Role of Valency of Copper in the Direct Decomposition of Nitrogen Monoxide over Well Characterized $La_{2x}A'_xCu_{1-y}B'_yO_4$

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Catalytic activity is closely related to the valency of copper in the direct decomposition of NO over well characterized $La_{2-x}A'_xCu_{1-y}B'_yO_4$ catalysts (K_2NiF_4 structure; A' = Sr, B' = Al, Zr, $x = 0—1.0$, $y = 0, 0.2$); the formal valency of copper was controlled in the range 1.60—2.30.

Mixed oxides which have the perovskite and related structures have attracted attention as useful catalysts for practical applications and for fundamental studies.[1] It has been reported that Cu-containing compounds such as Cu-ion-exchanged ZSM-5 and Cu-containing oxide showed high catalytic activities for the decomposition of NO.[2,3] However, little is known of the factors controlling the activities.

We have studied the direct decomposition of NO over $La_{2-x}A'_xCu_{1-y}B'_yO_4$, in which the valency of copper was controlled by substitution without changing the K_2NiF_4 structure.

The $La_{2-x}A'_xCu_{1-y}B'_yO_4$ catalysts were prepared by calcining the precipitate from the appropriate mixture of aqueous solutions of the metal acetates at 1123—1273 K for 5—20 h, as

Table 1. Structure, surface area, average oxidation number of copper, and stoicheiometry.

Catalyst	Calcination Temp. /K	Calcination Time /h	Structure	Surface area /m^2 g^{-1}	Oxidation number of copper[b]	δ[a]
$La_2Cu_{0.8}Zr_{0.2}O_4$	1123	5	$K_2NiF_4(O^c) + ZrO_2(tr.^d) + La_2Zr_2O_7$ (tr.)	10.5	1.60	0.04
$La_2Cu_{0.8}Al_{0.2}O_4$	1123	5	$K_2NiF_4(T^c) + LaAlO_3$ (tr.)	2.2	1.88	0.05
La_2CuO_4	1123	5	$K_2NiF_4(O)$	1.6	2.00	0.00
$La_{1.8}Sr_{0.2}CuO_4$	1173	20	$K_2NiF_4(T)$	1.3	2.20	0.00
$La_{1.6}Sr_{0.4}CuO_4$	1173	20	$K_2NiF_4(T)$	1.2	2.22	−0.09
$La_{1.5}Sr_{0.5}CuO_4$	1273	5	$K_2NiF_4(T)$	0.9	2.30	−0.10
$La_{1.4}Sr_{0.6}CuO_4$	1173	20	$K_2NiF_4{}^e(T)$	1.2	2.10	−0.25
$La_{1.0}Sr_{1.0}CuO_4$	1173	20	$K_2NiF_4{}^e(T)$	1.1	1.96	−0.52

[a] δ in $La_{2-x}A'_xCu_{1-y}B'_yO_{4+\delta}$. [b] Average oxidation number of copper. [c] O, orthorhombic K_2NiF_4 phase; T, tetragonal K_2NiF_4 phase. [d] Tr; trace. [e] Two tetragonal phases reported in refs. 7 and 8 were observed. The signal intensity of the peak assigned to the phase reported in ref. 7 was stronger than that reported in ref. 8.

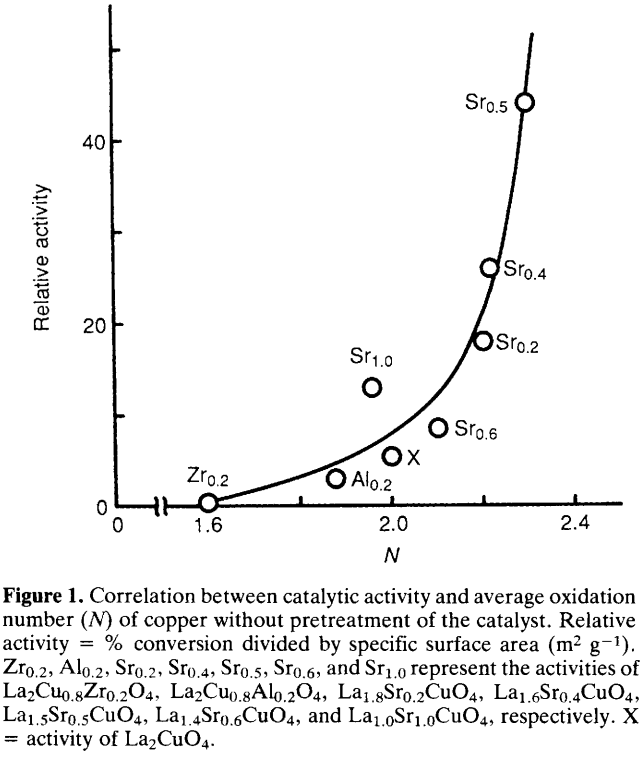

Figure 1. Correlation between catalytic activity and average oxidation number (N) of copper without pretreatment of the catalyst. Relative activity = % conversion divided by specific surface area (m^2 g^{-1}). $Zr_{0.2}$, $Al_{0.2}$, $Sr_{0.2}$, $Sr_{0.4}$, $Sr_{0.5}$, $Sr_{0.6}$, and $Sr_{1.0}$ represent the activities of $La_2Cu_{0.8}Zr_{0.2}O_4$, $La_2Cu_{0.8}Al_{0.2}O_4$, $La_{1.8}Sr_{0.2}CuO_4$, $La_{1.6}Sr_{0.4}CuO_4$, $La_{1.5}Sr_{0.5}CuO_4$, $La_{1.4}Sr_{0.6}CuO_4$, and $La_{1.0}Sr_{1.0}CuO_4$, respectively. X = activity of La_2CuO_4.

