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Reaction between Nitrogen Monoxide and Carbon Monoxide over Superconducting Bi-Sr-Ca-Cu and Related Mixed Oxides

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Synopsis. Bi-Sr-Ca-Cu-O mixed oxides having a $Bi_2Sr_2CaCu_2O_y$ structure were very active for reactions between nitrogen monoxide and carbon monoxide among the prepared catalysts having perovskite and related structures.

Nitrogen oxides (NO_x) from vehicle engines and industrial boilers cause air pollution and acid rain, and their removal or suppression is an urgent social necessity.[1)] The reductions of nitrogen monoxide (NO) by carbon monoxide (CO) and hydrocarbon are the major reaction pathways for the removal of NO_x from automobile exhaust.[2)]

It has been reported that superconducting $YBa_2Cu_3O_y$ shows interesting catalytic properties for the ammoxidation of toluene, oxidation of methane, and the dehydrogenation of methanol.[3)] Bi-Sr-Ca-Cu mixed oxides are new superconducting materials, and extensive studies of their electronic properties and structures have been reported. However, little is known of their catalytic properties.

Here, we wish to report on the high catalytic activity of a Bi-Sr-Ca-Cu mixed oxide having a $Bi_2Sr_2CaCu_2O_y$ structure for the reaction between nitrogen monoxide and carbon monoxide.

Experimental

All of the perovskite- and K_2NiF_4-type mixed oxides were prepared by calcining the precipitate from the appropriate mixture of aqueous solutions of the metal acetates or nitrates of each components at 1123—1273 K in air in the same manner as has been described previously.[4,5)] Although the actual compositions may be nonstoichiometric with respect to oxygen, i.e., $La_{1-x}Sr_xBO_{3\pm\delta}$($x$=0—0.4, B=Co, Mn, Cr, δ; nonstoichiometry) and $La_{2-x}A'_xCuO_{4\pm\delta}$($x$=0—0.5, A′=Ce, Sr), in this paper they are designated as $La_{1-x}Sr_xBO_3$ and $La_{2-x}A'_xCuO_4$, respectively. Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O mixed oxides were prepared by the calcination of appropriate mixtures of metal oxides and/or metal carbonates with nominal compositions of Y : Ba : Cu=1 : 2 : 3 and Bi : Sr : Ca : Cu=4 : 3 : 3 : 4 or 1 : 1 : 1 : 2, respectively, in O_2 at 1123—1193 K according to the methods described in the literature.[6,7)] Bi-Sr-Ca-Cu-O mixed oxide was further annealed at 1123 K for 24 h. Bi-Sr-Ca-Cu-O mixed oxides with nominal compositions of Bi : Sr : Ca : Cu=4 : 3 : 3 : 4 and 1 : 1 : 1 : 2 are designated as Bi-Sr-Ca-Cu-O (4 : 3 : 3 : 4) and Bi-Sr-Ca-Cu-O (1 : 1 : 1 : 2), respectively. These structures were confirmed by their X-ray diffraction patterns. A reaction between NO and CO was carried out in a closed circulation system (ca. 190 cm^3), as described previously.[5,6b)] The catalysts (25—200 mg) were mixed with inert SiC (250 mg) to prevent any undesirable temperature rise. The standard procedures were as follows: After the catalysts were treated in O_2 at 573 K for 1 h, the system was evacuated for 15 min. Then, the catalysts were exposed to the reaction gas mixture at ca. 8 kPa (NO : CO=1 : 1). Small portions of the reaction gas were intermittently taken from the system using a glass sampler and then analyzed with a gas chromatograph that was directly connected to the reaction system. The N and C balances were confirmed to be good.

Results and Discussion

The crystal structures and surface areas are summarized in Table 1. The X-ray diffraction pattern of Bi-Ca-Sr-Cu-O (4 : 3 : 3 : 4) showed only a $Bi_2Sr_2CaCu_2O_{y'}$ structure, while two extra peaks at 35.5 and 38.7° corresponding to CuO were observed for Bi-Sr-Ca-Cu-O (1 : 1 : 1 : 2), as was reported in Ref. 7. Although the nonstoichiometry of those catalysts was not determined, it is known that Bi-Sr-Ca-Cu-O, thus prepared, exhibits superconductivity. The X-ray diffraction patterns of the other catalysts showed only a perovskite-type, K_2NiF_4-type, or orthorhombic $YBa_2Cu_3O_y$ structure. It has been reported that y in $YBa_2Cu_3O_y$, thus prepared, ranges from 6.5 to 6.9[8)] and that y' in $Bi_2Sr_2CaCu_2O_{y'}$ was ca. 8.13.[7)]

