Direct Decomposition of NO into N2 and O2 over C-Type Cubic Y2O3-Tb4O7-ZrO2

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ABSTRACT

Catalytic activities for direct NO decomposition were investigated over C-type cubic Y2O3-Tb4O7-ZrO2 prepared by a co-precipitation method. The NO decomposition activity was enhanced by partial substitution of the yttrium sites with terbium in a (Y0.97Zr0.03)2O3.03 catalyst, which shows high NO decomposition activity. Among the catalysts synthesized in this study, the (Y0.67Tb0.30Zr0.03)2O3.33 catalyst exhibited the highest NO decomposition activity; NO conversion to N2 was as high as 67% at 900°C in the absence of O2 (NO/He atmosphere), and a relatively high conversion ratio was observed even in the presence of O2 or CO2, compared with those obtained over conventional direct NO decomposition catalysts. These results indicate that the C-type cubic Y2O3-Tb4O7-ZrO2 catalyst is a new potential candidate for direct NO decomposition.

Keywords: Nitrogen Monoxide; Direct Decomposition; Catalyst; Rare Earth Oxide; C-Type Cubic Structure

1. Introduction

Nitrogen oxides (NOx) are not only harmful to human beings, but are also responsible for photochemical smog and acid rain when present in relatively high levels in the atmosphere. NOx is mainly produced by the high-temperature combustion of fossil fuels such as petroleum in the engines of vehicles and ships, or coke in large-size boilers of factories. NOx species in exhaust gases emitted at high temperatures are composed principally of thermodynamically stable NO and a negligible amount of NO2. Therefore, studies on the catalytic decomposition of NO should focus on NO.

Several NO reduction processes have been proposed for NOx removal. Among them, selective catalytic reduction (SCR) methods employing ammonia or urea have been extensively studied and applied in diesel engines and large-size boilers [1]. The SCR methods have sufficient NO decomposition efficiency and a stable reaction process at high temperatures. However, separate specialized equipment is necessary to supply the reducing agents. Moreover, it is absolutely essential to ensure secure control systems due to the high toxicity and flammability of ammonia.

In contrast to the above processes employing ammonia or urea, direct catalytic decomposition of NO into N2 and O2 (2NO → N2 + O2) is the most ideal route for NOx removal, because no reducing agents and no special equipment are required. A number of materials, such as zeolites [2,3], perovskites [4-6], and other complex oxides [7-18], have been proposed as active catalysts for direct NO decomposition. However, the NO decomposition activity of these conventional catalysts is significantly decreased in the presence of O2 and CO2, due to strong adsorption of these molecules on the surface of the catalysts. Oxygen molecules produced by NO decomposition as well as those present in the gas phase adsorb on the catalyst surface and interfere with the catalytic reaction. In addition, a number of active direct NO decomposition catalysts contain highly basic alkaline and alkaline earth ions in the lattice. Among them, catalysts containing Ba typically exhibit high NO decomposition activities, because NO is acidic and adsorption of NO on the surface of the catalyst is significantly enhanced with increasing basicity of the catalyst. However, the high basicity also facilitates adsorption of CO2. As a result, catalyst poisoning by CO2 adsorption becomes a serious problem.

To realize high activities for direct NO decomposition, it is important to design a novel catalyst that is not influenced by the presence of CO2 or O2. Accordingly, we focused on C-type cubic rare earth oxides. Rare earth oxides can form three types of crystal structures, A-(hexagonal), B-(monoclinic), and C-types (cubic), depending on the ionic size of the respective rare earth element [19]. Among these, the C-type cubic structure
has the largest interstitial open space. It has been generally accepted that large open spaces in a catalyst play an important role in direct NO decomposition, and for this reason the C-type cubic rare earth oxide is suitable as a direct NO removal catalyst. Furthermore, in our previous works, we found that several C-type cubic rare earth oxide catalysts can exhibit high activities for direct NO decomposition even in the presence of O₂ [20-25] and that exclusion of alkaline earth ions from the catalyst lattice is significantly effective to induce CO₂ tolerance [25,26].

In the present study, \((\text{Y}_{0.97-x}\text{Zr}_{x}\text{O}_{2.03+\delta})\) solid solutions \((x = 0, 0.10, 0.20, 0.30, \text{and} 0.40)\), which adopt a C-type cubic structure, were designed as novel NO decomposition catalysts. In these catalysts, a fraction of the yttrium sites in \((\text{Y}_{0.97}\text{Zr}_{0.03})\) with \(\delta < 0\), which showed the highest NO decomposition activity in \((\text{Y}_{1-x}\text{Zr}_x)\) \((0 \leq y \leq 0.10)\) [24], was substituted with terbium to inhibit catalyst poisoning by O₂ and CO₂, utilizing the redox property of Tb³⁺/²⁺ [23,25] for effective direct NO decomposition.