described previously.[4] We represent them as $La_{2-x}A'_xCu_{1-y}B'_yO_4$, although the actual composition is $La_{2-x}A'_xCu_{1-y}B'_yO_{4\pm\delta}$. The average oxidation number of copper was chemically determined by iodometric titration[5] without treatment of the as-prepared samples. The stoicheiometry 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+}, Al^{3+}, Zr^{4+}, and O^{2-}, respectively.

The specific surface areas of the catalysts were measured by the Brunauer–Emmett–Teller (BET) method. The surface compositions of the catalysts before reaction were calculated from the X-ray photoelectron spectroscopic peak intensities as has been described previously.[4]

The NO decomposition reaction was carried out at 773—1073 K in a flow reactor by feeding a gas mixture of NO (3.17 vol.%) and He (balance) at a flow rate (F) of 30 cm^3 min^{-1} over 1 g of the catalyst (W/F = 2.0 g s cm^{-3}, W = catalyst weight) after pretreatment of the catalysts in a He stream (30 cm^3 min^{-1}) for 2 h at 1073 K. The reaction temperature was increased stepwise up and down in 100 K intervals from 773 to 1073 K and the reaction was carried out at each temperature for 1—2 h. The gas composition was analysed by gas chromatography with molecular sieve 5A and Porapak Q columns. The activity was evaluated in terms of the conversion of NO to N_2 according to the literature.[2,6] The mass balances of N and O were confirmed.

The crystal structure, surface area, average oxidation number of copper, and stoicheiometry are shown in Table 1. The X-ray diffraction patterns of Sr^{2+}-substituted catalysts showed only the K_2NiF_4-type structure. It is probable that most of the added Zr^{4+} and Al^{3+} ions was incorporated into the copper site if one takes into account the very weak intensities of the XRD main signals of their impurities.

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 and decreased with Al^{3+} or Zr^{4+} substitution. The highest oxidation state was observed for the Sr^{2+} substitution with $x = 0.5$. The composition became oxygen-rich upon Al^{3+} and Zr^{4+} substitution and oxygen-deficient with Sr^{2+} substitution. The average oxidation numbers of copper in the Sr^{2+}-substituted samples were close to the reported values.[7] The oxidation number is formal, and it is possible that O^- is present instead of Cu^{3+}.[9] The surface composition and the oxidation number of copper, which was estimated from the ratio of the satellite peak to the main peak of Cu $2p_{3/2}$ and the Auger parameter, were close to those of the catalysts listed in Table 1 except for a slight change for the Zr^{4+}-substituted sample as has been described in ref. 4.

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

With regard to the decomposition of NO, N_2O formation was slight, and the conversion did not change with time for each catalyst above 973 K. The conversion did not change when the flow rate was changed from 30 to 60 cm^3 min^{-1} at a constant W/F; changes in the crystal structure were not observed between the fresh and used catalysts by XRD.

Figure 1 shows the correlation between the average oxidation number of copper, measured for the as-prepared catalysts, and the relative activities (represented by % conversion divided by surface area) of the catalysts at 1073 K. The highest activity was observed for $La_{1.5}Sr_{0.5}CuO_4$, being about three times higher than that of $La_{0.8}Sr_{0.2}CoO_3$ which was the most active among perovskites studied by Teraoka *et al.*[6] It is noteworthy that the activities increased sharply with the increase in the average oxidation number of copper. These data were reproducible in two or more separate experiments with different batches of catalyst. We have reported previously that the average oxidation number of copper in $La_{2-x}Sr_xCuO_4$ (x = 0—1.0) changed little after the sampes had been heated to 1073 K at a constant rate of 20 K min^{-1} in a He stream.[10] No change in stoicheiometry below 1073 K was observed also for $La_{1.84}Sr_{0.16}CuO_4$.[11] Therefore, the treatment prior to the reaction must have had little effect on the average oxidation number of copper, and it is probable that the figures on the abscissa in Figure 1 also represent the oxidation number of copper on the surface during the reaction. Hence, it may be concluded that the activities for the direct decomposition of NO increased with the increase in the charge of copper for $La_{2-x}A'_xCu_{1-y}B'_yO_4$ catalysts.

The reason why the catalytic activity increases with increase in the average oxidation number of copper is not obvious at present. It could possibly be due to the easier reduction of Cu^{3+} in the redox cycle of $Cu^{2+} \leftrightarrow Cu^{3+}$. The presence of Cu^+ is unlikely because of its instability in the octahedral site of the K_2NiF_4-type structure; Cu^{3+} may correspond to Cu^{2+} and a positive hole at oxygen.[9]

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