# Pronounced Synergetic Effect in the Catalytic Properties of $LaMn_{1-x}Cu_xO_3$

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A pronounced synergetic effect has been found when $LaMn_{1-x}Cu_xO_3$ ($x = 0.3$—$0.5$) was prepared by a freeze-drying method from metal acetates of each component; $LaMn_{0.6}Cu_{0.4}O_3$ showed much higher catalytic activity for the reactions of $CO-O_2$ and NO–CO in comparison with $LaMnO_3$ and $La_2CuO_4$.

The perovskite structure is shown by binary oxides of the form $ABO_3$, in which the sum of the charges on the cations equals six, and where the cation B is much smaller than A. It is possible to control the valence of B-site ions and the amount of oxygen vacancies by changing the A- or B-site ions or by partial substitution with ions of different valence.[1] Catalytic activity is enhanced by A-site substitution,[1] but little is known of the effect of B-site element substitution.[2,3] Zhang *et al.* reported that the activity of $La_{0.4}Sr_{0.6}Mn_{0.8}Co_{0.2}O_3$ for the oxidation of butane was about 5 times higher than that of $LaMnO_3$,[2] but we found that substitution by Mn of Co in $LaCoO_3$ led to only slight enhancement of the catalytic activity for the oxidation of propane when the catalyst composition was made uniform by freeze-drying.[4]

We have now studied the catalytic reactions of $CO-O_2$ and NO–CO over $LaMn_{1-x}Cu_xO_3$ catalysts which were prepared by freeze-drying.

$LaMn_{1-x}Cu_xO_3$ catalysts were prepared by freeze-drying solutions containing the component metal acetates. $La_2CuO_4$ was prepared by evaporating an aqueous solution of lanthanum and copper acetates as described previously.[5] The powders obtained were first decomposed in air at 573 K for 3 h and then calcined in air at 1123 K for 5 h. We represent them as $LaMn_{1-x}Cu_xO_3$ although the actual composition may be $LaMn_{1-x}Cu_xO_{3\pm\delta}$. $LaMn_{0.6}Cu_{0.4}O_3$ was also prepared from the metal nitrates by the method of Gallagher *et al.*[6] The powder obtained by freeze-drying an aqueous solution of the metal nitrates was calcined at 1373 K for 4 h [denoted $LaMn_{0.6}Cu_{0.4}O_3(N)$].

The reactions of $CO-O_2$ (6 kPa, $CO:O_2$ 2:1) and NO–CO (8 kPa, CO:NO 1:1) were carried out in a closed recirculation system. The catalysts (10—50 mg) were used as a mixture with SiC (250 mg). The procedures were as follows: after pretreatment in $O_2$ (13 kPa) at 673 K for 1 h, the catalysts were cooled to 573 K in $O_2$ and were evacuated for 10 min at 573 K. They were then exposed to the reaction gas. Products were analysed by gas chromatography.