2. Experimental

2.1. Catalyst Preparation

The C-type cubic \((\text{Y}_{0.97-x}\text{Tb}_{x}\text{Zr}_{0.03})\) \((x = 0, 0.10, 0.20, 0.30, \text{and} 0.40)\) catalysts were synthesized by a co-precipitation method, where the zirconium content was fixed at 3 mol% for the reason mentioned above. A stoichiometric mixture of 1 mol·dm⁻³ \(\text{Y(NO₃)₃}, 0.1 \text{ mol·dm}^{-3} \text{Tb(NO₃)₃}, \text{and} 0.1 \text{ mol·dm}^{-3} \text{ZrO(NO₃)₂} \) aqueous solutions was added to a 1.0 mol·dm⁻³ ammonium carbonate solution with stirring. The pH of the mixture was adjusted to 10 by dropwise addition of 9% ammonia solution. After stirring at room temperature for 6 h, the resulting precipitate was collected by filtration, washed several times with deionized water, and then dried at 80°C for 6 h. The powder was then ground in an agate mortar and finally calcined at 900°C in air for 6 h.

2.2. Characterization

The catalysts were characterized by X-ray powder diffraction (XRD; Rigaku SmartLab) with CuKα radiation. XRD patterns were recorded in the 2θ range from 10° to 70°. The sample compositions were analyzed by X-ray fluorescence spectrometry (XRF; Rigaku, ZSX100e) and the specific surface area was measured by the Brunauer-Emmett-Teller (BET) method using nitrogen adsorption at −196°C with a Micromeritics TriStar 3000 adsorption analyzer.

2.3. Catalyst Test

The NO decomposition reaction was carried out in a conventional fixed-bed flow reactor with a 10-mm-diameter quartz glass tube. A gas mixture of 1 vol% NO and He (balance) was fed at a rate of 10 cm³·min⁻¹ over 0.5 g of catalyst. The W/F ratio, where W and F are the catalyst weight and gas flow rate, respectively, was adjusted to 3.0 g·s·cm⁻³. The gas composition was analyzed using a thermal conductivity detector (TCD), a molecular sieve 5 A column for NO, N₂, and O₂, and a Polapak-Q column for N₂O separation. The activity of each catalyst was evaluated in terms of NO conversion to N₂.

The effect of the presence of O₂ or CO₂ was measured by mixing each gas species with the reactant gas. 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 reactant flow rate of 10 cm³·min⁻¹.

2.4. Temperature Programmed Desorption

Temperature-programmed desorption (TPD) measurements of O₂ was carried out after adsorption of O₂ at 600°C for 1 h. After heating the catalyst in a flow of He (30 cm³·min⁻¹) at 600°C for 30 min, the catalytic was exposed to O₂ (1 atm) at the same temperature for 1 h, and then cooled to 50°C. After evacuation at 50°C for 30 min, the catalyst was heated under a flow of He at a heating rate of 10°C·min⁻¹ and the desorbed gas was monitored using a gas chromatograph with a TCD analyzer (BELCAT-B BEL JAPAN). In the case of CO₂-TPD, the catalyst was heated in a flow of He (30 cm³·min⁻¹) at 600°C for 1 h, and subsequently in a flow of H₂ (30 cm³·min⁻¹) at 600°C for 30 min. The catalyst was cooled in a flow of He to 50°C, and was then exposed to CO₂ (1 atm) at this temperature for 1 h. After evacuation at 50°C for 30 min, the catalyst was heated under a flow of He at a heating rate of 10°C·min⁻¹.

3. Results and Discussion

3.1. Characterization of the Catalysts

Figure 1 shows XRD patterns of the \((\text{Y}_{0.97-x}\text{Tb}_{x}\text{Zr}_{0.03})\) catalysts \((x = 0, 0.10, 0.20, 0.30, \text{and} 0.40)\). C-type cubic rare earth oxide with a single phase structure (PDF-ICDD 41-1105 for Y₂O₃) was successfully obtained for all samples and no crystalline impurities were observed. The catalyst compositions, as determined using XRF, the lattice constants, and the BET surface area of the \((\text{Y}_{0.97-x}\text{Tb}_{x}\text{Zr}_{0.03})\) catalysts are summarized in Table 1. The cubic lattice parameter of \((\text{Y}_{0.97-x}\text{Tb}_{x}\text{Zr}_{0.03})\) gradually decreased with the x value, because ionic sizes of Y³⁺ and Tb⁴⁺ with a six-fold coordination are 0.1040 nm [27] and 0.0900 nm [27], respectively. When the smaller Tb⁴⁺ occupies the lattice position of Y³⁺ in \((\text{Y}_{0.97}\text{Zr}_{0.03})\), the lattice parameter...
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Figure 1. XRD patterns of the (Y₀.₉₇₋ₓTbxZr₀.₀₃)₂O₃₊ₓ catalysts (x = 0, 0.10, 0.20, 0.30, and 0.40).

