Reactions of CO and NO over $La_{2-x}A'_xCu_{1-y}B'_yO_4$. A K_2NiF_4-Type Mixed Oxide

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Seven $La_{2-x}A'_xCu_{1-y}B'_yO_{4\pm\delta}$ (A' = Sr, Ce; B' = Al, Zr; x or y = 0–0.5) catalysts were prepared. It was demonstrated that the oxidation number of copper in the bulk and on the surface could be well controlled by the substitution of the constituent elements without change of the K_2NiF_4-type structure. For example, the average oxidation number of copper in the bulk, determined by iodometry, increased to 2.30 with Sr^{2+} substitution for La^{3+}, while it decreased to 1.65 with Zr^{4+} substitution for Cu^{2+}. The surface composition and the oxidation number of copper, which was estimated by the ratio of the satellite peak to main peak of Cu $2p_{3/2}$ and the Auger parameter, were close to those of the bulk. The reaction of NO and CO to give N_2 and CO_2 was carried out over these catalysts at 673 K in a recirculation system. It was found that the catalysts having an average oxidation number of copper close to 2 were most active for the reaction.

Introduction

A_2BO_4, which has the K_2NiF_4-type structure, consists of alternating layers of ABO_3 perovskite and AO rock salt.[1] It is possible to change the A- or B-site ions or substitute part of these ions with others of different valence ($A_{2-x}A'_xB_{1-y}B'_yO_4$), as was possible in the case of perovskite-type mixed oxides.[2,3] Therefore, it is possible to control the valence of transition metals at B-site ions, and hence these catalysts would be good models for the investigation of correlations between solid-state chemistry and catalytic properties.

The reaction of NO and CO is important for their removal from exhaust gas,[4] and Cu-containing oxides are active catalysts for this reaction.[5-8] Several schemes have been proposed for the reaction of NO and CO.[7,9-11] For example, London and Bell have reported that the reaction proceeded by a redox cycle of Cu^0 and Cu^+,[7] while Force and Ayen analyzed their kinetic data by assuming that the reaction proceeded between adsorbed CO and NO.[9] The adsorption behavior of NO and CO has been observed to change with the valences of copper; the amount of CO adsorption on Cu^{2+}–Y zeolite was much smaller than that on Cu^+–Y zeolite, and Cu^{2+} was reduced to form $Cu^+(NO^+)$ when NO was adsorbed on Cu^{2+}–Y zeolite.[12,13] Therefore, we were interested in investigating the possibility of a correlation between the valence of copper and the catalytic activity for the reaction between NO and CO, using catalysts for which the valences of copper are well defined. We have previously reported that the valence of the transition metal was controlled by Sr^{2+} substitution for La^{3+} in $LaCoO_3$, $LaMnO_3$, $LaFeO_3$,[14-18] and La_2CoO_4[19] and found a very high catalytic activity for oxidation in several cases.

In the present work, we controlled the valence of copper in La_2CuO_4 by substituting Sr or Ce for La, or Al or Zr for Cu, i.e., $La_{2-x}A'_xCu_{1-y}B'_yO_4$ (A' = Sr, Ce; B' = Al, Zr; x or y = 0–0.5). After the valence and composition were measured, we studied these materials as catalysts for the reaction between NO and CO and investigated the correlation between catalytic activity and the valence of copper.

Experimental Section

Catalyst Preparation. The $La_{2-x}A'_xCu_{1-y}B'_yO_4$ compounds were prepared from metal acetates as has been described previously.[14] 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 1123–1273 K for 5–10 h. The actual composition may be $La_{2-x}A'_xCu_{1-y}B'_yO_{4\pm\delta}$ (δ: nonstoichiometry), but in this paper they will be designated as $La_{2-x}A'_xCu_{1-y}B'_yO_4$.

The average oxidation numbers of the copper in the samples were chemically determined by an iodometric titration.[20,21] Portions were dissolved without pretreatment in dilute aqueous hydrochloric acid with an appropriate amount of KI. The amount of iodine formed was titrated with sodium thiosulfate solution. The nonstoichiometry of the sample was calculated on the assumption that copper was present as either a mixture of Cu^{2+} and Cu^{3+} or a mixture of Cu^+ and Cu^{2+}, and other elements were present as La^{3+}, Sr^{2+}, Ce^{4+}, Al^{3+}, Zr^{4+}, and O^{2-}, respectively.

