CHEMISTRY LETTERS, pp. 893 - 896, 1984.

OXYGEN-SORPTIVE PROPERTIES AND DEFECT STRUCTURE OF PEROVSKITE-TYPE OXIDES

Yasutake TERAOKA, Masahiro YOSHIMATSU, Noboru YAMAZOE,* and Tetsuro SEIYAMA
Department of Materials Science and Technology, Graduate School of
Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816

The nature of two types of oxygen desorption, α and β, from perovskite-type oxides was studied by TPD and TG experiments. The results show that α oxygen is accomodated in the oxygen vacancies formed by the partial substitution of A site cations, while the desorption of β oxygen corresponds to the reduction of B site cations to lower valencies.

Some perovskite-type oxides, in particular $LaCoO_3$ and $LaMnO_3$ families, are attracting great attention as catalysts for the complete oxidation of hydrocarbons as well as for electrode processes. The properties of these oxides can be easily modified by the substitution of A site cations, as in the case of $La_{1-x}Sr_xCoO_{3-\delta}$. In this oxide system, the partial or total substitution of La^{3+} for Sr^{2+} leads to the formation of Co^{4+} (or positive hole) and/or oxygen vacancies. Their high catalytic activities are considered to be related to such defect structure. It was reported that $La_{1-x}Sr_xCoO_{3-\delta}$ sorbed a large amount of oxygen[1)] and that two types of oxygen desorption, α and β, were discerned from TPD chromatograms.[2)] In this paper, we tried to elucidate the nature of α and β oxygen particularly in relation to the defect structure of perovskite-type oxides by using temperature programmed desorption (TPD) technique and thermogravimetry (TG).

The following four series of samples were used, $LaMO_3$ (M = Cr, Mn, Fe, Co, Ni), $La_{1-x}Sr_xCoO_{3-\delta}$ (x = 0, 0.2, 0.4, 1), $La_{0.8}Sr_{0.2}MO_{3\pm\delta}$ (M = Mn, Fe, Co), and $La_{0.8}A_{0.2}CoO_{3-\delta}$ (A = Na, Ca, Sr, Ba). All samples except $LaNiO_3$ were prepared by calcining the mixture of metal acetates at 1123 K in air for 10 h. $LaNiO_3$ was prepared by calcining the mixture of metal acetates at 1173 K in air for 10 h using Na_2CO_3 as flux. The products were identified by means of X-ray diffraction. All samples but $SrCoO_{2.5+\delta}$ had perovskite-type structure. $SrCoO_{2.5+\delta}$ had a tetragonal unit cell as reported before.[3)] The procedures of TPD experiments were described elsewhere.[2)] The oxygen stoichiometries of oxide samples were determined from the weight losses observed when heated in N_2 or $N_2 + H_2$ (5% or 10%) stream in an electrobalance (Cahn, Type RG).

In coincidence with our previous results on $La_{1-x}Sr_xCoO_{3-\delta}$,[2)] the TPD chromatograms of oxygen from partly alkali or alkaline earth metal substituted samples, $La_{0.8}A_{0.2}CoO_{3-\delta}$ (A = Na, Ca, Sr, Ba, La), were characterized by the appearance of two desorption peaks, α and β (Fig. 1). In every case the A site substitution increased both α and β desorption of oxygen. The β desorption was seen for the substituted as well as unsubstituted samples and similar in shape for all samples.

