JOURNAL OF MATERIALS SCIENCE 23 (1988) 1056–1059

Effects of thermal treatment on the catalytic properties of $LaCoO_3$ and $La_{0.8}Sr_{0.2}CoO_3$

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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 diffractometry using Cu$K\alpha$ 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 Al$K\alpha$ or Mg$K\alpha$ 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 3×10^{-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_2O 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

TABLE I Surface atomic ratio, Co/(La + Co), of $LaCoO_3$ as a function of annealing temperature (T_a)

T_a(K)	873	1073	1273	1473	1673
Co/(La + Co)	0.45	0.45	0.50	0.45	0.48

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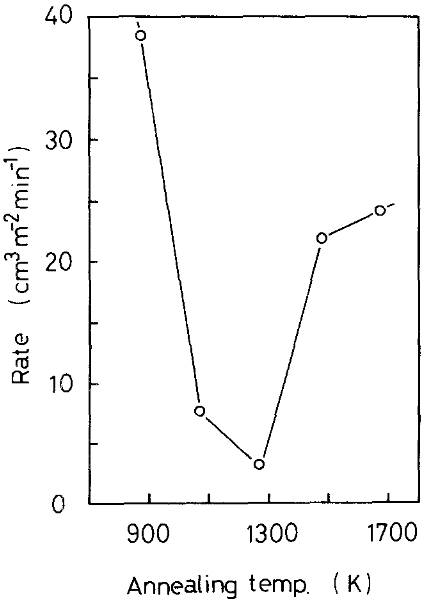

Figure 1 Effects of annealing temperature on the activity per unit surface area of $LaCoO_3$ in the oxidation of CO at 598 K (Space Velocity S.V. 7500 h^{-1}).

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 $Co2p_{3/2}$ and O1s of lattice oxygen [4]. Catalytic activity in Fig. 1 was related linearly to the ΔBE of $Co2p_{3/2}$ − 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 $LaCoO_3$.

3.4. Cobalt–oxygen separations in $LaCoO_3$

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 $LaCoO_3$ 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 $LaCoO_3$ 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 $LaCoO_3$ 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].

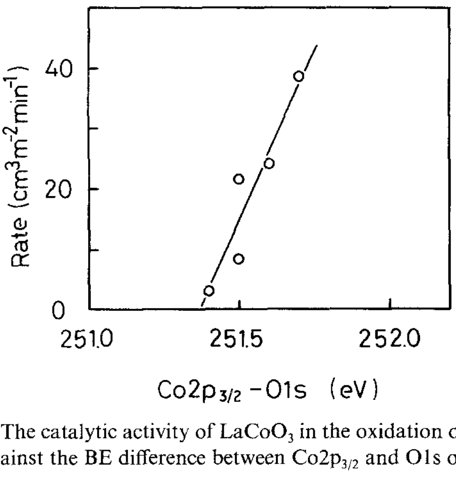

Figure 2 The catalytic activity of $LaCoO_3$ in the oxidation of CO at 598 K against the BE difference between $Co2p_{3/2}$ and O1s of lattice oxygen.

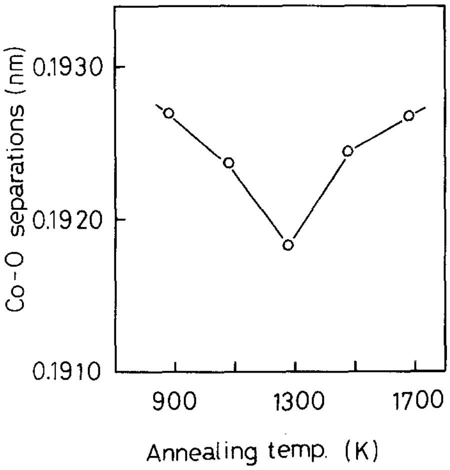

Figure 3 Co–O separation as a function of annealing temperature.

3.5. Crystal structure of $La_{0.8}Sr_{0.2}CoO_3$

The XRD patterns of all $La_{0.8}Sr_{0.2}CoO_3$ compounds were completely indexed on the basis of the perovskite-type structure.

3.6. Catalytic properties of $La_{0.8}Sr_{0.2}CoO_3$

Fig. 4 shows the effects of annealing temperature on the catalytic properties of $La_{0.8}Sr_{0.2}CoO_3$. The

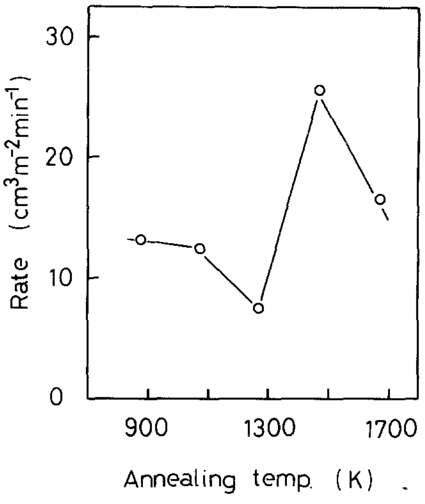

Figure 4 Effects of annealing temperature on the activity per unit surface area of $La_{0.8}Sr_{0.2}CoO_3$ in the oxidation of CO at 598 K (S.V. 7500 h^{-1}).

