Effect of oxygen vacancies on direct N$_2$O decomposition over ZrO$_2$-Y$_2$O$_3$ catalysts

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1. Introduction

Nitrous oxide (N$_2$O) has a high global warming potential, 310 times higher than that of carbon dioxide, and it also contributes to the destruction of the ozone layer in the stratosphere [1]. N$_2$O is emitted anthropogenically from manufacturing plants such as nitric acid and adipic acid plants, and the atmospheric N$_2$O concentration has increased continuously for several years [2]. The removal of N$_2$O from industrial exhaust gas to protect the environment is therefore an important issue.

Among the several N$_2$O decomposition methods, direct catalytic decomposition of N$_2$O into N$_2$ and O$_2$ is the ideal route, because this process is simple, clean, and sustainable. A large number of catalysts have been studied for N$_2$O decomposition: these include noble-metal-based catalysts [3–7], spinels [8,9], perovskites [10–12], hexa-aluminates [13,14], and zeolites [15,16].

The reaction for direct N$_2$O decomposition is thought to involve the following steps [2]: adsorption of N$_2$O on the active sites (Equation 1), decomposition to N$_2$ gas and adsorbed oxygen (Equation 2), and, finally regeneration through recombination of adsorbed oxygen species (Equation 3) or direct reaction with N$_2$O (Equation 4):

\[
\text{N}_2\text{O} + \ast \rightarrow \text{N}_2\text{O} \ast (\ast: \text{active site}) \quad (1)
\]

\[
\text{N}_2\text{O}\ast \rightarrow \text{N}_2 + \text{O} \ast \quad (2)
\]

\[
2\text{O}\ast \rightarrow \text{O}_2 + 2\ast \quad (3)
\]

\[
\text{O} \ast + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}_2 + \ast \quad (4)
\]

Since the reaction proceeds on the active sites in the lattice, the crystal structure is an important factor for N$_2$O decomposition. Recently, we have focused on the C-type rare-earth sesquioxide structure, which is related to the fluorite-type structure by removing one-quarter of the oxide anions. The oxygen vacancies worked as N$_2$O adsorption sites and catalytic active sites, with the highest activity realized by the YO$_{1.5}$ catalyst with a C-type structure, which contained the largest number of oxygen vacancies in the ZrO$_2$-Y$_2$O$_3$ system.

2. Experimental

Zr$_{1-x}$Y$_x$O$_2$-$\delta$ catalysts were synthesized using the co-precipitation method. Stoichiometric amounts of...
aqueous solutions of 1.0 mol·L\(^{-1}\) \(\text{Y(NO}_3\text{)}_3\) and 0.1 mol·L\(^{-1}\) \(\text{Zr(NO}_3\text{)}_2\) were mixed, and the resulting solution was added to a 1 mol·L\(^{-1}\) ammonium carbonate aqueous solution with stirring at room temperature. After the pH of the solution was controlled to 9 by dropwise addition of 4 mol·L\(^{-1}\) ammonia aqueous solution, the mixture was stirred for 6 h at room temperature. The precipitation product was collected by suction filtration, dried, and then calcined at 1600°C for 6 h in air.

The composition of the catalyst was measured by X-ray fluorescence spectrometry (XRF; Supermini 200, Rigaku). The Brunauer-Emmett-Teller (BET) surface area was measured at −196°C (Micromeritics TriStar 3000, Shimadzu) using nitrogen gas adsorption. The crystal structure was identified by X-ray powder diffraction (XRD; SmartLab, Rigaku) using Cu – Ka radiation (40 kV and 30 mA). The lattice constants were estimated by refining the XRD peak angles using α-alumina as an internal standard.

The catalytic tests for the \(\text{N}_2\text{O}\) direct decomposition were performed using a conventional fixed-bed flow reactor with a 10 mm diameter quartz glass tube. Catalytic activities were measured in the temperature range from 400°C to 950°C using thermal conductivity detection gas chromatography (GC-8AIT, Shimadzu). A gas mixture of 0.5 vol% nitrous oxide and 99.5 vol% helium was fed at a rate of 60 mL·min\(^{-1}\) over 0.2 g of the catalyst, a catalyst weight/gas flow rate (\(W/F\)) ratio of 0.2 g·s·mL\(^{-1}\). Before the catalytic activity tests, each catalyst was preheated at 200°C for 1 h in a helium flow.

