# Reaction between Carbon Monoxide and Nitrogen Monoxide over Perovskite-type Mixed Oxides

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Catalytic reactions between CO and NO and between CO and  $O_2$  over several perovskite-type mixed oxides, such as LaMO<sub>3</sub> and La<sub>1-x</sub>Sr<sub>x</sub>MO<sub>3</sub> (M = Co, Fe, Mn, Cr, Ni; x = 0-0.4), have been studied in a recirculation system at 473 and 573–673 K, respectively. It has been found that the catalytic activities for the two reactions depend on the B-site element in distinctly different ways; the activity pattern for CO–NO was Cr < Mn < Fe < Co > Ni and that for CO–O<sub>2</sub> was Cr < Mn > Fe < Co > Ni. It was suggested that the difference of the activity pattern was due to the ability of the B-site ion to activate NO and O<sub>2</sub>, based on the results of NO adsorption and the activity patterns reported for other oxidation reactions. The substitution of  $Sr^{2+}$  for the A site in ABO<sub>3</sub> (A = La, B = Co, Mn, Fe) decreased monotonically the catalytic activity for the CO–NO reaction in contrast to the increase observed previously for the oxidation of propane. The order of the rate of CO–N<sub>2</sub>O reaction was LaFeO<sub>3</sub> > La<sub>0.9</sub>Sr<sub>0.1</sub>FeO<sub>3</sub> > LaCoO<sub>3</sub> > LaMO<sub>3</sub>. The transformation of N<sub>2</sub>O to N<sub>2</sub> over LaFeO<sub>3</sub> and La<sub>0.9</sub>Sr<sub>0.1</sub>FeO<sub>3</sub> in the CO–NO reaction is due to the greater rates for the CO–N<sub>2</sub>O reaction.

Since nitrogen oxides  $(NO_x)$  cause air pollution and acid rain, the catalytic removal of  $NO_x$  is a reaction of social interest.<sup>1-6</sup> The reduction of nitrogen monoxide (NO) by carbon monoxide (CO) or hydrocarbon is an important reaction pathway for the removal of  $NO_x$  from automobile exhaust.<sup>1-6</sup> Therefore, elucidation of the controlling factor of the catalytic activity for the reduction of NO is very worthwhile.

It is possible to vary the concentrations of A- or B-site metal ions over a wide range for perovskite-type mixed oxides,  $^{7-20}$  and these materials efficiently catalyse various reactions.<sup>8,21</sup> Therefore, these catalysts would be good models for the investigation of correlations between solid-state chemistry and catalytic properties.

We have previously reported that catalytic activities can be controlled by changing the valency of the transition-metal ion, for example, by  $Sr^{2+}$  substitution for  $La^{3+}$  in  $LaCOO_3$ ,  $^{10-12}$  LaFeO<sub>3</sub>,  $^{13}$  LaMnO<sub>3</sub>,  $^{14}$  and  $La_2MO_4$  (M = Cu, Co, Ni).<sup>16,17,19</sup>

The catalytic activity of perovskite-type mixed oxides for the reaction between CO and NO has been reported, but little is known of the factors that control it.<sup>3</sup> In the present work, we prepared several perovskite-type mixed oxides having different B-site ions and investigated comparatively the role of the B-site ion and the effect of  $Sr^{2+}$  substitution at the A site in the reactions between CO and NO and between CO and O<sub>2</sub>.

#### Catalysts

### Experimental

The  $La_{1-x}Sr_xMO_3$  (M = Co, Fe, Mn, Cr, Ni; x = 0-0.4) catalysts were prepared from metal acetates as has been described previously.<sup>10</sup> Mixed acetate solutions were evaporated to dryness in a rotary evaporator. The solid obtained was first decomposed in air at 573 K for 3 h and then calcined in air at 1123 K for 5 h. The actual composition may be  $La_{1-x}Sr_xMO_{3\pm\delta}$  ( $\delta$ , non-stoichiometry; the values reported in the literature for the related samples are listed in Table 1 for reference, although the calcination temperature or the pretreatment for the chemical analysis differs slightly among the samples), but in this paper it will be designated as  $La_{1-x}Sr_{x}MO_{3}$ .

