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Catalytic Properties of $La_{2-x}Sr_xCoO_4$, a K_2NiF_4-Type Mixed Oxide

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Catalytic activities of $La_{2-x}Sr_xCoO_4$, a K_2NiF_4-type mixed oxide, for propane oxidation increased with the extent of Sr substitution upto $x = 1$, and then decreased for $x \geqq 1$. This variation was in parallel with the reducibility or the oxidizing power of the catalyst surface. Stoichiometry determined by the iodometry showed that the excess oxygen which was present for $x = 0$ decreased with x upto $x = 1$, and the oxide became oxygen-deficient for $x \geqq 1.5$.

K_2NiF_4-type mixed oxides (A_2BO_4) are a kind of two-dimensional analogue of a perovskite-type mixed oxide (ABO_3).$^{1)}$ It is possible to change the A- or B-site ion or substitute part of it by ions with different valence as in the case of perovskite-type mixed oxides. However, in contrast to the perovskite,$^{2)}$ the catalytic action of K_2NiF_4-type oxides has been reported only for Ln_2CuO_4 and Ln_2NiO_4 (Ln = rare earth ion),$^{3)}$ and no studies on the effect of valence control were reported.

In this work, we investigated the effect of Sr substitution of La_2CoO_4 on its catalytic properties, and compared it with the effects for the $La_{1-x}Sr_xCoO_3$,$^{2,4)}$ and $La_{1-x}Sr_xMnO_3$.$^{5)}$

Seven catalysts ($La_{2-x}Sr_xCoO_4$; x = 0, 0.5, 0.8, 1.0, 1.2, 1.5, 2.0) were prepared from mixtures of component metal acetates. They were calcined at 1000 °C for 10 h in air (x = 0.8-2.0) or in N_2 (x = 0-0.5). The products were identified by powder X-ray diffraction patterns. The first six samples (x = 0-1.5) had the K_2NiF_4-type structure. The last sample (x = 2.0) showed an unknown phase.

Sr_2CoO_4 having K_2NiF_4-type structure could not be synthesized even by the calcination in O_2 at 1200 °C. Surface areas of the samples measured by BET method (N_2 adsorption) were 1.0 $m^2\ g^{-1}$ ($x = 0$), 1.3 (0.5), 1.7 (0.8), 2.6 (1.0), 1.9 (1.2), 2.1 (1.5), 1.5 (2.0). The average oxidation numbers of cobalt ion were determined by the iodometric titration according to the literature.[6)]

The oxidation of propane was carried out by use of a conventional flow system. Prior to the reaction, catalysts (300 mg) were treated in an O_2 stream for 1 h at 300 °C. A gas mixture of propane (0.83%), O_2 (33.3%) and N_2 (balance) was used and the total flow rate was 60 ml min^{-1}. Products were analyzed by a gas chromatograph. The reduction of catalyst by CO was conducted by a pulse reactor. After the same pretreatment as above, a He stream was substituted for an O_2 stream and the catalysts (50 mg) were subjected to pulse reactions in a He stream. The size of each pulse was 0.1 cm^3. Products were analyzed by a gas chromatograph.

The catalytic activities of $La_{2-x}Sr_xCoO_4$ for propane oxidation are shown in Fig. 1. The oxidation activity increased gradually with Sr substitution at first, but decreased at higher extents of substitution, showing a maximum at $x = 1.0$. The activity at $x = 1.0$ was higher than $LaMnO_3$ and comparable with $LaCoO_3$. The results of the reduction by CO (% conversion of the first CO pulse) are shown also in Fig. 1. The amount of CO_2 formed by the first CO pulse for $x = 1.0$ corresponded to 1.2 surface monolayers. Therefore, the % conversion may be considered to represent the oxidizing power of the catalyst surface. It is obvious from this figure that the catalytic activity and the reducibility (or the oxidizing power) of La_2CoO_4 varied in parallel when the extent of Sr substitution, x, was increased. The parallel changes of two properties as shown in Fig. 1 were similar to those found for the Mn perovskites,[5)] but not like the Co perovskites.[2,4)] In the latter case, the reducibility increased monotonously with increasing x, while the catalytic activity was highest at $x = 0.2$.

