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Catalytic properties and surface states of $La_{1-x}Ce_xCoO_3$

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The correlations between the catalytic properties and the surface states, which were measured by X-ray photoelectron spectroscopy (XPS) were investigated for the perovskite-type cerium doped lanthanum cobalt oxides ($La_{1-x}Ce_xCoO_3$). The activities of the catalytic oxidation for the 1123 K calcined samples were correlated with the atomic ratio of cobalt on the surface. On the other hand, the activities of the catalytic oxidation for the 1673 K calcined samples had a peak at $x = 0.02$. The ionicity between surface cobalt and lattice oxygen increased by substituting cerium for lanthanum, and had a peak at $x = 0.02$.

1. Introduction

Voorhoeve *et al.* reported that the catalytic activity of oxidation was enhanced by partial substitution of 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 [1].

In the previous paper [2], we reported the effect of surface chemical states of $La_{1-x}Sr_xCoO_3$ ($0 \leqq x \leqq 0.5$) on the catalytic activity.

In this study, we investigate in more detail the effect of cerium substitution for lanthanum in $LaCoO_3$ on the catalytic activity. The relationship between the catalytic properties and the surface chemical states is reported.

2. Experimental Procedure

$La_{1-x}Ce_xCoO_3$ was prepared from mixtures of metal acetates of each component following the literature [3]. First, mixed acetate solution was evaporated to dryness in a rotary evaporator (343 to 363 K) and then the solid obtained was decomposed in air at 673 K for 1 h and then calcined in air at 1123 K or 1673 K for 5 h.

The structure of the catalysts were determined by means of XRD using Cu$K\alpha$ radiation (Philips APD-10). Surface area of the samples were measured by BET method (N_2 adsorption).

The XPS spectra were recorded on a V.G. ESCA LAB5 spectrometer with Al$K\alpha$ or Mg$K\alpha$ radiations. The binding energies (BE) were corrected by using the value of 285.0 eV for the C_{1s} level resulting from the contaminated carbon. Then, the core-level BE of palladium, silver and gold foils were measured. The $Pd_{3d_{5/2}}$, $Ag_{3d_{5/2}}$ and $Au_{4f_{7/2}}$ BEs were, respectively, 335.4 eV, 368.3 eV and 84.0 eV relative to the Fermi level [4]. The normal operating vacuum pressure was less than 3×10^{-8} Pa. The spectra of XPS were measured at room temperature without additional surface treatment. The shift due to charge up was not observed.

The O $KL_{23}L_{23}$ Auger electron spectra were also recorded on the same instrument in the constant analyser energy mode. The bulk composition of $La_{1-x}Ce_xCoO_3$ were measured by X-ray fluorescence spectroscopy (XRFS) by using a glass bead method (Rigaku model 3370). Catalytic activity for oxidations of both CH_4 and CO were measured with the conventional flow system. Prior to the reaction, the catalysts (CH_4: 1.0 g, CO: 0.2 g) were heated in a stream of air 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 (Shimadzu GC-R1A). (CH_4: activated charcoal column 1 m, kept at 363 K, CO: molecular sieve 5A column 1 m, kept at 363 K.)

3. Results and discussion

3.1. X-ray measurements of the samples calcined at 1123 K

The crystal structures of $LaCoO_3$ ($x = 0$) was purely rhombohedral perovskite-type, but other samples ($x = 0.1$ to 0.5) showed the peaks due to CeO_2, Co_3O_4, which increased with increasing x.

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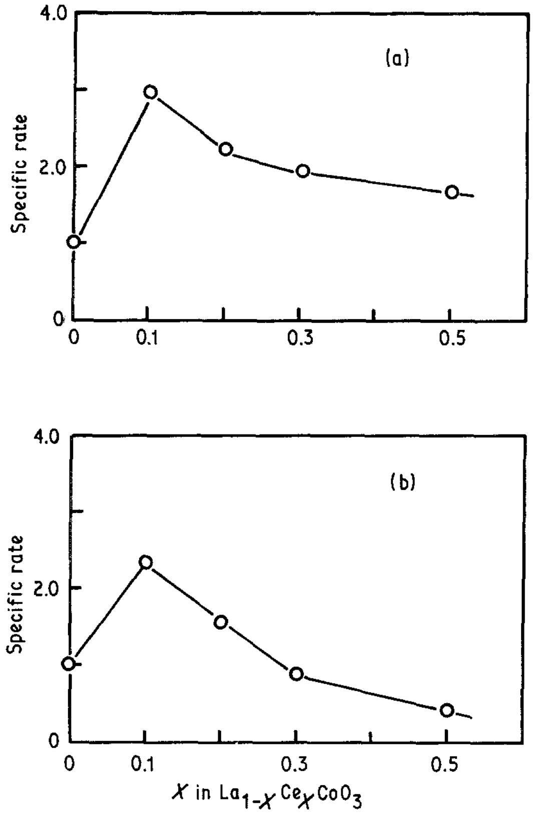

Figure 1 Catalytic activity of $La_{1-x}Ce_xCoO_3$ calcined at 1123 K for the oxidation of (a) CO (523 K, S.V. 7500 h^{-1}) and (b) CH_4 (733 K, S.V. 7500 h^{-1}).

