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Catalytic Activity of Perovskite-Type Oxides for the Direct Decomposition of Nitrogen Monoxide

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Perovskite-type oxides showed the catalytic activity for NO decomposition above 773 K, which depended largely on constituent metal cations and their composition. Results obtained indicate that perovskite-type oxides such as $La_{0.8}Sr_{0.2}CoO_3$ are a promising NO decomposition catalyst having high activity and thermal stability at elevated temperatures.

Nitrogen monoxide (NO) is one of serious air pollutants, and the development of the excellent process to remove NO from exhausts has remained important. Among the NO removal processes proposed, the direct decomposition of NO into N_2 and O_2 ($2NO \rightarrow N_2 + O_2$) over a solid catalyst is the simplest method without any need of reducing agents. In spite of extensive studies to develop an effective catalyst for NO decomposition,1) Cu ion-exchanged ZSM-5 is the only catalyst showing sufficiently high and stable steady-state activity for the reaction at temperatures around 773 K.2) It has been generally accepted that the desorption of oxygen generated through the NO decomposition is cardinal for a catalyst to show the steady-state activity and that for oxide catalysts oxide ion vacancies play an important role in the catalytic decomposition of NO. Thus defective perovskite-type oxides which easily desorb a large amount of oxygen from oxide bulk3) are the possible candidates for the NO decomposition catalysts.4-6) In this letter, we report the catalytic activity for NO decomposition of perovskite-type (ABO_3) and its relating mixed oxides which contain 3d transition metals at B sites.

Catalysts excepting $YBa_2Cu_3O_y$ were prepared by calcining an appropriate mixture of metal acetates or nitrates at 1123 K for 10 h in air. X-Ray diffraction analyses showed that the oxides thus prepared had K_2NiF_4-type ($La_{1.5}Sr_{0.5}CuO_4$) or perovskite-type (others) structure and that no significant structural changes were observed between the fresh and used catalysts. $YBa_2Cu_3O_y$ was synthesized from nitrates of Y, Ba, and Cu by adopting the two-step air calcination at 1173 K for 5 h and at 1223 K for 5 h.7) The obtained disk-form $YBa_2Cu_3O_y$ was pulverized and used as a catalyst. The resulting catalyst had an orthorhombic unit cell, which transformed into a tetragonal one under the reaction condition above 973 K. The specific surface areas of catalysts were measured by the BET method. The NO decomposition reaction was carried out in a flow reactor by feeding a gas mixture of NO (1 vol.%) and He (balance) at a rate of 15.0 cm^3 min^{-1} over 1 g catalyst (W/F = 4.0 g s cm^{-3}). The gas composition was analyzed before and after the reaction by gas chromatography using Molecular Sieve 5A for NO, N_2, and O_2 and Porapak Q for N_2O. The formation of N_2O was hardly detected for all the catalysts tested between 673 and 1073 K. In this study, the neat activity for NO decomposition was evaluated in terms of the conversion of NO to N_2 ($2[N_2]_{out}/[NO]_{in}$), because the decrease of NO is due to not only the decomposition of NO but also the oxidation of undecomposed NO by O_2 generated through NO decomposition ($NO + 1/2O_2 \longrightarrow NO_2$), which takes place in a cooler part of the reactor system on the downstream.

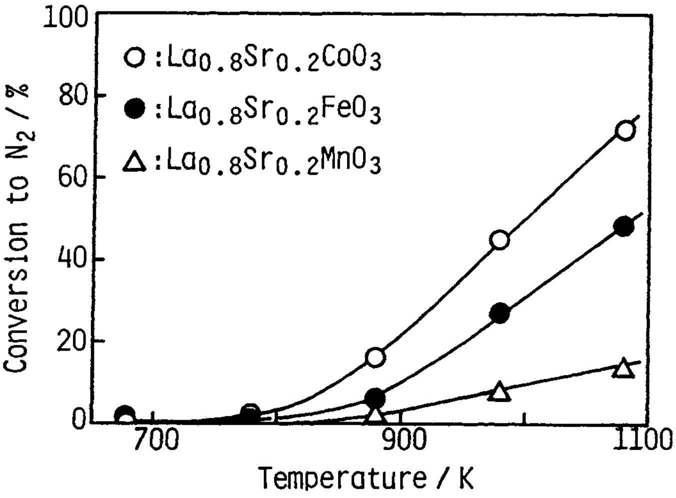

Fig. 1. Catalytic decomposition of NO over $La_{0.8}Sr_{0.2}MO_3$ (M=Mn, Fe, Co). W/F=4.0 g s cm^{-3}, Feed gas; 1% NO in He.