The valency of the iron in LaFeO<sub>3</sub> was chemically determined by an iodometric titration as described previously.<sup>19</sup> A portion of the oxide (as-prepared LaFeO<sub>3</sub>) was dissolved without treatment in dilute aqueous hydrochloric acid with an appropriate amount of KI. The amount of iodine formed was titrated with sodium thiosulfate solution. The valency of iron in LaFeO<sub>3</sub> was calculated on the assumption that other elements were present as La<sup>3+</sup> and O<sup>2-</sup>.

Powder X-ray diffraction patterns were recorded on a powder X-ray diffractometer (Rigaku Denki, Rotaflex, RU-200) using Cu-K $\alpha$  radiation. Surface areas were measured by the B.E.T. method (N<sub>2</sub> adsorption). Elemental analysis was carried out for LaCoO<sub>3</sub> and LaMnO<sub>3</sub> with atomic absorption spectroscopy.

### Reaction

The CO-NO, CO-O<sub>2</sub> and CO-N<sub>2</sub>O reactions were carried out in a closed circulation system (ca. 190 cm<sup>3</sup>) as described previously.<sup>5,6,18,19</sup> The catalysts (50 mg) were mixed with

**Table 1** Structures, surface areas and non-stoichiometry ( $\delta$ ) of La<sub>1-x</sub>Sr<sub>x</sub>MO<sub>3- $\delta$ </sub> (M = Co, Fe, Mn, Cr, Ni; x = 0-0.4) catalysts

catalyst	structure <sup>a</sup>	surface area $/m^2 g^{-1}$	δ	
			reported	ref. <sup>b</sup>
LaCoO <sub>3</sub>	P(R)	2.4	0.0	(a)
LaFeO <sub>3</sub>	P(O)	8.6	0.0	(b)
LaMnO <sub>3</sub>	P(O)	7.0	-0.12	(c)
LaCrO <sub>3</sub>	P(O)	3.2		
LaNiO <sub>3</sub>	P(R) <sup>c</sup>	2.3		
$La_{0.8}Sr_{0.2}CoO_3$	P(C)	2.8	$\pm 0.005$	(a)
$La_{0.6}Sr_{0.4}CoO_3$	P(C)	3.4	0.052	(a)
La <sub>0.9</sub> Sr <sub>0.1</sub> FeO <sub>3</sub>	P(C)	5.1	0.003	(d)
$La_{0.6}Sr_{0.4}MnO_3$	P(C)	9.6	0.023	(e)

<sup>a</sup> Deduced from the splitting of the main peaks of XRD. P, perovskite structure; R, rhombohedral; O, orthorhombic; C, cubic. <sup>b</sup> (a) Ref. 12. (b) This work. (c) B. C. Tofield and R. S. Roth, J. Solid State Chem., 1974, 10, 183. (d) T. Ishigaki, Ph.D. Thesis, The University of Tokyo, 1984. (e) T. Shimizu and Y. Morikawa, Nippon Kagaku Kaishi, 1978, 1462. The average of  $\delta$  values reported for La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> and La<sub>0.5</sub>Sr<sub>0.5</sub>MnO<sub>3</sub>. <sup>c</sup> This catalyst contained a distorted perovskite phase (ASTM card no. 12–751).

