Decomposition of Nitrous Oxide over Cu/TiO$_2$ Catalysts: The Effect of Cu Loading, TiO$_2$ Structure, and Reaction Conditions

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ABSTRACT

Decomposition of nitrous oxide (N$_2$O) over titania (TiO$_2$) supported copper (Cu) catalyst was investigated with the existence of oxygen and water vapor. The catalytic activity of TiO$_2$ was promoted by copper loading. It was found that there are optimum levels of copper loading on TiO$_2$, and these values are correlated to the specific surface area of TiO$_2$ support being used. The relationship between the catalytic activity for decomposition of N$_2$O and the crystal structure of TiO$_2$ was also investigated. The result revealed that Cu/TiO$_2$ catalysts with the rutile structure has a higher activity toward N$_2$O decomposition than those with the anatase structure. In this research, Cu(5wt%)/TiO$_2$ prepared from TiO$_2$ JRC-TIO-4 (reference catalyst provided by Catalysis Society of Japan) which was mainly constituted of rutile showed the highest activity for N$_2$O decomposition and it could decompose N$_2$O completely at 650$^\circ$C. The catalytic activity was inhibited by the existence of oxygen. However, there was no influence of water vapor to the catalytic activity of Cu/TiO$_2$ for N$_2$O decomposition.

1. INTRODUCTION

Nitrous oxide (N$_2$O) is one of the powerful greenhouse gases with a global warming potential per molecule of about 300 times higher than that of carbon dioxide (CO$_2$). N$_2$O is also identified as a contributor to the destruction of ozone layer in the stratosphere. Therefore, from the environmental point of view, it is important to investigate the decomposition of N$_2$O to minimize its adverse effect on the environment. A considerable number of studies have been
conducted on the catalytic decomposition and the selective catalytic reduction of N₂O (Haber et al., 2004; Dandekar and Vannice, 1999; Lin et al., 1996; Triawan et al., 2018; Tanaka et al., 2000; Chaki et al., 2003; Pophal et al., 1998; Yan et al., 2003; Sunnardianto et al., 2019).

Selective catalytic reduction of NO to N₂ over TiO₂-supported metal catalysts in the presence of hydrocarbon had been studied by Mitadera and Hinode (Mitadera and Hinode, 2002), and the results showed that TiO₂-supported metal catalysts had good activity for NO reduction (Mitadera and Hinode, 2002). The mechanism of NO reduction to N₂O which occurs at low temperature region. From this result, it could be interpreted that N₂O produced from NO reduction was completely decomposed at high temperature region. Therefore, it was assumed that TiO₂-supported metal catalysts would also show a good activity for N₂O decomposition. Furthermore, TiO₂ as a support also possesses advantages such as high tolerance to water vapor, which is an important property for N₂O decomposition catalyst in practical use, where oxygen and water vapor often exist in the N₂O containing stream. Therefore, it is desirable to investigate the activity of TiO₂-supported metal catalysts for decomposition of N₂O.

In this study, the direct decomposition of N₂O to N₂ by various Cu/TiO₂ catalysts was investigated to understand the influences of Cu loading, TiO₂ structure, as well as oxygen and water vapor on the catalytic activity of the catalyst.

2. METHODOLOGY AND MATERIALS

2.1 Catalyst preparation

In this research, Cu/TiO₂ catalyst was prepared by impregnation method. Various kinds of TiO₂ (JRC-TIO-1, 2, 4, and 6; reference catalyst provided by Catalysis Society of Japan) were used as supports. The specific surface area of JRC-TIO-1, 2, 4, and 6 are 82.0 m²/g, 15.9 m²/g, 52.9 m²/g, and 73.0 m²/g, respectively.

Parent TiO₂ was stirred in a aqueous solution of Cu(NO₃)₂ · 3H₂O (99.9%, Wako Co.) at room temperature for one day. Afterwards, the impregnated catalysts were dried up at approximately 60°C for one day, followed by calcination at 600°C for 5 hours under air flow. In order to reduce the pressure drop in the catalytic activity study, catalysts were pelletized, crushed and sieved to between 0.71 mm to 1.00 mm. The catalyst samples were expressed as: Cu( x wt%)/TiO₂ y where x means Cu loading level, and y represents reference support number (e.g. Cu(1wt%)/TiO₂ ① means JRC-TIO-1 loading by 1 wt% of Cu).

