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# Catalytic properties and surface states of $La_{1-x}(Th, Sr)_xCoO_3$

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The surface chemical states of the perovskite-type thorium- or strontium-doped lanthanum cobalt oxides ($La_{1-x}Th_xCoO_3$, $La_{1-x}Sr_xCoO_3$) have been investigated using X-ray photoelectron spectroscopy. Catalytic oxidations of CO have been also investigated by flow methods. The ionicity between cobalt and lattice oxygen was increased by substituting thorium for lanthanum, and had a peak at $x = 0.02$. The catalytic activity also had a peak at $x = 0.02$. However, the ionicity decreased for the case of strontium substitution, and the activity also decreased.

## 1. Introduction

Voorhoeve *et al.* [1] reported that the catalytic activity of oxidation was enhanced by partial substitution of the A-site ion. They reported that $Ce^{4+}$-substituted lanthanum cobalt oxides like $La_{0.9}Ce_{0.1}CoO_3$ were more active than $LaCoO_3$ for the oxidation of CO.

Nakamura *et al.* [2] reported that $Sr^{2+}$-substituted lanthanum cobalt oxides showed higher oxidative activities for hydrocarbons and carbon monoxides, $La_{0.8}Sr_{0.2}CoO_3$ being the most active. They also reported that the variation of catalytic activity was explained on the basis of the reduction–oxidation properties of the catalysts.

In a previous paper [3], we reported the effects of surface chemical states of $La_{1-x}Ce_xCoO_3$ ($0 \leqq x \leqq 0.03$) on the catalytic activity, and also suspected that the catalytic activity of oxidation increased in proportion to the ionicity between the cobalt and lattice oxygen.

In this study, we investigated the effects of thorium or strontium substitution for lanthanum in $LaCoO_3$ ($La_{1-x}Th_xCoO_3$, $La_{1-x}Sr_xCoO_3$) on the catalytic activity of oxidation. The relationship between the catalytic properties and the surface chemical states is also reported.

## 2. Experimental procedure

$La_{1-x}Th_xCoO_3$ and $La_{1-x}Sr_xCoO_3$ were prepared from mixtures of metal acetates of each component [4]. First, the mixed acetate solution was evaporated to dryness in a rotary evaporator at 343 to 363 K. The solid obtained was decomposed at 673 K for 1 h and calcined in air at 1673 K for 5 h.

The phases of the products were determined by means of X-ray diffraction (XRD) using CuKα radiation (Philips APD-10). The surface areas of the samples were measured by the BET method ($N_2$ adsorption).

The X-ray photoelectron spectroscopy (XPS) spectra were recorded on a V.G. (Sussex) Esca Lab5 spectrometer with AlKα or MgKα radiation. A shift due to charge-up was not observed. The binding energies (BEs) were corrected by using the value of 285.0 eV for the C1s level resulting from contaminating carbon. The core-level BEs of palladium, silver and gold foils were then mesured. The $Pd3d_{5/2}$, $Ad3d_{5/2}$ and $Au4f_{7/2}$ BEs were, respectively, 335.4, 368.3 and 84.0 eV relative to the Fermi level [5]. The experimental errors were within 0.1 eV. The normal operating vacuum pressure was less than $3 \times 10^{-8}$ Pa. The XPS spectra were measured at room temperature and without additional surface treatment.

The spectra of far infrared spectrometry (FIRS) were recorded with a Digilab (Chicago) SPS-15. The sample was dispersed using liquid paraffin and measured with polyethylene windows.

Catalytic activity for the oxidation of CO was measured with a conventional flow system. Prior to the reaction, the catalysts (0.2 g) were heated in a stream of air for 1 h at 473 K. A mixed gas (CO 1.0%, air balance) was fed at a flow rate of $300\,cm^3\,min^{-1}$. The reaction temperatures of $La_{1-x}Th_xCoO_3$ and $La_{1-x}Sr_xCoO_3$ were 498 and 523 K, respectively. Products were analysed by a gas chromatograph (Shimadzu, Kyoto, GC-R1A) (molecular sieve 0.5 nm, column 1 m, kept at 363 K).

