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Surface characterization and catalytic properties of $La_{1-x}Sr_xCoO_3$

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The surface chemical states of the perovskite-type compounds, strontium doped lanthanum cobalt oxides ($La_{1-x}Sr_xCoO_3$), have been investigated using X-ray photoelectron spectroscopy (XPS). Catalytic oxidations of both methane and CO have also been investigated using flow methods. The chemical composition of the surface of $La_{1-x}Sr_xCoO_3$ was very different from that in the bulk, which was measured by X-ray fluorescence spectroscopy (XRFS). The catalytic activity of $La_{1-x}Sr_xCoO_3$ increased with an increase in the quantity of cobalt atoms on the surface.

1. Introduction

Strontium doped lanthanum cobalt oxides ($La_{1-x}Sr_xCoO_3$) with a perovskite-type structure have been investigated with regard to their crystal structures, magnetic properties and electrical properties [1, 2]. Recently, Misono *et al.* [3] reported that $La_{1-x}Sr_xCoO_3$ showed high activity as an oxidation catalyst. Particularly, $La_{0.8}Sr_{0.2}CoO_3$ calcined at 1123 K was the most active, and its activity was comparable with platinum catalysts. They also reported that the variation of catalytic activity was explained on the basis of the reduction–oxidation properties of catalysts.

In this study, we investigated the surface chemical states and the bulk states of $La_{1-x}Sr_xCoO_3$. We attempted to elucidate the relationships between the catalytic properties and the surface states analysed by X-ray photoelectron spectroscopy (XPS).

2. Experimental procedure

$La_{1-x}Sr_xCoO_3$ was prepared from mixtures of $La(CH_3COO)_3 3/2H_2O$ (Mitsuwa Chemical Co.), $(CH_3COO)_2Co4H_2O$ and $Sr(CH_3COO)_2 1/2H_2O$ (Kanto Chemical Co.). First, mixed acetate solution was evaporated to dryness in a rotary evaporator (343 to 363 K) and then the solid obtained was first decomposed in air at 673 K for 1 h and calcined in air at 1123 K for 5 h in an electric furnace [3].

The phases of products were determined by means of X-ray powder diffractometry (XRD) using Cu*Kα* radiation (Philips APD-10) Lattice parameters of these compounds were determined using silicon as an internal standard.

The surface area of the samples was measured by the BET method (N_2 adsorption). The XPS spectra were recorded on a VG ESCA LAB 5 spectrometer with Al*Kα* or Mg*Kα* radiation. The charge shift was not observed. The binding energies (BE) were corrected by using the value of 285.0 eV for the C1s level resulting from the contaminated carbon. Then the core-level BE of palladium, silver and gold foils were measured. The $Pd3d_{5/2}$, $Ag3d_{5/2}$ and $Au4f_{7/2}$ BEs were 335.4 ± 0.1, 368.3 ± 0.1 and 84.0 ± 0.1 eV, respectively, relative to the Fermi level [4]. The experimental errors were within ± 0.1 eV. The normal operating vacuum pressure was less than 3×10^{-8} Pa. The spectra of XPS were measured at room temperature and without additional surface treatment. The bulk composition of $La_{1-x}Sr_xCoO_3$ was measured by X-ray fluorescence spectroscopy (XRFS) using a glass bead method (Rigaku model 3370).

Catalytic activities for oxidations of methane or CO were measured with the conventional flow system. Prior to the reaction, the catalysts (1.0 g) were heated in a dried air stream for 1 h at 473 K. A mixed gas (CH_4 or CO 1.0% air balance) was fed at the flow rate of 300 $cm^3 min^{-1}$. Products were analysed by a gas chromatograph (Shimazu GC-R1A). (CH_4, activated charcoal 1 m kept at 363 K; CO, molecular sieve 5A 1 m kept at 363 K).

3. Results

3.1. X-ray measurement

The X-ray powder diffraction patterns of $La_{1-x}Sr_xCoO_3$ samples were indexed on the basis of the perovskite-type structure, and no other phases were found. The crystal structure of $LaCoO_3$ ($x = 0$) was rhombohedral, but the structure of $La_{1-x}Sr_xCoO_3$ gradually became cubic as x was increased [2].

