Catalytic Activity of Perovskite-type $La_{0.8}Sr_{0.2}M_{1-2y}Cu_yRu_yO_3$ (M = Al, Mn, Fe, Co) for CO Oxidation and NO-CO Reactions. Influence of the Simultaneous Substitution of Cu and Ru

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The catalytic activity of perovskite-type $La_{0.8}Sr_{0.2}M_{1-2y}Cu_yRu_yO_3$ (M = Al, Mn, Fe, Co) for CO oxidation and NO-CO reactions was changed significantly by the simultaneous substitution of Cu and Ru for M at the B sites, and its effect was dependent on host M cations. The simultaneous Cu/Ru substitution into the inert host of $La_{0.8}Sr_{0.2}AlO_3$ gave a very active catalyst at a substitution level (y-value) of 0.1.

ABO_3 perovskite-type oxides are important catalytic materials not only for basic studies aiming to elucidate the relationship among structure, composition and catalytic property but also for practical application as substitutes for precious metal catalysts.[1-3] Since the catalytic activity of perovskite-type oxides is practically determined by the nature of B-site cations, almost all the perovskite catalysts so far reported contain 3d transition metals, especially Co and Mn, as B-site host cations.[3] Recently, Skoglundh et al.[4] reported that when an alumina washcoat was impregnated with an aqueous solution containing La^{3+}, Sr^{2+}, Cu^{2+} and Ru^{3+} ions and calcined at 900 °C, nano-sized perovskite particles of the nominal composition of $La_{1-x}Sr_xAl_{1-2y}Cu_yRu_yO_3$ were formed on the washcoat. This perovskite phase was reported to take an active part in the catalytic conversion of NO and CO into N_2 and CO_2, and might be used as an active ingredient of a three-way catalyst for automobiles.[4] In order to elucidate the intrinsic catalytic property of the given compounds and the influence of the simultaneous substitution of Cu and Ru for M at the B sites, we have investigated the preparation and the activity of $La_{0.8}Sr_{0.2}M_{1-2y}Cu_yRu_yO_3$ (M = Al, Mn, Fe, Co).[5]

Perovskite-type oxides listed in Table 1 were prepared by calcining an appropriate mixture of metal chloride (Ru) and nitrates (others) at 900 °C for 24 h, and they were characterized by powder X-ray diffraction (XRD) using CuKα radiation (Rigaku RINT2200). Catalytic activities for CO-NO and CO-O_2 reactions were measured in a fixed-bed flow reactor by feeding He-balanced CO(0.5%)-NO(0.5%) and CO(0.5%)-O_2(5%) gas mixtures with a contact time (W/F) of 0.4 g·s·cm^{-3}. Temperature programmed desorption (TPD) of oxygen was measured by the procedure described in Ref. 6.

Table 1. Perovskite-type oxide catalysts used in this study

Perovskites	Abbreviation	S_a / m^2·g^{-1}
$La_{0.8}Sr_{0.2}AlO_3$	AXX0	6.7
$La_{0.8}Sr_{0.2}Al_{0.9}Cu_{0.05}Ru_{0.05}O_3$	ACR5	8.1
$La_{0.8}Sr_{0.2}Al_{0.8}Cu_{0.1}Ru_{0.1}O_3$	ACR10	9.8
$La_{0.8}Sr_{0.2}Al_{0.6}Cu_{0.2}Ru_{0.2}O_3$	ACR20	4.7
$La_{0.8}Sr_{0.2}CoO_3$	CXX0	9.5
$La_{0.8}Sr_{0.2}Co_{0.9}Cu_{0.05}Ru_{0.05}O_3$	CCR5	7.4
$La_{0.8}Sr_{0.2}Co_{0.8}Cu_{0.1}Ru_{0.1}O_3$	CCR10	3.5
$La_{0.8}Sr_{0.2}MnO_3$	MXX0	6.9
$La_{0.8}Sr_{0.2}Mn_{0.8}Cu_{0.1}Ru_{0.1}O_3$	MCR10	3.5
$La_{0.8}Sr_{0.2}FeO_3$	FXX0	4.8
$La_{0.8}Sr_{0.2}Fe_{0.8}Cu_{0.1}Ru_{0.1}O_3$	FCR10	6.3