Each of the prepared oxides showed an activity more or less for NO decomposition at temperatures above 773 K. For examples, the temperature dependences of the NO decomposition activity of $La_{0.8}Sr_{0.2}MO_3$ (M=Mn, Fe, Co) are shown in Fig. 1. All experimental data were taken after 2 h on stream at respective temperatures, where the catalytic reaction practically reached a steady state. The catalytic activity appeared around 800 K and increased monotonically with increasing temperature. The conversion to N_2 of $La_{0.8}Sr_{0.2}CoO_3$ which is the most active in this study reached 72.0% at 1073 K. In addition, the activity of the oxide was not deteriorated even after 24 h on stream at 1073 K. These results suggest that perovskite-type oxides such as $La_{0.8}Sr_{0.2}CoO_3$ are promising as a highly active and stable catalyst for NO decomposition at elevated temperatures.

Table 1. NO decomposition activity of catalysts tested

Catalysts	Surface area/m^2g^{-1}	Conversion to N_2/% 973 K	Conversion to N_2/% 1073 K
$La_{0.8}Sr_{0.2}CoO_3$	8.1	45.0	72.0
$La_{0.8}Sr_{0.2}MnO_3$	9.1	7.6	13.5
$La_{0.4}Sr_{0.6}MnO_3$	4.0	10.8	25.1
$La_{0.8}Sr_{0.2}Co_{0.8}Fe_{0.2}O_3$	6.8	46.8	68.7
$La_{0.8}Sr_{0.2}Co_{0.4}Fe_{0.6}O_3$	5.1	24.9	56.2
$La_{0.8}Sr_{0.2}FeO_3$	6.7	26.9	48.8
$LaCo_{0.4}Fe_{0.6}O_3$	3.3	9.2	12.8
$La_{0.6}Sr_{0.4}Co_{0.4}Fe_{0.6}O_3$	2.1	17.5	37.1
$La_{0.2}Sr_{0.8}Co_{0.4}Fe_{0.6}O_3$	3.8	8.0	24.7
$SrCo_{0.4}Fe_{0.6}O_3$	3.3	9.8	27.9
$La_{0.8}Sr_{0.2}Co_{0.8}Cr_{0.2}O_3$	4.8	2.7	2.0
$La_{0.8}Sr_{0.2}Co_{0.8}Ni_{0.2}O_3$	5.6	34.2	70.5
$La_{0.8}Sr_{0.2}Co_{0.8}Cu_{0.2}O_3$	4.9	24.9	35.9
$La_{0.8}Sr_{0.2}Co_{0.8}Mn_{0.2}O_3$	4.6	30.4	43.4
$La_{0.6}Sr_{0.4}Co_{0.8}Mn_{0.2}O_3$	8.7	39.0	65.5
$La_{0.4}Sr_{0.6}Co_{0.8}Mn_{0.2}O_3$	7.2	37.6	67.9
$La_{0.4}Sr_{0.6}Co_{0.2}Mn_{0.8}O_3$	3.7	34.0	58.8
$LaMn_{0.8}Cu_{0.2}O_3$	2.6	6.4	9.8
$LaMn_{0.6}Cu_{0.4}O_3$	2.8	2.5	3.2
$La_{1.5}Sr_{0.5}CuO_4$	3.0	15.7	24.5
$YBa_2Cu_3O_y$	2.4	3.8	2.5

Table 1 summarizes the NO decomposition activity of the tested catalysts at 973 K and 1073 K. It can be seen that the activity depends largely on constituent metal cations and their composition. $La_{0.8}Sr_{0.2}Co_{0.8}M'_{0.2}O_3$ (M'=Fe, Co, Ni) and $La_{1-x}Sr_xCo_{0.8}Mn_{0.2}O_3$ (x=0.4, 0.6) showed an excellent activity: at 1073 K the conversion to N_2 is 65.5-72.0% over these catalysts. The specific surface area of a catalyst naturally affects the catalytic performance. However, the comparison between the catalysts having a comparable surface area, between $La_{0.8}Sr_{0.2}CoO_3$ and $La_{0.8}Sr_{0.2}MnO_3$ for example, indicates that the sort of constituent metals is primarily responsible for the difference in the activity.

Figure 2 shows the effect of Sr substitution for La in $La_{1-x}Sr_xCo_{0.4}Fe_{0.6}O_3$ on the catalytic activity for NO decomposition. The activity became maximum at x=0.2. In Mn-containing oxides, $La_{1-x}Sr_xMnO_3$ and $La_{1-x}Sr_xCo_{0.8}Mn_{0.2}O_3$, on the other hand, the activity tended to increase with an increase in x. These changes in the NO decomposition activity with Sr substitution essentially agree with those in the combustion activity,[8,9] suggesting that the existence of oxide ion vacancies and the ability to desorb oxygen are important for the catalytic activity for NO decomposition as observed in the combustion activity.[8,9]