Fig. 1 shows the lattice parameters on the base of the hexagonal indices. As shown in Fig. 1, the lattice parameters of the c-axis showed definite discontinuity in the range $0.2 < x < 0.3$. Similar discontinuities in the c-axis have been reported by Raccah

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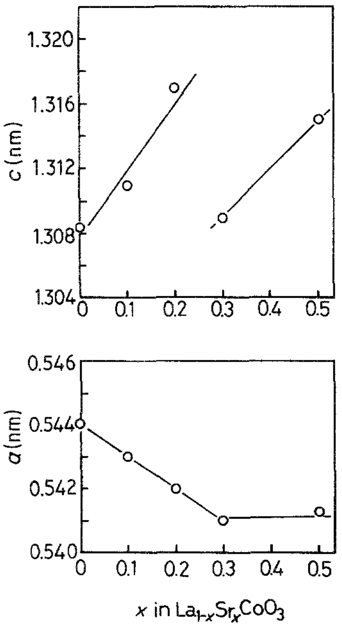

Figure 1 Lattice parameters of $La_{1-x}Sr_xCoO_3$.

and Goodenough [5] or Bhide and coworkers [6]. The hexagonal a-axis did not show any discontinuity.

3.2. Surface area and atomic ratio by XRFS

The surface area of $La_{1-x}Sr_xCoO_3$ measured by the BET method is shown in Table I. The surface area was almost constant except for $x = 0.5$. The atomic ratios of the samples measured by XRFS are also shown in Table I. These ratios show the bulk composition of $La_{1-x}Sr_xCoO_3$. It is noted from this table that all samples had a stoichiometric composition.

3.3. Oxidation of methane

Fig. 2 shows the results of the catalytic oxidation of CH_4 with these samples. The activity was measured at 723 K. Products other than CO_2 and H_2O were not detected. The activity was enhanced by substituting strontium and had a peak at $x = 0.2$. With further substitution of strontium the activity decreased monotonously. This result was consistent with the results of Misono *et al.* They also reported the peak at $x = 0.2$ for the oxidation of both C_3H_8 and CO by $La_{1-x}Sr_xCoO_3$.

3.4. Surface and bulk composition of $La_{1-x}Sr_xCoO_3$

As shown in Table I the chemical composition in these samples agreed well with the stoichiometric ratio. On the other hand, the surface atomic ratio of cobalt drastically changed, as shown in Fig. 3. That is, the surface atomic ratio of cobalt increased gradually with substituting strontium, and had a peak at $x = 0.2$. After that, the ratio decreased gradually.

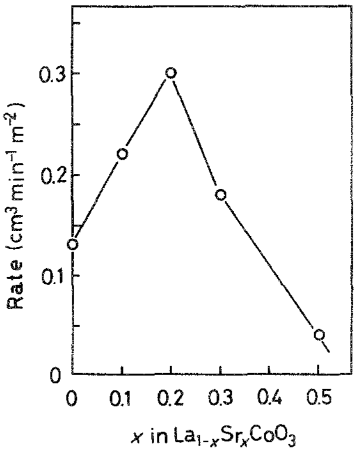

Figure 2 Effects of strontium substitution for lanthanum in the oxidation of methane at 723 K. (SV 7500 h^{-1}).

In Fig. 4, the atomic ratio of lanthanum to cobalt on the surface was less than that in the bulk except for $x = 0$ ($LaCoO_3$). On the contrary, the ratio on the surface of strontium to cobalt was considerably larger than that in the bulk ratio. It is interesting that the surface ratio of lanthanum to strontium came up to the values of the bulk ratio and the stoichiometry ratio at $x = 0.2$.

