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The Valence Control and Catalytic Properties of $La_{2-x}Sr_xNiO_4$

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A series of $La_{2-x}Sr_xNiO_4$ catalysts (x=0—1.0) with a K_2NiF_4-type structure were prepared, and the average oxidation number of the Ni ion and the stoichiometry of the oxygen in the catalysts were measured. We also investigated the relationships between the reactivity of the catalysts and their catalytic activity for oxidation. The average oxidation number of the Ni ion increased monotonously from 2.32 (x=0) to 2.90 (x=1.0) upon the Sr substitution, and the composition changed with the x value from oxygen-excess (x=0—0.2) to oxygen-deficient (x=0.6—1.0), via a stoichiometric composition at x=0.4. In the range of x=0—0.2 (oxygen excess), the desorption peaks of oxygen in TPD (temperature-programmed desorption) were observed at about 300 °C; these results were ascribable to the excess oxygen. In this range, the oxidizing power of the surface, which was measured by the reduction of the catalysts by CO, was comparatively high. For x=0.4—1.0 (stoichiometric to oxygen-deficient), the oxygen desorbed at a higher temperature, and the amounts increased in accordance with the increase in the oxygen deficiency. The oxidizing power of the surface similarly increased with x values up to x=0.8. The composition of metal on the surface generally reflected that in the bulk, as judged from XPS. The catalytic activity for the oxidation was in parallel with the oxidizing power of the surface in x=0.4—1.0.

K_2NiF_4-type mixed oxide (A_2BO_4) consists of alternating layers of ABO_3 perovskite and AO rock salt, being a kind of two-dimensional analogue of perovskite.[1] K_2NiF_4-type oxides with various A- and B-site metal ions are known,[2] as in the case of perovskite-type mixed oxides.[3] It is also possible to control the valence and stoichiometry by the appropriate substitution of constituent metal elements. Hence, a series of catalysts with a K_2NiF_4-type structure are suitable materials for research into the relationships between the reactivity of the oxygen on the surface and in the bulk and the catalytic activity, as in the case of such perovskites as $LnBO_3$ (Ln: rare earth, B: Mn, Fe, Co).[4—8]

Recently we reported the catalytic activity of $La_{2-x}Sr_xCoO_4$, a K_2NiF_4-type mixed oxide, and compared the results with those for $La_{1-x}Sr_xCoO_3$, perovskite.[9] In the case of simple 3d-transition metal oxides, nickel oxide shows a relatively high oxidation activity, coming next to cobalt and manganese oxides,[10] while $LaNiO_3$ perovskite shows an activity in the same level.[4,11] However, $LaNiO_3$ is not stable on a usual atmosphere, and the preparation of Sr-substituted $LaNiO_3$ is very difficult under ordinary conditions. Therefore, in the present study, we prepared a series of Sr-substituted La_2NiO_4 catalysts and determined the valence of the nickel ion at the B-site and the change in the nonstoichiometry of oxygen upon the Sr substitution. We also measured the catalytic activities for oxidation as well as the reactivity of the oxygen on the surface and in the bulk of the catalysts, and discussed the relationships between them.

Experimental

Preparation of $La_{2-x}Sr_xNiO_4$. The $La_{2-x}Sr_xNiO_4$ (x=0—1.5) catalysts (the actual compositions of these mixed oxides were, in general, nonstoichiometric, $La_{2-x}Sr_xNiO_{4+\delta}$, but the stoichiometric formulae will be used in this paper unless explicit presentation is necessary) were prepared from mixtures of acetates of the metal components. First, the mixed acetate solution was evaporated to dryness in a rotary evaporator (70 °C), and then the residual solid was decomposed in air at 300 °C for 3 h and finally calcined in a quartz crucible in air at 1000 °C for 10 h.

Powder X-ray diffraction patterns were recorded on a powder X-ray diffractometer (Rigaku Denki, Geigerflex, RAD-IIA) using Cu $K\alpha$ radiation. The surface area of the samples was measured by the BET method (static N_2 adsorption; Micromeritics; AccuSorb 2100).