TABLE II Surface atomic ratio, Co/(La + Sr + Co), of $La_{0.8}Sr_{0.2}CoO_3$ as a function of annealing temperature (T_a)

T_a(K)	873	1073	1273	1473	1673
Co/(La + Sr + Co)	0.34	0.34	0.37	0.36	0.34

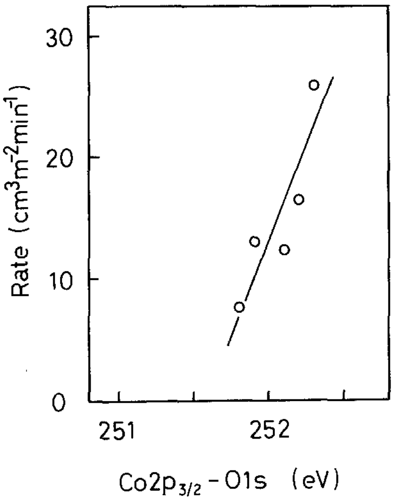

Figure 5 The catalytic activity for $La_{0.8}Sr_{0.2}CoO_3$ in the oxidation of CO at 598 K (S.V. 7500 h^{-1}).

oxidative activity of CO was measured at 598 K. Products other than CO_2 and H_2O were not detected. The activity had a minimum value at 1273 K. This result was consistent with that of $LaCoO_3$.

3.7. Surface states and catalytic activity of $La_{0.8}Sr_{0.2}CoO_3$ for different annealing temperature

Table II shows the surface atomic ratios of cobalt as measured by XPS. They were nearly constant in all samples.

Fig. 5 represents the catalytic reaction rate per surface area in $La_{0.8}Sr_{0.2}CoO_3$ against ΔBE between $Co2p_{3/2}$ and O1s of lattice oxygen [3]. Catalytic activity in $La_{0.8}Sr_{0.2}CoO_3$ was related linearly to the ΔBE of $Co2p_{3/2}$ and O1s of lattice oxygen, which was the same as that in $LaCoO_3$. Thus, the catalytic activity also seemed to increase in proportion to the ionicity between the surface cobalt and lattice oxygen.

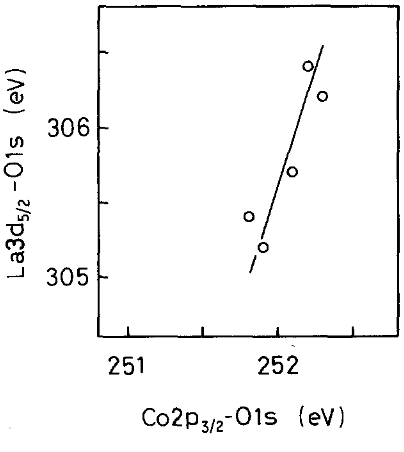

Figure 6 The BE difference between $La3d_{5/2}$ and O1s of lattice oxygen, plotted as a function of the BE difference between $Co2p_{3/2}$ and O1s of lattice oxygen.

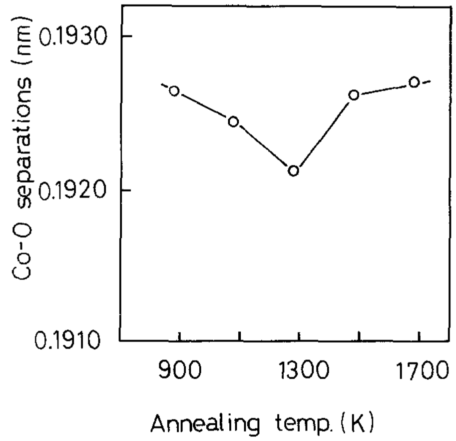

Figure 7 Co–O separation as a function of annealing temperature.

Fig. 6 shows the ΔBE between $La3d_{5/2}$ and O1s of lattice oxygen against the ΔBE between $Co2p_{3/2}$ and O1s of lattice oxygen. With increasing the ionicity of the Co–O bond, the ionicity of the La–O bond increased in parallel.

3.8. Cobalt–oxygen separations in $La_{0.8}Sr_{0.2}CoO_3$

Fig. 7 shows the Co–O separations which were calculated from the lattice parameters. As shown in Fig. 7, the separation decreased with increasing annealing temperature and had a minimum value for the sample annealed at 1273 K. This result was consistent with that for $LaCoO_3$ in Fig. 3. 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, as shown in Fig. 5, and this sample showed the lowest activity in the oxidation of CO (Fig. 4).

The change of the bulk state in $La_{1-x}Sr_xCoO_3$ ($0 \leq x \leq 0.5$) from room temperature to 1273 K was also investigated by Raccah and Goodenough [9]. They reported that the transition, which was detected in $LaCoO_3$ at about 1210 K, was also detected for all x in $La_{1-x}Sr_xCoO_3$ ($0 \leq x \leq 0.5$) by means of DTA. However, the DTA peak intensity decreased with x, and almost disappeared above $x = 0.4$.

The effects of annealing temperature in both $LaCoO_3$ and $La_{0.8}Sr_{0.2}CoO_3$ on the catalytic properties can be well explained by the changes in the surface state which were caused by the changes of bulk state.

Acknowledgements

The authors thank Messrs Yamada, Maki and Matsumoto for their support in this work. We also thank Professor Misono, Tokyo University and Dr Kido, Osaka Municipal Technical Research Institute, for their helpful advice.

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Received 29 May
and accepted 27 July 1987