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OXYGEN-SORPTIVE PROPERTIES OF DEFECT PEROVSKITE-TYPE $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$

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The substitution of Fe for Co of $La_{1-x}Sr_xCoO_{3-\delta}$ makes it possible to preserve perovskite-type structure at higher Sr contents. While the amount of oxygen reversibly absorbed or desorbed was mostly determined by the Sr content, the Fe substitution was found to enhance the oxygen desorption particularly in a lower temperature region as well as catalytic activities.

Perovskite-type oxide (ABO_3) possesses the posibility of modifying its properties by the partial or total substitution of A or B site cations by other metal ions. The effects of A site substitution on catalytic properties have been extensively studied by many workers. Temperature programmed desorption (TPD) of oxygen from $La_{1-x}Sr_xCoO_{3-\delta}$ was first reported by Misono et al.[1)] So far we have also applied TPD technique to clarify the effect of A site substitution on the oxygen-sorptive properties of $La_{1-x}A'_xMO_{3-\delta}$ (M=Cr, Mn, Fe, Co, Ni).[2,3)] On the other hand, there have been few reports which have dealt with the effect of B site substitution. We have found that the B site substitution is sometimes very effective to promote the oxygen desorption and catalytic activity. This letter describes the effects of Fe substitution at B site of $La_{1-x}Sr_xCoO_{3-\delta}$ on the oxygen-sorptive and catalytic properties.

$La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ series oxides were prepared by calcining the mixture of lanthanum, strontium, and cobalt acetates and iron nitrate at 1123 K in air for 10 h. The products were identified by means of X-ray diffraction. The procedures of TPD experiments were described in the previous report.[2)]

The XRD analyses showed that all oxides listed in Table 1 had perovskite-type structure. It was reported that the upper limit of Sr content for perovskite formation was about 0.6 in $La_{1-x}Sr_xCoO_{3-\delta}$ system.[4)] In the present Fe-containing system, however, perovskite structure could be maintained up to x=1.0, in accordance with the previous report.[5)] Thus Fe substitution makes it possible to preserve perovskite structure up to the highest Sr content.

Before going to the results on B site substituted samples, we describe the oxygen-sorptive properties of oxides with a single B site cation of Co or Fe. The results on $La_{1-x}Sr_xCoO_{3-\delta}$ were already published.[2)] The TPD chromatograms of oxygen from $La_{1-x}Sr_xFeO_{3-\delta}$ (x=0, 0.2, 0.4, 0.8, 1.0) are presented in Fig. 1. $LaFeO_3$ desorbed little oxygen in the temperature range examined (300-1123 K). The amount of desorbed oxygen increased with increasing x and oxides with higher Sr content, x=0.8 and 1.0, showed the desorption maxima in the lower temperature region. The onset temperature of oxygen desorption lowered with increasing x up to x=0.8 and rose for x=1.0. We reported previously[2,3] that two types of oxygen desorption from perovskite-type oxides, α and β, were discerned from TPD chromatograms: α oxygen is accomodated in the oxygen vacancies formed by the partial substitution of A site cations, while β is associated with the reduction of B cations to lower valence state. In the case of $La_{1-x}Sr_xFeO_{3-\delta}$, the oxygen desorbed below 1123 K is considered to be α because β desorption is expected to take place far above the temperature range examined.[3] The substitution of Sr^{2+} for La^{3+} of $LaFeO_3$ is expected to bring about the formation of oxygen vacancies, in good agreement with the observed enhancement of α desorption by Sr substitution which is intimately associated with oxygen vacancies.

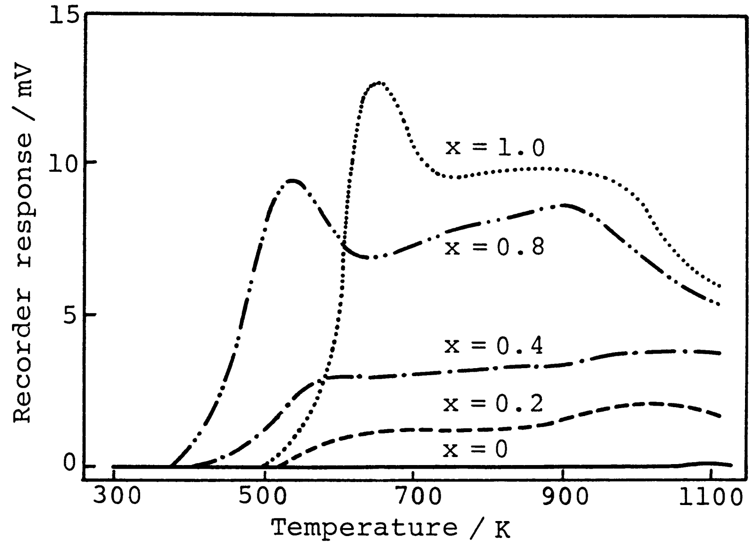

Fig. 1. TPD chromatograms of oxygen from $La_{1-x}Sr_xFeO_{3-\delta}$. Oxygen preadsorption; 1073 K → RT, 100 Torr. Heating rate; 10 K·min^{-1}.

