The effects of annealing temperature on the catalytic properties for CO oxidation and the surface state have been investigated with X-ray photoelectron spectroscopy in LaCoO$_3$ and La$_{0.8}$Sr$_{0.2}$CoO$_3$ compounds. The catalytic activity in both LaCoO$_3$ and La$_{0.8}$Sr$_{0.2}$CoO$_3$ depended on the ionicity between the surface cobalt and lattice oxygen. The change of ionicity on the surface can be explained by the change of Co–O separations in the bulk.

### 1. Introduction

The perovskite-type mixed oxides have been suggested as possible substitutes for noble metals in automotive exhaust catalysts [1]. Manganite and cobalite perovskite have been reported to be very active for the oxidation of CO [2].

In previous papers, we have reported the effects of calcination temperature on the catalytic properties of both La$_{0.9}$Ce$_{0.1}$CoO$_3$ [3] and La$_{0.8}$Sr$_{0.2}$CoO$_3$ [4].

In this study, we investigate the effects of annealing temperature on the catalytic properties in both LaCoO$_3$ and La$_{0.8}$Sr$_{0.2}$CoO$_3$. The catalytic properties and surface states are studied by X-ray photoelectron spectroscopy (XPS).

### 2. Experimental procedure

Both LaCoO$_3$ and La$_{0.8}$Sr$_{0.2}$CoO$_3$ were prepared by heating precipitates at 1673 K for 5 h in air, and then quenching to room temperature. The precipitates were made from mixtures of metal acetates. After heating both LaCoO$_3$ and La$_{0.8}$Sr$_{0.2}$CoO$_3$ samples were annealed at a given temperature (between 873 and 1673 K) for 5 h and then quenched to room temperature.

The phases of the products were examined by means of X-ray powder diffraction using CuK$_\alpha$ radiation (Philips APD-10). Lattice parameters were determined by using silicon as an internal standard.

Surface areas of the samples were measured by the BET method (N$_2$ adsorption).

The XPS spectra were recorded on a V.G. Esca LAB-5 spectrometer with AlK$_\alpha$ or MgK$_\alpha$ radiation. The binding energies (BE) 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 measured. The Pd3d$_{5/2}$, Ag3d$_{5/2}$ and Au4f$_{7/2}$ BEs were 335.4, 368.3 and 84.0 eV, respectively, 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 without additional surface treatment.

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 (1.0% CO, air balance) was fed at a flow rate of 300 cm$^3$ min$^{-1}$. The reaction temperature was 598 K. Products were analysed by a gas chromatograph (Shimadzu GC-R1A, molecular sieve 5A in 1 m column at 363 K).

### 3. Results and discussion

#### 3.1. Crystal structure of LaCoO$_3$

The X-ray powder diffraction patterns of all LaCoO$_3$ compounds were indexed on the basis of the perovskite-type structure. No other phases were detected. The crystal structure was rhombohedral in all samples.

#### 3.2. Catalytic activity of LaCoO$_3$

Fig. 1 shows the effects of annealing temperature on the catalytic properties of LaCoO$_3$. Products other than CO$_2$ and H$_2$O were not detected. The activity decreased greatly with increasing annealing temperature from 873 to 1273 K, and had a minimum value at 1273 K. On further increasing the annealing temperature the activity was enhanced again.

#### 3.3. Surface states and catalytic activity of LaCoO$_3$ for different annealing temperatures

The surface atomic ratios of the samples were measured by XPS at room temperature. Table I shows the surface atomic ratios, Co/(La + Co), of LaCoO$_3$ as a function of annealing temperature ($T_a$).

<table>
<thead>
<tr>
<th>$T_a$(K)</th>
<th>873</th>
<th>1073</th>
<th>1273</th>
<th>1473</th>
<th>1673</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co/(La + Co)</td>
<td>0.45</td>
<td>0.45</td>
<td>0.50</td>
<td>0.45</td>
<td>0.48</td>
</tr>
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atomic ratio of cobalt. There was no significant change in all samples in spite of a large difference in the oxidative activity as shown in Fig. 1.

Fig. 2 represents the catalytic reaction rate per surface area against the binding energy difference (ΔBE) between Co2p3/2 and O1s of lattice oxygen [4]. Catalytic activity in Fig. 1 was related linearly to the ΔBE of Co2p3/2 − O1s. According to Frost et al. [6], the increase in the BE of cobalt for cobalt halides from bromide to fluoride was due to the increase in ionicity of the compounds. Thus, the catalytic activity seemed to increase in proportion to the ionicity between the surface cobalt and lattice oxygen in LaCoO3.

3.4. Cobalt-oxygen separations in LaCoO3
To explain the minimum value of catalytic activity and the most covalent bond character for the sample annealed at 1273 K as seen in Figs 1 and 2, we considered the relation between the surface state and the bulk state. The change in bulk states of LaCoO3 in the temperature range 300 to 1273 K was investigated by Raccah and Goodenough [7] in detail with both high-temperature X-ray diffraction (XRD) and differential thermal analysis (DTA). They reported that there was a first-order transition at about 1210 K, and discontinuities in the hexagonal lattice parameters. The separations between the cobalt and oxygen atoms for the LaCoO3 compounds for different annealing temperatures were calculated, and the results are shown in Fig. 3. The separations decreased with increasing annealing temperature and had a minimum value for the sample annealed at 1273 K. We speculated that the appearance of the minimum Co−O separation at 1273 K annealed LaCoO3 seemed to correspond to the phase transition as reported by Raccah and Goodenough [7]. Since the crystal field may be strengthened for shorter Co−O separations, the bond state of Co−O both in the bulk and on the surface seemed to be most covalent for the sample annealed at 1273 K [8].

3.5. Crystal structure of La0.8Sr0.2CoO3
The XRD patterns of all La0.8Sr0.2CoO3 compounds were completely indexed on the basis of the perovskite-type structure.

3.6. Catalytic properties of La0.8Sr0.2CoO3
Fig. 4 shows the effects of annealing temperature on the catalytic properties of La0.8Sr0.2CoO3. The