Diffusion reflectance infrared fourier transform spectroscopy (DRIFTS) analysis was performed with an \textit{in situ} FT-IR spectrometer (FT/IR-6100, JASCO) under a 0.5 vol% nitrous oxide and 99.5 vol% helium flow (60 mL·min\(^{-1}\)). An environmental DRIFTS chamber was equipped with calcium fluoride windows to allow thermal and water resistance. Each spectrum was recorded by averaging 100 scans with a resolution of 4 cm\(^{-1}\), where the spectrum was compensated by the helium underflow. Prior to measurement, the sample was preheated at 400°C under a helium flow.

The oxygen-species desorption characteristics of the catalysts were evaluated by oxygen temperature-programmed desorption (\(\text{O}_2\)-TPD) measurement using oxygen gas as follows. After heating the catalyst in a flow of helium at 500°C for 30 min, the catalyst was exposed to oxygen gas at the same temperature for 1 h and then cooled to 50°C. The catalyst was heated again under a helium flow at a heating rate of 10°C·min\(^{-1}\), and the desorbed gas was monitored using a catalyst analyzer (BELCAT-B, MicrotracBEL).

The acidity of the catalysts was measured by ammonia temperature-programmed desorption (NH\(_3\) – TPD) measurement. The sample was exposed to a mixture of 0.5 vol % ammonia and 99.5 vol% nitrogen at 50°C for 1 h after annealing at 500°C for 30 min under a helium flow. Subsequently, the sample was heated under a helium flow (30 mL·min\(^{-1}\)) at a heating rate of 10°C·min\(^{-1}\) using the same analyzer (BELCAT-B, MicrotracBEL). The number of basic sites on the catalysts was estimated from the temperature-programmed desorption profile of carbon dioxide (\(\text{CO}_2\) – TPD), assuming that one carbon dioxide molecule is adsorbed on one basic site. Much as in the previous study [22], the sample was pretreated in a flow of hydrogen (30 mL·min\(^{-1}\)) at 500°C for 30 min, and exposed to carbon dioxide (30 mL·min\(^{-1}\)) at 50°C for 1 h. After evacuation at 50°C for 30 min, the catalyst was heated under a flow of helium at a rate of 10°C·min\(^{-1}\), and the desorbed gas was monitored using the same analyzer (BELCAT-B, MicrotracBEL).

### 3. Results and discussion

Table 1 shows the compositions of \(\text{Zr}_{1-x}\text{Y}_x\text{O}_{2-δ}\) measured by XRF and the number of oxygen vacancies (\(δ\)) simply estimated using the measured \(x\) i.e. \(δ = x/2\). Here, \(\text{YO}_{1.5}\) (\(\text{Y}_2\text{O}_3\)) was regarded as a distorted fluorite-related structure with a large number of oxygen vacancies (\(δ = 0.5\)). The measured compositions of the catalysts were consistent with their stoichiometric values within the range of experimental error. Table 1 also shows the BET surface area of the catalysts. The surface area decreased with increases in the Y content (\(x\)) due to the lower melting point of \(\text{YO}_{1.5}\) (ca. 2200°C) [23] compared to that of \(\text{ZrO}_2\) (ca. 2700°C) [24]. As for the crystal structure (Figure 2), the samples with \(x = 0.05, 0.11, \text{and 0.19}\) exhibited a single-phase cubic fluorite-type structure of
Table 1. Measured composition, number of oxygen vacancies (δ), BET surface area, crystal structure, and lattice constant of the Zr1−xYxO2−δ catalysts.

