doi:10.1246/cl.2011.708

Coexisting Gas-resistant C-type Cubic Yb_2O_3–Tb_4O_7 Catalysts for Direct NO Decomposition

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C-type cubic $(Yb_{1-x}Tb_x)_2O_{3\pm\delta}$ $(0 \le x \le 0.62)$ catalysts were synthesized by coprecipitation. Among the samples prepared, $(Yb_{0.50}Tb_{0.50})_2O_{3\pm\delta}$ showed the highest catalytic activity and high tolerability for O_2 or CO_2 coexistence was recognized. In particular, the negative effect of CO_2 on the NO decomposition activity is significantly reduced compared to those of conventional catalysts, and N_2 yield as high as 33% was obtained even in the presence of 5 vol % CO_2.

Nitrogen oxides (NO_x) are not only harmful to human beings but are also responsible for photochemical smog and acid rain when they are formed in relatively large quantities in the atmosphere. NO_x species in exhaust gases emitted at high temperatures are composed principally of thermodynamically stable nitrogen monoxide (NO) and a negligible amount of nitrogen dioxide (NO_2). Accordingly, research should be focused on NO with respect to catalytic NO_x decomposition.

In several processes for NO removal, direct decomposition of NO into N_2 and O_2 ($2NO \rightarrow N_2 + O_2$) is an optimum route, because this process is quite simple and no reductant is required. A number of materials, such as zeolites,[1–3] perovskites,[4–9] and other mixed or complex oxides[10–14] have been reported as active catalysts for direct NO decomposition, of which perovskite-type catalysts have been extensively studied. However, the NO decomposition activity of these conventional catalysts is significantly decreased in the presence of O_2 or CO_2, due to the strong adsorption of the coexisting gas on the surface of the catalysts. In particular, CO_2 inhibition is quite serious for the conventional perovskite-type catalysts, in which alkaline earth ions such as Sr^{2+} and Ba^{2+} are contained in the lattice,[4,9] because CO_2 is acidic and because adsorption of CO_2 on the Sr^{2+} and Ba^{2+} sites on the surface of the catalyst significantly inhibits the NO adsorption.

In our previous studies, we elucidated that a catalyst based on C-type cubic rare earth oxide can exhibit higher activity for direct NO decomposition than that of perovskite-type catalysts in the presence of O_2.[15–18] The C-type cubic oxides, R_2O_3 (R = rare earths), are related to the fluorite structure oxides, RO_2, from which the C-type oxides are derived by removing one-quarter of the oxide anions. In other words, C-type structure possesses large interstitial open spaces,[19] which have been identified to play an important role in direct NO decomposition in our laboratory.[17]

Among the series of rare earth elements, terbium forms intermediate oxides based on oxygen-deficient fluorite-related structures in narrow composition ranges with the generic formula Ln_nO_{2n-2m} (n is an integer or infinity, and m is between 1 and 8),[19] because terbium ion can take both trivalent (Tb^{3+}) and tetravalent (Tb^{4+}) states. The amount of oxide anions in the lattice is larger than that of the C-type structure but smaller than that of the fluorite structure. In our previous study, it was evidenced that introduction of $Tb^{3+/4+}$ into the lattice was highly effective for enhancing the NO decomposition activity and suggested the promotion of O_2 desorption from the catalyst surface caused by the redox property of $Tb^{3+/4+}$ as a possible reason for the improvement of catalytic activity.[18]

Furthermore, it has been suggested that surface basic sites of rare earth oxides are oxide anions on the surface.[20] Therefore, the coexisting CO_2 should be adsorbed on the oxide anions on the surface of the catalyst and block the adsorption of NO molecules. The redox ability of the catalysts would be also effective to prevent the negative effect of CO_2, because CO_2 adsorption on the surface of the catalyst is hindered by a similar mechanism suggested in the case of O_2.

In this study, therefore, we designed novel C-type cubic rare earth oxides without alkaline earth ions in the lattice for direct NO decomposition catalysts. Furthermore, the catalysts were composed of only rare earth ions, which can take multiple oxidation states, and heavier rare earth ions were selected for the component because they are originally inactive to react with CO_2.[21] Accordingly, the catalysts were based on Yb_2O_3 which can maintain C-type cubic structure even at temperatures above 1273 K,[19] and a part of the Yb^{3+} sites was substituted with $Tb^{3+/4+}$ to promote NO decomposition. Since ytterbium ion can also take multiple valence states such as Yb^{3+} and Yb^{2+}, the reduction of Yb^{3+} to Yb^{2+} will further promote O_2 and CO_2 desorption from the catalyst surface, in addition to that of $Tb^{3+/4+}$. Therefore, the $(Yb_{1-x}Tb_x)_2O_{3\pm\delta}$ $(0 \le x \le 0.62)$ catalysts were prepared, and their NO decomposition activities were investigated. Furthermore, the effects of the coexistence of O_2 or CO_2 on the catalytic activity were also examined.