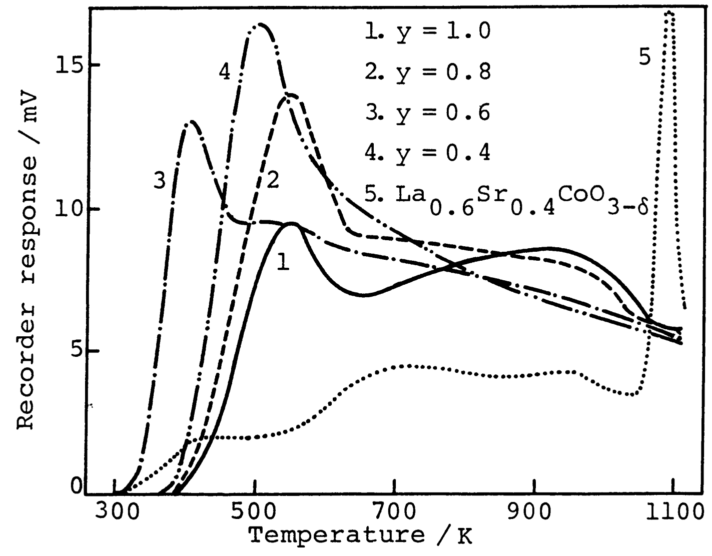

Fig. 2. TPD chromatograms of oxygen from $La_{0.2}Sr_{0.8}Co_{1-y}Fe_yO_{3-\delta}$. Oxygen preadsorption; 1073 K → RT, 100 Torr. Heating rate; 10 K·min^{-1}.

Figure 2 shows how TPD chromatograms of oxygen vary with the composition of B site cations by taking $La_{0.2}Sr_{0.8}Co_{1-y}Fe_yO_{3-\delta}$ system as an example. In this system single phase perovskite-type oxides were synthesized in the composition range y≥0.4. For comparison, the result of $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ is also illustrated in the figure. It is seen that the Fe-substitution enhances the oxygen desorption especially in a lower temperature region, granting that the amount of Sr substituted is different. Although $La_{0.2}Sr_{0.8}FeO_{3-\delta}$ desorbed a large amount of oxygen, mixing of Fe with Co at B site enhanced oxygen desorption in a lower temperature region and lowered the temperature for the onset of oxygen desorption and the temperature for the desorption maximum; for y=0.6 the lowest temperatures were obtained, 310 K and 420 K, respectively. This fact suggests that the bonding of sorbed oxygen in the lattice is influenced by the composition of Co and Fe and becomes weakest at y=0.6. As for β desorption, $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ exhibited a sharp β desorption peak around 1100 K, which was shown to correspond to the reduction of Co^{3+} to Co^{2+} 3), but the substituted samples (y≥0.4) showed no sharp peaks corresponding to β desorption. This indicates that trivalent Co ions are stabilized by the partial replacement of Co by Fe.

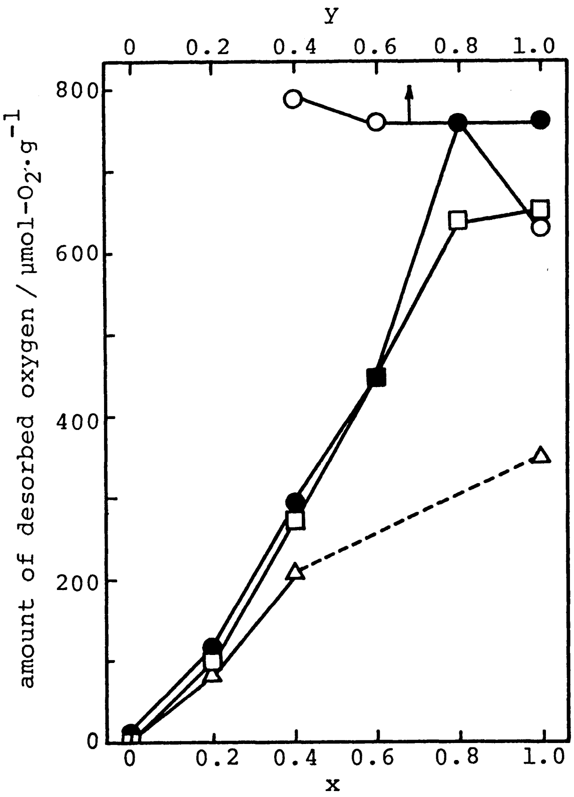

Fig. 3. Dependence of the amount of oxygen desorbed on A site (x) and B site (y) compositions.
△; $La_{1-x}Sr_xCoO_{3-\delta}$
□; $La_{1-x}Sr_xFeO_{3-\delta}$
●; $La_{1-x}Sr_xCo_{0.4}Fe_{0.6}O_{3-\delta}$
○; $La_{0.2}Sr_{0.8}Co_{1-y}Fe_yO_{3-\delta}$