| Catalyst          | Measured composition | δ   | BET surface area/m²·g⁻¹ | Crystal structure | Lattice constant/nm |
|-------------------|----------------------|-----|-------------------------|-------------------|--------------------|
| YO1.5             | 0.50                 | 1.24| C-type                  | 1.0616            |
| Zr0.05YO1.95O2−δ  | 0.480                | 2.55| C-type                  | 1.0612            |
| Zr0.10YO1.90O2−δ  | 0.450                | 2.92| C-type                  | 1.0607            |
| Zr0.20YO0.80O2−δ  | 0.400                | 3.48| C-type                  | 1.0600            |
| Zr0.30YO0.70O2−δ  | 0.345                | 3.88| C-type                  |                   |
| Zr0.40YO0.60O2−δ  | 0.250                | 3.36| Mixture                 |                   |
| Zr0.50YO0.50O2−δ  | 0.130                | 3.93| Mixture                 |                   |
| Zr0.60YO0.40O2−δ  | 0.095                | 6.20| Fluorite-type           | 0.5144            |
| Zr0.80YO0.20O2−δ  | 0.055                | 7.70| Fluorite-type           | 0.5121            |
| Zr0.95YO0.05O2−δ  | 0.025                | 8.10| Fluorite-type           | 0.5103            |

where r is the reaction rate, k is the apparent rate constant, C is the N₂O concentration, A is the pre-exponential factor, Eₐ is the apparent activation energy, R is the gas constant, and T is the absolute reaction temperature. The apparent activation energy of the N₂O decomposition can be obtained from the slope of the Arrhenius plot, in which ln(k) is plotted against the reciprocal temperature. The results are listed in Table 2. The apparent activation energy decreased with increases in x, the same tendency as that of the N₂O decomposition activity. Based on these results, it was determined that the oxygen vacancy (δ) was related to the catalytic activity and the apparent activation energy of the N₂O decomposition.

To investigate the role of oxygen vacancies in the N₂O decomposition process of Zr₁ₓYₓO₂−δ catalysts, in situ FT-IR measurements were carried out. Figure 4(a) shows the DRIFT spectra of Zr₁ₓYₓO₂−δ catalysts under a 0.5 vol% nitrous oxide-99.5 vol% helium flow at 50°C. There are doublet peaks at ca. 2240 and 2210 cm⁻¹, due to the asymmetric N-N stretching vibrations of N₂O adsorbed on the catalysts [28,29]. With increases in the x value, the N₂O adsorption peak intensity increased. Figure 4(b) presents the dependence of the N₂O adsorption peak area on the number of oxygen vacancies (δ). For each fluorite-type (0.05 ≤ x ≤ 0.19) or C-type (x ≥ 0.80) structure, the adsorption area increased linearly with increases in the number of oxygen vacancies (δ). In addition, the fluorite-type structure has a high potential for N₂O adsorption.

ZrO₂, Fm̅3m. In the case of large amounts of x (x = 0.80, 0.90, 0.95, or 1), the patterns were assigned as a cubic C-type structure of YO₁₅, 22. By contrast, the samples with x = 0.30, 0.50, 0.69 (Figure S1) were a mixture of a C-type structure and a monoclinic ZrO₂ phase. The crystal phase and the lattice constant are also summarized in Table 1. The lattice constant of the samples with fluorite-type structures increased with increases in x, because the Zr⁴⁺ ion sites (0.098 nm, coordination number [CN] = 8) [25] were partially replaced by larger Y³⁺ ions (0.116 nm, CN = 8) [25]. For catalysts with C-type structures, the lattice constant also increased with increases in x, indicating replacement of the Zr⁴⁺ sites (0.086 nm, CN = 6) [25] with Y³⁺ (0.104 nm, CN = 6) [25]. This structural change in the ZrO₂ — Y₂O₃ system is consistent with that observed in the previous studies [26,27].