Powder X-ray diffraction patterns were recorded on a powder X-ray diffractometer (Rigaku Denki, Rotaflex, RU-200) by using Cu Kα radiation. The surface areas measured by the BET method (N_2 adsorption) varied from 0.5 $m^2 \cdot g^{-1}$ for $La_{1.9}Ce_{0.1}CuO_4$ to 10.5 $m^2 \cdot g^{-1}$ for $La_2Cu_{0.8}Zr_{0.2}O_4$.

Adsorption of NO. The catalysts (ca. 300 mg) were evacuated at 773 K for 1 h and then exposed to NO gas (ca. 15 kPa) at 303 K. The amount of NO uptake was determined by the pressure

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Table I. Structure, Surface Area, Amount of NO Adsorbed, Average Oxidation Number of Copper, and Nonstoichiometry

catalyst	calcination temp, K	calcination time, h	structure	surface area, $m^2 \cdot g^{-1}$	amt of NO adsorbed, 10^{-6} $mol \cdot m^{-2}$ total[c]	amt of NO adsorbed, 10^{-6} $mol \cdot m^{-2}$ irr[d]	ox. no. of Cu[b]	δ[a]
$La_2Cu_{0.8}Zr_{0.2}O_4$	1123	5	K_2NiF_4 (O[e])	10.5	2.0	1.2	1.60	0.04
$La_2Cu_{0.8}Al_{0.2}O_4$	1123	5	K_2NiF_4 (T_e)	4.6			1.88	0.05
$La_{1.8}Ce_{0.2}CuO_4$	1123	5	K_2NiF_4 (O) + CuO(trace)	3.1	14.7	8.8	1.97	0.09
$La_{1.9}Ce_{0.1}CuO_4$	1123	5	K_2NiF_4 (O)	0.5				
La_2CuO_4	1123	5	K_2NiF_4 (O)	1.2	12.6	7.8	2.00	0.00
$La_{1.8}Sr_{0.2}CuO_4$	1173	10	K_2NiF_4 (T)	2.8	13.5	10.0	2.10	−0.05
$La_{1.5}Sr_{0.5}CuO_4$	1273	5	K_2NiF_4[f] (T)	1.2	3.5	3.5	2.30	−0.10

[a] δ in $La_{2-x}A'_xCu_{1-y}B'_yO_{4+\delta}$. [b] Average oxidation number of copper. [c] Total amount of NO adsorbed at 303 K. [d] Amount of irreversible adsorption of NO at 303 K. [e] Deduced from the XRD lines at about $2\theta = 33°$: O, orthorhombic; T, tetragonal. [f] The half-widths of these XRD lines were considerably broader than those of the others.

decrease measured with a Baratron pressure gauge, giving the total amount of NO adsorbed. After evacuation of the sample for 1 h at 303 K, the amount of NO uptake was measured again. This was used to determine the amount of reversible adsorption of NO. The amount of irreversible adsorption of NO was the difference between the total amount of NO uptake and the amount of reversible adsorption of NO.

Reaction. The reaction of NO and CO was carried out in a closed circulation system (ca. 190 cm^3). The catalysts (20–200 mg) were mixed with inert SiC (250 mg) to prevent an undesirable temperature rise. The procedures were as follows: After pretreatment in O_2 (ca. 13 kPa) at 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 (NO:CO = 1:1). Small portions of gases were taken from the system intermittently by using a glass sampler and analyzed with a gas chromatograph directly connected to the system.

X-ray Photoelectron Spectroscopy Measurement. XPS and X-ray-induced Auger measurements were made with a JEOL JPS-90SX spectrometer using a Mg Kα source (1253.6 eV). The powdered samples were pressed into disks, loaded into the spectrometer, and evacuated at 298 K overnight, prior to the XPS measurements.

The surface composition of the catalyst was calculated from eq 1. For the elements a and b, the relationship

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

where N is the peak intensity (integrated), n, atoms per unit volume, σ, ionization cross section, λ, mean free path of electron, and S, instrumental factor, was proposed.[18,22a] The peak areas of La 4d, Sr 3d, Cu 3p, Zr 3d, and Al 2s, including the satellite peak, were used for N, while the values of σ were taken from the literature.[22b] λS was assumed in this study to be proportional to (kinetic energy)$^{0.75}$, as has been confirmed in this apparatus. The binding energies were corrected by using the value of 285.0 eV (usually 284.4–285.0 eV) for the C 1s peak resulting from carbon contamination according to the literature.[18,22c,23]

