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TPD AND XPS STUDY ON THERMAL BEHAVIOR OF ABSORBED OXYGEN IN $La_{1-x}Sr_xCoO_3$

Noboru YAMAZOE, Yasutake TERAOKA, and Tetsuro SEIYAMA*
Department of Materials Science and Technology, Graduate School of
Engineering Sciences, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812

Two types of oxygen desorption from $La_{1-x}Sr_xCoO_3$ were revealed by the appearance of a broad desorption peak(α) below ca. 800°C and a sharp one(β) around 820°C. The binding energy of O 1s level for absorbed oxygen was clearly different from that for lattice oxygen. Close examination shows that α is ascribable to the desorption of the absorbed oxygen while β may be the desorption of a part of lattice oxygen.

Perovskite-type oxides are very interesting material in which the replacement of metal ions at A or B site by other metal ions often results in drastic changes in properties. The partly Sr-substituted lanthanum cobalt oxide, $La_{1-x}Sr_xCoO_3$, is known to exhibit high activity as oxygen electrodes1) or catalysts for complete oxidation.2) In this case, the partial substitution of Sr^{2+} for La^{3+} brings about the oxidation of Co^{3+} to Co^{4+} and/or the formation of O^{2-} vacancies.3) It has been reported that, on cooling in oxygen or heating in vacuo, the oxide absorbs or liberates a large amount of oxygen which increases with increasing x.4) However, little has been known of the nature of the absorbed oxygen in this oxide system. In this paper, we tried to collect information on the thermal behavior and nature of absorbed oxygen by using temperature programmed desorption(TPD) and X-ray photoelectron spectroscopy(XPS) techniques.

Four samples, $LaCoO_3$(x = 0), $La_{0.8}Sr_{0.2}CoO_3$(x = 0.2), $La_{0.6}Sr_{0.4}CoO_3$(x = 0.4) and $SrCoO_{2.5}$(x = 1), were prepared by calcining the mixtures of $Co(NO_3)_2 \cdot 6H_2O$, La_2O_3 and $SrCO_3$ at 850°C for 10-15 h. The products were identified by X-ray diffraction analysis. The first three samples(x = 0, 0.2, 0.4) have perovskite-type structure. The last(x = 1) has brownmillerite-like structure, which can be derived from the perovskite-type structure by taking off oxygen atoms(oxygen-deficient perovskite).5) TPD experiments were carried out as follows. Each sample was exposed to 100 torr of oxygen for 1 h at 800°C and cooled to room temperature in the same atmosphere. After evacuation, the sample was heated in a helium stream at the rate of $10°C \cdot min^{-1}$ and the desorbed oxygen was monitored by TCD. X-Ray photoelectron spectra were recorded on VG ESCA 3 MkII spectrometer with AlKα radiation. Binding energy(BE) was calibrated in reference to the Au $4f_{7/2}$ level(83.8 eV) of evaporated gold.

As seen from the TPD chromatograms in Fig. 1, large amounts of oxygen were desorbed between room temperature and 850°C. While Yoneda et al.4) reported only oxygen desorption below 600°C, desorption clearly extended to still higher temperature. In addition to the broad desorption peak(denoted α) appearing below ca. 800°C, each sample exhibited a sharp peak(β) around ca. 820°C. The shape of α peak was strongly dependent on x: The peak is very low for $x = 0$, or plateau-like for $x = 0.2$ or 0.4, while a very strong, broad peak centered at ca. 500°C was obtained for $x = 1$. In contrast, β peaks were all similar in shape but became larger as x increased. The amounts of oxygen desorbed in the temperature ranges of α and β peaks are presented in Table 1. The amounts of both α and β oxygen far exceeded a surface monolayer except for a case on $x = 0$ (assuming 4.0 $\mu mol\text{-}O_2 \cdot m^{-2}$ for one surface layer). This indicates that both α and β oxygen are not adsorbed on the surface but absorbed in the bulk. As stated later, at least α oxygen atoms are considered to be accommodated at the sites of lattice oxygen vacancies of the perovskite oxides. (If all Co atoms are assumed to be trivalent, y in $La_{1-x}Sr_xCoO_{3-y}$ can be as large as $1/2x$.) In Fig. 2 moles of desorbed oxygen per mole of perovskite are plotted against x. Apparently the amounts of α and β sharply increase with increasing x, though α is more dependent on x. The amounts, α + β, are equivalent to ca. 0.3($x = 0.2$ and 0.4) and 0.2 ($x = 1$) oxygen atoms per Sr atom, respectively. The correlation between the amount of absorbed oxygen and the content of Sr^{2+} suggests that the oxygen absorption is associated with some sort of lattice defect originating from the partial substitution of Sr^{2+}.