3.2. Oxidations of CO and CH_4 for the samples calcined at 1123 K

Fig. 1 shows the results of the catalytic oxidations of CO and CH_4 with $La_{1-x}Ce_xCoO_3$. The activities for CO and CH_4 were measured at 523 K and 733 K respectively. The activities were enhanced by the cerium substitution and showed a peak at $x = 0.1$ for both reactions. With further cerium substitution, the activities decreased monotonously. Products other than CO_2 and H_2O were not detected in both oxidation reactions.

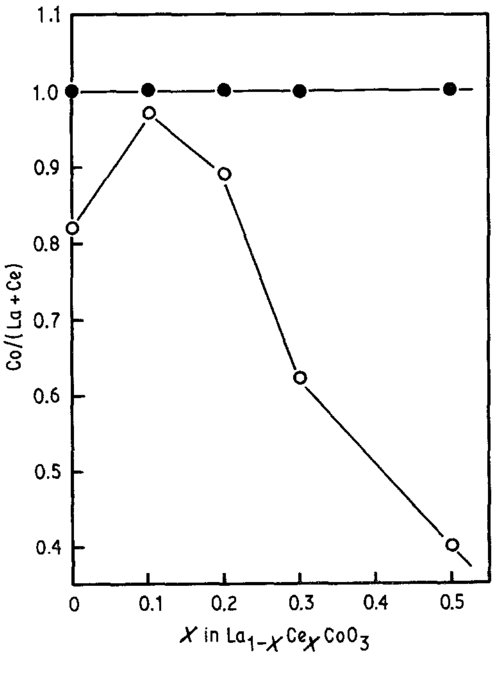

Figure 2 Surface atomic ratio (Co/La + Ce) of $La_{1-x}Ce_xCoO_3$ calcined at 1123 K. (●) XRFS, (○) XPS.

3.3. Bulk and surface compositions of the samples calcined at 1123 K

Fig. 2 shows both the bulk and surface atomic ratio of $La_{1-x}Ce_xCoO_3$ which were quantitatively analysed by XRFS and calculated from both main and satellite peaks of XPS respectively. In all samples, the averaged bulk composition agreed with the stoichiometric ratio. On the other hand, the atomic ratio of cobalt on the surface significantly changed as shown in Fig. 2. The surface atomic ratio of cobalt increased gradually with substituting cerium, and showed a peak at $x = 0.1$. Then, the ratio decreased gradually.

Overbury *et al.* reviewed the various thermodynamic models that permit practical determination of the surface composition of ideal or regular solid solutions [5]. They indicated that the surface tension of the components were important to determine the surface composition.

The Gibbs' free energy of formation (ΔG) for La_2O_3, CeO_2 and Co_3O_4 are $-1254.2\,KJ\,mol^{-1}$, $-1390.0\,KJ\,mol^{-1}$ and $-769.3\,KJ\,mol^{-1}$ respectively. Consequently, lanthanum oxide seemed to be formed at the early stage of the calcination. Since, ΔG for La_2O_3 is very large and the surface tension of La_2O_3 seemed to be small, lanthanum oxide came up to the surface. With increasing the compositional parameter x, cerium oxide also came up to the surface.

The catalytic activity of $La_{1-x}Ce_xCoO_3$ as shown in Fig. 1, was quite similar to the surface atomic ratio of cobalt. Since the reaction rate of both La_2O_3 and CeO_2 of reagents for the oxidation of CH_4 at 733 K were nearly zero, the catalytic activity seemed to depend on the cobalt on the surface. Thus the sample at $x = 0.1$, which had the maximum surface atomic ratio of cobalt, naturally showed the maximum of the catalytic activity.

3.4. X-ray measurement of the samples calcined at 1673 K

For examining in more detail the effects of cerium substitution for lanthanum in $LaCoO_3$ on the catalytic activity, we prepared the single phase samples which were calcined in air at 1673 K for 5 h. The X-ray powder diffraction patterns of $La_{1-x}Ce_xCoO_3$ samples were indexed on the basis of the perovskite-type structure, and no other phases were found in the composition range $x = 0$ to 0.03. The crystal structure was rhombohedral in all samples.

