



## Effect of the A-site cation on methane oxidation of perovskite-type $(\text{La}_{1-x}\text{M}_x)\text{CoO}_3$ ( $M=\text{Ca}$ , $\text{Sr}$ , and $\text{Ba}$ )

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### ABSTRACT

Perovskite-type  $(\text{La}_{1-x}\text{M}_x)\text{CoO}_3$  ( $M=\text{Ca}$ ,  $\text{Sr}$ , and  $\text{Ba}$ ) synthesized at 700 °C in air using the polymerizable complex method had a rhombohedral perovskite-type structure in the range of  $x \leq 0.06$ . The oxygen content of the samples was 2.98–2.99, and the specific surface area was 3.5–8.3 m<sup>2</sup>/g regardless of the  $M$  ion or  $x$ . The Rietveld method indicated that the Co–O distance was also constant regardless of the  $M$  ion or  $x$ , and that the Co–O–Co angle between two  $\text{CoO}_6$  octahedra increased with an increase in the ionic radius of the  $M$  ion. The temperature corresponding to the 50% conversion ( $T_{1/2}$ ) of  $\text{CH}_4$  oxidation was almost constant for the samples with  $x=0.04$ , while the  $T_{1/2}$  of the samples with  $x=0.06$  was linearly lowered with increases in the ionic radius of the  $M$  ion.

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### 1. Introduction

Methane ( $\text{CH}_4$ ) is an attractive fuel because of its low carbon-to-hydrogen ratio, but the global warming potential (GWP) of  $\text{CH}_4$  is 21 [1]. The ultimate goal in efforts to decrease its environmental impact as a fuel is to minimize the amount of  $\text{CH}_4$  emitted by converting it to  $\text{CO}_2$ . Perovskite-type oxides ( $\text{ABO}_3$ ) have been known as excellent catalysts of hydrocarbon ( $\text{C}_n\text{H}_{2n+2}$ ) oxidation [2–11]. The catalytic activity of  $\text{CH}_4$  oxidation on perovskite-type oxides is essentially controlled by the B-site cation and is improved by the substitution of other A- or B-site cations [2,5–10].  $\text{CH}_4$  oxidation occurs on the outmost surface of the catalyst. Therefore, it is necessary to synthesize perovskite-type oxides with good surface crystallinity (regularity of ions) and/or large specific surface areas.

Taguchi et al. synthesized  $\text{LaMO}_3$  ( $M=\text{Mn}$  and  $\text{Co}$ ) using poly (acrylic acid) (PAA) [12–14].  $\text{LaMO}_3$  ( $M=\text{Mn}$  and  $\text{Co}$ ) was shown to have a large specific surface area, but the rapid combustion of PAA caused cracks on the catalytic surface. Citric acid was added to an aqueous solution of metal nitrates for the purpose of reducing the number of cracks and improving the surface crystallinity [15,16]. Yi et al. prepared highly crystalline  $\text{LaCoO}_3$  in the host pores of mesoporous SBA-15 silica using a novel microwave-assisted process [7]. Two nano-sized  $\text{LaCoO}_3$  were prepared with co-precipitation

and with the citrate gel method [17]. Only the sample prepared with the citrate gel method provided a single phase in the results of X-ray powder diffraction (XRD). The sample prepared by this method had a low presence of hydroxyl groups and carbonate species from the results of X-ray photoelectron spectroscopy (XPS) and diffusion reflection infrared Fourier transform (DRIFT) spectroscopy. Cheng et al. prepared nano-sized  $\text{LaCoO}_3$  powder by an aqueous gel-casting method, and investigated the effect of the ratio of organic precursors to metal nitrates and the ratio of acrylamide (AM) and  $N,N'$ -methylenebisacrylamide (MBAM) [18]. The particle size of the sample was 31–60 nm and decreased with an increased ratio of the organic precursor to metal nitrates, but was not affected by the ratio of AM to MBAM.

Saracco et al. reported that  $\text{CH}_4$  oxidation was promoted by Mg/Cr substitution in  $\text{La}(\text{Cr}_{1-x}\text{Mg}_x)\text{O}_3$  [3]. According to Arai et al. [19],  $\text{CH}_4$  oxidation on  $(\text{La}_{1-x}\text{A}_x)\text{MO}_3$  ( $A=\text{Sr}$ ,  $\text{Ca}$ , and  $\text{Ba}$ ;  $M=\text{Mn}$ ,  $\text{Fe}$ , and  $\text{Co}$ ) occurred by means of parallel reactions involving both adsorbed oxygen and lattice oxygen. From the relationship between the crystal structure and  $\text{CH}_4$  oxidation on  $(\text{La}_{1-x}\text{Nd}_x)\text{CoO}_3$ , Taguchi et al. reported that both the Co–O distance and the Co–O–Co angle were very important for improving the catalytic activity [20]. In the present study, perovskite-type  $(\text{La}_{1-x}\text{M}_x)\text{CoO}_3$  ( $M=\text{Ca}$ ,  $\text{Sr}$ , and  $\text{Ba}$ ) was synthesized using the polymerizable complex method [21,22]. We then examined the crystal structure, oxygen content, specific surface area, and catalysis in order to elucidate the effect of the A-site cation in  $\text{CH}_4$  oxidation on perovskite-type  $(\text{La}_{1-x}\text{M}_x)\text{CoO}_3$  ( $M=\text{Ca}$ ,  $\text{Sr}$ , and  $\text{Ba}$ ).