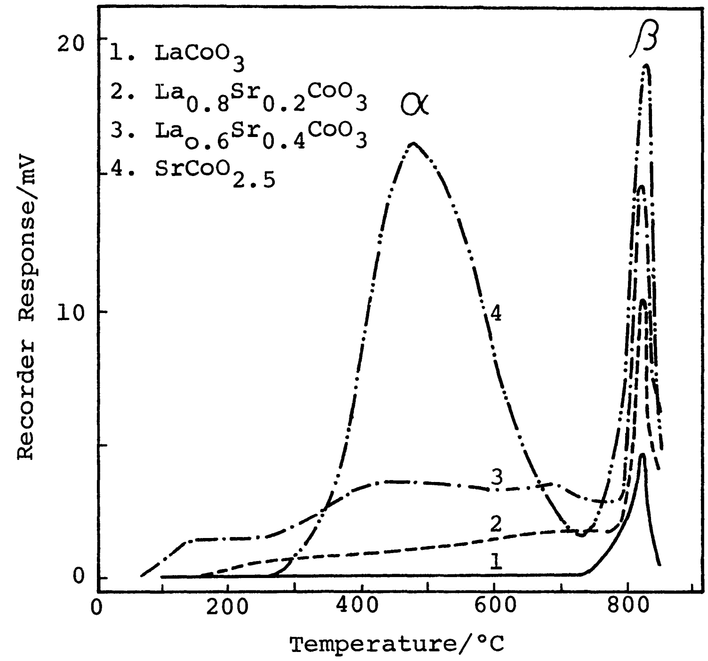

Fig. 1 TPD chromatograms of oxygen from $La_{1-x}Sr_xCoO_3$ (Oxygen preadsorption 800°C → R.T., 100 torr; heating rate = $10°C \cdot min^{-1}$).

The surface states were inspected by means of XPS. Special care was taken to eliminate surface contamination due to carbonate or hydrocarbons. After the oxygen absorption pretreatments under the same conditions in TPD, XPS measurements were carried out at room temperature. Particularly interesting informa-

Table 1 The amounts of oxygen desorbed from $La_{1-x}Sr_xCoO_3$

Catalyst	Surface area $m^2 \cdot g^{-1}$	Amount of oxygen desorbed$^{a)}$ $\mu mol\text{-}O_2 \cdot g^{-1}$ $\alpha(\theta_\alpha)$	 $\beta(\theta_\beta)$
$LaCoO_3$	2.2	2.7(0.3)	29.4(3.4)
$La_{0.8}Sr_{0.2}CoO_3$	5.2	81.6(3.9)	72.0(3.5)
$La_{0.6}Sr_{0.4}CoO_3$	5.7	207.3(9.1)	85.5(3.8)
$SrCoO_{2.5}$	13.4	348.0(6.5)	172.0(3.2)

a) θ_α and θ_β denote surface coverages(in unit of surface monolayer).

tion was obtained in the O 1s spectral region. The O 1s spectrum for each sample was a doublet as shown in Fig. 3. The signal(O_L) with lower BE is assigned to lattice oxygen judging from its binding energy, 528.2 eV. The signal(O_A) with higher BE(530.2 ~ 531.4 eV) was weak for x = 0 and increased in intensity as x increased. This behavior agrees well with that of the amounts of absorbed oxygen described previously and allows us to attribute the signal to the absorbed oxygen. Thus the absorbed oxygen can be distinguished from lattice oxygen, in disagreement with the assumption of Yoneda et al..$^{4)}$

The thermal behavior of the O 1s signal was pursued by evacuating samples at 300 and 500°C in situ or at 800°C outside the ESCA chamber. In the last case the evacuated sample was transfered to the ESCA chamber using a helium atmosphere to prevent from contacting to air. As an example, the O 1s spectra of $La_{0.6}Sr_{0.4}CoO_3$ after evacuation are illustrated in Fig. 4. The O_A signal diminished in intensity with the evacuation temperature up to 500°C, accompanied by gradual upward shifts of BE from 530.8 eV (evacuated at room temperature) to 531.5 eV(at 300°C) and 531.8 eV(at 500°C). After evacuation at 800°C, however, the O 1s signal was broadened considerably. First we consider the cases of evacuation below 500°C. Obviously the O_A signal is usually much broader than the O_L. We consider that this broadness reflects the heterogeneity of absorbed oxygen: The absorbed oxygen is not in a uniform state but in broadly dispersed states. The upward BE shift of the O_A signal with evacuation temperature is considered to result because the absorbed oxygen with lower BE is liberated more easily than that with