Fig. 5 shows XPS spectra of $Co2p_{3/2}$ for $La_{1-x}Sr_xCoO_3$. The peak of the spectrum at $x = 0$ ($LaCoO_3$) agreed quite well with the reported value of Co^{3+} (779.6 eV) by Lombardo *et al.* [7]. The value of spin-orbit splitting was 15.3 eV and this value also agreed well with that of Co^{3+} reported by Yasumori *et al.* [8]. From these results, the chemical state of cobalt seemed to be Co^{3+} at $x = 0$.

By substituting strontium, the peaks shifted slightly to higher binding energy and these peaks agreed with the value of Co^{2+} (780.3 eV) except for $x = 0.2$ [9]. The value of spin-orbit splitting for CoO was reported as 15.5 eV [10] or 16.0 eV [8]. The values of spin-orbit splitting for $La_{1-x}Sr_xCoO_3$ samples ($x = 0.1$ to 0.5) were within the limits of 15.5 eV to 16.0 eV. Thus the contribution of Co^{2+} appeared to increase on the surface by substituting with strontium.

For Co^{4+}, which was detected in the bulk by chemical analysis [3], we could not find notable evidence from these spectra.

For $x = 0.2$, the contribution of Co^{3+} is larger than the other strontium-substituted samples, because the BE of the peak at $x = 0.2$ shifted slightly to lower BE, i.e. near 779.6 eV as for Co^{3+} [7].

TABLE I Surface area by BET method and bulk composition by X-ray fluorescence spectroscopy (XRFS) of $La_{1-x}Sr_xCoO_3$

x in $La_{1-x}Sr_xCoO_3$	Surface area (m^2 g^{-1})	XRFS (atomic ratio)		
		Lanthanum	Strontium	Cobalt
0.0	3.4	1.00	–	1.00
0.1	3.7	0.90	0.10	1.00
0.2	4.0	0.81	0.19	1.00
0.3	3.7	0.69	0.31	1.00
0.5	5.8	0.49	0.51	1.00

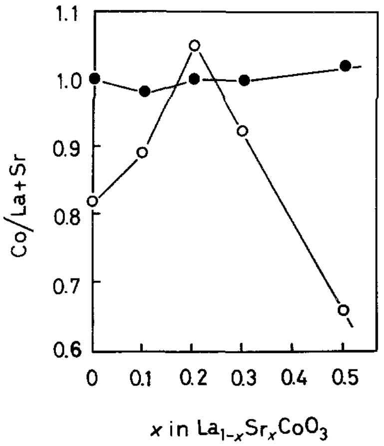

Figure 3 Surface atomic ratio (Co/La + Sr) of $La_{1-x}Sr_xCoO_3$ measured by XPS. ●, XRFS; ○, XPS.

Fig. 6 shows XPS spectra of Sr $3d_{5/2}$ for $La_{1-x}Sr_xCoO_3$. Obviously, the main peaks of the samples coincided well with the peak (132.6 eV) of SrO which was measured from the commercial reagent. The BE of SrO (132.6 eV) agreed quite well with the results of Young and Otagawa [11].

As well as this peak, there were two shoulders on both sides of the main peak. The shoulder of higher BE (134.2 eV) may be assigned as Sr^0 [12, 13]. For the other shoulder, of lower BE (130.5 eV), the component could not definitely be assigned. This value was different from the peak positions of our results for $Sr(OH)_2$ (134.2 eV) and $SrCO_3$ (133.6 eV). This value was separated by about 2 eV from the peak position of SrO.

Generally, the BE reflects the density of electric charge of the atom. The value of BE increases with valence number, and in cases of the same valence, the value of BE increases with the electronegativity of the binding atom or atomic group. Since the BE of the shoulder shifted to a lower binding energy side than that of SrO, the valence state of strontium appeared to be smaller than Sr^{2+}. We suspected that if the component was SrO_{1-x}, the peak would shift to a lower BE than that of SrO.