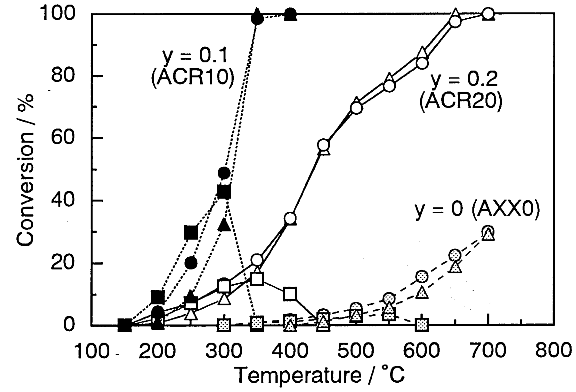

Figure 1. CO-NO reaction over $La_{0.8}Sr_{0.2}Al_{1-2y}Cu_yRu_yO_3$ (y=0, 0.1, 0.2). Conversion of CO into CO_2 (circle), Conversion of NO into N_2 (triangle) and N_2O (square).

We have already reported that the substitution of the Cu/Ru pair for Co in $La_{0.8}Sr_{0.2}Co_{1-2y}Cu_yRu_yO_3$ was possible up to y = 0.2 without changing the crystal symmetry.[6] In the Al-based system ($La_{0.8}Sr_{0.2}Al_{1-2y}Cu_yRu_yO_3$), ACR5 and ACR10 were practically monophasic and in ACR20 two by-products, possibly $LaRuO_3$ and La_2CuO_4, were detected in addition to the Al-based perovskite. Thus the substitution limit of the Cu/Ru pair in the Al-based system may be around y = 0.1 under the present preparation conditions. In Mn- and Fe-based systems, oxides with y = 0 and 0.1 were synthesized and they were monophasic.

Figure 1 shows the temperature dependence of the CO-NO reaction over $La_{0.8}Sr_{0.2}Al_{1-2y}Cu_yRu_yO_3$ (y = 0, 0.1 and 0.2). It can be seen that the Cu/Ru substitution at y = 0.1 resulted in a drastic enhancement of activity but further substitution (y = 0.2) reduced the activity. The effect of the Cu/Ru substitution in the Al-based system on catalytic activities for CO-NO and CO-O_2 reactions is depicted in Figure 2 in which the temperatures for 20% and 90% conversion ($T_{20\%}$ and $T_{90\%}$) of CO into CO_2 are taken as a measure of the activity (lower T indicating higher activity). On increasing the y value, the activities for both reactions progressively increased up to y = 0.1 and then decreased, indicating that ACR10 (y = 0.1) is the most active. The decrease in 90% conversion activity between y = 0.1 and 0.2 was more remarkable than that in 20% conversion activity due to the fact that the conversion *vs.* temperature curves of ACR20 (y = 0.2) became gentle above the conversion degree of 60%. This activity order held for the surface-area-normalized activity.

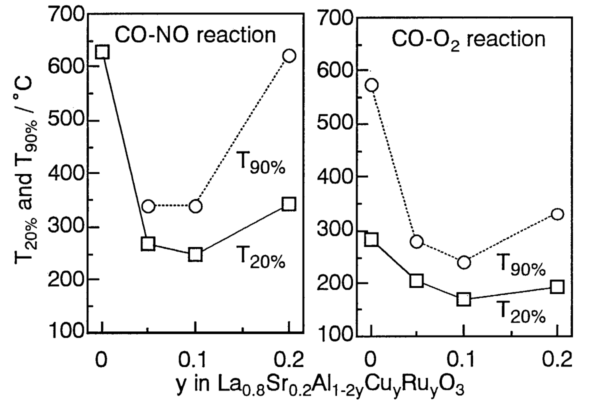

Figure 2. Effect of the Cu/Ru substitution on the catalytic activity of $La_{0.8}Sr_{0.2}Al_{1-2y}Cu_yRu_yO_3$ for CO-NO and CO-O_2 reactions. $T_{20\%}$, $T_{90\%}$; temperatures for 20 and 90% conversion of CO into CO_2.