The catalysts were synthesized by a coprecipitation method. A stoichiometric mixture of 1 $mol\,dm^{-3}$ aqueous $Yb(NO_3)_3$ and 0.1 $mol\,dm^{-3}$ aqueous $Tb(NO_3)_3$ was added to 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.

The catalysts were characterized by using X-ray powder diffraction (XRD), and the specific surface area was measured by the BET (Brunauer–Emmett–Teller) method. The catalytic tests were carried out in a conventional fix-bed flow reactor with a 10-mm-diameter quartz glass tube by feeding a gas mixture of NO (1.0 vol %) and He (balance) at a rate of 10 $cm^3\,min^{-1}$ over 0.5 g of catalyst. The W/F ratio 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 NO conversion to N_2. The effect of the presence of O_2 or CO_2 was measured by mixing each gas species with the reactant gas.

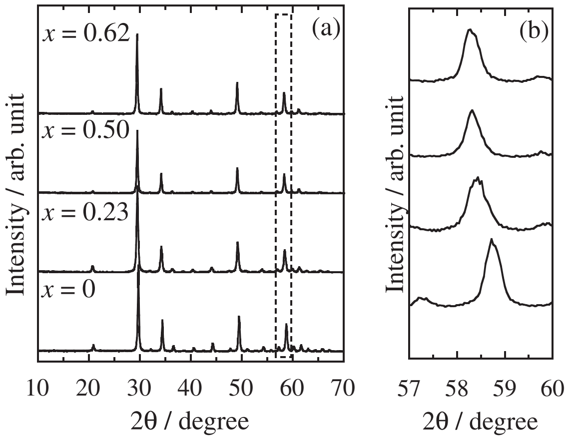

Figure 1. XRD patterns of the $(\mathrm{Yb}_{1-x}\mathrm{Tb}_x)_2\mathrm{O}_{3\pm\delta}$ catalysts in the 2θ ranges from 10 to 70° (a) and 57 to 60° (b).

The concentrations of the additional gases and NO were controlled by changing the feed rate of He as the balance gas to maintain a total flow rate of reactants constant at $10\,\mathrm{cm}^3\,\mathrm{min}^{-1}$.

Figure 1 shows XRD patterns of the $(\mathrm{Yb}_{1-x}\mathrm{Tb}_x)_2\mathrm{O}_{3\pm\delta}$ catalysts. All the diffraction patterns can be assigned to C-type cubic rare earth oxides, and no crystalline impurities were observed. Since the ionic sizes of Yb^{3+} and Tb^{3+} with six coordination number are 0.1008 and 0.1063 nm, respectively,[22] the diffraction peaks shifted to lower angles relative to those of $\mathrm{Yb}_2\mathrm{O}_3$ with the increase of the Tb^{3+} concentration. Therefore, the lattice parameters of the $(\mathrm{Yb}_{1-x}\mathrm{Tb}_x)_2\mathrm{O}_{3\pm\delta}$ catalysts became larger than that of $\mathrm{Yb}_2\mathrm{O}_3$, indicating that the C-type cubic solid solutions were successfully obtained. However, the crystalline structure gradually transformed to the oxygen-deficient fluorite-related structure with increasing the amount of terbium in the range of $0.50 \le x \le 0.62$.

Figure 2 depicts the temperature dependence of NO conversion to N_2 on the $(\mathrm{Yb}_{1-x}\mathrm{Tb}_x)_2\mathrm{O}_{3\pm\delta}$ catalysts. The formation of $\mathrm{N}_2\mathrm{O}$ was not detected between 673 and 1173 K. BET surface area of the catalysts is also depicted in parentheses in the figure, and the surface area decreased with increasing of $\mathrm{Tb}^{3+/4+}$ content. However, the NO decomposition activity was enhanced by the $\mathrm{Tb}^{3+/4+}$ addition, and the highest catalytic activity was obtained for the $(\mathrm{Yb}_{0.50}\mathrm{Tb}_{0.50})_2\mathrm{O}_{3\pm\delta}$ catalyst. On this oxide, the N_2 yield reached 54% at 1173 K in the absence of coexistence gas (NO/He atmosphere).