Table 1. Composition, lattice constant, and BET surface area of the (Y₀.₉₇₋ₓTbxZr₀.₀₃)₂O₃₊ₓ catalysts.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Lattice constant /nm</th>
<th>BET surface area /m²·g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Y₀.₆₇Tb₀.₃₀)₂O₃.₃₃</td>
<td>1.₀₅₆₁</td>
<td>2₁.₅</td>
</tr>
<tr>
<td>(Y₀.₇₇Tb₀.₂₀)₂O₃.₂₃</td>
<td>1.₀₅₈₈</td>
<td>1₆.₀</td>
</tr>
<tr>
<td>(Y₀.₈₇Tb₀.₁₀)₂O₃.₁₃</td>
<td>1.₀₆₀₀</td>
<td>1₅.₆</td>
</tr>
<tr>
<td>(Y₀.₹₇Zr₀.₀₃)₂O₃.₀₃</td>
<td>1.₀₆₀₉</td>
<td>2₀.₆</td>
</tr>
</tbody>
</table>

decreases monotonically with increasing Tb⁴⁺ content. The results indicate that C-type cubic solid solutions were successfully formed for all samples. The BET specific surface area was slightly affected by the introduction of Tb⁴⁺ into the (Y₀.₉₇Zr₀.₀₃)₂O₃.₀₃ lattice.

3.2. NO Decomposition Activity

Figure 2 depicts the temperature dependencies of the N₂ yield for the (Y₀.₉₇₋ₓTbxZr₀.₀₃)₂O₃₊ₓ catalysts (x = 0, 0.10, 0.20, 0.30, and 0.40). Initial NO decomposition activity appeared at 5₅₀°C and the N₂ yield increased monotonically with reaction temperature. The formation of N₂O was not detected between 4₀₀ and 9₀₀°C.

Figure 3 shows the dependence of NO conversion into N₂ at 9₀₀°C on the terbium concentration in the (Y₀.₉₇₋ₓTbxZr₀.₀₃)₂O₃₊ₓ catalysts. The catalytic activity increased with the x value, and the highest catalytic activity was obtained for the (Y₀.₆₇Tb₀.₃₀Zr₀.₀₃)₂O₃.₃₃ composition, where the N₂ yield obtained over this catalyst was 6₇%.

3.3. Effect of the Presence of O₂ or CO₂

The effect of the presence of O₂ or CO₂ on the N₂ yield obtained over the (Y₀.₆₇Tb₀.₃₀Zr₀.₀₃)₂O₃.₃₃ catalyst at 9₀₀°C was also examined, and the results are presented in Figure 4. In the presence of O₂, the N₂ yield for (Y₀.₆₇Tb₀.₃₀Zr₀.₀₃)₂O₃.₃₃ decreased from 6₇ to 5₃% until the content reached 1 vol%, but became almost constant in the range from 1 to 5 vol%. As a result, NO decomposition activity as high as 4₇% was maintained, even in the presence of 5 vol% O₂, and the activity did not deteriorate during the 1₀-h catalytic test. This conversion ratio in the presence of 5 vol% O₂ (4₇%) was higher than that for C-type cubic (Yb₀.₅₀Tb₀.₅₀)₂O₃±δ (₃₅%) [2₅].

In contrast, the effect of CO₂ on the NO decomposition activity was relatively larger than that for O₂, but the decreasing tendency of the N₂ yield with the increase in the partial pressure of CO₂ was similar to that observed for O₂. Since CO₂ is acidic, adsorption of CO₂ on the basic sites of the catalyst surface will inhibit NO adsorption on the open space sites of the catalyst. However, for the (Y₀.₆₇Tb₀.₅₀Zr₀.₀₃)₂O₃.₃₃ catalyst, a high N₂ yield of 3₆% was maintained even in the presence of 5 vol% CO₂, which is higher than those for the (Yb₀.₆₀Tb₀.₄₀)₂O₃±δ (3₄%) [2₅], Ba₀.₅La₀.₅Mn₀.₅Mg₀.₅O₃ (2₀% at 8₅₀°C) [1₂], and La₀.₈Sr₀.₂CoO₃ (1₀% at 8₀₀°C) catalysts [1₅].