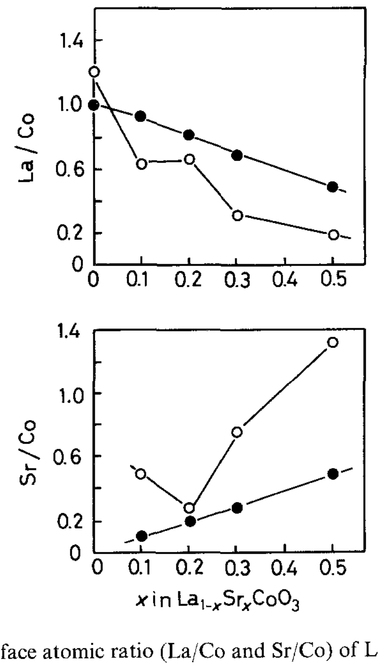

Figure 4 Surface atomic ratio (La/Co and Sr/Co) of $La_{1-x}Sr_xCoO_3$ measured by XPS. ●, XRFS; ○, XPS.

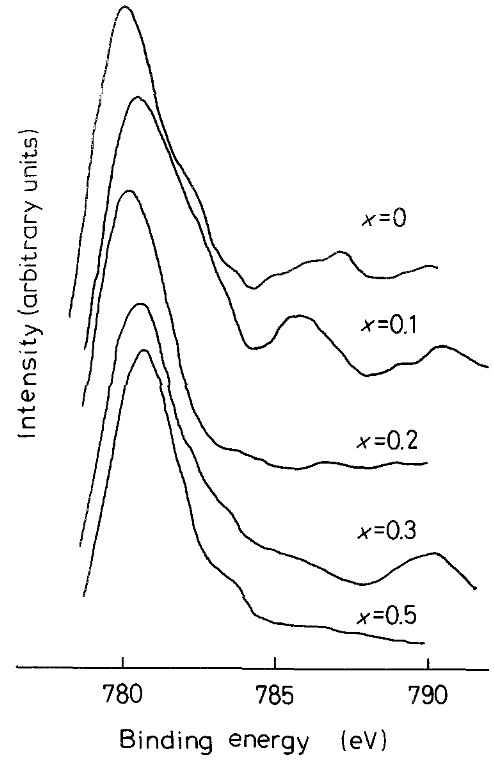

Figure 5 X-ray photoelectron spectra in the $Co2p_{3/2}$ of $La_{1-x}Sr_xCoO_3$.

Fig. 7 shows $La3d_{5/2}$ spectra of $La_{1-x}Sr_xCoO_3$. The spectra were very similar in all samples. These spectra were in good agreement with the results (for $LaCoO_3$) of Lam and co-workers [14]. The multiple splittings between the $3d_{3/2}$ and $3d_{5/2}$ level were almost identical

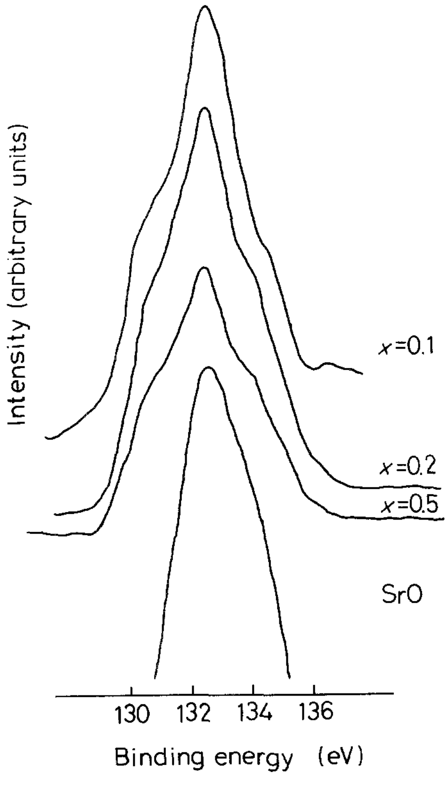

Figure 6 X-ray photoelectron spectra in the $Sr3d_{5/2}$ of $La_{1-x}Sr_xCoO_3$.