Results

Structures and Nonstoichiometry of Catalysts. The crystal structures, surface areas, nonstoichiometry, and the average oxidation numbers of the copper in the catalysts are summarized in Table I. The X-ray diffraction (XRD) patterns of Sr-, Ce-, Al-, and Zr-substituted catalysts showed only the K_2NiF_4-type structure except that a very weak line due to CuO was observed in the case of $La_{1.8}Ce_{0.2}CuO_4$. The structures of La_2CuO_4, $La_{1.9}Ce_{0.1}CuO_4$, $La_{1.8}Ce_{0.2}CuO_4$, and $La_2Cu_{0.8}Zr_{0.2}O_4$ were orthorhombic, while those of $La_{1.8}Sr_{0.2}CuO_4$, $La_{1.5}Sr_{0.5}CuO_4$, and $La_2Cu_{0.8}Al_{0.2}O_4$ were tetragonal.

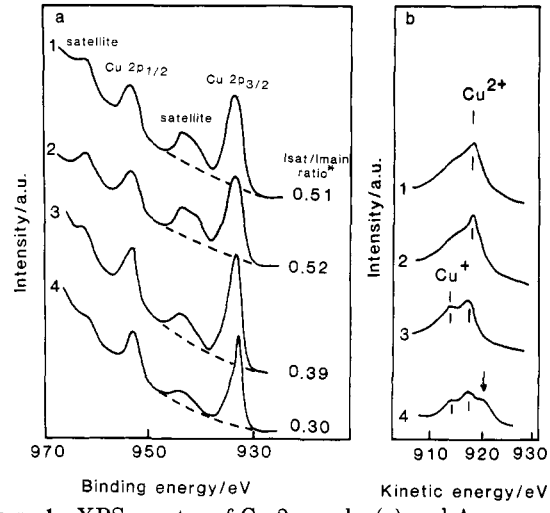

Figure 1. XPS spectra of Cu 2p peaks (a) and Auger spectra of Cu L_3VV peaks (b). Spectra 1, 2, 3, and 4 correspond to those of $La_{1.8}Sr_{0.2}CuO_4$, La_2CuO_4, $La_2Cu_{0.8}Al_{0.2}O_4$, and $La_2Cu_{0.8}Zr_{0.2}O_4$, respectively. Broken lines indicate the background spectra used for the calculation of the I_{sat}/I_{main} ratio of Cu $2p_{3/2}$. The asterisk designates the I_{sat}/I_{main} ratio of Cu $2p_{3/2}$. The feature designated by the arrow shown in the spectrum of $La_2Cu_{0.8}Zr_{0.2}O_4$ in Figure 1b is probably due to Zr^{4+} and not to Cu^0. (No XRD line due to Cu^0 was observed.)

The average oxidation number of copper in the as-prepared samples increased from 2.00 for La_2CuO_4 up to 2.30 with Sr^{2+} substitution for 25% of La^{3+} ions and decreased with Al^{3+}, Zr^{4+}, or Ce^{4+} substitution for Cu^{2+}. Here, an oxidation number higher than 2 is due to the presence of either Cu^{3+} or a positive hole at oxygen as discussed later. The composition became oxygen-rich upon Al^{3+}, Ce^{4+}, and Zr^{4+} substitutions and oxygen-deficient with Sr^{2+} substitution. When La_2CuO_4 was treated in O_2 (13 kPa) at 673 K for 1 h and then evacuated at the same temperature for 15 min, the average oxidation number of copper was 1.99. This is almost the same as the average oxidation number of La_2CuO_4 without this pretreatment.

NO Adsorption. The amounts of NO adsorption at 303 K (both total and irreversible) are also shown in Table I. Both showed maxima at the average oxidation number of about 2. A similar trend was also observed for the reversible adsorption of NO. When the density of copper ion was assumed to be 2.6×10^{18} ions$\cdot m^{-2}$, the total amount of NO adsorbed on La_2CuO_4 was about 3 times greater than that of copper ion on the surface, as in the previous cases of $LaFeO_3$ or $LaMnO_3$.[23] These data are for the catalysts preevacuated at 773 K. When La_2CuO_4 was treated in O_2 (13 kPa) at 673 K for 1 h followed by evacuation at the same temperature for 15 min, the total amount of NO uptake increased from 12.6×10^{-6} to 13.0

