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REDUCTION-OXIDATION AND CATALYTIC PROPERTIES OF PEROVSKITE-TYPE MIXED OXIDE CATALYSTS ($La_{1-x}Sr_xCoO_3$)

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The reducibility of $La_{1-x}Sr_xCoO_3$ (a perovskite-type mixed oxide) remarkably increased with the Sr^{2+} content, x, but the rate of re-oxidation of the reduced catalysts decreased with x. These trends well explain the catalytic activity for oxidation on the basis of redox mechanism.

When Sr^{2+} ion is substituted for La^{3+} (A-site) of $LaCoO_3$, the charge compensation is accomplished by both or either of the following two mechanisms; i) oxidation of Co^{3+} ion (B-site) to Co^{4+} ion, and ii) formation of oxygen vacancies.1) We reported previously that $La_{1-x}Sr_xCoO_3$ (x=0—0.4) calcined at about 850°C showed very high activity for the oxidation of C_3H_8, CH_4, and CO.2) The catalytic activity increased by the Sr^{2+} substitution upto the Sr^{2+} content of x=0.2, but it slightly decreased by further substitution.

In this communication, we wish to report reduction-oxidation properties of $La_{1-x}Sr_xCoO_3$ which explain above changes in the catalytic activity and characterize the oxygen species responsible for the catalytic oxidation over $La_{1-x}Sr_xCoO_3$.

The catalysts were prepared from mixtures of metal acetates. They were calcined at 850°C in air for 5 h.2) It was confirmed by the X-ray diffraction analysis that the samples had the perovskite-type structure. The oxidation of CO was carried out by use of a closed circulation system (ca. 250 cm^3). The standard pre-treatment was as follows; the catalyst (300 mg or 50 mg) was heated in O_2 (ca. 10 cmHg: 1 cmHg=1.33 kPa) for 1 h at 300°C, cooled to 150°C and then evacuated for 1 h at 150°C. CO_2 formed was collected by a trap kept at liquid nitrogen temperature. The reaction was followed by the pressure decrease. Temperature programmed desorption (TPD) of O_2 was carried out with a flow system by using He as a carrier gas. Temperature was raised at the rate of 20 deg. min^{-1} and O_2 desorbed was detected with the aid of a quadrupole mass spectrometer (NEVA, NAG-531).

Reduction of the catalysts by CO was measured at 150°C after the standard pre-treatment. Extent of reduction was about 5% (e.g., from $La_{1-x}Sr_xCoO_3$ to $La_{1-x}Sr_xCoO_{2.85}$).3) Then the catalysts were evacuated for 0.5 h at 150°C, and the rate of re-oxidation by O_2 was measured at the same temperature. The rates of the reduction (r_R) and the re-oxidation (r_O) are plotted against the degree of reduction in Fig. 1. It is noted in this figure that r_R gradually decreased with the extent of reduction, while r_O rapidly increased. When the extent of preceding reduction was lowered, r_O increased slightly at the same degree of reduction. But the change was not as much as to affect the following discussion. When r_R is compared at the same degree of reduction, it increased with the Sr^{2+} content, x: The Sr^{2+} substitution greatly enhanced the reducibility. Similar trends were observed previously in a CO pulse method.[4)] On the contrary, r_O markedly decreased with x. Re-oxidation was completed within 1 min for x=0.2. But as for x=0.6 the rate was so slow that complete re-oxidation required more than 100 min. Carbon balance of the reduction process ($CO \rightarrow CO_2$) was satisfactory and no CO_2 was formed in the re-oxidation process. Therefore, carbide or carbon deposit which was observed in the case of iron oxide in the reduction process by CO[5)] was negligible.