As mentioned above, B site composition mainly affects the properties of sorbed oxygen. On the other hand, A site composition was found to influence the amount of sorbed oxygen. In Fig. 3 the amounts of oxygen desorbed under α desorption peaks are plotted against A site (x) and B site (y) compositions. Apparently the amount of oxygen desorbed sharply increases with increasing x, while it remains almost unchanged by changing y. This indicates that the amount of oxygen desorbed is mostly determined by the composition of A site cations, i.e., the concentration of oxygen vacancies. The desorption amount for $La_{1-x}Sr_xCo_{0.4}Fe_{0.6}O_{3-\delta}$ is far larger than that for $La_{1-x}Sr_xCoO_{3-\delta}$, while it is almost equal to that for $La_{1-x}Sr_xFeO_{3-\delta}$. This means that Fe is superior to Co in an ability to take oxygen into the sites of oxygen vacancies.

The amount of oxygen desorbed below 1123 K are presented in Table 1. The amount of oxygen desorbed far exceeded a surface monolayer except for the cases of $LaFeO_3$ and $LaCo_{0.4}Fe_{0.6}O_3$ (assuming 4.0 $\mu mol\text{-}O_2m^{-2}$ for one surface layer), indicating that the desorbed oxygen is liberated not only from the surface but also from the bulk. The amounts of desorbed oxygen atoms per Sr atoms (O/Sr) are presented in the last column of Table 1. If it is assumed that the oxygen desorbed from present Fe-containing oxides have been accomodated in the oxygen vacancies formed by the substitution of Sr^{2+} for La^{3+}, O/Sr can take values between 0 to 0.5. As seen from Table 1, it is ca. 0.4 for $La_{0.2}Sr_{0.8}Co_{1-y}Fe_yO_{3-\delta}$ (y=0.4, 0.6, 0.8) and ca. 0.3 for the others. These results allow us again to confirm that the desorbed oxygen are accomodated in the oxygen vacancies.

Finally we briefly describe the relation to catalysis. Perovskite-type oxides which contain Co and Fe at B site were found to be more active than those

Table 1. The amount of oxygen desorbed from $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$

Catalyst	Surface area	Amount of oxygen desorbed		$O/Sr^{b)}$
	$m^2 \cdot g^{-1}$	$\mu mol\text{-}O_2 \cdot g^{-1}$	$\theta^{a)}$	
$LaFeO_3$	4.4	1.8	0.1	——
$La_{0.8}Sr_{0.2}FeO_{3-\delta}$	4.7	99.6	5.3	0.23
$La_{0.6}Sr_{0.4}FeO_{3-\delta}$	4.6	268.7	14.6	0.30
$La_{0.2}Sr_{0.8}FeO_{3-\delta}$	3.2	639.4	50.0	0.32
$SrFeO_{3-\delta}$	4.6	651.3	35.4	0.25
$LaCo_{0.4}Fe_{0.6}O_3$	3.3	12.1	0.9	——
$La_{0.8}Sr_{0.2}Co_{0.4}Fe_{0.6}O_{3-\delta}$	6.1	116.5	4.8	0.27
$La_{0.6}Sr_{0.4}Co_{0.4}Fe_{0.6}O_{3-\delta}$	7.5	282.9	9.4	0.32
$La_{0.4}Sr_{0.6}Co_{0.4}Fe_{0.6}O_{3-\delta}$	4.7	444.7	23.7	0.32
$La_{0.2}Sr_{0.8}Co_{0.6}Fe_{0.4}O_{3-\delta}$	3.8	785.0	51.6	0.40
$La_{0.2}Sr_{0.8}Co_{0.4}Fe_{0.6}O_{3-\delta}$	4.2	756.3	45.0	0.38
$La_{0.2}Sr_{0.8}Co_{0.2}Fe_{0.8}O_{3-\delta}$	3.2	755.9	59.1	0.38
$SrCo_{0.4}Fe_{0.6}O_{3-\delta}$	3.3	759.0	57.5	0.29

a) Surface coverage (in unit of surface monolayer).

b) Amount of desorbed oxygen atoms per Sr atom.

with a single kind of B site cations in electrochemical reduction of oxygen.[6)] It is well known that perovskite-type oxide which has Co at B site is one of the most active catalysts, while one which has Fe is less active. Accordingly the results obtained here suggest a possibility of finding more excellent catalysts by selecting proper combinations of cations not only for A site but also for B site.

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