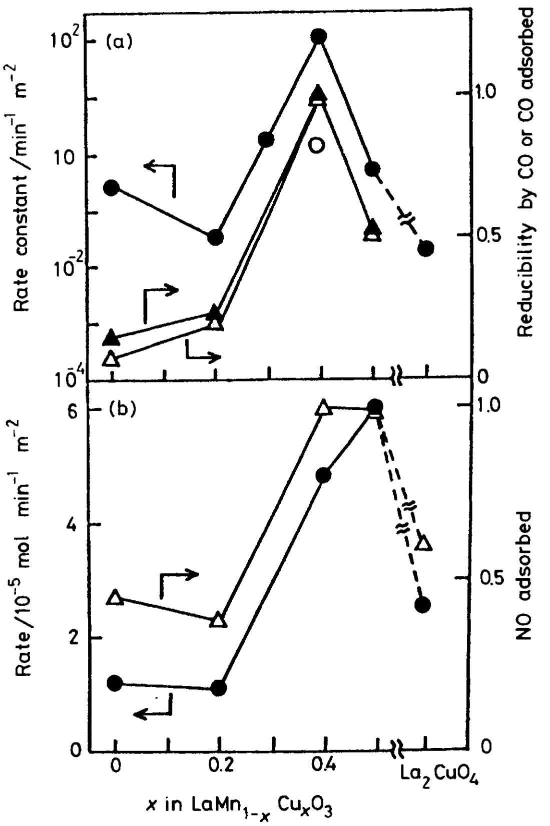

**Figure 1.** Effect of Cu substitution for Mn in $LaMnO_3$. Catalysts: $LaMn_{1-x}Cu_xO_3$ ($x$ = 0—0.5) and $La_2CuO_4$. (a) Rate constant for the reaction of CO–$O_2$ (●); (right-hand axis) reducibility by CO (▲), and amount of CO adsorbed relative to surface area (△), arbitrary units. ○: catalytic activity of $LaMn_{0.6}Cu_{0.4}O_3$(N) for the oxidation of CO. (b) Rate of the reaction of NO–CO (●) and (right-hand axis) amount of adsorption of NO (△) relative to surface area, arbitrary units.

**Table 1.** The structures and surface areas of $LaMn_{1-x}Cu_xO_3$ ($x$ = 0—0.5) (calcination at 1123 K unless noted otherwise).

| Composition | Structure | Surface area/ $m^2 g^{-1}$ |
|---|---|---|
| $LaMnO_3$ | P(R)[a] | 3.1 |
| $LaMn_{0.8}Cu_{0.2}O_3$ | P(R) | 3.8 |
| $LaMn_{0.7}Cu_{0.3}O_3$ | P(C)[b] | 4.2 |
| $LaMn_{0.6}Cu_{0.4}O_3$ | P(C) | 2.3 |
| $LaMn_{0.5}Cu_{0.5}O_3$ | P(C) + CuO (tr.)[c] + $La_2CuO_4$(O)[d] (0.14)[e] | 2.8 |
| $La_2CuO_4$ | $La_2CuO_4$(O) | 1.2 |
| $LaMn_{0.6}Cu_{0.4}O_3$(N)[f] | P(C) + unidentified phase (tr.) | 0.8 |

[a] P(R): rhombohedral perovskite phase. [b] P(C): cubic perovskite phase. [c] The intensity ratio of main signal of CuO phase to that of perovskite phase, tr.: trace. [d] O: orthorhombic. [e] The intensity ratio of main signal of $La_2CuO_4$ phase to that of perovoskite phase. [f] Calcination at 1373 K.

The reduction of the catalyst and the catalytic oxidation of propane were conducted at 573 K as in the previous study.[7] The catalysts (25—50 mg) were heated in an $O_2$ stream (1 atm) for 1 h at 673 K and then cooled to 573 K in an $O_2$ stream prior to the reactions.

The amounts of chemisorption of CO and NO under an equilibrium pressure of 14.7 kPa were measured at 298 K after evacuation at 773 K for 2 h.[8] The surface compositions of the catalysts were calculated from the *X*-ray photoelectron spectroscopic peak intensities of La $3d_{5/2}$, Mn $2p_{3/2}$, and Cu $2p_{3/2}$.

The structures and the surface areas are summarized in Table 1. The *X*-ray diffraction patterns of $LaMn_{1-x}Cu_xO_3$ ($x$ = 0—0.4) showed the formation of a single perovskite phase, while weak signals due to $La_2CuO_4$ and CuO were observed for $LaMn_{0.5}Cu_{0.5}O_3$.