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inert SiC (250 mg). The procedures for CO-NO and  $CO-N_2O$  reactions were as follows: After pretreatment in  $O_2$ (ca. 13 kPa) at 573 K or 673 K for 1 h, the catalysts were evacuated at the same temperature for 15 min. Then the catalysts were exposed to the reaction gas mixture at ca. 8 kPa (CO: NO = 1:1), or ca. 6 kPa (CO:  $N_2O = 1:2$ ) at the same temperature. The CO-O<sub>2</sub> reaction temperature was lowered to 473 K because the reaction proceeded too rapidly at higher temperatures (573 or 673 K) for the rate to be measured. The procedure for CO-O2 reaction was as follows; after the catalysts were pretreated in  $O_2$  (ca. 13 kPa) at 573 K for 1 h, the catalysts were exposed to the reaction gas mixture at 6 kPa (CO :  $O_2 = 2$  : 1) evacuated at the same temperature and then cooled to 473 K. Products and reactants were analysed with a gas chromatograph using Porapak Q and molecular sieve 5A columns.

## Results

# Structure and Composition

The structures and surface areas of the perovskite catalysts prepared are summarized in Table 1. The surface areas varied from 2.3 m<sup>2</sup> g<sup>-1</sup> for LaNiO<sub>3</sub> to 9.6 m<sup>2</sup> g<sup>-1</sup> for La<sub>0.6</sub>Sr<sub>0.4</sub>MnO<sub>3</sub>. All catalysts showed a single perovskite phase except for LaNiO<sub>3</sub> which showed rhombohedral and distorted rhombohedral perovskite phases. The elemental analysis showed that the atomic ratios of La/Co in LaCoO<sub>3</sub> and La/Mn in LaMnO<sub>3</sub> were close to unity, 0.99.

# Reaction between CO and NO over $LaMO_3$ (M = Co, Mn, Fe, Cr, Ni) Catalysts

Fig. 1(a) and (b) show the time courses of the reactions between CO and NO over LaCoO<sub>3</sub> and LaFeO<sub>3</sub> at 573 K, respectively. The broken and dotted lines are the results for a second run (vide infra). The products detected by gas chromatography were N<sub>2</sub>, N<sub>2</sub>O and CO<sub>2</sub>. The nitrogen and carbon balances were better than 95%, suggesting that the formation of NO<sub>2</sub> by the oxidation of NO or by the disproportionation of NO hardly took place, as in the case of La<sub>0.85</sub>Ba<sub>0.15</sub>CoO<sub>3</sub>.<sup>4</sup> CO<sub>2</sub> and N<sub>2</sub>O were the main products, and the amount of N<sub>2</sub> formed was small for the LaMO<sub>3</sub> (M = Co, Mn, Cr, Ni) catalysts. In the case of LaFeO<sub>3</sub>, the N<sub>2</sub>O initially formed was transformed to N<sub>2</sub>. The CO-NO reaction over LaMO<sub>3</sub> (M = Co, Mn) at 673 K was similar to that over LaFeO<sub>3</sub> at 573 K.

The variations of the amounts of CO and NO in the second run were indicated by the broken and dotted lines, respectively, in Fig. 1(*a*) and (*b*). The rate and selectivity did not change significantly in repeated runs, as was the case for the other LaMO<sub>3</sub> (M = Mn, Cr, Ni) catalysts. The total turn-

J. CHEM. SOC. FARADAY TRANS., 1992, VOL. 88

greater than 20, demonstrating that the reaction is catalytic. The concentration-time data for each LaMO<sub>3</sub> catalyst can be approximately represented by the rate equation, -d[CO]/dt = k[CO][NO], as was reported by Force et al.<sup>22</sup> and by us,<sup>19</sup> where t, k, [CO] and [NO] are the time, rate constant and partial pressures of CO and NO, respectively. The rate and the initial selectivity to  $N_2$  are summarized in Table 2. In this work, the stationary rate constant was calculated in the second run according to the equation -d[CO]/ dt = k[CO][NO] and the selectivity was defined by the product distribution obtained after 10 min in the second run, since the selectivity changed little over the first 60 min, except in the cases of  $LaFeO_3$  and  $La_{0.9}Sr_{0.1}FeO_3$  as shown in Table 2. The rate decreased as follows:  $LaCoO_3 >$  $LaFeO_3 > LaMnO_3 > LaCrO_3 > LaNiO_3$ . The selectivity for  $N_2$  formation did not change much among the LaMO<sub>3</sub> catalysts (M = Co, Mn, Cr, Ni).