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Table II. Surface Composition of the $La_{2-x}A'_xCu_{1-y}B'_yO_4$ (A' = Sr; B' = Al, Zr; x = 0, 0.2; y = 0, 0.2)

catalyst	surface comp La	surface comp Cu	surface comp A' or B'	bulk comp[a] La	bulk comp[a] Cu	bulk comp[a] A' or B'
$La_2Cu_{0.8}Zr_{0.2}O_4$	0.72	0.17	0.12	0.67	0.27	0.07
$La_2Cu_{0.8}Al_{0.2}O_4$	0.68	0.23	0.09	0.67	0.27	0.07
La_2CuO_4	0.66	0.34	0	0.67	0.33	0
$La_{1.8}Sr_{0.2}CuO_4$	0.67	0.27	0.07	0.60	0.33	0.07

[a] These values were calculated from the quantity of the starting materials.

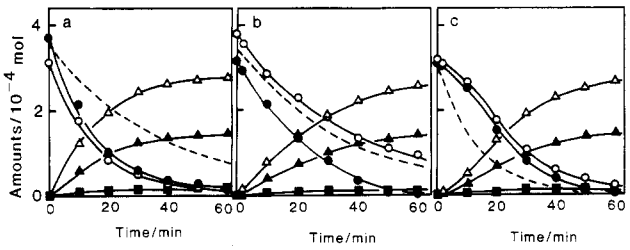

Figure 2. Time courses for the reaction of NO and CO over La_2CuO_4 (a), $La_{1.8}Sr_{0.2}CuO_4$ (b), and $La_{1.5}Sr_{0.5}CuO_4$ (c) at 673 K. ●, ▲, ■, ○, and △ correspond to the amounts of NO, N_2, N_2O, CO, and CO_2, respectively. Dotted lines represent the amounts of CO in the second runs. Weights of the catalysts were 50, 20, and 50 mg for La_2CuO_4, $La_{1.8}Sr_{0.2}CuO_4$, and $La_{1.5}Sr_{0.5}CuO_4$, respectively.

$\times 10^{-6}$ mol·m^{-2}. There was little change in NO uptake after two successive pretreatments.

Surface Properties of Catalysts. X-ray photoelectron spectra of the Cu 2p region and the X-ray-induced Cu L_3VV Auger peak are shown in Figure 1, parts a and b, respectively. The XPS spectra of the catalysts have intense shake-up satellite peaks on the high binding energy sides of the Cu $2p_{1/2}$ and Cu $2p_{3/2}$ peaks. The assignment leaves room for discussion,[39] but the assignment does not influence the discussion in this paper. The satellites can be a measure of the oxidation state of copper as discussed in the Discussion. The Cu $2p_{3/2}$ binding energies decreased as follows: $La_{1.8}Sr_{0.2}CuO_4$ (933.8 eV) ≈ La_2CuO_4 (933.8 eV) > $La_2Cu_{0.8}Al_{0.2}O_4$ (933.6 eV) > $La_2Cu_{0.8}Zr_{0.2}O_4$ (933.4 eV). The Cu $2p_{3/2}$ binding energy of $La_{1.8}Sr_{0.2}CuO_4$ and La_2CuO_4 was in general agreement with those of $La_{1.85}Sr_{0.15}CuO_4$[24] (933.6 eV) and $La_{1.4}Sr_{0.6}CuO_4$[25] (934.3 eV) and a little lower than Cu^{2+} in the channels of Na–A, –X, and –Y zeolites[26] (936.0 eV). The intensity ratios of the satellite peak to the main peak, I_{sat}/I_{main}, of Cu $2p_{3/2}$ of La_2CuO_4, $La_2Cu_{0.8}Al_{0.8}O_4$, and $La_2Cu_{0.8}Zr_{0.2}O_4$ were 0.52, 0.39, and 0.30, respectively.

Only one L_3VV Auger peak (ca. 917 eV) due to Cu^{2+} was observed for $La_{1.8}Sr_{0.2}CuO_4$ and La_2CuO_4, while a Cu^+ L_3VV Auger peak was also observed for $La_2Cu_{0.8}Al_{0.2}O_4$ and $La_2Cu_{0.8}Zr_{0.2}O_4$ on the lower kinetic energy side of Cu^{2+} peak as discussed in the Discussion.

The surface compositions of the metallic elements calculated from the integrated intensity of the XPS peaks are summarized in Table II, together with those of the bulk, which were calculated from the quantities of the starting materials. The surface compositions generally agreed with the bulk compositions, except for $La_2Cu_{0.8}Zr_{0.2}O_4$, for which the surface Cu content was significantly smaller.

