyst at low temperature below 500 °C.

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