The effect of the presence of O_2 or CO_2 on the N_2 yield at 1173 K is presented in Figure 3 for the $(\mathrm{Yb}_{0.50}\mathrm{Tb}_{0.50})_2\mathrm{O}_{3\pm\delta}$ catalyst, which shows the highest catalytic activity for direct NO decomposition among the samples prepared. Also in these cases, $\mathrm{N}_2\mathrm{O}$ was not detected, as that in the absence of these interfering gases. In the presence of O_2, the catalytic activity monotonically decreased from 54 to 35% with the increase in the O_2 concentration until the content reached 5 vol %. The N_2 yield in the presence of 5 vol % O_2 at 1173 K (35%) was higher than that of the conventional perovskite-type $\mathrm{La}_{0.8}\mathrm{Sr}_{0.2}\mathrm{CoO}_3$ catalyst (20% at 1073 K)[4] but was comparable to that of the $\mathrm{Ba}_{0.8}\mathrm{La}_{0.2}\mathrm{Mn}_{0.8}\mathrm{Mg}_{0.2}\mathrm{O}_3$ catalyst (40% at 1123 K).[7] However, the decreasing degree of the N_2 yield from 0 to 5 vol % O_2 at 1173 K was only 19% (54 → 35%) on the present $(\mathrm{Yb}_{0.50}\mathrm{Tb}_{0.50})_2\mathrm{O}_{3\pm\delta}$ catalyst, which is obviously smaller than those of the $\mathrm{La}_{0.8}\mathrm{Sr}_{0.2}\mathrm{CoO}_3$ (35% at 1073 K; 55 → 20%)[4] and the $\mathrm{Ba}_{0.8}\mathrm{La}_{0.2}\mathrm{Mn}_{0.8}\mathrm{Mg}_{0.2}\mathrm{O}_3$ (35% at 1123 K; 75 → 40%)[7] catalysts.

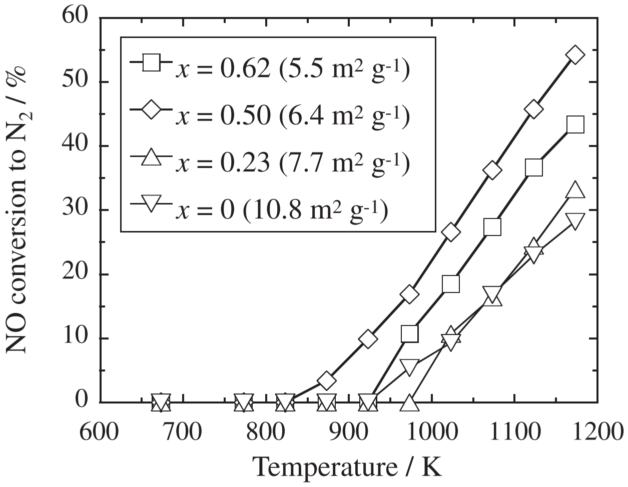

Figure 2. Temperature dependences of NO conversion to N_2 over the $(\mathrm{Yb}_{1-x}\mathrm{Tb}_x)_2\mathrm{O}_{3\pm\delta}$ catalysts (NO: 1 vol %; He balance; $W/F = 3.0\,\mathrm{g\,s\,cm}^{-3}$).

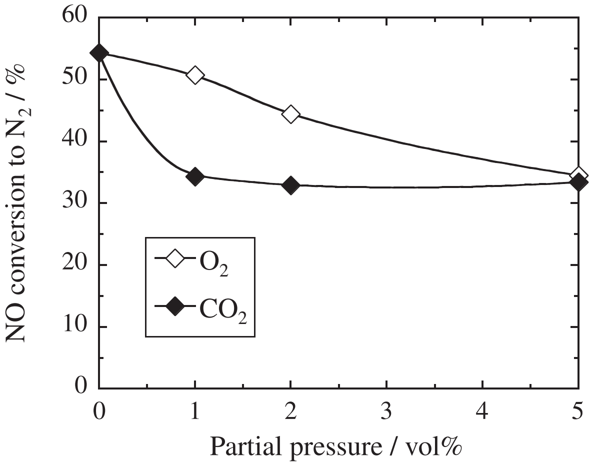

Figure 3. Effects of partial pressures of O_2 and CO_2 in the feed gas on the conversion of NO to N_2 over the $(\mathrm{Yb}_{0.50}\mathrm{Tb}_{0.50})_2\mathrm{O}_{3\pm\delta}$ catalyst (1173 K; NO, 1 vol %; He balance; $W/F = 3.0\,\mathrm{g\,s\,cm}^{-3}$).