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## 2. Experimental

$(\text{La}_{1-x}\text{M}_x)\text{CoO}_3$  ( $M=\text{Ca}$ ,  $\text{Sr}$ , and  $\text{Ba}$ ;  $x=0.04$ ,  $0.06$ ) powder was synthesized using a polymerized complex route [21,22]. High-purity powders of lanthanum nitrate hexahydrate (Nacalai Tesque, Japan, 99.9%), calcium carbonate (Kanto Kagaku, Japan, 99.5%), strontium nitrate (Kanto Kagaku, Japan, 98.0%), barium nitrate (Kanto Kagaku, Japan, 99.0%) and cobalt nitrate hexahydrate (Kanto Kagaku, Japan, 98.0%) were weighed to the desired proportions. Citric acid (CA, Kanto Kagaku, 99.0%) and ethylene glycol (EG, Kanto Kagaku, 99.5%) were then added to make the gel, resulting in a molar ratio of  $\text{La}+\text{A}:\text{Co}:\text{CA}:\text{EG}=1:1:1:3$ . The solution was left to sit at  $100\text{ }^\circ\text{C}$  for 12 h until it had gelled. The gel was heated at  $700\text{ }^\circ\text{C}$  for 3 h in air. The heating rate was  $7.5\text{ }^\circ\text{C}/\text{min}$ .

The crystal phase of the sample was identified by powder X-ray diffraction (XRD, Model RAD-1C, Rigaku, Japan) using monochromatic  $\text{CuK}\alpha$  radiation. The structural refinement was carried out by the Rietveld method with XRD data [23]. The XRD data at room temperature were collected by step scanning over an angular range of  $20^\circ \leq 2\theta \leq 100^\circ$  in increments of  $0.02^\circ$  ( $2\theta$ ). The oxygen content of the sample was determined by iodometry. After potassium iodide solution and hydrochloric acid had been added to dissolve the sample in a beaker, the solution was titrated with a standard thiosulfate solution [24]. The average particle size of the sample was measured using scanning electron microscopy (SEM, Model JSM-7001FD, Jeol, Japan). The BET surface area was determined by an automatic surface analyzer (HM model-1208, Mountech, Japan). The catalytic activity of  $\text{CH}_4$  oxidation was measured as follows. The sample (0.5 g) was preheated at  $300\text{ }^\circ\text{C}$  in air. A mixed gas of  $\text{CH}_4$  (3.0%),  $\text{O}_2$  (6.0%), and He (balance) was fed into a flow reactor at a flow rate of  $30\text{ cm}^3/\text{min}$ . The space velocity was approximately  $5700\text{ h}^{-1}$  in all measurements. The product was analyzed by gas chromatography (Model D-2500, Hitachi, Japan) using a column (molecular sieve 13X) kept at  $40\text{ }^\circ\text{C}$  during the measurement.

## 3. Results and discussion

Gel was formed at  $\text{CA}/\text{EG}=1/3$ , and brown smoke from the decomposition of the nitrate ion was given off at  $100\text{ }^\circ\text{C}$  or less. After heating the gel at  $700\text{ }^\circ\text{C}$  in air, the amount of the sample overflowing from the crucible decreased by the addition of ethylene glycol. As a result, the yield of the sample increased. The XRD measurement indicated that  $(\text{La}_{1-x}\text{M}_x)\text{CoO}_3$  ( $M=\text{Ca}$  and  $\text{Sr}$ ) heated at  $700\text{ }^\circ\text{C}$  had a rhombohedral perovskite-type structure in the range of  $x > 0.06$ . By contrast,  $(\text{La}_{1-x}\text{Ba}_x)\text{CoO}_3$  heated at  $700\text{ }^\circ\text{C}$  had an impurity phase in the range of  $x > 0.06$ . According to Taguchi et al. [25],  $(\text{La}_{1-x}\text{Ba}_x)\text{CoO}_3$  heated at  $1300\text{ }^\circ\text{C}$  had a rhombohedral perovskite-type structure in the range of  $0 \leq x \leq 0.6$ . It is considered that  $\text{CH}_4$  oxidation on  $(\text{La}_{1-x}\text{Ba}_x)\text{CoO}_3$  heated at  $1300\text{ }^\circ\text{C}$  decreases because the specific surface area is very small. In the present study, therefore, we investigated the crystal structure and  $\text{CH}_4$  oxidation of the samples ( $x=0.04$  and  $0.06$ ) heated at  $700\text{ }^\circ\text{C}$ . From the chemical analysis, the oxygen content of the samples was 2.98–2.99 regardless of the  $M$  ion or  $x$  as shown in Table 1.