The oxidation number of the nickel ion in the catalysts was measured by means of iodometry. This method has usually been used as a direct method for the measurement of the excess oxygen in nickel oxide[12] and for the measurement of the average oxidation number of a Co or Ni ion in mixed oxides.[13] A sample (ca. 100 mg) which was dried at 100 °C for 3 h was dissolved in 25 ml of 0.4 mol l^{-1} HCl plus 25 ml of 0.16 mol l^{-1} KI aqueous solution. The solution was then titrated with a standard thiosulfate solution.

The composition of metal ions was determined with the aid of inductively coupled plasma spectrometry (ICP) (Nippon Jarrell-Ash, ICAP-575-II). The X-ray photoelectron spectra (XPS) were obtained with a Shimadzu ESCA-750 apparatus employing Mg $K\alpha$ radiation (1253.6 eV) under a high vacuum of 10^{-6} Pa. The binding energy was calibrated by using a Cls electron line (285.0 eV) coming from the background.

Apparatus. Conventional flow and pulse systems described previously were used.[4—6]

Procedure. Temperature Programmed Desorption (TPD) of Oxygen: The TPD of oxygen was carried out with a flow system using helium as the carrier gas. Prior to each run, the sample (1.0 g) was pretreated in an O_2 stream for 1 h at 800 °C and then cooled to room temperature. Then, O_2 was replaced by He at room temperature. Any oxygen impurity in He was removed by the use of a Molecular Sieve (MS) 5A trap kept at the temperature of liquid nitrogen. The temperature of the sample was raised at a constant rate of 20 deg min^{-1} in the He stream (25 cm^3 min^{-1}), and the oxygen desorbed was detected with a thermal conductivity detector. It was confirmed by a gas chromatograph that only oxygen existed in the effluent He gas. The TPD curves were reproduced in repeated runs (3 times) after the pretreatments above.

Reduction of Catalysts by CO: The reduction of the catalysts by CO was conducted in the pulse reactor. Prior to the reaction, the catalysts (50 mg) were treated in an O_2 stream (20 cm^3 min^{-1}) for 1 h at 300 °C, and then the O_2 stream was replaced by a He stream purified by the use of a MS-5A trap kept at the temperature of liquid N_2. The flow rate of the carrier gas (He) was 25 cm^3 min^{-1}, and the size of each pulse was 0.1 cm^3. The products were analyzed by means of a gas chromatograph.

Oxidation of Propane: The catalytic oxidation of propane was carried out with a flow system. Prior to each reaction, the 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 fed into the reactor. The flow rate of the mixed gas was 60 cm^3 min^{-1}. The products were analyzed by means of a gas chromatograph.

Results

Catalysts and Their Physical Properties. The surface area, the crystal structure, and the compositions of the prepared catalysts, $La_{2-x}Sr_xNiO_4$, are summarized in Table 1. In the range of x=0—1.0, samples with a tetragonal K_2NiF_4-type structure were obtained, judging from the XRD patterns. At x=1.5, the sample was a mixture of K_2NiF_4-type oxide, SrO, and NiO, the content of the latter two both being about 10—20%. No XRD peaks of La_2O_3 were observed. The surface areas of the samples were all less than 3 m^2 g^{-1} because of the high calcination temperature, and they tended to increase with the x value. The bulk compositions of the metal ions measured by ICP are shown in Fig. 1. The bulk composition agreed well with the nominal composition expected from the quantities of starting materials, within the limits of experimental error. Hence, there was no substantial loss of any specific components during the preparation of the catalysts (for example, evaporation during the calcination).

Figure 2 shows the average oxidation number of the nickel ion at the B-site, as measured by iodometry. The average oxidation number of the nickel ion increased monotonously from 2.32 (x=0) to 2.90 (x=1.0) with the increase in x, as has been expected. It should further be noted that the nonstoichiometry varied from an oxygen-excess composition for x=0—0.2, through almost a stoichiometric one for x=0.4, to an oxygen-deficient one (x=0.6—1.0).

