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A Pronounced Catalytic Activity of La–Cu Oxide Supported on ZrO_2 for Reaction between Nitrogen Monoxide and Carbon Monoxide

The reductions of nitrogen monoxide (NO) by carbon monoxide (CO) and hydrocarbon are the fundamental reaction pathways for the removal of NO_x from automobile exhaust (*1*, *2*). Therefore, it is meaningful from the standpoint of basic research to develop and investigate a high-activity catalyst for the reduction of NO by CO, although for the actual exhaust the effects of H_2O and SO_2 cannot be ignored.

It has been reported that copper-containing mixed oxides having perovskite-related structures such as $Bi_2Sr_2CaCu_2O_y$, $YBa_2Cu_3O_{y'}$, and La_2CuO_4 show high catalytic activities for the reaction between NO and CO (*3*, *4*) and that the catalysts having the valence of copper ion close to two are active for the reaction (*4*). We have reported that the perovskite-type mixed oxide, La CoO_3, can be highly dispersed on ZrO_2 and gave an enhanced catalytic activity (*5*, *6*). ZrO_2 is also known as a suitable substrate for preparing copper-containing superconducting oxide films (*7*).

We attempted in this study to prepare La_2CuO_4 highly dispersed on the surface of ZrO_2 and obtained a very high catalytic activity for the reaction between NO and CO.

ZrO_2 was prepared from zirconyl nitrate. Al_2O_3 (JRC-ALO-4) and SiO_2 (Fuji-Davison) were commercially obtained. They were used as supports after calcination in air at 1123 K for 5 h. The surface areas of ZrO_2, Al_2O_3, and SiO_2 supports were 22, 136, and 176 $m^2 \cdot g^{-1}$, respectively. These supports were impregnated with an aqueous solution of copper acetate or with an aqueous solution of a stoichiometric mixture of copper and lanthanum acetates with respect to La_2CuO_4 by an incipient wetness method. The loading amount of copper was 0.60% except for 1.5% of copper-loaded SiO_2 catalyst. They were calcined in air at 1123 K for 5 h. Surface areas of the catalysts after the calcination are given in Table 1. Although the formation of CuO, Cu_2O, and La–Cu mixed oxide could not be confirmed by XRD, the resulting catalysts are denoted by CuO/SiO_2, CuO/Al_2O_3, CuO/ZrO_2, and La_2CuO_4/ZrO_2, respectively. Studies are in progress to identify the supported oxide. In the case of $LaCoO_3$ dispersed on ZrO_2 (*5*, *6*), although $LaCoO_3$ was not detected by XRD, it was made very probable by several characterizations that thin films of La–Co oxide in the ratio of La/Co = 1 were formed on the surface of ZrO_2. Transmission electron micrographs were obtained with a JEOL JEM 1250 electron microscope (1000 keV; final magnification, ×150,000).

The reaction between NO and CO was carried out in a closed circulation system (ca. 190 cm^3) as described previously (*3*, *4*). The catalysts (50 mg) were mixed with inert SiC (250 mg) to prevent an undesirable temperature rise. The standard procedure was as follows: After the catalysts were treated in O_2 at 573 K for 1 h, the system was evacuated for 15 min at 573 K or the system was cooled to 473 K followed by the evacuation for 15 min at 473 K. Subsequently the catalysts were exposed to the reaction gas mixture at ca. 8 kPa (NO : CO = 1 : 1). The reaction was carried out at 473 or 573 K. The reaction gas

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TABLE 1

Catalytic activity and selectivity

Catalyst	Surface area ($m^2 \cdot g^{-1}$)	Reaction temp. (K)	Rate[a] (10^{-14} mol $\cdot$ min^{-1} $\cdot$ g^{-1})	Selectivity[b] (%) N_2	N_2O
La_2CuO_4/ZrO_2	12.7	473	1.0×10^{10}	12	88
CuO/ZrO_2	14.2	473	9.0×10^{8}	16	84
CuO/Al_2O_3	132	473	1.0×10^{9}	0	100
CuO/SiO_2	170	473	8.0×10^{8}	0	100
Bi–Sr–Ca–Cu–O[c]	0.7–0.8	573	$0.8\text{–}1.0 \times 10^{10}$	ca. 90	ca. 10
Y–Ba–Cu–O[c]	0.7–0.8	573	$0.5\text{–}1.0 \times 10^{10}$	ca. 90	ca. 10
Rh/Al_2O_3[d]		473	2.0	100	0

[a] La_2CuO_4/ZrO_2, Bi–Sr–Ca–Cu–O, and Y–Ba–Cu–O; the average rates of the CO consumption for the first 10 min. CuO/ZrO_2, CuO/Al_2O_3, and CuO/SiO_2; the average rates of the CO consumption for the first 60 min because of their very small rate.