3.5. CO oxidation of the samples calcined at 1673 K

Fig. 3 shows the results of the catalytic oxidation of CO with the samples calcined at 1673 K. The activity was measured at 523 K. The activity was enhanced by substituting cerium and had a peak at $x = 0.02$. With further substitution by cerium, the activity decreased monotonously.

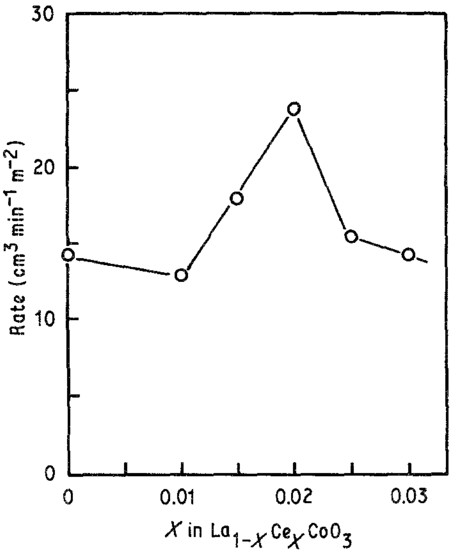

Figure 3 Catalytic activity of $La_{1-x}Ce_xCoO_3$ calcined at 1673 K for the oxidation of CO. (523 K, S.V. 7500 h^{-1}.)

3.6. Surface atomic ratio of the samples calcined at 1673 K

The surface atomic ratio of these samples were measured by XPS at room temperature. Fig. 4 shows the surface atomic ratio of cobalt. They were almost constant and agreed with the stoichiometric ratio.

3.7. Surface states of the samples calcined at 1673 K

Fig. 5 represents the catalytic reaction rate per surface area as a function of the binding energy difference (ΔBE) between $Co_{2p_{3/2}}$ and O_{1s} of lattice oxygen. Catalytic activity increased with increasing ΔBE of $Co_{2p_{3/2}}-O_{1s}$. According to Frost *et al.* [6], the increase in the BE of cobalt for the 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 of the sample.

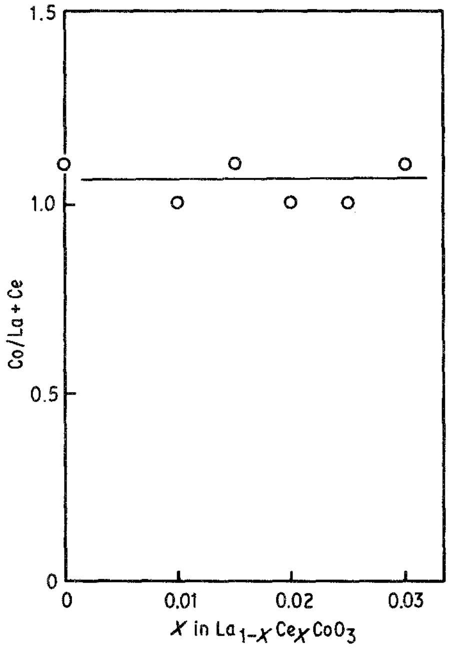

Figure 4 Surface atomic ratio (Co/La + Ce) of $La_{1-x}Ce_xCoO_3$ calcined at 1673 K.

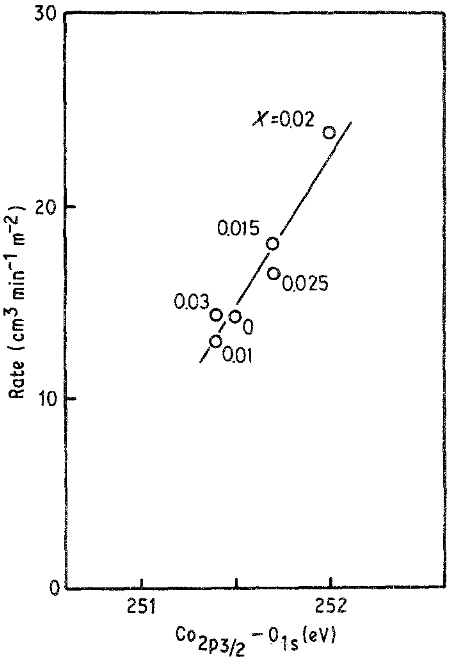

Figure 5 Catalytic activity of $La_{1-x}Ce_xCoO_3$ calcined at 1673 K for the oxidation of CO at 523 K is plotted as a function of the BE difference between $Co_{2p_{3/2}}$ and O_{1s} of the lattice oxygen.