TPD of Oxygen. Figure 3 shows the TPD profiles of oxygen from the catalysts, where the rate of desorption, as calculated from the oxygen concentration in the effluent gas, is plotted against the catalyst temperature. As is shown in this figure, the amount of the oxygen desorbed below 800 °C decreased with the

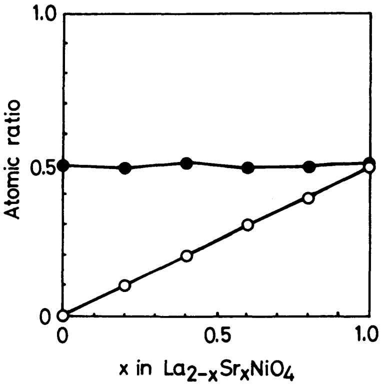

Fig. 1. The metal ion composition in the bulk. ○: Sr/La+Sr, ●: Ni/La+Sr.

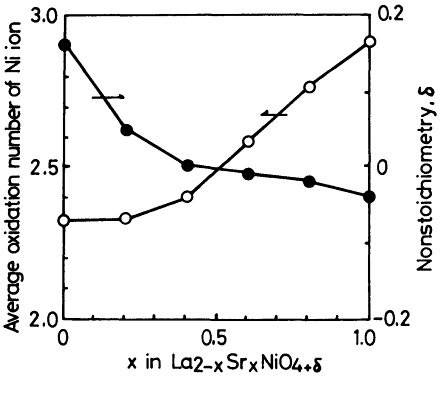

Fig. 2. The average oxidation number of Ni ion and the nonstoichiometry (δ) of $La_{2-x}Sr_xNiO_4$.

Table 1. The Surface Areas, Structures, and Compositions of Catalysts

x	Surface area/m^2 g^{-1}	Structure	Composition$^{a)}$
0	1.6	K_2NiF_4-type	$La_{2.0}\ Ni^{2+}{}_{0.68}Ni^{3+}{}_{0.32}O_{4.16}$
0.2	2.0	K_2NiF_4-type	$La_{1.8}Sr_{0.2}Ni^{2+}{}_{0.67}Ni^{3+}{}_{0.33}O_{4.07}$
0.4	1.9	K_2NiF_4-type	$La_{1.6}Sr_{0.4}Ni^{2+}{}_{0.60}Ni^{3+}{}_{0.40}O_{4.00}$
0.6	2.5	K_2NiF_4-type	$La_{1.4}Sr_{0.6}Ni^{2+}{}_{0.42}Ni^{3+}{}_{0.58}O_{3.99}$
0.8	2.9	K_2NiF_4-type	$La_{1.2}Sr_{0.8}Ni^{2+}{}_{0.24}Ni^{3+}{}_{0.76}O_{3.98}$
1.0	2.5	K_2NiF_4-type	$La_{1.0}Sr_{1.0}Ni^{2+}{}_{0.09}Ni^{3+}{}_{0.91}O_{3.96}$
1.5	2.5	K_2NiF_4-type, NiO, SrO	—

a) The metal ions were measured by ICP. The contents of oxygen were calculated from the oxidation number of the Ni ion, as measured by iodometry.

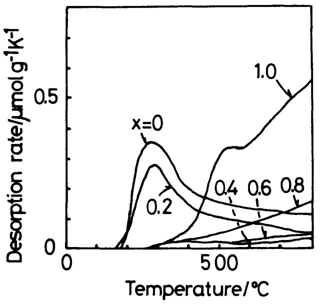

Fig. 3. TPD profiles of oxygen from $La_{2-x}Sr_xNiO_4$.