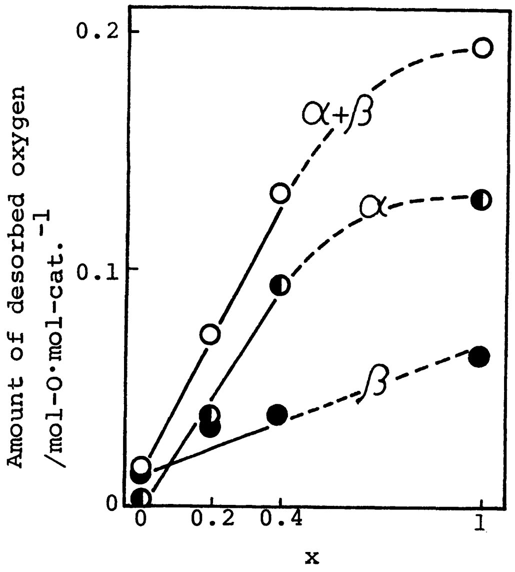

Fig. 2 Dependence of the amount of desorbed oxygen on x.

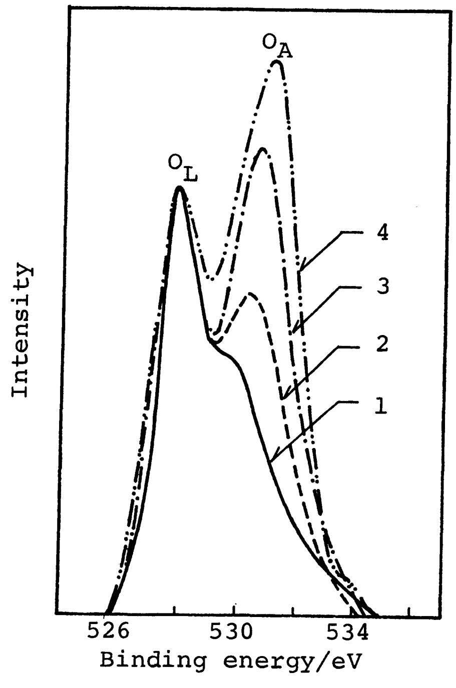

Fig.3 XPS for O 1s level of $La_{1-x}Sr_xCoO_3$.
(1) $LaCoO_3$ (2) $La_{0.8}Sr_{0.2}CoO_3$
(3) $La_{0.6}Sr_{0.4}CoO_3$ (4) $SrCoO_{2.5}$

higher BE. It may be interesting how the O_A signal is related with α and β oxygen observed in TPD. As is obvious from Fig. 1, of the two oxygen species, α and β, only α can be subjective to desorption at lower temperature, being diminished almost to one half at 500°C. Since this behavior is consistent with that of the O_A signal in Fig. 4, it is reasonable to ascribe the O_A signal to α oxygen. In contrast, the evacuation at 800°C, which should eliminate β oxygen, resulted in the broadening of O 1s signal(Fig. 4). Taking also into account the sharpness of the β peaks(Fig. 1), β oxygen may correspond to a part of lattice oxygen and its elimination may lead to the signal broadening via the formation of some new type of lattice defect.

As for the XPS signals of metal cations, no significant changes in intensity or BE were observed for Co $2p_{3/2}$ and La $3d_{5/2}$ levels with oxygen absorption or desorption. It was found, however, that BE of Sr $3p_{3/2}$ level shifted from 267.4 eV at room temperature to 267.9 eV after evacuation at 500°C. Thus the desorption of α oxygen influenced only the BE of Sr ions. This may mean that α oxygen has been taken into oxygen vacancies near Sr ions, and that its desorption weakens the negative crystal field around Sr ions to increase their BE. However, further investigation is necessary to confirm such an explanation.

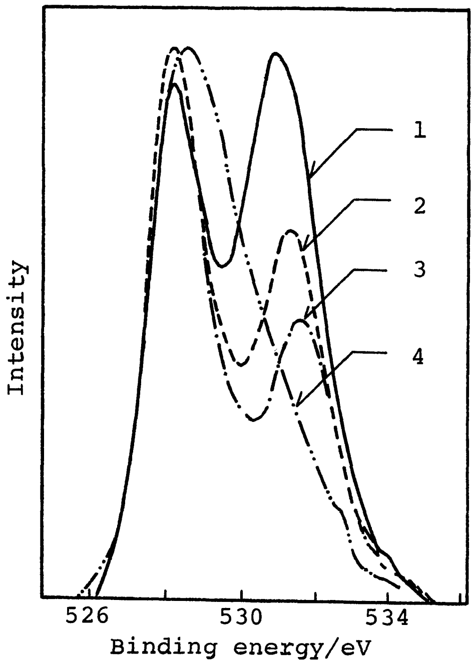

Fig. 4 XPS for O 1s level of $La_{0.6}Sr_{0.4}CoO_3$ evacuated at 1) R.T. 2) 300°C 3) 500°C 4) 800°C.

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