2.2 Experimental procedure and characterizations

The catalytic reaction was carried out in a fixed-bed flow reactor under atmospheric pressure. A 1.0 g sample was packed in a quartz tube with 6 mm inner diameter. The reactant gas was prepared by mixing N₂O, O₂, and He gas. The mixed gas of 1,000 ppm of N₂O and 10% of O₂ (He as balance gas) was fed to the catalyst at a flow rate of 5.0-6.0 ml/s, which corresponded to space velocity of 16,000 h⁻¹. Water vapor was introduced to the reactor by bubbling system with concentration of approximately 5 vol%.

Gas chromatograph (GC323w; GL Science Co., with Porapak N, Porapak Q and Molecular Sieve 13X column) was used to analyze the concentration of N₂O, N₂ and O₂ after leaving the catalyst system. Characterization of catalyst was performed by X-ray Diffraction (XRD) Method (MultiFlex; Rigaku) and N₂ Adsorption-Desorption Method (SA3100; COULTER).
3. RESULT AND DISCUSSION

3.1 The decomposition of N\textsubscript{2}O over Cu/TiO\textsubscript{2}

The catalytic activities of Cu/TiO\textsubscript{2} catalysts with different TiO\textsubscript{2} support (JRC-TIO-1, 2, 4, and 6) for the decomposition of N\textsubscript{2}O were investigated. The experimental results without the presence of water vapor is shown in Figures 1 to 4.

Figure 1 shows the effect of Cu loading level of Cu/TiO\textsubscript{2}\textsuperscript{①} on the decomposition of N\textsubscript{2}O to N\textsubscript{2}. The catalyst with Cu loading of 10wt% showed the highest catalytic activity, and the decomposition began at the temperature of 400\textdegree C. Complete conversion of N\textsubscript{2}O to N\textsubscript{2} was obtained in the temperature range of 650 to 700\textdegree C.

Figure 2 shows the effect of Cu loading level of Cu/TiO\textsubscript{2}\textsuperscript{②} on the decomposition of N\textsubscript{2}O to N\textsubscript{2}. In this case, the catalyst with Cu loading of 5wt% showed the highest catalytic activity. However, the difference of catalytic activity with respect to the change of Cu loading level was not significant.

Figure 3 shows the effect of Cu loading level of Cu/TiO\textsubscript{2}\textsuperscript{④} on the decomposition of N\textsubscript{2}O to N\textsubscript{2}. It can be seen from Figure 3 that JRC-TIO-4 decomposed only approximately 35% of N\textsubscript{2}O to N\textsubscript{2} at 700\textdegree C. Supporting copper on JRC-TIO-4 resulted in the improvement of catalytic activity. In this case, the catalyst with Cu loading level of 5wt% showed the highest catalytic activity.
Figure 4 shows the effect of Cu loading level of Cu/TiO$_2$ on the decomposition of N$_2$O to N$_2$. In this case, the catalysts with 5wt% and 10wt% Cu loading levels showed almost the same catalytic activity for the decomposition.

3.2 The relationship between the optimum Cu loading level and specific surface area of TiO$_2$

In Section 3.1, it was observed that the optimum Cu loading levels of Cu/TiO$_2$ for each TiO$_2$ support were as followed: JRC-TIO-1; 10wt%, JRC-TIO-2; 1wt%, JRC-TIO-4; 5wt%, and JRC-TIO-6; 5wt%. This difference of the optimum Cu loading level was considered to be correlated with the difference of the specific surface area of each TiO$_2$ support.