## 3. Results and discussion

### 3.1. X-ray measurements on $La_{1-x}Th_xCoO_3$

The X-ray powder diffraction patterns of all $La_{1-x}Th_xCoO_3$ ($0 \leqq x \leqq 0.03$) samples were indexed on the basis of a perovskite-type structure, and no

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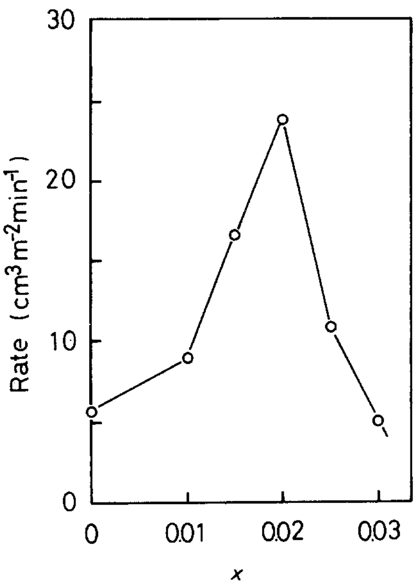

*Figure 1* Effects of substituting thorium for lanthanum in $La_{1-x}Th_xCoO_3$ on the oxidation of CO (498 K, S.V. (Space Velocity) 7500 h$^{-1}$).

other phases were found. The crystal structure was rhombohedral in all samples.

## 3.2. Catalytic activity of $La_{1-x}Th_xCoO_3$

Fig. 1 shows the results of the catalytic oxidation of CO for $La_{1-x}Th_xCoO_3$. The activity was measured at 498 K. Products other than $CO_2$ and $H_2O$ were not detected. The activity was enhanced by substituting thorium and had a peak at $x = 0.02$. With further substitution by $Th^{4+}$, the activity decreased monotonously. These results were consistent with that of $La_{1-x}Ce_xCoO_3$ [3].

## 3.3. Far infrared spectra for $La_{1-x}Th_xCoO_3$

Fig. 2 shows the far infrared spectra for $La_{1-x}Th_xCoO_3$. The peak at 176 cm$^{-1}$ seemed to show the states of cobalt in the perovskite structure [6]. From the result of the XRD pattern at $x = 0$, which showed only the $LaCoO_3$ phase, the peak is probably due to the $Co^{3+}$ state. Since this peak was little shifted in all samples, the state of cobalt in the perovskite structure seemed to remain unchanged.

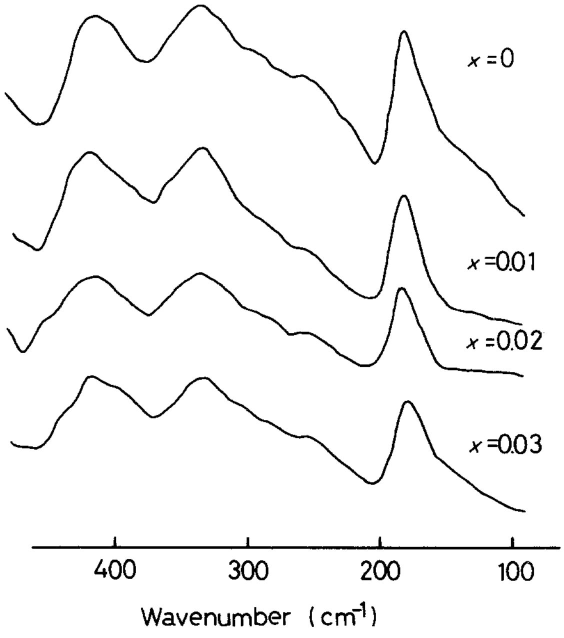

*Figure 2* FIRS spectra for $La_{1-x}Th_xCoO_3$.