Figure 3 shows the temperature dependence of the N₂O conversion for the Zr₁₋ₓYₓO₂−δ catalysts with a single-phase fluorite-type or C-type structure. The catalytic activity increased continuously with increases in x, regardless of any decrease in the surface area. A high level of activity was obtained for YO₁₅ (x = 1) with a C-type structure. The apparent activation energy of the N₂O decomposition was calculated using the following equations:

\[
    r = k \cdot C
\]

\[
    k = A \exp\left(-\frac{E_a}{RT}\right)
\]

Figure 2. XRD patterns of Zr₁₋ₓYₓO₂−δ (x = 0.05, 0.11, 0.19, 0.80, 0.90, 0.96, and 1).
compared to the C-type structure when the same number of oxygen vacancies is assumed. Practically speaking, samples with a large number of oxygen vacancies (δ ≥ 0.40) exhibited the C-type phase, not the fluorite-type phase. Figure 5 shows the dependence of the apparent activation energy on the N₂O adsorption peak area. The apparent activation energy was lowered monotonically by increasing the amount of N₂O adsorption, irrespective of the crystal structure. YO₁.₅ solids with a large number of oxygen vacancies exhibited high catalytic activity. Oxygen vacancies are therefore considered to work as active sites for N₂O decomposition.

For further investigation of the catalysts, O₂-TPD measurements were carried out (Figure S2). Two O₂ desorption peaks were observed: O₂ desorption peaks at lower and higher temperatures were assigned to desorption of physisorbed and chemisorbed oxygen, respectively [8]. The amounts of physisorbed and chemisorbed oxygen species are listed in Table 3. Both the amounts of physisorbed and chemisorbed oxygen increased with increases in the number of oxygen vacancies (δ), a tendency similar to that reported in the previous paper [21]. Thus, the O₂-TPD results also support the proposition that the oxygen vacancies are gas adsorption sites.

Several researchers have reported that the gas adsorption on catalyst surfaces is related to the acidity

| Catalyst          | Apparent activation energy/kJ·mol⁻¹ |
|-------------------|------------------------------------|
| YO₁.₅             | 77.2                               |
| Zr₀.₀₄Y₀.₉₆O₂−δ   | 79.4                               |
| Zr₀.₁₀Y₀.₉₀O₂−δ   | 82.7                               |
| Zr₀.₂₀Y₀.₈₀O₂−δ   | 86.3                               |
| Zr₀.₆₁Y₀.₃₉O₂−δ   | 88.0                               |
| Zr₀.₈₀Y₀.₁₀O₂−δ   | 92.2                               |
| Zr₀.₉₅Y₀.₀₅O₂−δ   | 96.7                               |

Figure 3. Temperature dependence of N₂O conversion by Zr₁₋ₓYₓO₂₋δ catalysts.

Table 2. Apparent activation energy of Zr₁₋ₓYₓO₂₋δ catalysts.

Figure 4. (a) DRIFTS spectra of Zr₁₋ₓYₓO₂₋δ and (b) the relationship between oxygen vacancies and the N₂O peak area.

Figure 5. Relationship between the N₂O peak area and apparent activation energy of Zr₁₋ₓYₓO₂₋δ catalysts.
Table 3. Volumes of oxygen physisorbed and chemisorbed by 
\( \text{Zr}_{1-x}\text{Y}_{2-\delta} \text{O}_2 \) catalysts.

| Catalyst | Amount of physisorbed oxygen/mm\text{ol\textsuperscript{-1}} | Amount of chemisorbed oxygen/mm\text{ol\textsuperscript{-1}} |
|----------|----------------------------------------------------------|----------------------------------------------------------|
| \( \text{YO}_{1.5} \)                | 0.035                                                      | 0.099                                                    |
| \( \text{Zr}_{0.04}\text{Y}_{1.96}\text{O}_{2-\delta} \) | 0.023                                                      | 0.097                                                    |
| \( \text{Zr}_{0.10}\text{Y}_{1.90}\text{O}_{2-\delta} \) | 0.019                                                      | 0.093                                                    |
| \( \text{Zr}_{0.15}\text{Y}_{1.85}\text{O}_{2-\delta} \) | 0.014                                                      | 0.090                                                    |
| \( \text{Zr}_{0.20}\text{Y}_{1.80}\text{O}_{2-\delta} \) | 0.011                                                      | 0.087                                                    |
| \( \text{Zr}_{0.25}\text{Y}_{1.75}\text{O}_{2-\delta} \) | 0.007                                                      | 0.085                                                    |
| \( \text{Zr}_{0.30}\text{Y}_{1.70}\text{O}_{2-\delta} \) | 0.005                                                      | 0.082                                                    |