# Effect of $Sr^{2+}$ Substitution for the Reaction between CO and NO

When the CO-NO reaction was carried out over the  $La_{1-x}Sr_{x}CoO_{3}$  (x = 0.2, 0.4) catalysts, it was noticed from the oxygen balance in the reaction system that  $La_{1-x}Sr_xCoO_3$  (x = 0.2, 0.4) catalysts were reduced during the first run, but were hardly reduced at all during the second run. By contrast, the other catalysts were reduced only a little during the entire reaction. The degree of reduction, calculated on the basis of the oxygen balance, is indicated by the  $\Delta\delta$ value given in Table 3. For the calculation, we ignored the formation of  $NO_2$ , since this was negligible as noted above. The time course of the reaction between CO and NO over  $La_{0.6}Sr_{0.4}CoO_3$  at 573 K is shown in Fig. 1(c). The amount of CO reacted in the second run was smaller than that in the first [see  $\bullet$  and broken line in Fig. 1(c)], suggesting that the reduction of the catalyst by CO took place only in the first run. A similar decrease in the CO consumption in the second run was also observed for  $La_{0.8}Sr_{0.2}CoO_3$ .

The decrease of NO content in the second run is shown by the dotted line in Fig. 1(c), and was greater than in the first run. The amounts of  $N_2$  and  $N_2O$  formed in the second run were also greater than those formed in the first. These facts suggest that the reaction was accelerated by the reduction of the catalyst. The rate of CO or NO consumption and the selectivity in the third run were equal to those in the second run. The time courses of the second runs for the other  $Sr^{2+}$ substituted catalysts were also similar to those of the corresponding third runs.

The concentration-time data of the second and third runs for  $Sr^{2+}$ -substituted catalysts may also be represented by the

**Table 2** Rates of the reaction between CO and NO or  $N_2O$  at 573 K

	NO-CO	CO N O		
catalyst	$rate^{a}/10^{-5} mol min^{-1} m^{-2}$	selectivity to $N_2^{b}$ (%)	$rate^{c}/10^{-6} \text{ mol min}^{-1} \text{ m}^{-2}$	
LaCoO <sub>3</sub>	3.1	13 (14)	4.1	
LaFeO	1.4	15 (59)	10.9	
LaMnO <sub>3</sub>	0.6	8 (7)	1.8	
LaCrO	0.3	13 (13)		
LaNiO	0.1	7 (7)		
$La_0 Sr_0 CoO_3$	1.3	13 (11)		
$La_{0.6}Sr_{0.4}CoO_3$	0.6	11 (12)		
$La_{0.9}Sr_{0.1}FeO_3$	1.0	8 (19)	6.2	
$La_{0.6}Sr_{0.4}MnO_3$	0.5	7 (9)		

<sup>*a*</sup> Estimated from the rate equation, -d[CO]/dt = k[CO][NO]. <sup>*b*</sup> The numbers in parentheses are the selectivities to N<sub>2</sub> after 60 min. <sup>*c*</sup> Estimated from the equation,  $-d[CO]/dt = -d[N_2O]/dt = k[N_2O]$ .



**Fig. 1** Time courses for the reaction between CO and NO over  $LaCoO_3$  (a),  $LaFeO_3$  (b) and  $La_{0.6}Sr_{0.4}CoO_3$  (c) at 573 K. NO,  $\bigcirc$ ; N<sub>2</sub>,  $\triangle$ ; N<sub>2</sub>O,  $\square$ ; CO,  $\blacksquare$ ; CO<sub>2</sub>,  $\blacktriangle$ . Broken and dotted lines represent the amounts of CO and NO in the second runs, respectively. Weight of catalysts, 50 mg

equation -d[CO]/dt = k[CO][NO]. The rate and the initial selectivity to N<sub>2</sub> are summarized in Table 2. The rate decreased monotonically with increase in the Sr<sup>2+</sup> content [ $\bigcirc$  in Fig. 2(*a*) and  $\bigcirc$ ,  $\triangle$  and  $\square$  in Fig. 2(*b*)] in contrast to the great or slight increase observed for the catalytic activity of La<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3</sub> for the C<sub>3</sub>H<sub>8</sub>-O<sub>2</sub> reaction<sup>10</sup> [ $\blacktriangle$  in Fig. 2(*a*)] or NO decomposition<sup>23</sup> [ $\blacksquare$  in Fig. 2(*a*)], respectively.