This suggests that β desorption is more specific to B cation than α. This suggestion was examined by using various B cations. Figure 2 shows TPD chromatograms of oxygen from $LaMO_3$, where M are the 3d transition metals from Cr to Ni. $LaCoO_3$ and $LaMnO_{3+\delta}$ exhibited large desorption peaks (β peaks) in a high temperature range, while $LaNiO_3$ showed, in addition to desorption above 850 K (β), a plateau-like one in the temperature range of 500 K - 850 K. In contrast to these samples, $LaCrO_3$ and $LaFeO_3$ showed no oxygen desorption in the temperature range examined. It was found that the onset temperature of β peaks for the Mn-, Co-, Ni-containing samples coincided fairly well with the thermal decomposition (reduction) temperature of the respective component oxides of B cations (Table 1). It is noted that the onset temperature for $LaMnO_{3+\delta}$ is close to the temperature for reduction of tetravalent Mn to trivalent. The oxides of Cr and Fe are reduced thermally far above the temperature range examined, in agreement with the observation that no desorption peaks appeared for the corresponding perovskite samples. These results indicate that the desorption of β oxygen is ascribable to the reduction of B cations to lower valencies.

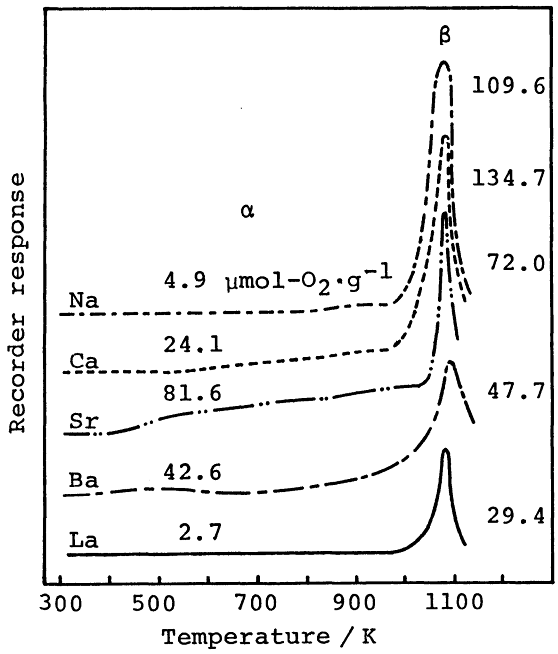

Fig. 1. TPD chromatograms of oxygen from $La_{0.8}A_{0.2}CoO_{3-\delta}$ (A = Na, Ca, Sr, Ba, La). (Oxygen preadsorption; 1073 K→RT, 13kPa)

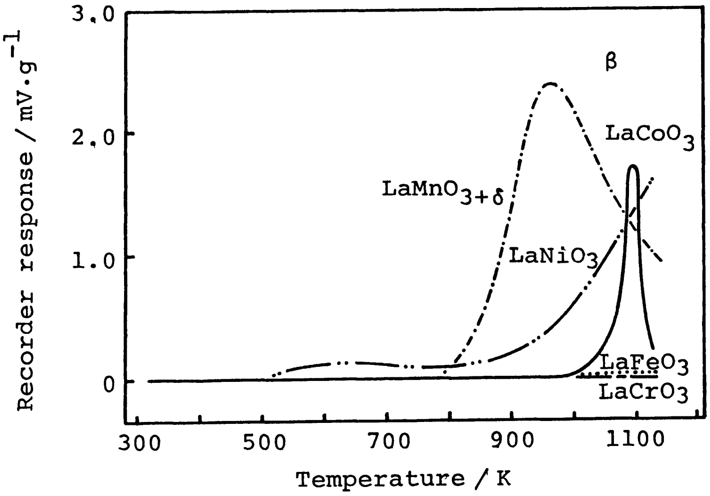

Fig. 2. TPD chromatograms of oxygen from $LaMO_3$ (M = Cr, Mn, Fe, Co, Ni). (Oxygen preadsorption; 1073 K→RT, 13kPa)

In order to elucidate the nature of α oxygen, Sr^{2+} substituted $LaCoO_3$, $LaFeO_3$, and $LaMnO_{3+\delta}$ were subjected to TPD experiments (Fig. 3). As stated before, Sr substitution for La of $LaCoO_3$ increased α desorption. A similar trend was observed also for $LaFeO_3$. In the case of $LaMnO_{3+\delta}$, Sr substitution for 20% La simply reduced β desorption, while that for 40% La brought about the slight appearance of