The X-ray Diffraction (XRD) analysis showed CuO was identified as the copper species on TiO$_2$. Therefore, the projected area of one molecule of CuO on the surface of TiO$_2$ can be geometrically calculated by using equation (1) to approximately 7.59 Å$^2$.

$$S = \int_{-4.40}^{0.355} \sqrt{1.40^2 - x^2} \, dx + \int_{0.355}^{1.95} \sqrt{0.69^2 - (x-1.95)^2} \, dx \quad (1)$$

However, during impregnation, Cu(NO$_3$)$_2$ was dispersed rather than CuO and loaded on the surface of TiO$_2$. Therefore the projected area of Cu(NO$_3$)$_2$ on TiO$_2$ surface was also calculated.

The necessary amount of CuO or Cu(NO$_3$)$_2$ molecule to make the monolayer on the surface of TiO$_2$ can be calculated by assuming the TiO$_2$ surface was uniform and the molecules of CuO or Cu(NO$_3$)$_2$ composed the first monolayer on the surface of TiO$_2$. Table 1 shows the relationship between the specific surface area of TiO$_2$ and the optimum Cu loading level of Cu/TiO$_2$ from the catalytic activity experiments and from the geometrical calculation of CuO and Cu(NO$_3$)$_2$ projected area.

The results from Table 1 indicated that the optimum Cu loading level of Cu/TiO$_2$ obtained by the catalytic activity experiments showed a good correlation with the calculated value from the projected area of CuO. This finding suggested that when the TiO$_2$ surface was completely covered with CuO, the catalytic activity for the decomposition of N$_2$O reached maximum. If the amount of CuO loading exceeded the optimum loading, the catalytic activity remained the same or declined because of sintering of copper.

3.3 The relationship between crystal structure of TiO$_2$ and catalytic activity

Figure 5 shows the comparison of the catalytic activities of catalyst prepared from JRC-TIO-1, 2, 4, and 6. The Cu loading level for each sample was selected from loading level of the sample with the best result presented in section 3.1.
Table 1. Relationship between the specific surface area of TiO$_2$ and ideal Cu loading level for the decomposition of N$_2$O

<table>
<thead>
<tr>
<th>Support</th>
<th>Specific surface area [m$^2$/g]</th>
<th>Optimum Cu loading level [wt%]</th>
<th>Geometrical calculation of CuO</th>
<th>Geometrical calculation of Cu(NO$_3$)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Experimental data</td>
<td></td>
<td></td>
</tr>
<tr>
<td>JRC-TIO-1</td>
<td>82.0</td>
<td>10</td>
<td>11.4</td>
<td>2.25</td>
</tr>
<tr>
<td>JRC-TIO-2</td>
<td>15.9</td>
<td>1</td>
<td>2.21</td>
<td>0.436</td>
</tr>
<tr>
<td>JRC-TIO-4</td>
<td>52.9</td>
<td>5</td>
<td>7.35</td>
<td>1.45</td>
</tr>
<tr>
<td>JRC-TIO-6</td>
<td>73.0</td>
<td>5</td>
<td>10.1</td>
<td>2.00</td>
</tr>
</tbody>
</table>

The specific surface area of JRC-TIO-2 was 15.9m$^2$/g, and this value was evidently smaller than other samples. Accordingly, optimum Cu loading level of Cu/TiO$_2$ prepared from JRC-TIO-2 was 1wt% which was also lower than other samples. This low loading level was considered as the cause of the low activity of Cu(1wt%)/TiO$_2$ ②.

The Cu(5wt%)/TiO$_2$ ④ and Cu(5wt%)/TiO$_2$ ⑥ showed higher catalytic activity than Cu(10wt%)/TiO$_2$ ①, even though the optimum Cu loading levels of Cu/TiO$_2$ prepared from JRC-TIO-4 and JRC-TIO-6 were lower than that prepared from JRC-TIO-1. This result can be explained using the results of XRD analysis (Figure 6). The crystal structure of JRC-TIO-1 and JRC-TIO-2 was anatase and remained as anatase after the preparation of Cu/TiO$_2$. The crystal structure of JRC-TIO-6 was rutile, and it remained rutile structure after the preparation of Cu/TiO$_2$. Moreover, the main crystal structure of JRC-TIO-4 was anatase, and it changed to rutile after the preparation of Cu/TiO$_2$. Therefore, the crystal structure of Cu(5wt%)/TiO$_2$ ④ and Cu(5wt%)/TiO$_2$ ⑥ was rutile, and the crystal structure of Cu(10wt%)/TiO$_2$ ① and Cu(1wt%)/TiO$_2$ ② was anatase.