The sort of B site cations affected the activity as well. Among $La_{0.8}Sr_{0.2}MO_3$ (M=Mn, Fe, Co), Co-containing oxide was most active, followed by Fe- and Mn-containing oxides as shown in Fig. 1. It was reported that $La_{0.8}Sr_{0.2}CoO_3$ and $La_{0.8}Sr_{0.2}FeO_3$ showed an oxygen-deficient nonstoichiometry[3] while $La_{0.8}Sr_{0.2}MnO_3$ showed an oxygen-excess nonstoichiometry.[9] Thus the lower activity of $La_{0.8}Sr_{0.2}MnO_3$ than the other two also indicates the importance of oxide ion vacancies. Because Co_3O_4 was reported to be more active for NO decomposition than Fe_2O_3,[10] the superiority in activity of $La_{0.8}Sr_{0.2}CoO_3$ over $La_{0.8}Sr_{0.2}FeO_3$ may imply that the nature of B site cations is important even when they are incorporated in the perovskite matrix. It has also turned out that the substitution of only 20% of Co in $La_{0.8}Sr_{0.2}CoO_3$ by other transition metal cations brought about the drastic change in activity (Fig. 3): Fe- and Ni-substituted oxides showed activity comparable

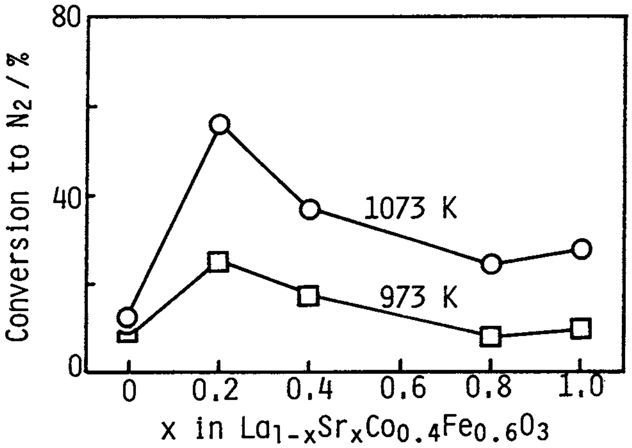

Fig. 2. Change in the NO decomposition activity with x in $La_{1-x}Sr_xCo_{0.6}Fe_{0.4}O_3$.

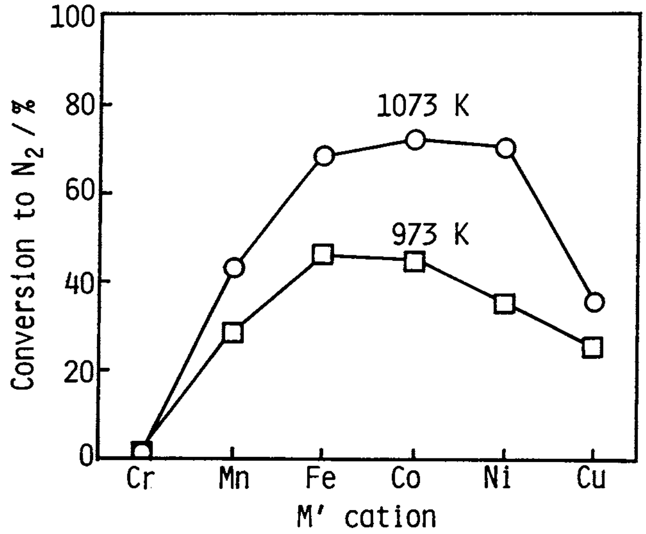

Fig. 3. Effect of B site substitution on the NO decomposition activity in $La_{0.8}Sr_{0.2}Co_{0.8}M'_{0.2}O_3$ (M'=Cr, Mn, Fe, Co, Ni, Cu).

to that of host $La_{0.8}Sr_{0.2}CoO_3$, while Cr-, Mn-, and Cu-substituted oxides were less active. The change in activity by B site substitution seems to result mainly from that in the specific surface area except for Cr-substituted oxides. Nevertheless, the above result would be sufficient to verify the possibility of modifying the NO decomposition activity of perovskite-type oxides by the partial substitution of B site cations.

Shimada et al.$^{6)}$ reported that Y-Ba-Cu-O mixed oxide supported on MgO was very active for NO decomposition at elevated temperatures and that the conversion to N_2 at 1073 K reached ca. 73% or 35% when W/F was set at 7.5 or 1.5 g s cm^{-3}, respectively (feed gas: 3%NO/He). Although the present experimental condition (W/F=4.0 g s cm^{-3}, feed gas: 1%NO/He) was different from their condition, the activity of Co-based perovskite-type oxides examined in this study seems to stand comparison with that of Y-Ba-Cu-O/MgO. Accordingly, it is concluded that the Co-based perovskite-type oxides are also the possible candidates for the NO decomposition catalysts at elevated temperatures. Furthermore, the variation of the catalytic property of the oxides by the partial substitution of cations strongly suggests the possibility of finding more excellent catalysts by selecting proper combinations of cations not only at A site but also at B site and their composition. It is also proposed that oxide ion vacancies and the catalytic nature of transition metals at B site for NO decomposition play an important role in the catalysis for NO decomposition over perovskite-type oxides.

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