#### Reaction between N<sub>2</sub>O and CO

The products detected by gas chromatography were  $N_2$  and  $CO_2$ . The balances of nitrogen and carbon were close to 100% in accordance with the reaction  $N_2O + CO \rightarrow N_2 + CO_2$ . The initial rapid CO uptake in the first run that was

**Table 3** Change in the non-stoichiometry ( $\delta$ ) during the reaction between NO and CO over La<sub>1-x</sub>Sr<sub>x</sub>MO<sub>3- $\delta$ </sub> (M = Co, Mn, Fe, Cr; x = 0-0.4) at 573 K

catalyst	$\Delta \delta^a$	δ <sup>a</sup>	average valency of B-site ion <sup>b</sup>
LaCoO <sub>3</sub>	0.00	0.00	3.0
La <sub>0</sub> Sr <sub>0</sub> CoO <sub>3</sub>	0.05	0.05-0.06	3.1
$La_0 Sr_0 CoO_3$	0.10	0.15	3.1
LaMnO <sub>3</sub>	0.02	-0.10	3.2
$La_0 Sr_0 MnO_3$	-0.03	-0.01	3.4
LaFeO,	-0.01	-0.01	3.0
La <sub>0</sub> Sr <sub>0</sub> FeO	0.01	0.01	3.1
LaČrO <sub>3</sub>	-0.03		

<sup>a</sup>  $\Delta\delta$ , the increase in  $\delta$  during the CO-NO reaction, estimated from the oxygen balance in the CO-NO reaction.  $\delta$ , sum of  $\Delta\delta$  in this table and  $\delta$  in Table 1 (see text). <sup>b</sup> Calculated from  $\delta$  in this table.



Fig. 2 Effects of  $Sr^{2+}$  substitution on the catalytic activity of perovskite-type mixed oxides. (a) Changes in the catalytic activity of  $La_{1-x}Sr_xCoO_3$  for  $C_3H_8-O_2(\triangle)$ ,<sup>10</sup> NO decomposition ( $\blacksquare$ )<sup>23</sup> and CO-NO ( $\bigcirc$ , this work) reactions. The catalytic activity of  $LaCoO_3$  for each reaction was taken as unity. (b) Changes in the catalytic activity for the CO-NO reaction at 573 K.  $\bigcirc$ ,  $\Box$  and  $\triangle$  are the activities of  $La_{1-x}Sr_xCoO_3$ ,  $La_{1-x}Sr_xMnO_3$  and  $La_{1-x}Sr_xFeO_3$ , respectively

**Table 4** Rates of the reaction between CO and O<sub>2</sub> at 473 K

catalyst	$rate^{a}/10^{-6} mol min^{-1} m^{-2}$
LaCoO <sub>3</sub>	8.4
LaFeO <sub>3</sub>	4.1
LaMnÕ <sub>3</sub>	8.1
LaCrO	1.1
LaNiO <sub>3</sub>	0.8

<sup>*a*</sup> Estimated from the equation, -d[CO]/dt = k[CO].

observed for the CO-NO reaction over  $La_{1-x}Sr_xCoO_3$ (x = 0.2, 0.4) catalysts was not observed in this case, and the rate changed little in the repeated runs. The total turnovers of more than 60 show that the reaction is catalytic. The concentration-time data for each catalyst are well reproduced by the equation  $-d[N_2O]/dt = k[N_2O] (= -d[CO]/dt)$ , which was reported by Krupay *et al.*,<sup>24</sup> where  $[N_2O]$ corresponds to the partial pressure of N<sub>2</sub>O. The rates are shown in Table 2.