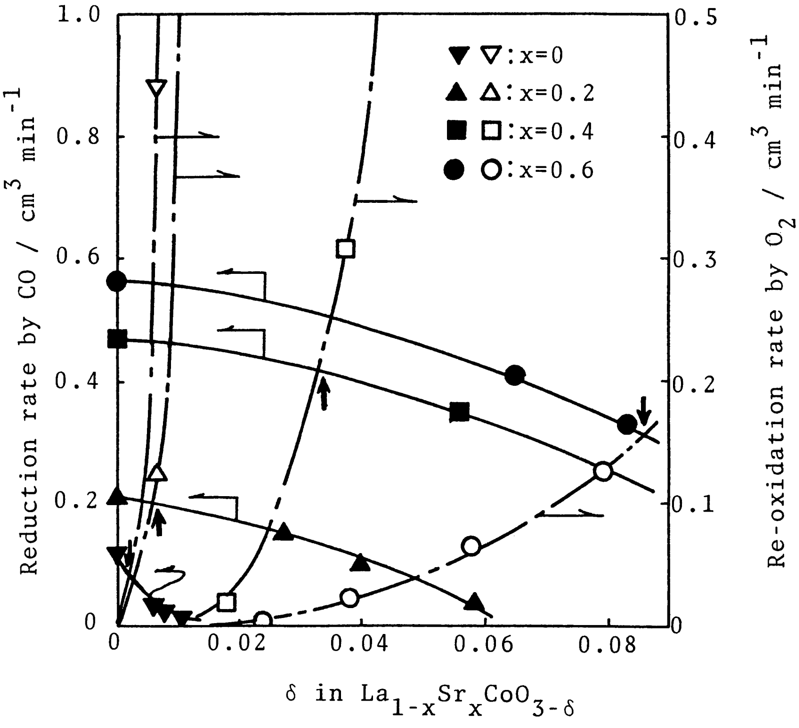

Fig. 1. Rates of reduction (r_R) and re-oxidation (r_O) of $La_{1-x}Sr_xCoO_{3-\delta}$ as a function of degree of reduction (δ).[3)]

Catalyst weight : 300 mg
Reaction temperature : 150°C

The X-ray diffraction peaks of the catalysts reduced by about 5% shifted by about 0.2—0.5°(2θ) to lower angles for x=0.2. For x=0 and 0.6 new small peaks appeared in addition to these shifts. However, the initial diffraction patterns were restored reversibly by the re-oxidation for all samples. Therefore, the reduction and the re-oxidation of the catalysts were reversible and probably the structure of the catalysts did not change significantly by the reduction. Even if a structural change might have taken place to some extent, this does not seem to be the reason of slow re-oxidation for x=0.6. Uptake of oxygen at 300°C after evacuation at the same temperature was also very slow for the samples having high Sr^{2+} contents. Oxygen desorbed by the evacuation was so small[4)] that significant structural change should not have occurred in this case.

In Fig. 1, the ordinateds are normalized considering the stoichiometry of $CO + 1/2O_2 \rightarrow CO_2$. The crosspoints of r_R and r_O curves, at which the two rates become identical, are indicated by arrows for each sample in Fig. 1. If the catalytic oxidation of CO to CO_2 proceeded by the repetition of the reduction of the catalyst by CO and the re-oxidation by O_2, namely a redox mechanism, it is expected, to the first approximation, that the rate at the crosspoint is equal to the rate of catalytic oxidation at the stationary state. The rate at the crosspoint initially increases with x and becomes nearly constant or slightly smaller at high x. This trend is in general agreement with the change found for the rate of catalytic oxidation of CO measured by the flow method.[2)] Therefore, we may conclude on the basis of the present findings that the catalytic oxidation proceeds essentially by a redox mechanism and the rate at the stationary state show a maximum at a certain value of x (possibly, 0.2—0.4). Figure 1 further indicates that the stationary catalytic oxidation proceeds in a more reduced state as x increases. This was also confirmed qualitatively in the case of CO oxidation in a closed circulation system.

However, the agreement was not satisfactory when examined more quantitatively. The catalytic oxidation of CO was measured in the circulation system with a gas mixture of CO (1.6 cmHg) and O_2 (4.1 cmHg). The catalysts (50 mg) was diluted by SiC (250 mg) to avoid the temperature rise caused by the heat of reaction. This rate was compared in Table 1 with the rate of reduction by CO (1.6 cmHg) under the same conditions. There was only a small difference between the two rates in the case of x=0.6, indicating that the catalytic oxidation proceeds essentially by the redox mechanism. The catalytic oxidation became significantly faster than the reduction for smaller x, although both decreased with decrease in x. Therefore, it appears necessary for smaller x to consider additional contribution from a mechanism in which adsorbed oxygen takes part.