Table 2. The Amount of Oxygen Desorption, the Corresponding Layers, and the Change in the Nonstoichiometry (see text)

x	Amount of oxygen desorbed/cm³ g⁻¹	Corresponding layer	$\Delta\delta$
0	2.48	8.6	0.09
0.2	1.77	5.0	0.06
0.4	0.26	0.8	0.01
0.6	0.30	0.7	0.01
0.8	0.78	1.5	0.03
1.0	3.25	6.3	0.10

a) The amount of oxygen in TPD desorbed up to 800 °C. The surface layers corresponding to the amounts of desorbed oxygen (assuming that the amount of oxygen in the surface monolayer was 0.96×10^{19} atom m⁻²). The change in the nonstoichiometry attributed to the oxygen desorption ($\Delta\delta$: $La_{2-x}Sr_xNiO_{4+\delta-\Delta\delta}$).

increase in the Sr content in the range of x=0—0.4, showed a minimum at x=0.4, and then increased with x (x=0.4—1.0). The TPD profiles for x=0 and 0.2 were similar to each other, both having a peak at around 300 °C, but were quite different from those for x=0.4—1.0. This difference in the TPD profiles seems to correspond to the transition of the nonstoichiometry of the catalysts from an oxygen-excess (x=0—0.2) to a stoichiometric and an oxygen-deficient composition (x=0.4—1.0).

The amounts of oxygen desorbed below 800 °C, as well as the number of surface layers and the change in the nonstoichiometry (δ) corresponding to the amounts of oxygen, are shown in Table 2, where the surface layers were calculated by assuming that the density of the oxygen in the monolayer is 0.96×10^{19} atom m⁻² and where the change of the nonstoichiometry, $\Delta\delta$, caused by desorption was expressed by; $La_{2-x}Sr_xNiO_{4+\delta-\Delta\delta}$. All of these values varied in a similar way, showing a minimum at x=0.4—0.6. The amounts of oxygen desorbed were always more than one surface monolayer except for the values of x=0.4 and 0.6. This indicates that the desorption of the lattice oxygen in the bulk took place in addition to the adsorbed oxygen. In the range of x=0.4—0.6, the nonstoichiometry and the average oxidation number of the Ni ion in catalysts, being nearly stoichiometric, are less influenced by the change in the atmosphere (partial oxygen pressure) or the temperature.

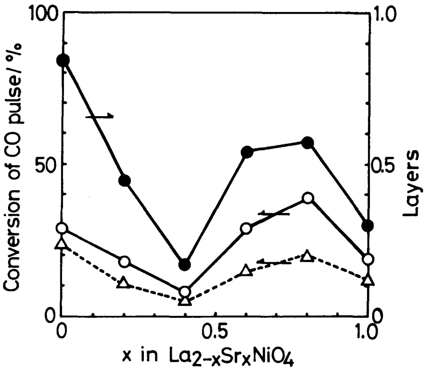

Fig. 4. The % conversion of CO to CO_2 in the first and in the fifth pulse and the amount of oxygen consumed by the first CO pulse in the unit of surface layers.

○: the first pulse, △: the fifth pulse, ●: layers.

Reduction of the Catalyst by CO (Oxidizing Power of the Surface). The % conversions of CO to CO_2 decreased gradually upon repeated pulses (at 10 min intervals). The decrease was smaller for x=0—0.2 (oxygen-excess) than for x=0.6—1.0 (oxygen-deficient). The values in the first and fifth pulses are shown in Fig. 4, where the amount of oxygen consumed by the first CO pulse is also given in the unit of surface layers. The conversion may be regarded as a measure of the oxidizing power per unit of catalyst weight. The oxidizing power expressed by the % conversion in the first pulse decreased first with the increase in x, showing its lowest value at x=0.4. It then increased with x up to x=0.8 and decreased at x=1.0. The amount of oxygen consumed by the first CO pulse for x=0 corresponded to about 6% of the excess oxygen. As this amount was less than the monolayer, this value may express the oxidizing power of the catalyst surface (the reducibility of the surface).

