Editor's Choice

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Direct Decomposition of NO on C-type Cubic Rare Earth Oxides Based on Y_2O_3

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C-type cubic $(Y_{0.99-x}Tb_xBa_{0.01})_2O_{2.99+\delta}$ $(0 \leq x \leq 0.4)$ catalysts were prepared by coprecipitation. The NO decomposition activities at 1173 K were higher than that of $(Gd_{0.7}Y_{0.26}Ba_{0.04})_2O_{2.96}$ reported previously. The highest catalytic activity was obtained for $(Y_{0.69}Tb_{0.3}Ba_{0.01})_2O_{2.99+\delta}$, and 100% NO conversion into N_2 and O_2 was realized at 1173 K on this catalyst. Furthermore, the conversion ratio was maintained as high as 70.8% even in the presence of 5 vol % oxygen.

The emission of nitrogen oxides (NO_x) is strictly regulated, because they are not only harmful to human beings but also responsible for photochemical smog and acid rain. The NO_x species in the exhaust gas emitted at high temperatures is principally thermodynamically stable NO and the amount of NO_2 is negligible. Accordingly, research should be focused on the NO decomposition in the case of catalytic NO_x remediation.

For the methods of NO removal, selective catalytic reduction processes using ammonia, urea, or hydrocarbons are the mainstream procedures.[1] In these processes, the decomposition efficiency is sufficient, and the reaction process is stable at high temperatures. However, separate specialized equipment is necessary to supply the reducing agents and secure control is indispensable, because ammonia is both toxic and flammable.

In contrast to the above methods that utilize selective catalytic reduction, direct decomposition of NO into N_2 and O_2 ($2NO \rightarrow N_2 + O_2$) is an appropriate route for NO removal, because this process is simple and reductants mentioned above are not required. A number of materials have been reported as active catalysts for direct NO decomposition, such as zeolites,[2] perovskites,[3–5] and other mixed or complex oxides.[6–14] However, the activity of conventional catalysts for NO decomposition decreases in the presence of oxygen, due to strong oxygen adsorption.

In contrast, it was found that C-type cubic rare earth oxides based on Gd_2O_3, $(Gd_{1-x-y}Y_xBa_y)_2O_{3-y}$ $(0 \leq x \leq 0.26,\ 0 \leq y \leq 0.08)$, can exhibit higher activity for direct NO decomposition than that of the perovskite-type catalysts in the presence of oxygen, as reported in our previous study.[14,15] There are three types of crystal structure in rare earth oxide, namely, A- (hexagonal), B- (monoclinic), and C-type (cubic), according to the ionic size of the respective rare earth element.[16] The lattice volume of the rare earth oxides increases in the order of A-type < B-type < C-type, and for this reason the C-type structure possesses the largest interstitial open space suitable for NO decomposition among the three types.

It has been generally accepted that oxide vacancies in the catalyst play an important role in the direct catalytic decomposition of NO.[3–7] Additional introduction of oxide anion vacancies by partial substitution of the trivalent rare earth cations with divalent Ba^{2+} ions will enhance the catalytic activity. In some of conventional catalysts, it has been suggested that the removal of surface oxygen can be easily achieved when the reduction of the tetravalent cation to the trivalent state proceeds easily.[4,5,8] In this study, Y_2O_3, which is a thermally more stable C-type cubic oxide than Gd_2O_3, was selected as the mother material, and a portion of Y^{3+} sites is substituted with Tb^{3+}/Tb^{4+} to promote direct NO decomposition, because the reduction of Tb^{4+} to Tb^{3+} cant take place smoothly.

Therefore, $(Y_{0.99-x}Tb_xBa_{0.01})_2O_{2.99+\delta}$ $(0 \leq x \leq 0.4)$ catalysts were prepared and their direct NO decomposition activities were investigated in this study. The molar fraction of barium in the catalysts was fixed to 1 mol %, because the addition of Ba^{2+} in concentrations more than 1 mol % induced formation of $BaTbO_3$ as a secondary impurity phase.