The compositions and the oxidation states of the cobalt ions in $La_{2-x}Sr_xCoO_4$ were calculated from the average oxidation number of cobalt ion on the assumption that cobalt ions were present as either a mixture of cobalt(II) and (III) or a mixture of (III) and (IV). The results are summarized in Table 1. The oxidation state of cobalt increased with Sr substitution as expected. It is further noted that $La_{2-x}Sr_xCoO_4$ had oxidative nonstoichiometry (excess oxygen) in the range of $0 \leqq x \leqq 0.8$, almost a stoichiometric composition in $1.0 \leqq x \leqq 1.2$ and an anion-deficient structure for $x \geqq 1.5$. These changes of stoichiometry resemble those

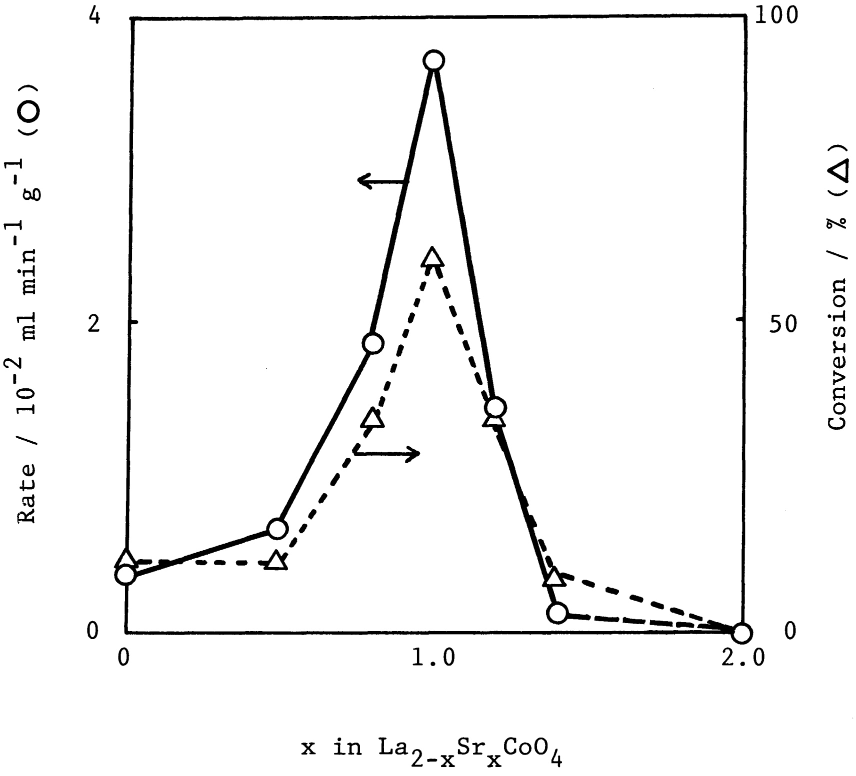

Fig. 1. Changes in the catalytic activity for oxidation of propane at 227 °C and the reducibility (% conversion of CO) of $La_{2-x}Sr_xCoO_4$.

Table 1. The stoichiometry of $La_{2-x}Sr_xCoO_4$

x	Average oxidation number of Co ion	Composition	State of Co ion		
			Co^{2+}	Co^{3+}	Co^{4+}
0	2.283	$La_{2.0}CoO_{4.14}$	71.7	28.3	-
0.5	2.585	$La_{1.5}Sr_{0.5}CoO_{4.04}$	41.5	58.5	-
0.8	2.868	$La_{1.2}Sr_{0.8}CoO_{4.03}$	13.2	86.8	-
1.0	3.009	$La_{1.0}Sr_{1.0}CoO_{4.00}$	-	99.1	0.9
1.2	3.209	$La_{0.8}Sr_{1.2}CoO_{4.00}$	-	79.1	20.9
1.5	3.344	$La_{0.5}Sr_{1.5}CoO_{3.92}$	-	65.6	34.4
2.0	3.360	$Sr_{2.0}CoO_{3.68}$	-	64.0	36.0

presumed for the Mn perovskites, in which, as the x in $La_{1-x}Sr_xMnO_3$ increased, the composition varied from $LaMnO_{3+\delta}$ ($\delta \simeq 0.1$) probably to $La_{0.2}Sr_{0.8}MnO_{3-\delta}$ (δ is not known but positive) via nearly stoichiometric $La_{0.4}Sr_{0.6}MnO_3$.[5] In contrast, the value of δ of $La_{1-x}Sr_xCoO_{3-\delta}$ was almost zero for x = 0-0.2, and monotonously increased with x for $x \geq 0.4$.[4]

Therefore, the increases of the catalytic activity and reducibility with Sr substitution may be explained in a way similar to the Mn perovskites by the easier desorption of surface oxygen and/or the increased number of coordinatively unsaturated cobalt ions on the surface, although further studies are needed to prove this. The reason for the decreases in the catalytic activity and reducibility for $x \geq 1.0$ is not clear at present. Nevertheless, it may be concluded based on the parallel variation of the two properties (Fig. 1) that the oxidizing power of the catalyst (reducibility of catalyst) is an important factor to determine the catalytic activity of $La_{2-x}Sr_xCoO_4$ for oxidation, and is closely related to the oxidation state of cobalt.

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