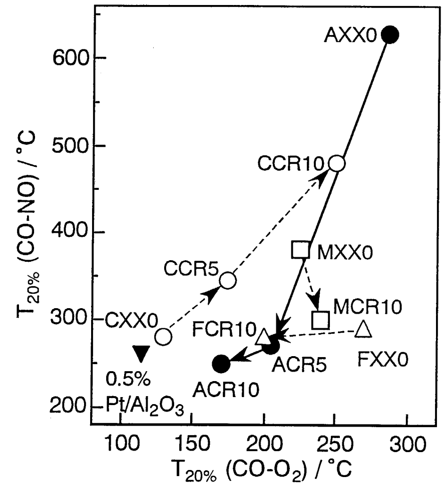

Figure 3. Comparison of temperature for 20% conversion of CO into CO_2 in CO-NO and CO-O_2 reactions.

Since the solubility limit of the Cu/Ru pair in this system is around y = 0.1, the maximum activity shown by ACR10 may imply that Cu and Ru are active sites only as far as they are incorporated in the crystal lattice of the Al-based perovskite. As can be seen from Figure 2, the decrease in the activity for CO-NO reaction between y = 0.1 and 0.2 due to the formation of impurity phases was more remarkable than that for the CO oxidation.

In order to compare the effect of the Cu/Ru substitution among Al-, Mn-, Fe- and Co-based systems, the $T_{20\%}$ values for CO-NO and CO-O_2 reactions are plotted in Figure 3. The effect of Cu/Ru substitution was dependent on host M cations. In the Co-based system, both activities decreased progressively with increasing Cu/Ru substitution.[6] The Cu/Ru substitution in the Fe-based system caused an enhancement of the CO-O_2 activity, while the NO-CO activity being almost unchanged, and the reverse was true in the Mn-based system. A drastic enhancement of activities for both reactions was observed only when the Cu/Ru pair was incorporated into the inactive host of $La_{0.8}Sr_{0.2}AlO_3$. In addition to the activity modification, the Cu/Ru substitution in every system caused an increase in the selectivity to N_2 in the NO-CO reaction, $N_2/(N_2+N_2O)$: *e.g.* CXX0 (16.3%) < CCR5 (45.1%), FXX0 (26.3%) < FCR10 (41.5%) at 300 °C, MXX0 (19.7%) < MCR10 (51.9%) at 350 °C.

The TPD investigation showed that the desorption amount of weakly bonded lattice oxygen, *i.e.* the redox capacity of the oxide lattice, from $La_{0.8}Sr_{0.2}Co_{1-2y}Cu_yRu_yO_3$ decreased monotonically with increasing y value[6] while the Cu/Ru substitution in the Al-based system caused an apparent increase of oxygen desorption. The agreement between the dependence on Cu/Ru substitution of activity for redox-type CO-O_2 and CO-NO reactions and oxygen desorption in each of Al- and Co-based systems suggests that such a modification of the redox properties of catalysts would be implicated in the activity modification. A detailed investigation is in progress for the full understanding of the effect of Cu/Ru substitution.

It has already been reported that perovskites containing Ru as a host B cation (*e.g.* $SrRuO_3$) or a substituent (*e.g.* $La_{0.7}Pb_{0.3}Mn_{0.9}Ru_{0.1}O_3$, $La_{0.7}Pb_{0.3}Mn_{0.92}Ru_{0.04}Ni_{0.04}O_3$) are active for the reduction of NO with CO or H_2[1,7,8] and that the substitution of Cu into $LaMnO_3$ enhances the activity for CO-O_2 and CO-NO reactions.[9-11] The present study revealed that the incorporation of Cu and Ru simultaneously into the inactive $La_{0.8}Sr_{0.2}AlO_3$ host gave a quite active catalyst (ACR10) for both CO-NO and CO-O_2 reactions. In addition, the activity of ACR10 especially for CO-NO reaction was comparable to that of 0.5 wt% Pt/Al_2O_3 (N.E. CHEMCAT) or $La_{0.8}Sr_{0.2}CoO_3$ (CXX0) which is one of most active perovskite catalysts (*cf.* Figure 3). Almost all reports on perovskite catalysts have been devoted to perovskites with active B-site cations, *e.g.* Co and Mn.[1-3] The present results demonstrate that a less active host perovskite can be made active by adequate partial substitution.

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References and Notes

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