Surface Composition of the Catalyst. The surface compositions of the catalysts were measured by XPS; the results are shown in Fig. 5, where Eq. 1[14] was used for the calculation.

$$(N_a/N_b) = (n_a/n_b)(\lambda_a/\lambda_b)(\sigma_a/\sigma_b)(S_a/S_b) \qquad (1)$$

where N: peak intensity, n: atoms per unit volume, λ: mean free path of the electron, σ: ionization cross section, and S: instrumental factor. The peak areas of La4d, Sr3d, and Ni3p, including the satellite peak, were used for N, while the values of σ were taken from the literature.[15] "$\lambda\cdot S$" was assumed to be constant, as in a previous work.[16] The surface compositions of the catalysts, as determined by Eq. 1, are not very accurate, but they may be sufficient to compare the relative change in the surface composition for a series of catalysts. As may be seen from this figure, though the

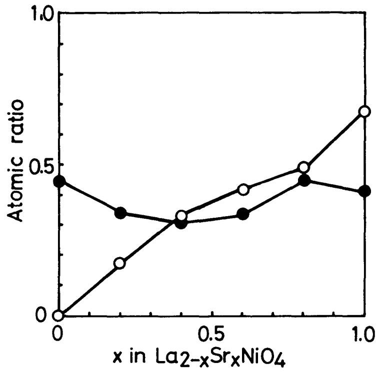

Fig. 5. The surface composition of metal ion determined by XPS.
○: Sr/La+Sr, ●: Ni/La+Sr.

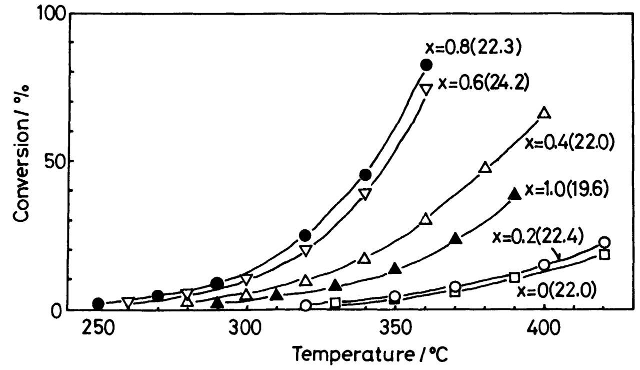

Fig. 6. The catalytic activity for propane oxidation over $La_{2-x}Sr_xNiO_4$. The activation energy in parenthesis: kcal mol^{-1}.

atomic ratio at Sr in the A-site (○) increased monotonously with x, this value was generally higher than that in the bulk composition. On the other hand, the atomic ratio of the Ni ion was considerably lower than that in the bulk, except for the values of $x=0$ and 0.8. The ratio of La:Sr:Ni, as calculated from Eq. 1, was 51:25:24 (54:13:33 in the bulk) at $x=0.4$ and 33:34:31 (bulk, 40:27:33) at $x=0.8$. The binding energies of La4d, Sr3d, and Ni3p in XPS changed little from one catalyst to another.

Catalytic Activity for the Complete Oxidation of Propane. The activity for the propane oxidation is shown in Fig. 6. The only reaction products were CO_2 and H_2O for all the catalysts. As is shown in this figure, the oxidation activities per unit of weight of the catalysts were very low at $x=0$—0.2; they then became higher with x up to $x=0.8$ and then decreased at $x=1.0$, showing a maximum at $x=0.8$. The activation energy obtained from the data at a low conversion level (below 10%) was 19.6—24.1 kcal mol^{-1}, as is shown in parentheses in Fig. 6.

Discussion

Structure and Composition of $La_{2-x}Sr_xNiO_4$. As K_2NiF_4-type mixed oxides often show interesting electrical properties, quite a few studies have been reported about this type of mixed oxides, formed by various A- and B-site ions.[2] The structure and the electrical properties of $La_{2-x}Sr_xNiO_4$ have also been studied.[17–19] All of these reports show that $La_{2-x}Sr_xNiO_4$ has a K_2NiF_4-type structure in the range of $x=0$—1.0, in agreement with the results of the present study. However, the formation of a K_2NiF_4 structure with $x=1.5$ has not been reported. The reason may be the necessity of an extremely high and unstable oxidation state of tetravalent Ni. This corresponds to the difficulty of Sr substitution in $LaNiO_3$ perovskite.