Table 1. Rates of CO_2 formation with and without O_2 in the circulation system at 150°C

$La_{1-x}Sr_xCoO_3$	Rate/$cm^3\ g^{-1}\ min^{-1}$ without O_2	Rate/$cm^3\ g^{-1}\ min^{-1}$ with O_2	with O_2/without O_2
x=0	0.15	1.7∿ 1.8	11.3∿12.0
x=0.2	2.6	16.2∿19.8	6.2∿ 7.6
x=0.6	7.6	10.4∿17.0	1.4∿ 2.2

TPD experiments were carried out to examine the mechanism in which adsorbed oxygen takes part. Figure 2 shows TPD of oxygen, where the rate of desorption increased with x, as expected. Oxygen desorbed at a higher temperature is clearly lattice oxygen, since its amount is comparable or greater than monolayer oxygen. It is not certain whether the oxygen desorbed at a low temperature is adsorbed oxygen or weakly bonded lattice oxygen. But, as seen in Fig. 2, the transition from the adsorbed (or weakly bonded lattice) oxygen to the strongly bonded lattice oxygen is continuous and these two oxygen species are hardly distinguishable. Moreover, the shapes of the TPD curves are more or less similar among the catalysts. In other words, the oxygen desorbed at low temperatures reflects the reducibility of the bulk lattice oxygen even if the former were adsorbed oxygen. In this sense, redox mechanism may be applied to all of these catalysts, and the redox properties of the bulk is essential in determining the catalytic activity.

The oxygen species which is desorbed and re-supplied readily at 150—300°C is probably the active oxygen species, and is or closely resembles lattice oxygen. This oxygen species can be supplied from both gaseous and bulk oxygen. Probably in the case of x=0—0.2 the supply from gaseous oxygen is faster than from the bulk, so that $La_{1-x}Sr_xCoO_3$ is in a higher oxidation state and becomes more reactive in the presence of gaseous oxygen than in its absence.

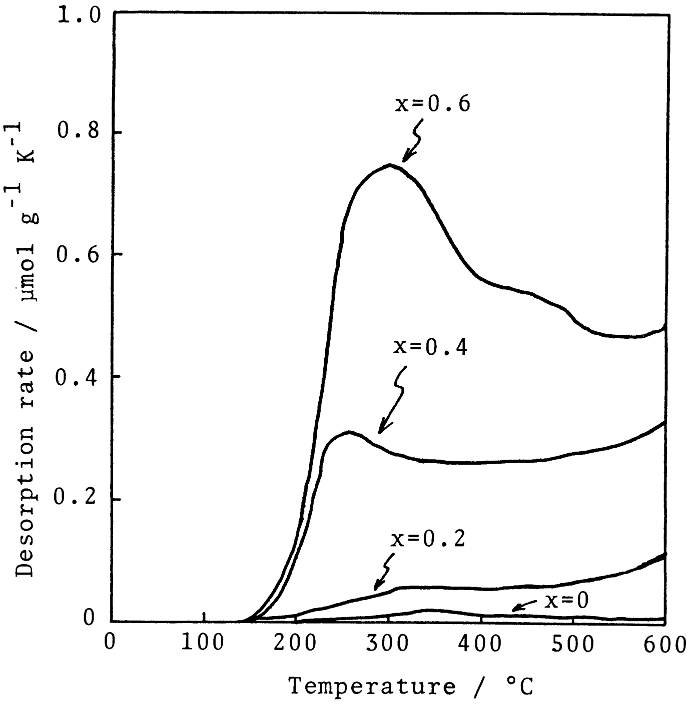

Fig. 2. TPD curves of oxygen from $La_{1-x}Sr_xCoO_3$ (x=0—0.6). rate of temperature rise = 20 deg. min^{-1}

References

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3) Non-stoichiometry, δ in $La_{1-x}Sr_xCoO_{3-\delta}$, of starting samples was tentatively assumed to be zero ($La_{1-x}Sr_xCoO_3$) in this communication, although chemical analyses indicated that δ is close to zero for x=0 and 0.2, but 0.098 for x=0.6.[4]

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