In Fig. 6, the catalytic activity was plotted as a function of the Auger parameter (α_a) of lattice oxygen in these samples. The Auger parameter of oxygen (α) is defined as

$$\alpha = \mathrm{BE}\,(O_{1s}) + \mathrm{KE}\,(\mathrm{O\ KLL}) \qquad (1)$$

In a practical point of view, α is convenient because it is independent of absolute energy calibration and of sample charging. If two compounds are examined, the difference can be designated as follows

$$\Delta\alpha = 2\,R_{ex}(0_{2p}) \qquad (2)$$

by Kowalczyk *et al.* [7] and Wagner [8]. The value of 1/2 ($\Delta\alpha$) is equivalent to the difference in extra-atomic

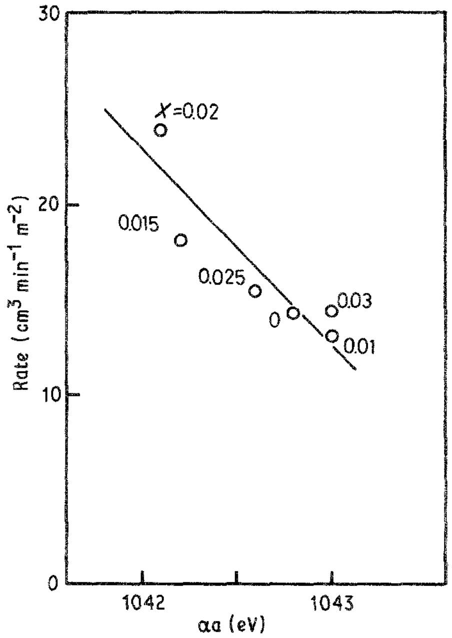

Figure 6 Catalytic activity of $La_{1-x}Ce_xCoO_3$ calcined at 1673 K for the oxidation of CO at 523 K is plotted as a function of the Auger parameter (α_a) of the lattice oxygen.

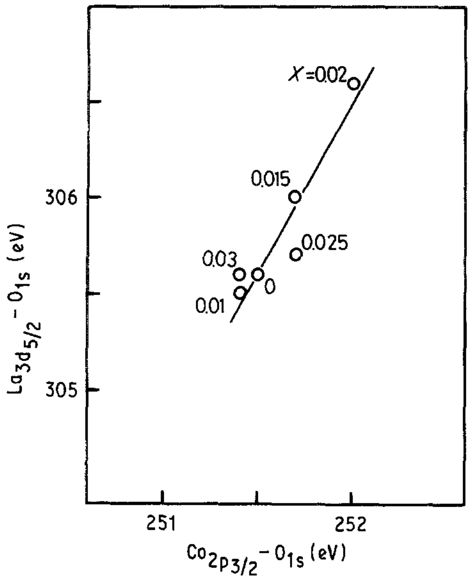

Figure 7 The BE difference between $La_{3d_{5/2}}$ and O_{1s} is plotted as a function of the BE difference between $Co_{2p_{3/2}}$ and O_{1s} of the lattice oxygen.

relaxation energy for a singly charged final state of the atom under study in the two compounds. Bahl *et al.* [9] reported that in ionic bond, the extra-atomic relaxation energy shift was a useful scale of electronegativity. Then, the increase of the Auger parameter implies that the electronegativity of the ionic bond become smaller, namely, ionicity of the bond decreases. As shown in Fig. 6, the increase of the ionicity of the lattice oxygen brought the increase of catalytic activity as the same results in Fig. 5.

Fig. 7 shows the ΔBE between $La_{3d_{5/2}}$ and O_{1s} of lattice oxygen as a function of the ΔBE between $Co_{2p_{3/2}}$ and O_{1s} of lattice oxygen. With increasing ionicity of the Co–O bond, that of the La–O bond increased in parallel.

The O_{1s} spectrum for each sample was doublet as reported by Seiyama *et al.* for $La_{1-x}Sr_xCoO_3$ [10].

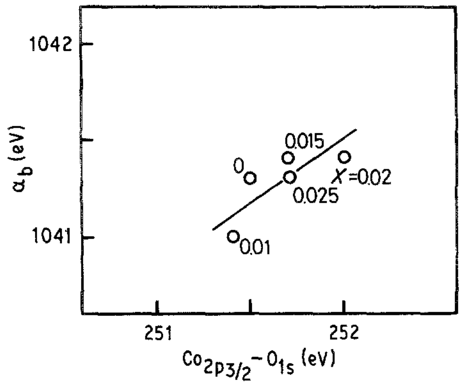

Figure 9 The Auger parameter (α_b) of the adsorbed oxygen is plotted as a function of the BE difference between $Co_{2p_{3/2}}$ and O_{1s} of the lattice oxygen.