In the case of La_2NiO_4, a part of the Ni ion is oxidized to make it trivalent, since its tolerance factor is close to the lower limit of the tetragonal K_2NiF_4-type structure.[2] Hence, the composition becomes oxygen-excess. The average oxidation number of the Ni ion (2.32) and the oxygen-excess composition observed for $x=0$ in the present work are consistent with those data. It is probable that cation deficiencies at both A- and B-sites were formed in La_2NiO_4, as in the case of $LaMnO_3$.[20] The oxidation number of the Ni ion increased monotonously from 2.32 ($x=0$) to 2.90 ($x=1.0$) with the increase in the extent of the Sr substitution for the A-site (Table 1). Gopalakrishnan et al. also reported a monotonous increase in the number from 2.15 ($x=0$) to 3.00 ($x=1.0$)[17] with a change in the stoichiometry with x from an oxygen-excess to a stoichiometric composition. This trend is consistent with that found in the present work, except that the composition in the present work became oxygen-deficient at a higher x value.. This difference may be due to the different calcination conditions. In this work, the oxides were calcined in air at 1000 °C, while in the oxygen these were caclined at 1200 °C for more than 72 h for $x=0.4$—1.0 in their case.

The valence control of the B-site ion as well as the variation in the nonstoichiometry upon the Sr substitution obtained in this work may be compared with those results previously obtained for perovskites and $La_{2-x}Sr_xCoO_4$. In the case of $La_{2-x}Sr_xCoO_4$, the average oxidation number of the Co ion increased monotonously from 2.28 ($x=0$) to 3.34 ($x=1.5$) with the increase in x, and its composition varied from $La_2CoO_{4.14}$ to $La_{0.5}Sr_{1.5}CoO_{3.92}$.[9] This variation is very similar to that found in this study for $La_{2-x}Sr_xNiO_4$. The change in nonstoichiometry was also similar for $La_{1-x}Sr_xMnO_3$.[8] On the other hand, in the case of the $La_{1-x}Sr_xCoO_3$ or $La_{1-x}Sr_xFeO_3$ system,[6,7] although the averag oxidation number of the B-site ion increased monotonously with the x value, the composition varied from stoichiometric to oxygen-deficient. This variation corresponds to that found in the present study for $La_{2-x}Sr_xNiO_4$ above $x=0.4$.

Thus, it may be stated that the $La_{2-x}Sr_xNiO_4$

catalysts prepared in the present study have well-controlled oxidation numbers of the Ni ion and nonstoichiometry, in general agreement with those of the previous studies of related mixed oxides.

The Effect of Sr Substitution on the Oxidizing Power of the Surface, the Surface Composition, and the TPD. The oxidizing power of the surface, as measured by the CO pulse, varied as is shown in Fig. 4. This trend appears to correspond closely to the changes in the nonstoichiometry and the TPD profiles. The initial decrease in the oxidizing power (x=0—0.4) apparently parallels the desorption peak at about 300 °C in the TPD.21) On the other hand, the variation in the oxidizing power of the surface in the range of x=0.4—0.8 corresponds to the variation in the oxygen desorption in TPD in the high-temperature region. The low oxidizing power of the surface at x=1.0 may be due to the stability of the oxygen-deficient composition or to the formation of a Sr− rich phase on the surface, as will be described below.

The reactivity of the oxide ion in the bulk may be seen in the TPD profiles (Fig. 3). In x=0—0.2, the large peaks in the TPD profiles at about 300 °C are ascribed to the desorption of the excess oxygen (the amount of oxygen desorbed was about 4 times the monolayer).

