Characterization of Pt/TiO$_2$ catalyst for NO-CO-H$_2$O reaction

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Abstract: To develop a new ammonia synthesis process, NH$_3$ formation for NO-CO-H$_2$O reaction over Pt/TiO$_2$ was investigated. Pt/TiO$_2$ catalysts were characterized by XRD, N$_2$ adsorption, and CO pulse adsorption. These results indicate that catalytic activity for NO conversion to NH$_3$ was influenced to Pt particle size.

Keywords: ammonia, NO-CO-H$_2$O, Pt/TiO$_2$.

1. Introduction

Ammonia is an important chemical compound as a fertilizer. Recently, ammonia synthesis has been studied extensively due to much concern of NH$_3$ usage as a hydrogen carrier. Ammonia is normally produced by catalytic process, called Haber-Bosch process. Although this process consumes a large amount of fossil fuels, ammonia production can be obtained with high efficiency. Development of other ammonia synthesis process rather than the Haber-Bosch process has been attained. We focus that Pt/TiO$_2$ catalyst showed high activity and NH$_3$ selectivity from NO and CO reaction in the presence of H$_2$O under ambient pressure and low temperature. The crystal structure of TiO$_2$ used in the literature was anatase, which was the most effective support material. Here, we aimed to clarify the influence of the physical properties of anatase TiO$_2$ on the activity of NO-CO-H$_2$O reaction to form NH$_3$.

2. Experimental

Pt/TiO$_2$ catalysts were prepared by means of incipient wetness method. TiO$_2$(HS) (Nakai Chemical: SSP-M), TiO$_2$(MS) (Nakai Chemical: CS-300S-12) and TiO$_2$(LS) (Wako Pure Chem) were used as the support materials. H$_2$PtCl$_6$ (Wako Pure Chem) was used as a Pt precursor. After 1wt% Pt loading, the samples were calcined at 500°C for 4h, and then reduced in 10vol% H$_2$ at 400°C for 1h. Catalytic activity test was measured by a fixed bed tubular reactor. Product gases were analyzed by FT-IR (Thermo Fischer: iS50) equipped multi-reflection gas cell and Gas Chromatograph (INFICON: 3000 micro GC). The catalysts were characterized by X-ray diffraction (RIGAKU: RINT Ultima+: 2θ = 20°~60°), N$_2$ adsorption measurement (Microtrec-Bell: Belsorp mini-II, -196°C, pretreatment at 300°C, BET method) and CO pulse adsorption (Okura Riken: model R6015H).

3. Results and discussion

Fig. 1 showed temperature dependence of NO conversion over Pt/TiO$_2$ catalysts. NO conversions over Pt/TiO$_2$(HS) and Pt/TiO$_2$(MS) reached to 100% above 300°C. Pt/TiO$_2$(LS) was showed about 50% at 300°C. NH$_3$ selectivity (table 1.) were more than 94% on all catalysts even at 150°C except for Pt/TiO$_2$(LS). The small amounts of N$_2$ and N$_2$O were confirmed.

Fig. 2 showed XRD patterns (2θ = 20°~60°). The diffraction peak assigned to Pt metal exhibited at 39.8° on Pt/TiO$_2$(LS). On the other hand, there is no peak for Pt metal on Pt/TiO$_2$(HS) and Pt/TiO$_2$(MS). Table 1 showed $S_{BET}$, Pt dispersion, and Pt particle size. The specific surface area ($S_{BET}$) were in the order of Pt/TiO$_2$(HS) > Pt/TiO$_2$(MS) >> Pt/TiO$_2$(LS). The activities of Pt/TiO$_2$(HS) and Pt/TiO$_2$(MS) were almost same, suggesting that specific surface area of Pt/TiO$_2$ catalyst was not responsible for the catalytic activity. The Pt particle size calculated by CO dispersion. Pt dispersion were in the order of Pt/TiO$_2$(HS) $\approx$ Pt/TiO$_2$(MS) $>$ Pt/TiO$_2$(LS). Fig.3 shows the relationship between Pt particle size and T$_{30}$ (temperature...
achieved NO conversion 30%). From this results, the smaller particle size of Pt the higher catalytic activity for NO-CO-H₂O reaction.

**Figure 1.** NO conversion of each catalysts

**Figure 2.** XRD patterns of each catalysts from 20° to 60°

**Figure 3.** Relation between Pt particle size and Tₚ₃₀

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>S_BET [m²/g]</th>
<th>Pt dispersion [%]</th>
<th>Pt particle size [nm]</th>
<th>NH₃ selectivity [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/TiO₂(LS)</td>
<td>11</td>
<td>4</td>
<td>13</td>
<td>0</td>
</tr>
<tr>
<td>Pt/TiO₂(HS)</td>
<td>96</td>
<td>32</td>
<td>1.5</td>
<td>95</td>
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<tr>
<td>Pt/TiO₂(MS)</td>
<td>72</td>
<td>29</td>
<td>1.7</td>
<td>96</td>
</tr>
</tbody>
</table>

### 4. Conclusions
Pt/TiO₂ catalysts for NO-CO-H₂O reaction were prepared same method using various TiO₂ as a support. These catalysts were characterized by XRD, N₂ adsorption and CO pulse adsorption measurement. As a result, catalytic activity were in the order of Pt/TiO₂(HS) ≅ Pt/TiO₂(MS) > Pt/TiO₂(LS). As the specific surface area of the catalyst became larger, the result was higher activity. However, it was suggested that the small particle size of Pt is favorable for obtaining high NO conversion to NH₃ even at 150°C.

### References