In Figure 5, Cu(5wt%)/TiO$_2$ ④ and Cu(5wt%)/TiO$_2$ ⑥ (rutile) exhibited higher catalytic activity for N$_2$O decomposition than Cu(10wt%)/TiO$_2$ ① and Cu(1wt%)/TiO$_2$ ② (anatase). This result suggested that the crystalline structure of the support contributed to the catalytic activity of samples, and rutile is considered to be more effective than anatase for the decomposition of N$_2$O.

Figure 5. The decomposition of N$_2$O to N$_2$ over Cu/TiO$_2$ prepared from each TiO$_2$.
3.4 The influence of oxygen and water vapor on the $\text{N}_2\text{O}$ decomposition to $\text{N}_2$

Figure 7 shows the influence of oxygen and water vapor on the decomposition of $\text{N}_2\text{O}$ to $\text{N}_2$ over Cu(5wt%)/TiO$_2$ ④. In the absence of oxygen and water vapor, the decomposition of $\text{N}_2\text{O}$ to $\text{N}_2$ over Cu(5wt%)/TiO$_2$ ④ began from the temperature of 400°C, and the conversion of $\text{N}_2\text{O}$ to $\text{N}_2$ reached 100% at the temperature of 550°C. However, in the presence of oxygen, $\text{N}_2\text{O}$ decomposition shifted to higher temperature. The temperature for 100% decomposition of $\text{N}_2\text{O}$ to $\text{N}_2$ was higher than non-existent case.

$\text{N}_2\text{O}+\text{O}_2$ system and $\text{N}_2\text{O}+\text{O}_2+\text{H}_2\text{O}$ system in Figure 7 showed no difference of the catalytic activity for $\text{N}_2\text{O}$ decomposition. Previous research reported that the catalytic activity for the decomposition of $\text{N}_2\text{O}$ increased because of the existence of water vapor [8]. However, our result in Figure 7 showed that no difference of the catalytic activity for $\text{N}_2\text{O}$ decomposition in $\text{N}_2\text{O}+\text{O}_2$ system and $\text{N}_2\text{O}+\text{O}_2+\text{H}_2\text{O}$ system. This indicates that the existence of water vapor does not influence this catalytic system, and the catalyst could be used in the water treatment process.

4. CONCLUSION

The decomposition of $\text{N}_2\text{O}$ over various TiO$_2$-supported copper catalysts was investigated. Cu/TiO$_2$ catalyst exhibits catalytic activity for the decomposition of $\text{N}_2\text{O}$ to $\text{N}_2$. Optimum Cu loading level is related to the specific surface area of TiO$_2$ support being used. The optimum Cu loading level increases with the specific surface area of TiO$_2$ support. Furthermore, when the TiO$_2$ surface is covered with CuO completely, the catalytic activity for the decomposition of $\text{N}_2\text{O}$ reaches maximum value. On the basis of catalytic activity towards the decomposition of $\text{N}_2\text{O}$ and XRD pattern of Cu/TiO$_2$ prepared from each TiO$_2$, rutile is considered to be more effective than anatase for the decomposition of $\text{N}_2\text{O}$. Therefore, Cu(5wt%)/TiO$_2$ ④ and Cu(5wt%)/TiO$_2$ ⑥ that constitute of rutile has the highest
catalytic activity for the decomposition of N\textsubscript{2}O to N\textsubscript{2}.

The catalytic activity for N\textsubscript{2}O decomposition decreases in the existence of oxygen. However, the catalytic activity of Cu/TiO\textsubscript{2} for the decomposition of N\textsubscript{2}O is not affected by water vapor. This water vapor tolerance of Cu/TiO\textsubscript{2} catalyst for the decomposition of N\textsubscript{2}O is an advantage in the practical use.

5. REFERENCES


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