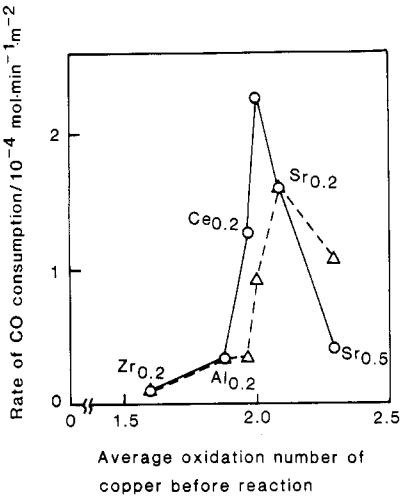

Figure 3. Correlation between the rate of the reaction of NO and CO and the average oxidation number of copper. The rate is the average rate of CO consumption for the first 10 min. The average oxidation number of copper was obtained before the reaction (see Table I). ○ and △ correspond to the rates in the first and third runs, respectively. $Zr_{0.2}$, $Al_{0.2}$, $Ce_{0.2}$, $Sr_{0.2}$, and $Sr_{0.5}$ represent the rates of $La_2Cu_{0.8}Zr_{0.2}O_4$, $La_2Cu_{0.8}Al_{0.2}O_4$, $La_{1.8}Ce_{0.2}CuO_4$, $La_{1.8}Sr_{0.2}CuO_4$, and $La_{1.5}Sr_{0.5}CuO_4$, respectively. ○ and △ without notation represent the rates for La_2CuO_4.

Reaction of NO and CO. Figure 2 shows the time courses of the reaction of NO and CO over La_2CuO_4 (a), $La_{1.8}Sr_{0.2}CuO_4$ (b), and $La_{1.5}Sr_{0.5}CuO_4$ (c) at 673 K. The main products were also N_2 and CO_2 for the other catalysts. The selectivity to N_2O was 10–20%. When the reaction was repeated, the rate varied in different ways depending on the catalysts, although the selectivity to N_2 did not change significantly.

In the case of La_2CuO_4 (Figure 2a), the reaction proceeded rapidly in the initial stage of the first run, and deactivation was observed (the broken line indicates a decrease in the amount of CO in the second run). Deactivation was also observed for $La_{2-x}Ce_xCuO_4$ (x = 0.1, 0.2).

The activity and XRD patterns remained unchanged for $La_{1.8}Sr_{0.2}CuO_4$ (Figure 2b), $La_2Cu_{0.8}Al_{0.2}O_4$, and $La_2Cu_{0.8}Zr_{0.2}O_4$. The concentration–time data for $La_{1.8}Sr_{0.2}CuO_4$ were approximately reproduced by the equation $-d[NO]/dt = k[CO][NO]$, which was reported by Force and Ayen,[9] where t, k, [CO], and [NO] correspond to time, the rate constant, and the concentrations of CO and NO, respectively. In contrast, for $La_{1.5}Sr_{0.5}CuO_4$ (Figure 2c) an induction period was observed in the first run and an increase in activity was observed in repeated runs.

The time courses of $La_{2-x}Ce_xCuO_4$ (x = 0.1, 0.2), La_2CuO_4, and $La_{1.5}Sr_{0.5}CuO_4$ in the third runs were similar to those in the fourth runs. The total turnover (i.e., the number of CO reacted per number of copper ions contained in the whole catalyst) for runs 1–4 was greater than 7. These results show that the reaction is catalytic. In this work, the activity at the "stationary state" was defined by the average rate for the first 10 min in the third run. The initial activities were obtained when the used catalysts were treated in O_2 at 673 K. After O_2 treatment, the catalytic activity increased in the case of the used and deactivated La_2CuO_4, while it decreased in the case of $La_{1.5}Sr_{0.5}CuO_4$.