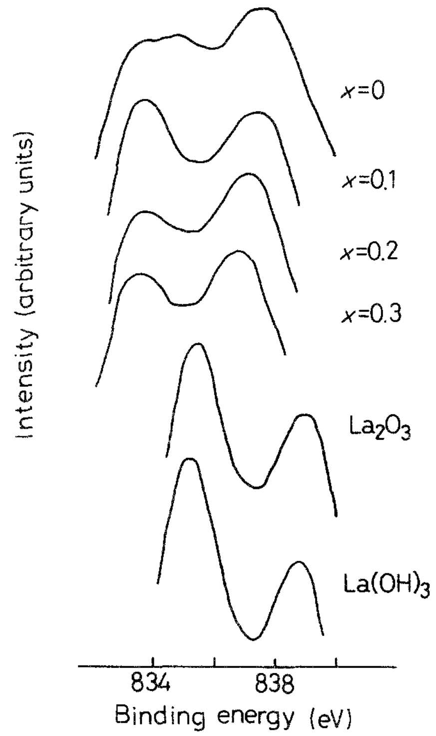

Figure 7 X-ray photoelectron spectra in the La3d$_{5/2}$ of La$_{1-x}$Sr$_x$CoO$_3$.

in all samples (16.8 eV), and this value also agreed with Lam and co-workers [14]. The satellite lines on the high BE side of the 3d levels were separated from the main peak by 4 eV and were fairly constant over the entire composition. These satellites may be interpreted in terms of excitation of an electron from the anion valence band into the lanthanum f band [15].

Fig. 8 shows the O1s spectra of La$_{1-x}$Sr$_x$CoO$_3$. The O1s spectrum for each sample was a doublet as reported by Seiyama *et al.* [16]. According to them, the peak with lower BE was assigned to the lattice oxygen (O^a). The assignment of the other peak (O^b) is controversial. It is possibly due to oxygen weakly bound on the surface [16], surface hydroxyls or oxygen bound to a basic element (La$_2$O$_3$, SrO) [17]. As shown in Fig. 8, the peak O^b increased but the peak O^a decreased with increasing the compositional parameter x. These changes seem to be correlated with the change of the atomic ratio of strontium to cobalt on the surface shown in Fig. 4. Our results about the peak of the O1s spectrum of SrO was 531.2 eV, that is, the O1s spectrum of SrO should be included in the peak of O^b of La$_{1-x}$Sr$_x$CoO$_3$. As shown in Fig. 4, the ratio of strontium to cobalt on the surface measured by XPS was considerably larger than that of the bulk measured by XRFS except for $x = 0.2$. Thus the peak O^b in Fig. 8 was clearly increased by substituting strontium, except for $x = 0.2$.

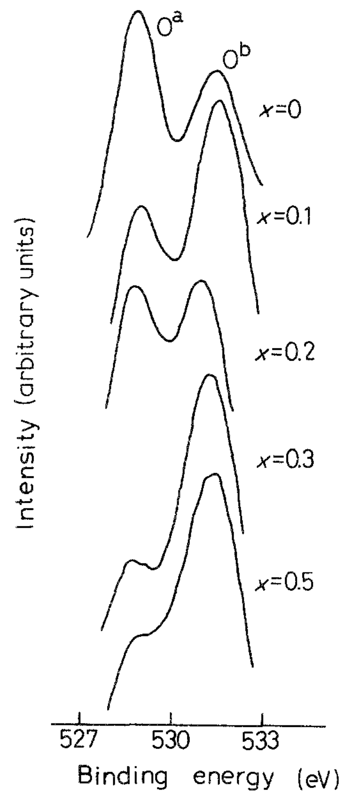

Figure 8 X-ray photoelectron spectra in the O1s of La$_{1-x}$Sr$_x$CoO$_3$.

4. Discussion

4.1. Surface composition

Only recently, through the application of XPS or Auger electron spectroscopy, has it been possible to analyse the chemical composition of the surface. According to these experimental results, the surface composition was usually very different from the composition in the bulk for most multicomponent systems.

Overbury *et al.* [18] reviewed the various thermodynamic models that permit practical determination of the surface composition of ideal or regular solid solutions. They indicated that the surface tension of the components was important in determining the surface composition.