Table 1. Comparison of β desorption from $LaMO_3$ with thermal reduction of component oxides (MO_n)

Catalyst	Onset of β desorption K	Reduction	Thermal reduction temperature (in air)[4)] K
$LaCrO_3$	—	$Cr^{3+} \rightarrow Cr^{2+}$	2173
$LaMnO_{3+\delta}$	770	$Mn^{4+} \rightarrow Mn^{3+}$	808
		$Mn^{3+} \rightarrow Mn^{2+}$	1353
$LaFeO_3$	—	$Fe^{3+} \rightarrow Fe^{2+}$	1833
$LaCoO_3$	1050	$Co^{3+} \rightarrow Co^{2+}$	1173
$LaNiO_3$	850	$Ni^{3+} \rightarrow Ni^{2+}$	873

α desorption accompanied by a further decrease of β desorption. In $LaCoO_3$ and $LaFeO_3$, Sr substitution is expected to lead to the formation of oxygen vacancies. The observed promotion of α desorption by A site substitution suggests that α oxygen is associated with oxygen vacancies. On the other hand, $LaMnO_{3+\delta}$ is known to show an oxidative nonstoichiometry;[5)] a part of Mn ions are of tetravalent state, the charges being compensated by cation vacancies at both A and B sites. As stated before, β desorption from the unsubstituted sample corresponds to the reduction of tetravalent Mn ions. The substitution of small amounts of Sr simply decreases these cation vacancies and the Mn^{4+} concentration without leading to the formation of oxygen vacancies. This is why the 20% substitution was not effective to promote α desorption but decreased β desorption. When the concentration of substituted Sr becomes high enough (40% in this case), Sr substitution effectively brings about the formation of oxygen vacancies and the appearance of α desorption.

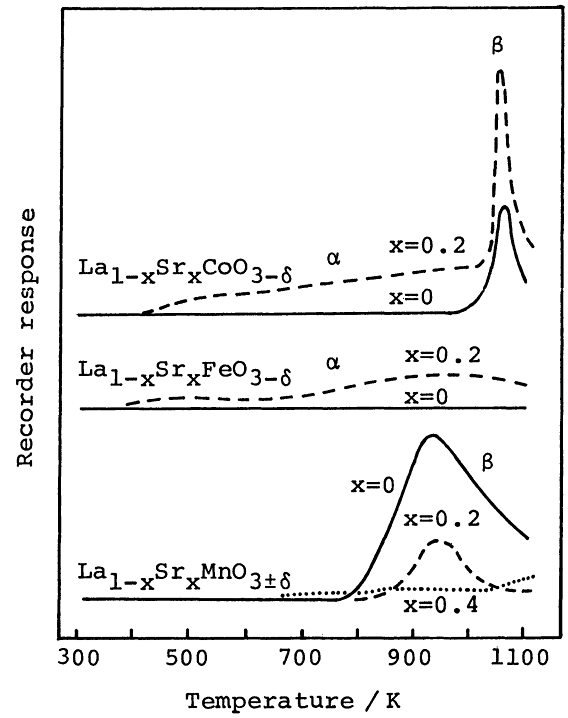

Fig. 3. TPD chromatograms of oxygen from $La_{1-x}Sr_xMO_{3\pm\delta}$ (x = 0, 0.2; M = Mn, Fe, Co). (Oxygen preadsorption; 1073 K → RT, 13 kPa)

The nature of α and β oxygen described above was supported by the determination of exact oxygen composition of $La_{1-x}Sr_xCoO_{3-\delta}$ (x = 0, 0.2, 0.4, 1) before and after the respective desorption peaks. The observed oxygen compositions and the corresponding oxidation states of Co ions estimated from the oxygen compositions are listed in Table 2. After α desorption, Co ions take essentially normal oxidation states, namely trivalent in every case. This means that, at this stage, the