The average rates for the first 10 min in the first and third runs are plotted against the average oxidation number of copper, which was measured before the reaction, in Figure 3. These data were reproducible in two or more separate determinations. It is noteworthy that the rate in the first run (circles) reached a maximum when the

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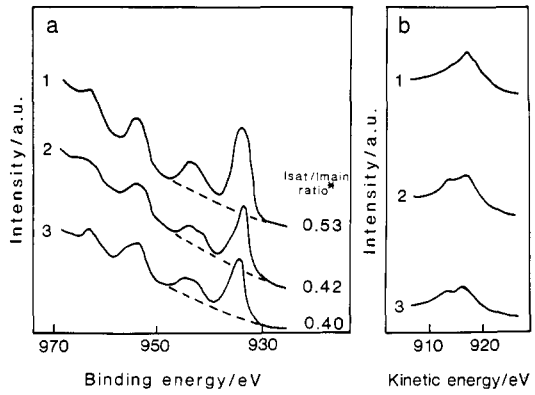

Figure 4. XPS spectra of Cu 2p peaks (a) and Auger spectra of Cu L_3VV peaks (b) after the reaction of NO and CO. Spectra 1, 2, and 3 correspond to those of $La_{1.8}Sr_{0.2}CuO_4$, La_2CuO_4, and $La_2Cu_{0.8}Al_{0.2}O_4$, respectively. Broken lines indicate the background spectra used for the calculation of the I_{sat}/I_{main} ratio of Cu $2p_{3/2}$. The asterisk designates the I_{sat}/I_{main} ratio of Cu $2p_{3/2}$.

oxidation number of copper was about 2. This trend is similar to that observed for the amount of NO adsorbed. Similar trends were also observed when the rates were normalized by the total and irreversible amounts of NO adsorbed. The maximum for the third run (triangles, steady-state activity) shifted to higher oxidation number (2.10).

Figure 4 shows the XPS spectra of $La_{1.8}Sr_{0.2}CuO_4$, La_2CuO_4, and $La_2Cu_{0.8}Al_{0.2}O_4$. If these are compared with the spectra shown in Figure 1a, it is noted that I_{sat}/I_{main} of Cu $2p_{3/2}$ decreased from 0.52 to 0.42 for La_2CuO_4 after it was used in the reaction. Further, the L_3VV Auger peak due to Cu^+ appeared for La_2CuO_4 in addition to Cu^{2+} (compare spectrum 2 in Figure 4b and spectrum 2 in Figure 1b). On the other hand, little change after use was observed for $La_{1.8}Sr_{0.2}CuO_4$ and $La_2Cu_{0.8}Al_{0.2}O_4$: I_{sat}/I_{main} of Cu $2p_{3/2}$ for $La_{1.8}Sr_{0.2}CuO_4$ and $La_2Cu_{0.8}Al_{0.2}O_4$ were 0.51 vs 0.53 and 0.39 vs 0.40, respectively, before vs after use, and the binding energies of Cu $2p_{3/2}$ after use for the reaction were 933.7 and 933.6 eV for $La_{1.8}Sr_{0.2}CuO_4$ and $La_2Cu_{0.8}Al_{0.2}O_4$, respectively, as compared with 933.8 and 933.6 eV before use.

Discussion

Structure and Valence Control of the Bulk Catalyst. A tolerance factor t is defined for A_2BO_4 oxides as

$$t = r(\text{A–O})/2^{1/2}r(\text{B–O}) \quad (2)$$

where r(A–O) and r(B–O) are distances obtained from ionic radii.[2] The value of t determines the stability of tetragonal or orthorhombic structures. For example, the tetragonal K_2NiF_4-type structure is usually stable in the range $1.02 > t > 0.85$. It has been reported that the structure of La_2CuO_4 becomes orthorhombic because the value (t = 0.85) is equal to the lower limit.[2] This agrees with the present results. When Sr^{2+} was substituted for La^{3+} in La_2CuO_4, the structure changed from orthorhombic to tetragonal (Table I). The change can be explained by an increase of the average radius of the A-site ion, in other words, the increase of the t value. Similar changes in the structures were observed for Sr^{2+}-substituted samples[27] and Ba^{2+}-substituted samples.[28] The fact that the structure of $La_2Cu_{0.8}Al_{0.2}O_4$ is tetragonal can also be explained by the increase of the t value. On the other hand, $La_{1.9}Ce_{0.1}CuO_4$ and $La_{1.8}Ce_{0.2}CuO_4$ maintained the orthorhombic structures, since the smaller ionic radii of the Ce^{4+} introduced decreases the t values. $La_2Cu_{0.8}Zr_{0.2}O_4$ also maintained the orthorhombic structure. This is probably because the ionic radii of Zr^{4+} is close to that of Cu^{2+} and only slightly changes the t value.