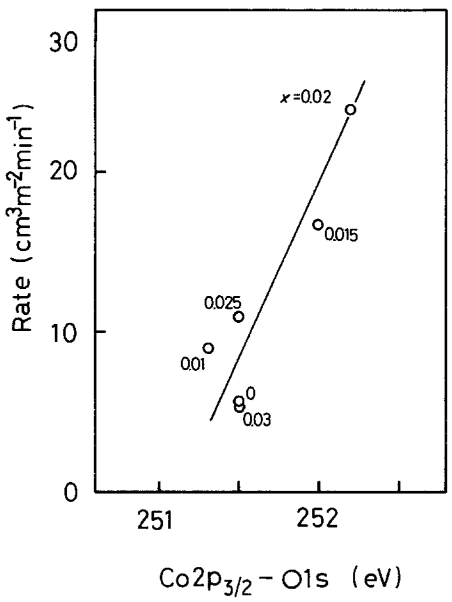

*Figure 3* The catalytic activity of $La_{1-x}Th_xCoO_3$ in the oxidation of CO at 498 K against the BE difference between $CO2p_{3/2}$ and O1s of lattice oxygen.

## 3.4. Surface chemical states of $La_{1-x}Th_xCoO_3$

The surface atomic ratio of cobalt was measured from the results of the XPS spectra, and it was nearly constant in all $Th^{4+}$-substituted samples.

Fig. 3 represents the catalytic reaction rate per surface area against the binding energy difference ($\Delta$BE) between $Co2p_{3/2}$ and O1s of lattice oxygen [3]. Catalytic activity increased with increasing the $\Delta$BE of $Co2p_{3/2}$–O1s. The catalytic activity of $La_{1-x}Th_xCoO_3$ also increased in proportion to the ionicity between the surface cobalt and lattice oxygen, as was the same case in $La_{1-x}Ce_xCoO_3$ [3].

Fig. 4 shows the intensity ratio of the lattice oxygen ($O^a$) to the oxygen weakly bound on the surface ($O^b$) (oxygen hydrated on the oxide surface may be included) [7, 8]. From this result and Fig. 3, it was found that in the most ionic sample ($x = 0.02$), the oxygen intensity

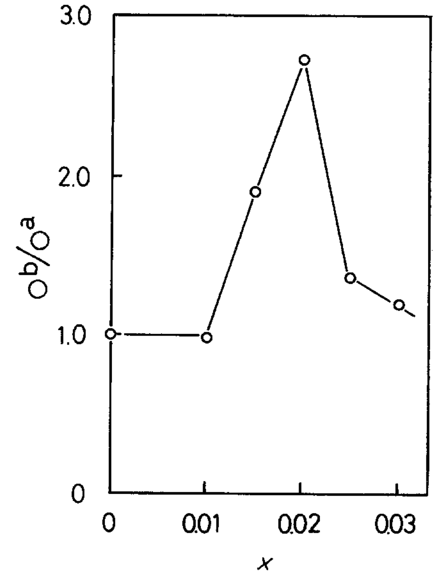

*Figure 4* The intensity ratio of $O^b$ to $O^a$ of $La_{1-x}Th_xCoO_3$.

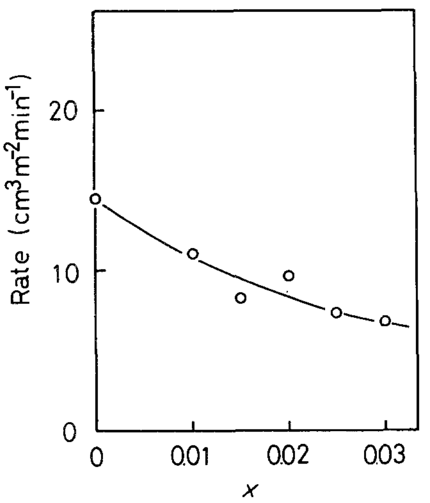

*Figure 5* Effects of substituting strontium for lanthanum in $La_{1-x}Sr_xCoO_3$ on the oxidation of CO (523 K, S.V. 7500 h$^{-1}$).

ratio was largest. It seemed to show that oxygen molecules in the gas might be adsorbed more easily in the more ionic sample. The same results were obtained for $La_{1-x}Ce_xCoO_3$ [3].