The $(Y_{0.99-x}Tb_xBa_{0.01})_2O_{2.99+\delta}$ catalysts were synthesized by coprecipitation. A stoichiometric mixture of aqueous solutions of $Y(NO_3)_3$ (1 mol dm^{-3}), $Tb(NO_3)_3$ (0.1 mol dm^{-3}), and $Ba(NO_3)_2$ (0.1 mol dm^{-3}) was added into a 1.0 mol dm^{-3} ammonium carbonate solution with stirring, adjusting the total amount of cations to be 10 mmol. The pH value of the mixture was adjusted to 10 by the dropwise addition of aqueous ammonia. After stirring for 6 h at room temperature, the resulting precipitate was collected by filtration, washed with deionized water several times, and then dried at 353 K for 6 h. The dried powder was ground in an agate mortar and finally calcined at 1173 K in air for 6 h.

Figure 1 shows X-ray powder diffraction (XRD) patterns of the $(Y_{0.99-x}Tb_xBa_{0.01})_2O_{2.99+\delta}$ catalysts. All the diffraction patterns can be assigned as C-type cubic rare earth oxides. Figure 2 depicts the temperature dependence of NO conversion

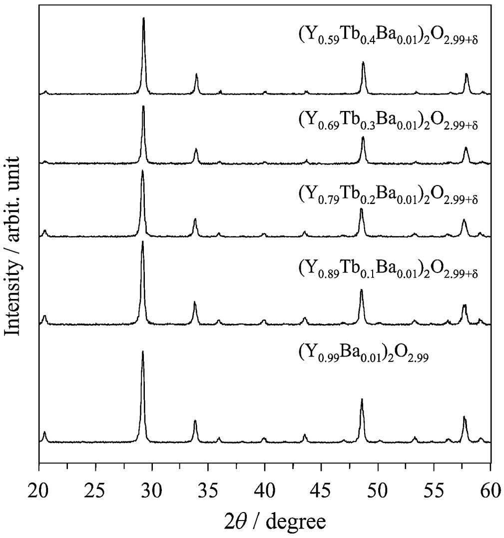

Figure 1. XRD patterns of the $(Y_{0.99-x}Tb_xBa_{0.01})_2O_{2.99+\delta}$ catalysts.

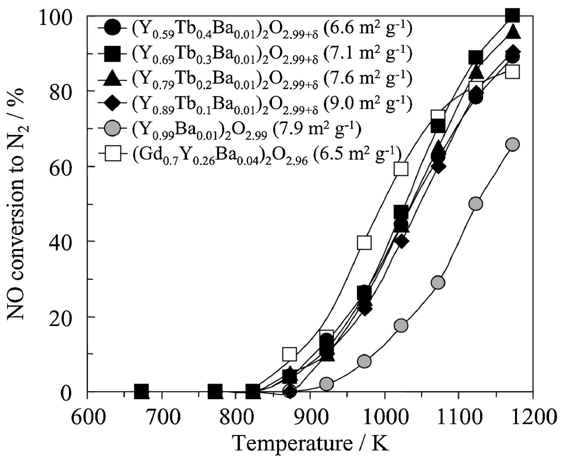

Figure 2. Temperature dependence of NO conversion into N_2 on $(Y_{0.99-x}Tb_xBa_{0.01})_2O_{2.99+\delta}$ and on $(Gd_{0.7}Y_{0.26}Ba_{0.04})_2O_{2.96}$ catalysts reported in ref 14 (NO: 1 vol %; He balance; $W/F = 3.0\,g\,s\,cm^{-3}$).