It has been noted that the electrical conductivity of La_2CuO_4 is very sensitive to various treatments and La_2CuO_4 tends to be nonstoichiometric.[29,30] However, as shown in Table I the average valence of copper in La_2CuO_4 was 2.00 and there is no oxygen vacancy in the bulk. This result was consistent with that reported by Nguyen et al.[31] When Sr^{2+} is partially substituted for La^{3+} in La_2CuO_4, the average oxidation number of copper increases up to 2.30 for $x = 0.5$, and the oxygen vacancy is formed for $x \geq 0.2$ as shown in Table I. These changes in stoichiometry closely resemble that of $La_{1-x}Sr_xCoO_3$[15] and partially those of $La_{2-x}Sr_xNiO_4$,[32] $La_{1-x}Sr_xMnO_3$,[17] and $La_{2-x}Sr_xCoO_4$.[19] In the latter cases, the composition changed from oxygen-rich to stoichiometric and then became oxygen-deficient as x increased. Those differences may be understood if one considers the relative stability of each B-site ion in the higher oxidation state and normal oxidation state in each structure. In contrast to the Sr^{2+} substitution, Ce^{4+} substitution for La^{3+} decreased the oxidation number of copper below 2.00 and the compositions became oxygen-rich. When Al^{3+} or Zr^{4+} was partially substituted for Cu^{2+}, greater changes were observed. For example, the Al^{3+} substitution resulted in $La_2Cu^{2+}{}_{0.7}Cu^{+}{}_{0.1}Al_{0.2}O_{4.05}$. The composition would be represented by $La_2Cu^{2+}{}_{0.6}Cu^{+}{}_{0.2}Al_{0.2}O_4$ if the Al^{3+} substitution caused only partial reduction of copper ($Cu^{2+} \rightarrow Cu^+$). So, the 7% increase in positive charge of copper is compensated for by excess oxygen.

As discussed above, the valence of copper can be well controlled by the substitution of the constituent elements without change of the K_2NiF_4-type structure.

Surface Properties. The cuprous compounds show no satellite peaks for the Cu 2p peaks as described before, while cupric compound have intense satellite peaks on the Cu 2p peaks.[8,25] The I_{sat}/I_{main} ratio of Cu $2p_{3/2}$ can be used as a measure of the valence of the copper. The ratio for La_2CuO_4 was 0.52, which was nearly equal to the reported value for CuO (0.53).[33] Here, we assume that the ratio is 0.53 for Cu^{2+} and that the intensity ratio is proportional to the fraction of Cu^{2+}. Then we can obtain from the observed ratio the oxidation state of copper to be 1.98, 1.74, and 1.57 for La_2CuO_4, $La_2Cu_{0.8}Al_{0.2}O_4$, and $La_2Cu_{0.8}Zr_{0.2}O_4$, respectively. These values were in general agreement with those for the bulk shown in Table I, and the order was the same. The 2-D chemical-state plots[34] of Cu $2p_{3/2}$ binding energy and the kinetic energy of L_3VV Auger peak of La_2CuO_4 also indicated that the oxidation state of copper in La_2CuO_4 is close to 2.00.

As for $La_{2-x}Sr_xCuO_4$, copper in the bulk is considered to be in a mixed valence state of Cu^{2+} and Cu^{3+}. But the position and width of the Cu $2p_{1/2}$ and Cu $2p_{3/2}$ peaks

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shown in Figure 1a were close to those of CuO, and no peak due to Cu^{3+} was observed as reported in the literature.[35] This phenomenon has been explained by the assumption that doped holes are predominantly O 2p-like rather than Cu 3d-like.[36] So, it is probable that the oxidation numbers of copper on the surface of $La_{2-x}Sr_xCuO_4$ (x = 0.2, 0.5) are close to those in the bulk as in the case of La_2CuO_4, $La_2Cu_{0.8}Al_{0.8}O_4$, and $La_2Cu_{0.8}Zr_{0.2}O_4$.

Therefore, in the case of the present work, the bulk properties well reflected those of the surface for both A-site and B-site substitutions. These results were also supported by the general agreement of the composition between the bulk and the surface except for the Zr^{4+}-substituted sample (Table II). It is probable in the latter case that ZrO_2 (or CuO) was segregated on the surface to a certain extent.