NO reacted with CO at 573 K over Bi-Sr-Ca-Cu-O (1 : 1 : 1 : 2, Fig. 1) to form N_2 and CO_2 in an approximately stoichiometric ratio in accordance with the reaction $NO+CO \rightarrow 1/2N_2+CO_2$; the amount of NO uptake was comparable with that of CO uptake and the amount of N_2O formed was small. The reaction proceeded over Bi-Sr-Ca-Cu-O (4 : 3 : 3 : 4) at 573 K in a similar way to that of Bi-Sr-Ca-Cu-O (1 : 1 : 1 : 2). A similar time course was observed upon performig a repeated reaction. Absorption of NO was not observed for either Bi-Sr-Ca-Cu-O (1 : 1 : 1 : 2) or Bi-Sr-Ca-Cu-O (4 : 3 : 3 : 4) mixed oxides. No change in the XRD pattern of Bi-Sr-Ca-Cu (1 : 1 : 1 : 2) was observed between fresh and used catalysts.

The selectivities and rates changed little when the reaction was repeated over perovskite-type mixed oxides, while the rates of K_2NiF_4-type mixed oxides and $YBa_2Cu_3O_y$ varied in various ways, depending on the catalysts, as reported previously.[5,6b)]

The rate and selectivity of Bi-Sr-Ca-Cu-O (4 : 3 : 3 : 4) were close to those of Bi-Sr-Ca-Cu-O (1 : 1 : 1 : 2), while the former has a CuO phase in addition to the $Bi_2Sr_2CaCu_2O_{y'}$ phase. We previously reported that the catalytic activity of $La_{1.8}Ce_{0.2}CuO_4$ for the reaction of NO and CO was little affected by the small amount of coexisting CuO.[5)] These facts indicate that the coexisting Cu or CuO had little influence on the rate and selectivity.

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Table 1. Structure, Surface Area, and Catalytic Activity

Catalyst	Structure	Reaction temp./K	Surface area	Rate[a]	Selectivity[b]/%	
			$m^2 g^{-1}$	10^{-6} mol $min^{-1} m^{-2}$	N_2	N_2O
Bi-Sr-Ca-Cu-O (4 : 3 : 3 : 4)	$Bi_2Sr_2CaCu_2O_{y'}$ (T[c])	573	0.7	114	88	12
Bi-Sr-Ca-Cu-O (1 : 1 : 1 : 2)	$Bi_2Sr_2CaCu_2O_{y'}$ (T) +CuO (0.23[d])	573	0.8	128	90	10
Y-Ba-Cu-O	YBa_2Cu_3-O_y (O[c])	573	0.7—0.8	68—140	ca. 90	ca. 10
$La_{1.9}Ce_{0.1}CuO_4$[e]	K (O)	673	0.5	60	78	22
La_2CuO_4[e]	K (O)	673	1.2	96	83	17
$La_{1.8}Sr_{0.2}CuO_4$	K (T)	573	2.8	16	78	22
$La_{1.8}Sr_{0.2}CuO_4$[e]	K (T)	673	2.8	159	90	10
$La_{1.5}Sr_{0.5}CuO_4$	K (T)	673	1.2	106	88	12
$LaCoO_3$	P (R[c])	573	2.4	40	11	89
$La_{0.8}Sr_{0.2}CoO_3$	P (C[c])	573	2.8	22	11	89
$LaMnO_3$	P (O)	573	7.0	12	7	93
$LaCrO_3$	P (O)	573	3.2	5	13	87

a) The average rates of the CO consumption for the first 10 min. b) The selectivity of the reaction products of NO after 10 min. The composition was nearly constant for the first 10 min. c) T; tetragonal. O; orthorhombic. R; rhombohedral. C; cubic. d) The intensity ratio of main signal of $Bi_2Sr_2CaCu_2O_{y'}$ phase to that of CuO phase. e) Cited from Ref. 5.