According to them, the peak with lower BE side was assigned to the lattice oxygen (O^a). The other peak (O^b) may be due to oxygen weakly bound on the surface or hydrate of oxide surface [11].

Fig. 8 shows the intensity ratio of O^b to O^a. The ratio had a peak at $x = 0.02$. From this result, the oxygen in the gas seemed to be adsorbed more easily on the ionic sample.

The Auger parameter (α_b) of the adsorbed oxygen (O^b) increased with increasing the BE between $Co_{2p_{3/2}}$ and O_{1s} of the lattice oxygen (O^a) as shown in Fig. 9. This figure seemed to imply that the ionicity of Co–O^b bond decreased slightly with increasing the ionicity of the Co–O^a bond. The electron of the adsorbed oxygen (O^b) seemed to pour into the adsorbents (cobalt, lanthanum) when ionicity between the Co–O^a bond was increased. From these results, we schematized, the effects of substituting cerium for lanthanum in Fig. 10. In this figure a and b represent the surface states of $LaCoO_3$ and $La_{0.98}Ce_{0.02}CoO_3$, respectively. The broken line expresses the change of the electron cloud by substituting cerium for lanthanum in $LaCoO_3$.

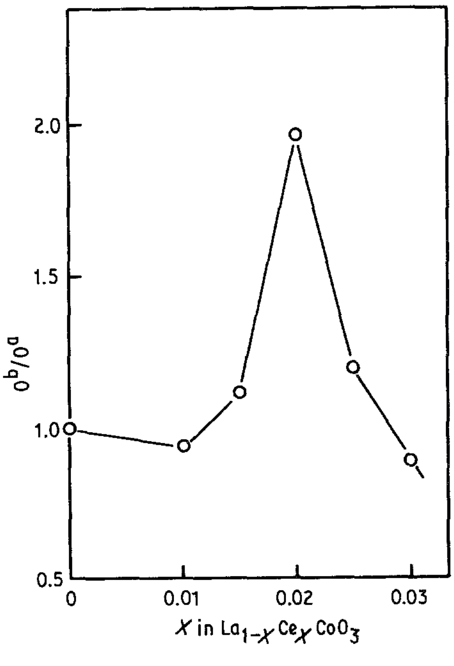

Figure 8 Intensity ratio of the adsorbed oxygen (O^b) to lattice oxygen (O^a) of $La_{1-x}Ce_xCoO_3$ calcined at 1673 K.

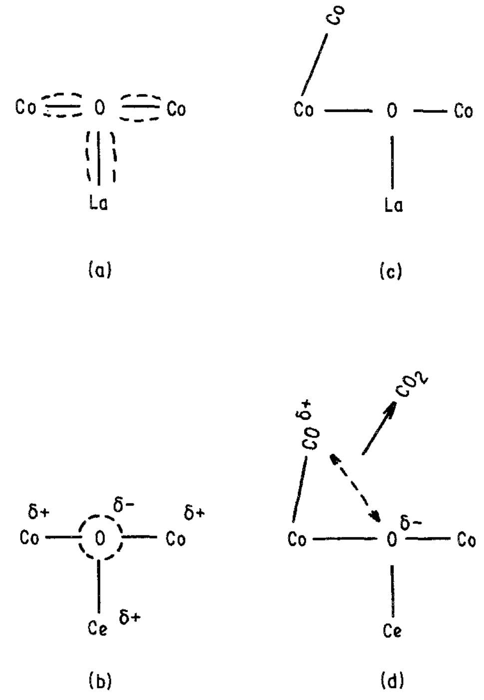

Figure 10 Reaction scheme.

Since the electron from CO, adsorbed on the surface of $La_{0.98}Ce_{0.02}CoO_3$ (d), seemed to pour easily to the surface cobalt, as was the case of the adsorbed oxygen (O^b) in Fig. 9. Thus, the adsorbed CO on the surface of $La_{0.98}Ce_{0.02}CoO_3$ seemed to be more positive than that adsorbed on $LaCoO_3$ (c). This $CO^{\delta+}$ seemed to react easily with the ionic lattice oxygen ($O^{\delta-}$), and produce CO_2. The oxidative reactivity of partly cerium substituted lanthanum cobalt oxides can be well explained by the surface states of compound.

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