[b] La_2CuO_4/ZrO_2, Bi–Sr–Ca–Cu–O, and Y–Ba–Cu–O; the selectivities to the reaction products of NO after 10 min. CuO/ZrO_2, CuO/Al_2O_3, and CuO/SiO_2; the selectivities to the reaction products of NO after 60 min because of their very small rate. The product distribution was nearly constant for the first 10 min and 60 min or the former catalysts and the latter catalysts, respectively.

[c] Cited from Ref. (*3*).

[d] Calculated from Ref. (*1*), assuming that Rh loading was 0.01 wt% and the Rh dispersion was 12%.

and products were analyzed with a gas chromatograph that was directly connected to the reaction system as described previously (*3*, *4*). The N and C balances were confirmed to be good.

NO reacted with CO at 473 K over La_2CuO_4/ZrO_2 to form N_2O, N_2, and CO_2. The main products were N_2O and CO_2, and the amount of N_2 formed was small. The ratio of the amount of NO uptake to that of CO uptake was 1.7, close to 2, showing that N_2O is formed by the reaction, $2NO + CO \rightarrow N_2O + CO_2$. A similar time course was observed upon repeated reactions. The reaction proceeded over the other copper-loaded catalysts at 473 K in a manner similar to that over La_2CuO_4/ZrO_2; the main products were CO_2 and N_2O and the selectivities and the rates changed little upon a repeated run over each catalyst. By contrast, when the reaction was carried out at 573 K over La_2CuO_4/ZrO_2, the main products changed to N_2 (selectivity 80%) and CO_2 as was observed for the perovskite- and K_2NiF_4-type mixed oxides, Bi–Sr–Ca–Cu–O and Y–Ba–Cu–O (*3*).

The total turnover number of La_2CuO_4/ZrO_4 (i.e., the number of CO reacted per number of copper loaded) for runs 1–2 was greater than 50 showing that the reaction is catalytic. It is noteworthy that the catalytic activity of La_2CuO_4/ZrO_2 for the reaction between NO and CO was the highest among the catalysts listed in Table 1, which summarizes the stationary rates and selectivities (*8*). The difference in the activities among the catalysts supported on various oxides cannot be explained by the difference in the surface areas of the catalysts. It was reported that the catalytic activities of Bi–Sr–Ca–Cu and Y–Ba–Cu mixed oxides having $Bi_2Sr_2CaCu_2O_y$ and $YBa_2Cu_3O_{y'}$, structures, respectively, were of the highest level among the perovskite-type and its related mixed oxides (*3*).

Furthermore, even using the number of the whole copper atoms of the catalysts, the calculated turnover frequency of La_2CuO_4/ZrO_2 was still 1.8×10^{-2} molecules $\cdot$ s^{-1} $\cdot$ (total Cu-atom)$^{-1}$. This value is ca. 10^7 times higher than the turnover frequency of Rh/Al_2O_3 catalyst (2.9×10^{-9} molecules $\cdot$ s^{-1} $\cdot$ (surface Rh-atom)$^{-1}$ at 473 K, extrapolated value based on the data in Ref. (*1*)) and comparable to the turnover frequency of active Rh(111) (2.2×10^{-2} molecules · s^{-1} · (surface Rh-atom)$^{-1}$ at 473 K, extrapolated value of Ref. (*1*)). The automotive exhaust contains a variable amount of SO_2 that often poisons copper catalysts. Therefore, this comparison does not necessarily mean the superiority of the present catalyst for automotive exhaust. However, it is noteworthy that copper ion-exchanged zeolites are fairly resistant to SO_2 in actual automotive exhausts (*9*).

The high activity of La_2CuO_4/ZrO_2 may be explained by (1) high dispersion of copper on the surface of ZrO_2 resulting from the suppression of the reaction between copper and ZrO_2 caused by the added lanthanum and/or (2) maintenance of the valence of copper close to 2, where the activity for the reaction between NO and CO was the highest (*4*). In favor of the former idea, any segregated particles of La_2CuO_4 were not detected by TEM and no formation of CuO, Cu_2O, or La–Cu oxide was observed by XRD. Although the structure of La_2CuO_4 on ZrO_2 is not yet known exactly, it may at least be stated that La-Cu oxide supported on ZrO_2 is an excellent catalyst for the reduction of NO by CO.

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