Structural refinement of  $(\text{La}_{1-x}\text{M}_x)\text{CoO}_3$  ( $M=\text{Ca}$ ,  $\text{Sr}$ , and  $\text{Ba}$ ) was carried out by the Rietveld method assuming the space groups of the rhombohedral to be  $R\bar{3}c$  [26]. Tables 2 and 3 show the structure refinement parameters of the samples.  $R_{\text{Wp}}$ ,  $R_{\text{p}}$ , and  $R_{\text{e}}$  are an  $R$ -weighted pattern,  $R$ -pattern, and  $R$ -expected, respectively. In Tables 2 and 3, rhombohedral lattice parameters are shown as hexagonal lattice parameters. The  $R_{\text{Wp}}$  of all samples was less than 9.86%, and the low value of  $R_{\text{Wp}}$  suggested that the structural model for the samples was reasonable.

**Table 1**

The oxygen content, specific surface area, and temperature corresponding to the 50% conversion ( $T_{1/2}$ ) of  $\text{CH}_4$  oxidation of perovskite-type  $(\text{La}_{1-x}\text{M}_x)\text{CoO}_3$  ( $M=\text{Ca}$ ,  $\text{Sr}$ , and  $\text{Ba}$ ).

	$3-\delta$	Specific surface area ( $\text{m}^2/\text{g}$ )	$T_{1/2}$ ( $^\circ\text{C}$ )
$x=0.04$			
Ca	2.99	4.3	541
Sr	2.98	3.8	534
Ba	2.98	7.6	538
$x=0.06$			
Ca	2.99	4.3	526
Sr	2.98	3.5	503
Ba	2.98	8.3	488

**Table 2**

The structure refinement parameters of  $(\text{La}_{0.96}\text{M}_{0.04})\text{CoO}_3$  ( $M=\text{Ca}$ ,  $\text{Sr}$ , and  $\text{Ba}$ ;  $x=0.04$ ).

	Ca	Sr	Ba
Cell data			
$a$ ( $\text{\AA}$ )	5.4327(6)	5.4333(5)	5.4342(5)
$c$ ( $\text{\AA}$ )	13.1274(10)	13.1305(10)	13.1333(10)
$V$ ( $\text{\AA}^3$ )	335.54(6)	335.69(5)	335.87(5)
$R$ factor (%)			
$R_{\text{Wp}}$	8.81	9.15	9.05
$R_{\text{p}}$	6.61	6.93	6.81
$R_{\text{e}}$	5.62	5.68	5.55
Atomic parameters <sup>a</sup>			
La/M			
$B$ ( $\text{\AA}^2$ )	0.33(14)	0.38(11)	0.46(9)
Co			
$B$ ( $\text{\AA}^2$ )	0.19(14)	0.18(11)	0.20(9)
O			
$x$	0.455(1)	0.456(1)	0.459(1)
$B$ ( $\text{\AA}^2$ )	0.86(17)	0.79(15)	1.08(14)

<sup>a</sup> Atomic position: La/M (6a) 0, 0, 1/4; Co (6b) 0, 0, 0; O (18e)  $x$ , 0, 1/4.

**Table 3**

The structure refinement parameters of  $(\text{La}_{0.94}\text{M}_{0.06})\text{CoO}_3$  ( $M=\text{Ca}$ ,  $\text{Sr}$ , and  $\text{Ba}$ ;  $x=0.06$ ).

	Ca	Sr	Ba
Cell data			
$a$ ( $\text{\AA}$ )	5.4300(7)	5.4338(5)	5.4348(5)
$c$ ( $\text{\AA}$ )	13.1231(13)	13.1357(10)	13.1377(10)
$V$ ( $\text{\AA}^3$ )	335.09(7)	335.89(5)	336.06(5)
$R$ factor (%)			
$R_{\text{Wp}}$	9.14	9.24	9.86
$R_{\text{p}}$	6.89	6.99	7.06
$R_{\text{e}}$	5.62	5.72	5.73
Atomic parameters <sup>a</sup>			
La/M			
$B$ ( $\text{\AA}^2$ )	0.45(10)	0.34(10)	0.54(9)
Co			
$B$ ( $\text{\AA}^2$ )	0.32(10)	0.14(10)	0.27(9)
O			
$x$	0.455(1)	0.458(1)	0.459(1)
$B$ ( $\text{\AA}^2$ )	1.11(14)	0.86(14)	1.26(16)

<sup>a</sup> Atomic position: La/M (6a) 0, 0, 1/4; Co (6b) 0, 0, 0; O (18e)  $x$ , 0, 1/4.

When the value of  $x$  was fixed, the hexagonal lattice parameters of  $(\text{La}_{1-x}\text{M}_x)\text{CoO}_3$  ( $M=\text{Ca}$ ,  $\text{Sr}$ , and  $\text{Ba}$ ) increased with increases in the ionic radius of the  $M$  ion. Fig. 1 shows the

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