Table 2. Oxygen compositions and oxidation states of Co ions of $La_{1-x}Sr_xCoO_{3-\delta}$

x	after O_2 sorption (1073 K → RT)			after α desorption			after β desorption		
	Co^{4+} a)	Co^{3+}	Co^{2+}	Co^{4+} a)	Co^{3+}	Co^{2+}	Co^{4+} a)	Co^{3+}	Co^{2+}
0	$LaCoO_{3.000}$			$LaCoO_{3.000}$			$LaCoO_{2.987}$		
	0%	100%	0%	0%	100%	0%	0%	97.4%	2.6%
0.2	$La_{0.8}Sr_{0.2}CoO_{2.930}$			$La_{0.8}Sr_{0.2}CoO_{2.906}$			$La_{0.8}Sr_{0.2}CoO_{2.882}$		
	6%	94%	0%	1.2%	98.8%	0%	0%	96.4%	3.6%
0.4	$La_{0.6}Sr_{0.4}CoO_{2.895}$			$La_{0.6}Sr_{0.4}CoO_{2.796}$			$La_{0.6}Sr_{0.4}CoO_{2.750}$		
	19%	81%	0%	0%	99.2%	0.8%	0%	90%	10%
1	$SrCoO_{2.618}$			$SrCoO_{2.506}$			$SrCoO_{2.473}$		
	23.6%	76.4%	0%	1.2%	98.8%	0%	0%	94.6%	5.4%

a) Co^{4+} may be replaced by "positive hole".

electric charges resulting from Sr substitution are compensated solely by the formation of oxygen vacancies. Thus we understand that α oxygen is accomodated in these oxygen vacancies, resulting in the formation of Co^{4+} ions or positive holes. On the other hand, β desorption is accompanied by the partial reduction of trivalent Co ions to divalent. The amounts of α and β oxygen estimated from the above oxygen compositions coincided well with the results obtained from the TPD experiments.

In conclusion, α oxygen is accomodated in the oxygen vacancies formed by the partial substitution of A site cations, while β desorption is ascribable to the reduction of B cations to lower valencies. The uptake of α and β oxygen may be described by (1) and (2), respectively.

$$La_{1-x}Sr_xCo^{3+}O_{3-\frac{x}{2}}Vo_{\frac{x}{2}} + \frac{y}{2}O_2 \xrightleftharpoons{\alpha} La_{1-x}Sr_xCo^{3+}_{1-2y}Co^{4+}_{2y}O_{3-\frac{x}{2}+y}Vo_{\frac{x}{2}-y} \quad (1)$$

$$(\text{or} \quad V_o^{\cdot\cdot} + \frac{1}{2}O_2 \xrightleftharpoons{\alpha} O_o^{\times} + 2\,h^{\cdot})$$

$$La_{1-x}Sr_xCo^{2+}_{2z}Co^{3+}_{1-2z}O_{3-\frac{x}{2}-z}Vo_{\frac{x}{2}+z} + \frac{z}{2}O_2 \xrightleftharpoons{\beta} La_{1-x}Sr_xCO^{3+}O_{3-\frac{x}{2}}Vo_{\frac{x}{2}} \quad (2)$$

$$(\text{or} \quad 2\,Co'_{Co} + V_o^{\cdot\cdot} + \frac{1}{2}O_2 \xrightleftharpoons{\beta} 2\,Co^{\times}_{Co} + O_o^{\times})$$

References

1) T. Nakamura, M. Misono, and Y. Yoneda, Chem. Lett., 1981, 1589.
2) N. Yamazoe, Y. Teraoka, and T. Seiyama, Chem. Lett., 1981, 1767.
3) N. Yamazoe, S. Furukawa, Y. Teraoka, and T. Seiyama, Chem. Lett., 1982, 2019.
4) "Mukikagaku Handbook", Gihodo Shuppan, Tokyo (1981), Chap. 1.
5) B. C. Tofield and W. R. Scott, J. Solid State Chem., 10, 183 (1974).

(Received March 16, 1984)