### Reaction between CO and O<sub>2</sub>

As for the reaction between CO and  $O_2$  over LaMO<sub>3</sub> (M = Co, Mn, Fe, Cr, Ni) at 473 K, the balances of carbon and oxygen were close to 100% from the beginning, showing that the oxidation state of LaMO<sub>3</sub> (M = Co, Mn, Fe, Cr, Ni) catalysts change little during the reaction. Moreover, the rate also remained unchanged in the repeated runs. The concentration-time data for each catalyst followed the rate equation -d[CO]/dt = k[CO], which was reported by Yao.<sup>25</sup> The rates are shown in Table 4.

# Discussion

**Reaction Scheme** 

Two possible reaction mechanisms have been proposed for the CO–NO reaction.<sup>2.4</sup> (a)  $N_2$  is formed through  $N_2O$ according to the following equations:

$$2NO + CO \rightarrow N_2O + CO_2 \tag{1}$$

$$N_2O + CO \rightarrow N_2 + CO_2 \tag{2}$$

(b)  $N_2$  is formed directly from CO and NO:

$$NO + CO \rightarrow 1/2N_2 + CO_2 \tag{3}$$

The fact that a large amount of N<sub>2</sub>O was formed from the initial stage over LaMO<sub>3</sub> (M = Co, Mn, Fe, Cr, Ni) at 573 K favours the former mechanism, eqn. (1) and (2). Since N<sub>2</sub> was formed at 573 K over La<sub>1-x</sub>Sr<sub>x</sub>MO<sub>3</sub> (x = 0-0.4; M = Co, Mn, Cr, Ni) even at the initial stages there may be a contribution from eqn. (3). However, the contribution would be small because the amount of N<sub>2</sub> formed was much smaller than that of N<sub>2</sub>O. Therefore, the CO-NO reaction at 573 K proceeds mainly by the first mechanism [eqn. (1) and (2)].

The transformation of N<sub>2</sub>O to N<sub>2</sub> was observed for LaFeO<sub>3</sub> and La<sub>0.9</sub>Sr<sub>0.1</sub>FeO<sub>3</sub>, while the reaction was not significant for the other La<sub>1-x</sub>Sr<sub>x</sub>MO<sub>3</sub> (x = 0-0.4; M = Co, Mn, Cr, Ni) catalysts. The increase is due to the greater rates of the CO-N<sub>2</sub>O reaction for the former catalysts, as shown in Table 2.

### **Activity Pattern**

The nature of B-site ion is an important factor affecting the oxidation reactions over perovskite-type mixed oxides. For example, we have previously reported that the catalytic activities of  $LaMO_3$  (M = Fe, Co, Mn) for the oxidation of hydrocarbons are of a similar order of magnitude to those of the

oxides of the corresponding B-site metals, and that the catalytic properties reflect mainly the nature of B-site ions.<sup>10,15</sup> The dominance of B-site ions has also been pointed out by other investigators and explained in terms of the various properties of the B-site ion.<sup>26-30</sup> In agreement with the previous observation, the activity pattern for the CO-O<sub>2</sub> reaction found in the present work shows twin peaks at Co and Mn [Fig. 3(b)]. By contrast, an activity pattern with one peak at Co was found for the CO-NO reaction [Fig. 3(a)]. If one considers that CO is a common reactant for the two reactions, an idea emerges that the activation of NO is important for the CO-NO reaction and the activation of  $O_2$  for the CO-O<sub>2</sub> reaction. In accordance with this idea, similar patterns to that of the CO-O<sub>2</sub> reaction exist for the oxidation of propene<sup>26</sup> and isobutene<sup> $\tilde{3}1$ </sup> over LaMO<sub>3</sub>. Note also that single-metal oxides as well as LaMO<sub>3</sub> <sup>11,13,14</sup> showed activity patterns with twin peaks at Co and Mn for the  ${}^{16}\text{O}_2 - {}^{18}\text{O}_2$  exchange reaction as shown in Fig. 3(b),<sup>32</sup> which renders further support for this idea.