Reaction of NO and CO. The average oxidation numbers of copper in La_2CuO_4 that had been treated in O_2 (ca. 13 kPa) for 1 h at 673 K and subsequently evacuated at the same temperature for 15 min was 1.99, which was only slightly different from that observed without pretreatment (2.00, Table I). Further, the amount of NO adsorbed, which changes with the oxidation number of copper,[23] only slightly changed for La_2CuO_4 after two successive treatments. These results show that the average oxidation number of copper is little changed by the treatment prior to the NO–CO reaction. No change in nonstoichiometry below 1073 K has also been reported for $La_{1.84}Sr_{0.16}CuO_4$.[37] Therefore, the oxidation numbers plotted on the abscissa of Figure 3 may be considered to be the values just before the NO–CO reaction. If one considers the general agreement of the chemical state between the bulk and the surface as discussed above, it is probable that the figures on the abscissa in Figure 3 also represent the oxidation numbers of copper on the surface just before reaction. On the basis of the above discussion, the correlation for the first run in Figure 3 may be considered to be for the initial oxidation state of copper and the catalytic activity. Hence, it is concluded that the $La_{2-x}A'_xCu_{1-y}B'_yO_4$ catalysts are most active for the reaction of NO and CO when the formal charge of copper is in the +2 state.

Next we briefly discuss the reason Cu^{2+} is active for the reaction of NO and CO. It was reported that Cu^{2+} was reduced to the form $Cu^+(NO^+)$ when NO was adsorbed on Cu^{2+}–Y zeolite,[12] that the rate of NO–CO reaction over Rh catalysts increased with the increase of the amount of $NO^{\delta+}$ detected by IR,[38] and that CO was preferentially adsorbed on Cu^+.[13] It was also reported that reducing agents such as CO promoted adsorption and dissociation of NO over Co/SiO_2.[10] If these results are taken into account, it is probable that NO adsorbs on Cu^{2+} to form $Cu^+(NO)^+$ and the dissociation of NO is promoted with the coexistence of CO. Consequently, Cu^{2+} is active for the reaction of NO and CO. The fact that the amount of NO adsorbed showed a maximum at the average oxidation number of about 2 is consistent with the above idea. It has been suggested in the literature that Cu^+ or Cu^0 are the catalytically active sites for the NO–CO reactions.[7] But Teranishi et al. showed that Cu^{2+} is more active for the same reaction than Cu^+ and Cu^0.[8] The present result is not consistent with the former results.[7] Although the reason for this difference is not obvious, it must be considered that the structures of the catalysts are entirely different and the catalysts in the present work are more uniform. If one considers that Cu^{2+} is more stable than Cu^+ in the octahedral sites of the K_2NiF_4-type structure and the reaction proceeds by the mechanism mentioned above (Cu^{2+}–Cu^+ cycle), it may be reasonable that the oxidation number of copper during the reaction is close to +2.

The average oxidation number of copper at the maximum rate of reaction was different for the third runs as shown in Figure 3, consistent with the altered catalytic activity compared with the initial stage of the first run. This is most likely due to a change of the oxidation state of copper during the NO–CO reaction as described below. The copper atoms on the surface of La_2CuO_4 and $La_{1.5}Sr_{0.5}CuO_4$ were actually reduced during the reaction, as is supported by the following facts: (1) When the oxidation number of copper on the surface of La_2CuO_4 was estimated from the I_{sat}/I_{main} ratio of Cu $2p_{3/2}$ (see Figure 4), it decreased from 1.98 to 1.79 during reaction. On the other hand, the oxidation numbers of copper similarly estimated (Figure 4) for $La_{1.8}Sr_{0.2}CuO_4$ and $La_2Cu_{0.8}Al_{0.2}O_4$, which were not deactivated, only slightly changed during the reaction. (2) The activity returned to the initial value when La_2CuO_4, which had been deactivated by repeated runs, was treated with O_2. Moreover, $La_{1.5}Sr_{0.5}CuO_4$, which showed an increase of activity after repeated runs, was deactivated after O_2 treatment.

The increase or the decrease of the oxidation number during the NO–CO reaction was not simply correlated with whether the initial oxidation number was larger or smaller than 2. The oxidation number is determined, for example, for Sr^{2+} substitution, by the reaction

$$La_{2-x}Sr_xCu^{2+}{}_{1-x}Cu^{3+}{}_xO_4 \rightleftarrows La_{2-x}Sr_xCu^{2+}{}_{1-x+2\delta}Cu^{3+}{}_{x-2\delta}O_{4-\delta} + \delta/2O_2 \quad (3)$$

(Cu^{3+} could be a positive hole at oxygen). Therefore, the stable oxidation states of copper under the reaction conditions may vary with x, as the initial oxidation number did, and cannot simply be predicted. The present results indicate that the stable oxidation number during the reaction was close to 2.1 for x = 0.2 and smaller than 2 and 2.3 for x = 0 and 0.5, respectively.

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