![Figure 2. Temperature dependence of the N₂ yield obtained over the (Y₀.₉₇₋ₓTbxZr₀.₀₃)₂O₃₊ₓ catalysts (x = 0, 0.10, 0.20, 0.30, and 0.40) (NO: 1 vol%, He; balance, W/F = 3.₀ g·s·cm⁻³).](image)

![Figure 3. Dependence of NO conversion into N₂ at 9₀₀°C on the terbium concentration in the (Y₀.₉₇₋ₓTbxZr₀.₀₃)₂O₃₊ₓ catalysts (NO: 1 vol%, He; balance, W/F = 3.₀ g·s·cm⁻³).](image)
Furthermore, the catalytic activity was recovered when the catalytic test was carried out again in the absence of CO\textsubscript{2} (1 vol\% NO/He), which indicates that the decrease in NO decomposition activity is caused by the adsorption of CO\textsubscript{2} on the catalyst. In addition, the XRD patterns of the \((Y_{0.67}Tb_{0.30}Zr_{0.03})_2O_{3.33}\) catalyst were the same before and after the reactions.

### 3.4. O\textsubscript{2} and CO\textsubscript{2} Desorption Profiles

As mentioned above, the present \((Y_{0.67}Tb_{0.30}Zr_{0.03})_2O_{3.33}\) catalyst showed relatively high catalytic activity even in the presence of O\textsubscript{2} or CO\textsubscript{2}. To facilitate direct NO decomposition, it is important that these coexisting gases desorb from the surface of the catalyst easily. Therefore, desorption behavior of O\textsubscript{2} and CO\textsubscript{2} adsorbed on \((Y_{0.67}Tb_{0.30}Zr_{0.03})_2O_{3.33}\) was characterized by TPD measurements.

**Figure 5** shows O\textsubscript{2} and CO\textsubscript{2} desorption profiles (O\textsubscript{2}-TPD and CO\textsubscript{2}-TPD) for \((Y_{0.67}Tb_{0.30}Zr_{0.03})_2O_{3.33}\). In references [5,6,12], catalysts that demonstrated low-temperature O\textsubscript{2} desorption exhibited high activities for NO decomposition. In the present case, a single O\textsubscript{2} desorption peak was observed at 470\degree C for the \((Y_{0.67}Tb_{0.30}Zr_{0.03})_2O_{3.33}\) catalyst, whereas that for \((Yb_{0.50}Tb_{0.50})_2O_{3.33}\) was 510\degree C. In general, catalysts with weak oxygen adsorption exhibit higher NO decomposition activities. Therefore, the \((Y_{0.67}Tb_{0.30}Tb_{0.03})_2O_{3.33}\) catalyst showed high NO decomposition activity even in the presence of O\textsubscript{2}

In the case of CO\textsubscript{2}, the CO\textsubscript{2} desorption peak was observed at 115\degree C, which is much lower than those seen for \(Ba_{0.8}La_{0.2}Mn_{0.8}Mg_{0.2}O_3\) (700\degree C) [14] and \(La_{0.8}Sr_{0.2}CoO_3\) (750\degree C) [15]. The desorption strength of CO\textsubscript{2} correlates with the desorption temperature observed in TPD, and the lower the CO\textsubscript{2} desorption temperature is, the weaker the adsorption strength becomes. Although the weakly adsorbed CO\textsubscript{2} may block the active site for NO decomposition in the \((Y_{0.67}Tb_{0.30}Zr_{0.03})_2O_{3.33}\) catalyst, the adsorption strength of CO\textsubscript{2} on this catalyst is quite weak. As a result, the NO decomposition activity was not significantly suppressed by the CO\textsubscript{2} coexistence. This consideration is supported by the result mentioned above that the N\textsubscript{2} yield obtained at 900\degree C in the presence of 5 vol\% CO\textsubscript{2} over the present \((Y_{0.67}Tb_{0.30}Zr_{0.03})_2O_{3.33}\) catalyst (36\%) was almost equivalent to that over \((Yb_{0.50}Tb_{0.50})_2O_{3.33}\) (34\%), because the CO\textsubscript{2} desorption peak was observed at 115\degree C and 125\degree C for the former and the latter, respectively.

### 4. Conclusion

C-type cubic \((Y_{0.97-x}Tb_xZr_{0.03})_2O_{3.03+δ}\) \((x = 0, 0.10, 0.20, 0.30, and 0.40)\) catalysts, in which the yttrium site was partially substituted with terbium, were found to exhibit high catalytic activity for direct NO decomposition. The highest catalytic activity was obtained for \((Y_{0.67}Tb_{0.30}Zr_{0.03})_2O_{3.33}\). It is noteworthy that the catalytic activity was maintained at a high conversion ratio even in the presence of O\textsubscript{2} or CO\textsubscript{2}. Therefore, the \((Y_{0.67}Tb_{0.30}Zr_{0.03})_2O_{3.33}\) catalyst is expected to be a new potential candidate as a direct NO decomposition catalyst.

### 5. Acknowledgements

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