The Gibbs' free energies (ΔG) for La$_2$O$_3$, Co$_3$O$_4$ and SrO are -1254.2, -769.3 and $-561.9\,\mathrm{kJ\,mol^{-1}}$, respectively. Consequently, lanthanum oxide seemed to be firstly constructed during the calcination. Since ΔG for La$_2$O$_3$ is very large and the surface tension of La$_2$O$_3$ seemed to be small in the case of LaCoO$_3$ ($x = 0$), lanthanum oxide seemed to come up to the surface as shown in Fig. 4.

In the La$_{1-x}$Sr$_x$CoO$_3$ ($0.1 \leqslant x \leqslant 0.5$) compounds, the valence state of cobalt seemed to be smaller than that of cobalt at $x = 0$. As for strontium, Sr^0 can be seen in Fig. 6. Thus both cobalt and strontium, whose ΔG values are smaller than that of La$_2$O$_3$, seemed to be reduced during the calcination. Since the ratio of strontium to cobalt on the surface far exceeded that in the bulk except for $x = 0.2$ as shown in Fig. 4, the reduced strontium seemed to melt on the surface.

For $x = 0.2$, the conduct of the surface atomic ratio of strontium was different from the other samples and comparatively near the stoichiometric ratio. The sample at $x = 0.2$ may be unstable because the lattice constant of the c-axis was discontinuous at $x = 0.2$ as shown in Fig. 1. This unstability of the system may make the diffusion of atoms easy. Therefore, the atomic ratio of the surface and the bulk might easily coexist with each other.

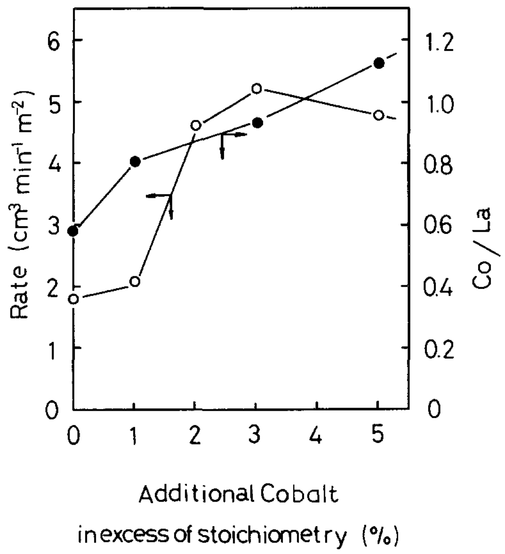

Figure 9 Effects of the additional cobalt in excess of the stoichiometry ratio on arrangement at $LaCoO_3$ in the oxidation of CO at 523 K (SV 7500 h^{-1}), and the surface atomic ratio measured by XPS.

4.2. Catalytic properties

The catalytic activity showed the peak at $x = 0.2$ as shown in Fig. 2. The catalytic activity of $La_{1-x}Sr_xCoO_3$ was quite similar to the surface atomic ratio of cobalt measured by XPS in Fig. 3. Since the reaction rates of La_2O_3 and SrO of the reagents at the same temperature were nearly zero, the catalytic activity seemed to depend on the cobalt on the surface. Thus, the sample at $x = 0.2$, which has the maximum surface atomic ratio of cobalt, naturally showed the maximum catalytic activity.

To examine the relation between the catalytic activity and the surface states, we prepared samples to which were added further cobalt in excess of the stoichiometric ratio of $LaCoO_3$, and measured the catalytic activity for oxidation of CO at 523 K, and also measured surface chemical states by XPS. All the samples showed X-ray diffraction peaks as for the perovskite-type structure. The surface atomic ratio of cobalt measured by XPS increased linearly as shown in Fig. 9. The catalytic activity also increased. But the activity of the sample, whose surface atomic ratio of cobalt exceeded the stoichiometry ratio, did not increase.

From these results, the catalytic activity seems to depend not only on the surface concentration of cobalt but also on the chemical states of cobalt.

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