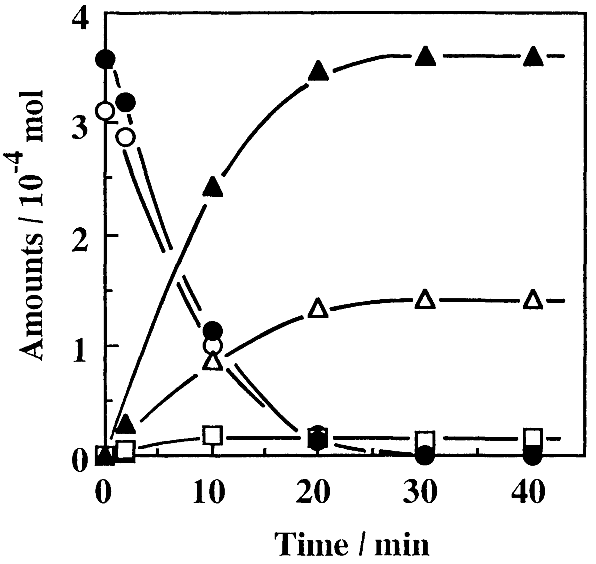

Fig. 1. Reaction between NO and CO at 573 K over Bi-Sr-Ca-Cu-O (1 : 1 : 1 : 2) catalyst.
○, NO; △, N_2; □, N_2O; ●, CO; and ▲, CO_2.
Catalyst weight, 0.2 g.

The number of surface copper ions for Bi-Sr-Ca-Cu-O (4 : 3 : 3 : 4), calculated from the crystallographic data of the $Bi_2Sr_2CaCu_2O_y$ structure (assuming that the most frequently exposed plane is CuO_2 plane where the concentration of copper ions is the highest in this structure), is 6.8×10^{18} ions$\cdot$$m^{-2}$. The total turnover number of Bi-Sr-Ca-Cu-O (i.e., the number of CO reacted per number of surface copper ions) for Runs 1—4 was greater than five hundred, showing that the reaction is catalytic. It is noteworthy that the catalytic activity of Bi-Sr-Ca-Cu-O mixed oxides for the reaction of NO and CO, as well as the selectivity to N_2, were of the highest level among the catalysts listed in Table 1, which summarizes the stationary rates and selectivities.[9] The formal charge of copper for $Bi_2Sr_2CaCu_2O_{8.13}$ is 2.13. It is remarkable that this value is close to that of $La_{1.8}Sr_{0.2}CuO_4$ (2.10), which was the most active for the reaction of NO and CO among $La_{2-x}A'_xCu_{1-y}B'_yO_4$($A'$=Sr, Ce; B'=Al, Zr; x or y=0—0.5) catalysts.[5]

Even using the highest number of surface copper ions (6.8×10^{18} ions$\cdot$$m^{-2}$), the calculated turnover frequency was still 1.7×10^{-1} mol s^{-1}(Cu-atom)$^{-1}$, which was 10^2 times higher than the turnover frequency of Rh/Al_2O_3 catalyst (1.7×10^{-3} mol s^{-1}(Rh-atom)$^{-1}$ at 573 K, extrapolated value in Ref. 1b).

As for the other catalysts, the following trends were noted. The rate decreased with Sr^{2+}-substitution for $LaCoO_3$, and $LaMnO_3$ (perovskite-type structure), while the rate increased in the case of La_2CuO_4.[5] Copper-containing catalysts showed the high selectivity to N_2.

The activity of $YBa_2Cu_3O_{y'}$ which changed among the different lots, was comparative to, or a little lower than, that of Bi-Sr-Ca-Cu-O. The difference in the rates between the lots of $YBa_2Cu_3O_y$ may be due to the water which was either absorbed or adsorbed.[10] In fact, the activity of $YBa_2Cu_3O_y$ changed considerably after its exposure to water vapor. The more NO that was absorbed, the higher the activity of Y-Ba-Cu-O for the reaction between NO and CO was. It has been reported for Ba-Cu-O that NO is absorbed into the bulk as in the case of $YBa_2Cu_3O_y$[5b] and that the absorptivity of NO is accelerated by the coexistence of Cu^{3+}.[11] Therefore, the valence of copper may be another influential factor regarding the activity for the reaction between NO and CO.

In contrast, the activity of Bi-Sr-Ca-Cu-O was reproducible. It is noteworthy in the above respect that Bi-Sr-Ca-Cu-O is stable in water vapor and carbon dioxide.[12]

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9) The time course of each catalyst in the second run was similar to that in the third run. In this work, the stationary rate and selectivity were defined by those for the first 10 min in the second run.

10) The effect of water vapor on the chemical and catalytic properties of $YBa_2Cu_3O_y$ is significant. For example, the treatment of $YBa_2Cu_3O_y$ with water vapor remarkably accelerated the absorption of NO (H. Toyama, N. Mizuno, and M. Misono, 1989 Intl. Chem. Congr. Pacific. Basin Soc., Honolulu, Dec.1989). Further study is in progress. The reaction of $YBa_2Cu_3O_y$ with water vapor has also been reported (H. S. Horowitz, R. K. Bordia, R. B. Flippen, R. E. Johnson, and U. Chowdhry, *Mat. Res. Bull.,***23**, 821 (1988)).

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