A parallel variation between the catalytic activity for the CO-NO reaction and the amount of NO adsorbed is present, as shown in Fig. 3(a). A similar parallel variation was also observed for  $La_{2-x}A'_xCu_{1-y}B'_yO_4$  (A' = Sr, Ce; B' = Al, Zr; x or y = 0-0.5) catalysts.<sup>19</sup> These facts support the suggestion that the change in the catalytic activity of  $LaMO_3$  (M = Co,



Fig. 3 Catalytic activities of LaMO<sub>3</sub> (M = Cr, Mn, Fe, Co, Ni) perovskites for the reactions between CO and NO at 573 K (a) or O<sub>2</sub> (b). (•) Catalytic activities for the reactions between CO and NO (a) and between CO and O<sub>2</sub> (b) at 473 K; ( $\blacksquare$ ) amount of NO irreversively adsorbed and LaMO<sub>3</sub> (a)<sup>3</sup> and the rate of isotopic exchange between <sup>16</sup>O<sub>2</sub> and <sup>18</sup>O<sub>2</sub> on a single-metal oxide (b),<sup>32</sup> respectively

### J. CHEM. SOC. FARADAY TRANS., 1992, VOL. 88

Mn, Fe, Cr, Ni) catalysts, shown in Fig. 3(*a*), is controlled by the ability of the B-site ion to activate NO.

# Effect of Sr<sup>2+</sup> Substitution

As shown in Table 3,  $LaCoO_3$ ,  $LaMnO_3$ ,  $LaFeO_3$ ,  $La_{0.6}Sr_{0.4}MnO_3$ , and  $La_{0.9}Sr_{0.1}FeO_3$  were reduced little, in contrast to  $La_{1-x}Sr_xCoO_3$  (x = 0.2, 0.4) catalysts. This is reasonable because  $La_{1-x}Sr_xCoO_3$  (x = 0.2, 0.4) catalysts were most readily reduced by CO.<sup>11-14</sup>

The valencies of B-site ions during the reaction were estimated using the  $\delta$  values at room temperature shown in Table 1, plus the  $\Delta\delta$  values shown in Table 3, assuming that the other elements were present as  $La^{3+}$ ,  $Sr^{2+}$  and  $O^{2-}$ . Although the temperatures of measurement were different, it has been reported that there is little difference in the valency (less than 0.1) of cobalt in  $La_{1-x}Sr_xCoO_3$  (x = 0-0.4) between room temperature and 573 K,<sup>12</sup> even though the amount of oxygen desorbed from  $La_{0.6}Sr_{0.4}CoO_3$  below 573 K in a temperature-programmed desorption experiment was the greatest among the catalysts listed in Table 1.<sup>11,13,14</sup> Therefore, the  $\delta$  value and valency shown in Table 3 may be very close to the corresponding values during the CO-NO reaction.

As shown in Fig. 2, the catalytic activity for the CO-NO reaction decreased with increasing  $Sr^{2+}$  content, while the valency of the B-site ion during the reaction was greater for the  $Sr^{2+}$ -substituted catalysts, as indicated in Table 3. It is known that NO<sup>-</sup> (adsorbed) more readily dissociates than neutral NO (adsorbed), and NO<sup>-</sup> is produced by the transfer of an electron from the metal ion to the antibonding orbital of NO. Therefore, the decrease of the catalytic activity for the CO-NO reaction upon  $Sr^{2+}$  substitution may be due to the decrease in electron donation caused by the increase in the oxidation state of cobalt. The acceleration of the reaction rate of La<sub>0.6</sub>Sr<sub>0.4</sub>CoO<sub>3</sub> in the second run (after reduction), as shown in Fig. 1(c), supports this idea, because this catalyst is in a less oxidized state.

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