For x=0.4—1.0, the TPD profiles were similar, with no peak at about 300 °C, and the amount of the desorbed oxygen increased with the x. The oxygen desorbed at a higher temperature may be assigned to the formation of the oxygen deficiency if one considers the relationship between the amounts of desorbed oxygen, the valence change in the B-site ion, and the change in the nonstoichiometry (Table 2). Consequently, the valence control by the following scheme, as in the $La_{1-x}Sr_xCoO_3$ system,4—6) is probable for x=0.4—1.0.

$$La_2^{3+}Ni^{2+}O_4 \xrightarrow{Sr^{2+}} La_{2-x}^{3+}Sr_x^{2+}Ni_{1-x}^{2+}Ni_x^{3+}O_4 \qquad (2)$$

$$La_{2-x}Sr_xNi_{1-x}^{2+}Ni_x^{3+}O_4 \longrightarrow La_{2-x}Sr_xNi_{1-x+2\delta}^{2+}Ni_{x-2\delta}^{3+}O_{4-\delta} + \delta/2O_2 \qquad (3)$$

First, a some of the divalent Ni ions are oxidized to the trivalent state upon the Sr substitution (Eq. 2). With further Sr substitution, the oxygen desorbs, forming a lattice oxygen deficiency, therefore, a some of the trivalent Ni ions are reduced to the divalent state (Eq. 3). The lattice oxygen deficiency should tend to increase with the increase in x and the rise in the temperature, as reflected in the TPD profiles at x=0.4—1.0.

The concentration of Sr on the surface was higher than that in the bulk in the whole range of x values studies. Especially at x=1.0, Sr occupied about half of the metal ions on the surface layer (about 33%, in bulk). Accordingly, a Sr-rich phase on the surface, which may be formed in this catalyst, is a possible reason for the lower oxidizing power of the surface at x=1.0. The Ni concentration on the surface varied with the x value, but it accounted for 24—33% of the total metal ions; this value did not change much among the catalysts, though it was always lower than the concentration in the bulk. On the whole, though the bulk composition was generally reflected in the surface composition, caution must be exercised when the property in the bulk is used for the discussion of the surface properties.

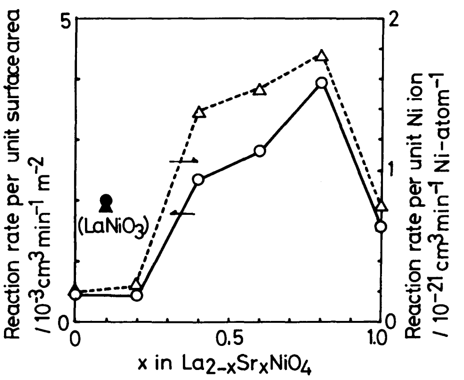

Fig. 7. The reaction rate for propane oxidation at 227 °C per unit surface area and unit Ni ion on the surface.

The Effect of Sr Substitution on the Catalytic Activity for Oxidation. Though the catalytic properties of $LaNiO_3$ perovskite have been reported in several papers,22) there have been only a few studies of the catalysis of La_2NiO_4,23—25) and no studies on the effect of the valence control have been reported. When the catalytic activity for oxidation is compared per unit of surface area of the catalysts, the catalytic activities of x=0.4—0.8 in this work were comparable with or higher than that of $LaNiO_3$4) (Fig. 7). The reaction rate of the propane oxidation, normalized to the Ni atom on the surface, is also shown in Fig. 7; it was calculated from the surface composition (Fig. 5).26) The activity per surface Ni ion thus calculated was higher for $La_{2-x}Sr_xNiO_4$ (x=0.4—0.8) than for $LaNiO_3$.

The catalytic activity for oxidation increased steeply from x=0.2 to 0.4 (Fig. 7). If one considers this result together with the changes in the composition, the TPD profiles, and the oxidizing power of the surface described above, the catalysts may be divided again into two groups, x=0—0.2 and 0.4—1.0.