Table 4. Number of acidic and basic sites on \( \text{Zr}_{1-x}\text{Y}_{2-\delta} \) catalysts.

| Catalyst | Amount of acidic sites/ mmol\text{g\textsuperscript{-1}} | Amount of basic sites/ mmol\text{g\textsuperscript{-1}} |
|----------|----------------------------------------------------------|----------------------------------------------------------|
| \( \text{YO}_{1.5} \)                | 0.168                                                      | 0.130                                                    |
| \( \text{Zr}_{0.04}\text{Y}_{1.96}\text{O}_{2-\delta} \) | 0.162                                                      | 0.135                                                    |
| \( \text{Zr}_{0.10}\text{Y}_{1.90}\text{O}_{2-\delta} \) | 0.160                                                      | 0.138                                                    |
| \( \text{Zr}_{0.15}\text{Y}_{1.85}\text{O}_{2-\delta} \) | 0.156                                                      | 0.142                                                    |
| \( \text{Zr}_{0.20}\text{Y}_{1.80}\text{O}_{2-\delta} \) | 0.144                                                      | 0.150                                                    |
| \( \text{Zr}_{0.25}\text{Y}_{1.75}\text{O}_{2-\delta} \) | 0.133                                                      | 0.153                                                    |
| \( \text{Zr}_{0.30}\text{Y}_{1.70}\text{O}_{2-\delta} \) | 0.130                                                      | 0.155                                                    |

and basicity of the catalyst surface [30–32]; the NH\textsubscript{3}-TPD and CO\textsubscript{2}-TPD levels were therefore measured to investigate the number of acidic and basic sites, respectively, on the \( \text{Zr}_{1-x}\text{Y}_{2-\delta} \) catalysts. The NH\textsubscript{3}-TPD (Figure S3) and the CO\textsubscript{2}-TPD (Figure S4) profiles were used to calculate the numbers of acidic and basic sites, and the results are listed in Table 4. The number of acidic sites increased with increases in \( x \), suggesting that oxygen vacancies with a positive charge served as acidic sites. Here, the O species in the \( \text{N}_2\)O molecule possesses a stronger negative charge than the N species, since the electronegativity of oxygen is higher than that of nitrogen. O in \( \text{N}_2\)O is therefore considered to be adsorbed on the acidic site preferentially, a conclusion supported by the DFT calculations reported previously [33]. On the other hand, the number of basic sites decreased with increases in \( x \), probably due to a decrease in the number of oxide anions in the lattice. This result suggests that basic sites have a negative effect on \( \text{N}_2\)O adsorption. For these reasons, it is clear that the active sites for \( \text{N}_2\)O decomposition are the oxygen vacancies in the \( \text{Zr}_{1-x}\text{Y}_{x}\text{O}_{2-\delta} \) lattice.

4. Conclusion

In summary, \( \text{Zr}_{1-x}\text{Y}_{2-\delta} \) Catalysts with fluorite-related structures were synthesized to investigate the relationship between oxygen vacancies and direct \( \text{N}_2\)O decomposition activity. The \( \text{N}_2\)O decomposition activity was enhanced by increases in the Y\textsuperscript{3+} content (x), or the number of oxygen vacancies (\( \delta \)). In situ FT-IR measurement showed that the amount of \( \text{N}_2\)O adsorption increased with increases in the number of oxygen vacancies. Here, when the same number of oxygen vacancies is assumed, the fluorite-type structure possesses greater potential for \( \text{N}_2\)O adsorption; however, catalysts with a large number of oxygen vacancies (\( \delta \geq 0.40 \)) have C-type structures. The amounts of \( \text{N}_2\)O adsorption and activation energy employed for \( \text{N}_2\)O decomposition have a simple relationship, irrespective of the crystal structure. The highest activity was obtained for \( \text{YO}_{1.5} \) solids with C-type structures, which possess the largest number of oxygen vacancies in the \( \text{ZrO}_2 - \text{Y}_2\text{O}_3 \) system.

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