into N_2 on $(Y_{0.99-x}Tb_xBa_{0.01})_2O_{2.99+\delta}$ with that on $(Gd_{0.7}Y_{0.26}Ba_{0.04})_2O_{2.96}$ reported previously.[14] The catalytic tests were carried out in a conventional fix-bed flow reactor with 10-mm-diameter quartz glass tube by feeding a gas mixture of NO (1.0 vol %) and He (balance) at a rate of 10 cm³ min⁻¹ over 0.5 g catalyst. W/F was adjusted to be 3.0 g s cm⁻³, where W and F are the catalyst weight and gas flow rate, respectively. The activity of each catalyst was evaluated in terms of the conversion of NO to N_2. BET specific surface area of the catalysts is also depicted in parentheses in the figure, but there is no clear relationship with the catalytic activity. However, the NO decomposition activities were significantly enhanced by the Tb addition to $(Y_{0.99}Ba_{0.01})_2O_{2.99}$, and the highest NO decomposition activity was obtained for the $(Y_{0.69}Tb_{0.3}Ba_{0.01})_2O_{2.99+\delta}$. On this oxide, 100% NO decomposition into N_2 and O_2 was realized at 1173 K, which has not been achieved by the $(Gd_{0.7}Y_{0.26}Ba_{0.04})_2O_{2.96}$ catalyst. In the stoichiometric direct NO decomposition, the O_2 yield should be equivalent to that of N_2. However, O_2 yield detected at 1173 K was 76.5%, because of strong adsorption on the surface of the catalyst, arising from the oxidation of Tb^{3+} to Tb^{4+}.

The effect of the presence of oxygen on the NO conversion to N_2 at 1173 K is presented in Figure 3. As mentioned above, it has been reported that the presence of O_2 significantly lowers the catalytic activity for NO decomposition.[3–6,10–14] The NO decomposition activity of the present $(Y_{0.69}Tb_{0.3}Ba_{0.01})_2O_{2.99+\delta}$ catalyst was also affected by the presence of oxygen, and the NO to N_2 conversion was decreased with increasing the O_2 partial pressure. However, the conversion ratio on the present $(Y_{0.69}Tb_{0.3}Ba_{0.01})_2O_{2.99+\delta}$ catalyst was 77.8% under an oxygen partial pressure of 2 vol %. Even in the presence of 5 vol % O_2, high NO decomposition activity was sustained at 70.8%, which is higher than that of C-type cubic $(Gd_{0.7}Y_{0.26}Ba_{0.04})_2O_{2.96}$.

In summary, C-type cubic $(Y_{0.99-x}Tb_xBa_{0.01})_2O_{2.99+\delta}$ was prepared as a novel catalyst for direct NO decomposition. In particular, $(Y_{0.69}Tb_{0.3}Ba_{0.01})_2O_{2.99+\delta}$ can realize 100% NO conversion into N_2 and O_2 for the first time at 1173 K, and the activity is maintained at high conversion ratio, even in the presence of 5 vol % oxygen. Therefore, the C-type cubic $(Y_{0.69}Tb_{0.3}Ba_{0.01})_2O_{2.99+\delta}$ catalyst can be a new potential candidate as a direct NO removal catalyst.

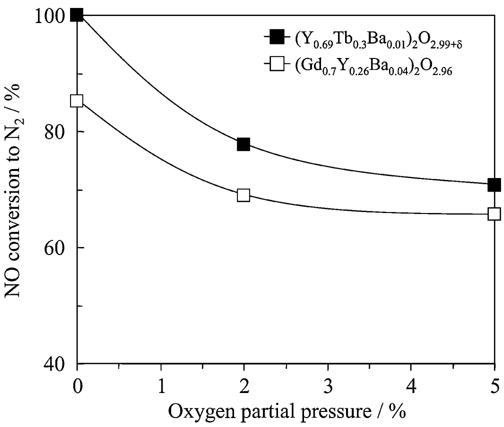

Figure 3. Effect of oxygen pressure on the N_2 formation rate on $(Y_{0.69}Tb_{0.3}Ba_{0.01})_2O_{2.99+\delta}$ and $(Gd_{0.7}Y_{0.26}Ba_{0.04})_2O_{2.96}$ (1173 K; NO: 1 vol %; He balance; $W/F = 3.0\,g\,s\,cm^{-3}$).

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