The rate constants† shown by $LaMn_{1-x}Cu_xO_3$ ($x$ = 0—0.5) for the oxidation of CO are shown in Figure 1a. The rate constant reached a maximum at $x$ = 0.4 (note that the ordinate is a log scale). The rate constants for $LaMn_{0.6}Cu_{0.4}O_3$ were about 400 and 5000 times greater than those for $LaMnO_3$ and $La_2CuO_4$, respectively, and about 100 times higher than that for $La_{0.8}Sr_{0.2}CoO_3$, which has approximately the same activity as Pt/$Al_2O_3$.[1] Thus, the Cu substitution for Mn in $LaMnO_3$ resulted in a marked enhancement of the catalytic activity. The catalytic activity varied in parallel with the reducibility of the catalysts by CO (▲ in Figure 1a) and the amount of adsorption of CO (△ in Figure 1a), although the catalytic activity showed a much greater variation. In separate experiments, it was found that $LaMn_{0.6}Cu_{0.4}O_3$ showed slightly lower activity for the oxidation of propane and $^{16}O_2$–$^{18}O_2$ equilibration than $LaMnO_3$. So, the synergetic effect is confined to the oxidation of CO.

We thus assume that the synergetic effect arises from an appropriate combination of activation (adsorption) of CO by Cu and the high reactivity of the lattice oxygen of Mn oxides.

The rate constant for $LaMn_{0.6}Cu_{0.4}O_3$ was 100 times greater than that for $LaMn_{0.6}Cu_{0.4}O_3$(N) (○ in Figure 1a) prepared by the method of Gallagher *et al.*[6] Further, when the CO–$O_2$ reaction was carried out with a flow system under similar conditions to those reported in the literature,[6] the rate for $LaMn_{0.6}Cu_{0.4}O_3$ (prepared from acetates) was about 20 and 50 times larger than that for $LaMn_{0.6}Cu_{0.4}O_3$(N) and that reported in the literature,[6] respectively. The fact that a weak signal due to an unidentified phase was observed for $LaMn_{0.6}Cu_{0.4}O_3$(N) (see Table 1) and that the surface composition (La : Mn : Cu atomic ratio 1.0 : 0.62 : 0.68) was different from that of the bulk (La : Mn : Cu 1.0 : 0.60 : 0.40) suggest that the perovskite phase was not formed uniformly in this case. This heterogeneity was also suggested in the literature.[6] In the present work, $LaMn_{0.6}Cu_{0.4}O_3$ was more nearly homogeneous judged from its *X*-ray diffraction pattern and the closeness of its surface composition (La : Mn : Cu 1.0 : 0.56 : 0.53) to that of the bulk. This may be the reason why the activity of $LaMn_{0.6}Cu_{0.4}O_3$ prepared from the metal

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† If the decrease of activity in the presence of $CO_2$ is taken into account, equation (i) may be obtained, where $k$, [CO], and [$CO_2$] are the rate constant and partial pressures of CO and $CO_2$, respectively, $b$ being a constant. A first order dependence on the partial pressure of CO and a zero order dependence on $O_2$ are consistent with the data in the literature (Y. Y. Yao, *J. Catal.*, 1975, **36**, 266). The experimental data fitted this equation well. The value of $k$ in the first run was thus used as a measure of the initial activity. The value of $b$ decreased in the order $La_2CuO_4 \approx LaMn_{0.5}Cu_{0.5}O_3 \geqslant LaMn_{0.6}Cu_{0.4}O_3 > LaMn_{0.7}Cu_{0.3}O_3 > LaMn_{0.8}Cu_{0.2}O_3 > LaMnO_3$.

$$-d[CO]/dt = k[CO]/(1 + b[CO_2]) \qquad (i)$$

acetates was much higher than that of $LaMn_{0.6}Cu_{0.4}O_3$ prepared from the metal nitrates.

Figure 1b shows the average rates for the first 10 min in the first run of the reaction of NO–CO over $LaMn_{1-x}Cu_xO_3$. The rate increased with Cu-substitution ($x$), being several times faster than that for $LaMnO_3$ and $La_2CuO_4$ at $x = 0.4$ and 0.5. The rates for these catalysts changed little when the reaction was repeated.

The activity pattern was similar to the pattern observed for the amounts of adsorption of NO at room temperature (△ in Figure 1b). It is probable that the strongly adsorbed NO was effective for the reaction of NO–CO as was reported for $Co/SiO_2$.[9]

In summary, a marked synergetic effect was found for catalytic activities for both $CO–O_2$ and NO–CO reactions when Cu was partially substituted for Mn in $LaMnO_3$.

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