### 3.5. X-ray measurements on $La_{1-x}Sr_xCoO_3$

We also investigated the effects on the catalytic activity and surface chemical states of $La_{1-x}Sr_xCoO_3$ ($0 \leq x \leq 0.03$).

The XRD patterns of all samples were indexed on the basis of a perovskite-type structure and no other phases were found. The crystal structure was rhombohedral in all samples.

### 3.6. Catalytic activity of $La_{1-x}Sr_xCoO_3$

Fig. 5 shows the results of the catalytic oxidation of CO for $La_{1-x}Sr_xCoO_3$. The activity was measured at 523 K. Products other than $CO_2$ and $H_2O$ were not detected. The activity decreased monotonously with $Sr^{2+}$ substitution. This result was consistent with that of Voorhoeve *et al.* [1].

### 3.7. Surface chemical states of $La_{1-x}Sr_xCoO_3$

The surface atomic ratio of cobalt was measured by XPS, and it was nearly constant in all $Sr^{2+}$-substituted samples, as shown in Table I. In Fig. 6, the catalytic reaction rate per surface area was plotted as a function of the ΔBE between $Co2p_{3/2}$ and O1s of lattice oxygen. Catalytic activity decreased with decreasing ΔBE. The catalytic activity of $La_{1-x}Sr_xCoO_3$ decreased monotonously in proportion to the decrease of the ionicity between the surface cobalt and lattice oxygen ($O^a$).

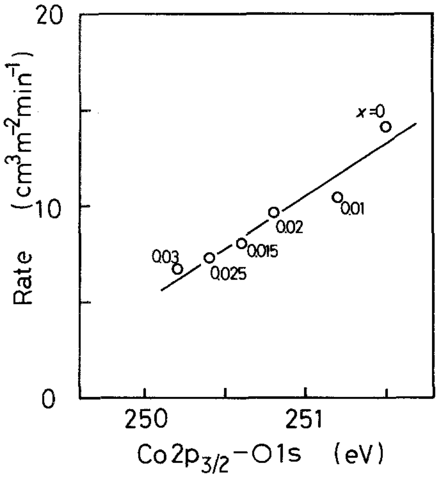

*Figure 6* The catalytic activity of $La_{1-x}Sr_xCoO_3$ in the oxidation of CO at 523 K is plotted as a function of the BE difference between $Co2p_{3/2}$ and O1s of lattice oxygen.

TABLE I Surface atomic ratio of $La_{1-x}Sr_xCoO_3$ measured by XPS

| $x$ in $La_{1-x}Sr_xCoO_3$ | Atomic ratio Co/(La + Sr + Co) |
|---|---|
| 0 | 0.52 |
| 0.01 | 0.54 |
| 0.015 | 0.54 |
| 0.02 | 0.57 |
| 0.025 | 0.53 |
| 0.03 | 0.46 |

Characterizations of the bulk state of $La_{1-x}Sr_xCoO_3$ have been performed by many workers [9–11]. Goodenough *et al.* [9] reported from their measurements of both magnetic susceptibility and electrical conductivity that the relation between the cobalt and oxygen in $La_{1-x}Sr_xCoO_3$ became covalent with strontium substitution. This result for the bulk state seemed to agree with our results for the surface state of $La_{1-x}Sr_xCoO_3$.

As for the decrease of the catalytic activity in $La_{1-x}Sr_xCoO_3$, we supposed that the decrease in the ionicity between the surface cobalt and lattice oxygen brought about a decrease in the degree of ionization of adsorbed CO, as reported for $La_{1-x}Ce_xCoO_3$ [3].

The oxidative reactivity of partly thorium- or strontium-substituted lanthanum cobalt oxides can be well explained by considering the surface chemical states of the compounds.

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