In the case of the effect of CO_2 coexistence on the NO decomposition activity, N_2 yield on the $(\mathrm{Yb}_{0.50}\mathrm{Tb}_{0.50})_2\mathrm{O}_{3\pm\delta}$ catalyst at 1173 K was decreased from 54 to 34% when the concentration of CO_2 reached 2 vol %. However, the N_2 yield was almost constant in the CO_2 partial pressure range between 2 and 5 vol %. As a result, on the $(\mathrm{Yb}_{0.50}\mathrm{Tb}_{0.50})_2\mathrm{O}_{3\pm\delta}$ catalyst, a high N_2 yield was sustained at 33% even in the presence of 5 vol % CO_2, which is appreciably higher than those for the conventional perovskite-type $\mathrm{La}_{0.8}\mathrm{Sr}_{0.2}\mathrm{CoO}_3$ (10% at 1073 K)[4] and $\mathrm{Ba}_{0.8}\mathrm{La}_{0.2}\mathrm{Mn}_{0.8}\mathrm{Mg}_{0.2}\mathrm{O}_3$ (18% at 1123 K)[9] catalysts. Furthermore, the decreasing degree of the N_2 yield from 0 to 5 vol % CO_2 was only 20% (54 → 34%) on the present $(\mathrm{Yb}_{0.50}\mathrm{Tb}_{0.50})_2\mathrm{O}_{3\pm\delta}$ catalyst at 1173 K, which is also significantly smaller than those of $\mathrm{La}_{0.8}\mathrm{Sr}_{0.2}\mathrm{CoO}_3$ (48% at 1073 K;

58 → 10%)[4] and $Ba_{0.8}La_{0.2}Mn_{0.8}Mg_{0.2}O_3$ (54% at 1123 K; 72 → 18%).[9] These results clearly elucidate the advantage of the present $(Yb_{0.50}Tb_{0.50})_2O_{3\pm\delta}$ catalyst that alkaline earth ions are not contained in the lattice and that both rare earth ions in the catalyst can take multiple valence states. Therefore, the negative effect of CO_2 is significantly reduced compared to those of the conventional catalysts.

As mentioned above, the present $(Yb_{1-x}Tb_x)_2O_{3\pm\delta}$ catalysts show high tolerability of O_2 or CO_2 coexistence. Furthermore, the catalytic activity steadily recovered to the original state without the interfering gas, when the cofeeding of O_2 or CO_2 in the reaction gas was cut off. The XRD pattern of the $(Yb_{0.50}Tb_{0.50})_2O_{3\pm\delta}$ catalyst remains unchanged before and after the reactions. These results suggest that the decrease in the NO decomposition activity is caused by the strong adsorption of O_2 or CO_2 on the catalyst surface, but the negative effects are not permanent. Similar recovery behavior is observed in the case of typical perovskite-type catalysts containing alkaline earth ions such as $La_{0.8}Sr_{0.2}CoO_3$[4] and $Ba_{0.8}La_{0.2}Mn_{0.8}Mg_{0.2}O_3$.[9] However, the deleterious impact of the coexisting O_2 or CO_2 on the catalytic activities is significantly larger than that of the present $(Yb_{0.50}Tb_{0.50})_2O_{3\pm\delta}$ catalyst as mentioned above.

In summary, C-type cubic $(Yb_{1-x}Tb_x)_2O_{3\pm\delta}$ was prepared as a novel catalyst for direct NO decomposition. The catalysts were designed from the innovative concept not only that any alkaline earth ions such as Ba^{2+} and Sr^{2+} are not contained in the lattice but also that the catalysts are composed of only heavier rare earth ions which can take multiple valence states. The highest catalytic activity was obtained for $(Yb_{0.50}Tb_{0.50})_2O_{3\pm\delta}$ in the samples we prepared. Furthermore, the $(Yb_{0.50}Tb_{0.50})_2O_{3\pm\delta}$ catalyst was highly tolerant against not only O_2 but also CO_2 coexistence. In particular, a high N_2 yield was maintained in the presence of CO_2 compared with those of the conventional perovskite-type catalysts. Therefore, the C-type cubic $(Yb_{1-x}Tb_x)_2O_{3\pm\delta}$ catalysts can be a new potential candidate for a direct NO decomposition catalyst.

This work was supported by the Steel Industry Foundation for the Advancement of Environmental Protection Technology (SEPT) and the Industrial Technology Research Grant Program '08 (Project ID: No. 08B42001a) from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

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