First we will discuss the latter group. In this range (x=0.4—1.0), the oxygen deficiency and the reactivity of the lattice oxygen increased with the x value up to x=0.8. A similar increase in the catalytic activity has already been reported for $La_{1-x}Sr_xCoO_3$ perovskite.4—6) Further, the oxidizing power of the surface and the oxidation activity showed parallel variations in this range of x, as in the cases of $La_{1-x}Sr_xMnO_3$ and $La_{2-x}Sr_xCoO_4$.8,9) It is noteworthy that the oxidizing power of the surface showed a maximum where the composition of the catalysts was slightly shifted from stoichiometric to oxygen-deficient. It is probable that, in this state, the redox cycles of the desorption and adsorption of oxygen on the surface and/or in the vicinity of the surface occurred smoothly; therefore, the catalytic activity increased. Hence, the catalytic activity in the present Ni system is closely related to the reactivity of the oxygen on the surface, as in $La_{1-x}Sr_xMnO_3$,[8] but the contribution of the oxygen in the bulk may not be neglected, especially in x=0.4—1.0, as in $La_{1-x}Sr_xCoO_3$.[4—6]

On the other hand, in the range of x=0—0.2, the oxidation activity was low, although large peaks were observed around 300 °C (due to the excess oxygen) in TPD and the oxidizing power of the surface was comparatively high. It may be suggested as the reason for this discrepancy that the excess oxygen is inactive for the catalytic oxidation reaction, although it is responsible for the TPD peaks at about 300 °C and the reducibility of the surface. In the cases of $La_{1-x}Sr_xMnO_3$ and $La_{2-x}Sr_xCoO_4$, the composition for low x values was oxygen-excess[8,9] and the catalytic activities were lower than for those with higher x values. This result also indicates that the low catalytic activity is correlated to the oxygen-excess composition. The reason for this is not clear at present, but it is possible that the ability of the dissociation or the activation of the oxygen is low because of the very small oxygen deficiency on the surface, as in the case of $La_{1-x}Sr_xMnO_3$.[8]

Conclusion

A series of $La_{2-x}Sr_xNiO_4$ (x=0—1.0) catalysts with a K_2NiF_4-type structure were prepared. With the increase in the x value, the average oxidation number of the Ni ion increased monotonously from 2.32 (x=0) to 2.90 (x=1.0) and the nonstoichiometry changed from an oxygen-excess to an oxygen-deficient composition via a stoichiometric one.

Based on the variation in the TPD of oxygen and the oxidizing power of the catalyst surface (as measured by the CO pulse), the catalysts were divided into two groups; (1) x=0—0.2 (oxygen-excess composition) and (2) x=0.4—1.0 (stoichiometric and oxygen-deficient). In Group (1), the desorption peak of oxygen ascribable to the excess oxygen was observed at about 300 °C, and the oxidizing power of the surface was comparatively high. On the other hand, in Group (2) oxygen desorbed at a relatively high temperature, with the formation of a lattice oxygen deficiency. The amount of oxygen desorbed and the oxidizing power of the surface increased from x=0.4 to x=0.8, much as with other perovskites and K_2NiF_4-type oxides.

The catalytic activity for the oxidation was in parallel with the oxidizing power of the surface in Group (2). However, the catalytic activity of Group (1) was low in spite of the considerable oxidizing power of the surface. Though the reason for this is not clear at present, it appears that the excess oxygen was inactive for the catalytical oxidation and/or that the ability of dissociation and activation of the oxygen on the surface was low.

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21) Here, it must be considered that, in the CO pulse experiments, the catalysts were pretreated in a He stream at 300 °C, so the oxidation state may be different between the CO pulse and TPD experiments. In the TPD profile of x=0 after the pretreatment in the CO pulse, the peak about 300 °C did not appear, while oxygen desorption started at 320 °C. However, the composition of this sample was $La_2NiO_{4.11}$, still an oxygen-excess composition; therefore, the oxidizing power of the surface measured as in the CO pulse experiment must be related to this excess oxygen.

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26) The calculation was carried out by assuming that the amounts of the surface oxygen of a perovskite and a K_2NiF_4-type oxide are the same and that the total numbers of metal ions on the surface are 2/3 (perovskite) and 3/4 (K_2NiF_4-type oxide) the number of oxygen atoms. The La:Ni ratio was used as the surface composition of $LaNiO_3$ (unpublished data by T. Nitadori and M. Misono).