Characterization of Pt/TiO_2 catalyst for NO-CO-H_2O reaction

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Abstract: To develop a new ammonia synthesis process, NH_3 formation for NO-CO-H_2O 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_2O, 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_2O under ambient pressure and low temperature[1]. The crystal structure of TiO_2 used in the literature was anatase, which was the most effective support material[2]. Here, we aimed to clarify the influence of the physical properties of anatase TiO_2 on the activity of NO-CO-H_2O reaction to form NH_3.

2. Experimental

Pt/TiO_2 catalysts were prepared by means of incipient wetness method. TiO_2(HS) (Sakai Chemical: SSP-M), TiO_2(MS) (Sakai Chemical: CS-300S-12) and TiO_2(LS) (Wako Pure Chem) were used as the support materials. H_2PtCl_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+: $2\theta = 20^o$~60^o), N_2 adsorption measurement (Microtrac-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_2O were confirmed.

Fig. 2 showed XRD patterns ($2\theta = 20^o$~60^o). 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) ≒ 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-H_2O reaction.

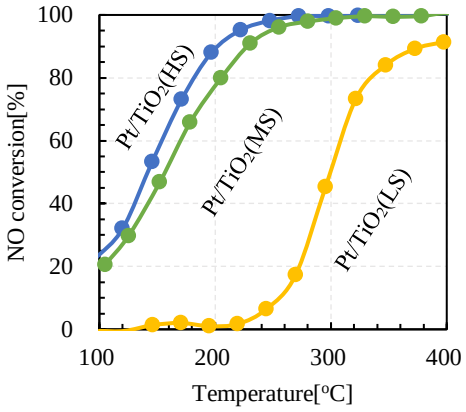

Figure 1. NO conversion of each catalysts

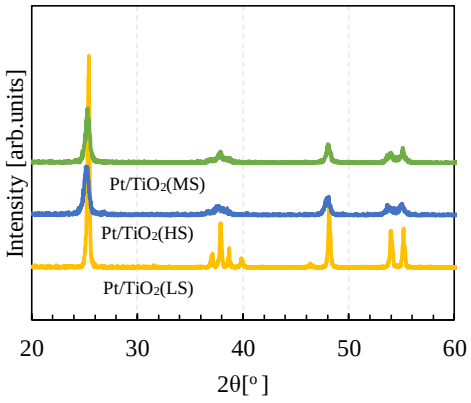

Figure 2. XRD patterns of each catalysts from 20° to 60°

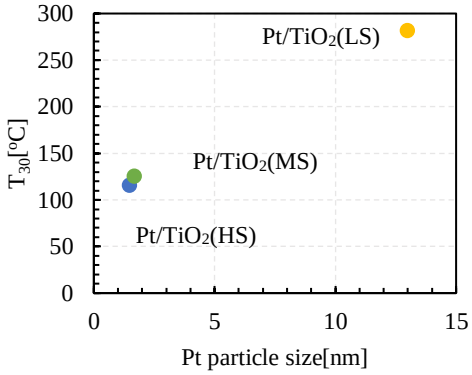

Figure 3. Relation between Pt particle size and T_{30}

Table 1. Characterization of each catalysts

Catalyst	S_{BET}[m^2/g]	Pt dispersion[%]	Pt particle size[nm]	NH_3 selectivity[%]		
				150	200	250
Pt/TiO_2(LS)	11	4	13	0	0	90
Pt/TiO_2(HS)	96	32	1.5	95	97	99
Pt/TiO_2(MS)	72	29	1.7	96	94	99

4. Conclusions

Pt/TiO_2 catalysts for NO-CO-H_2O reaction were prepared same method using various TiO_2 as a support. These catalysts were characterized by XRD, N_2 adsorption and CO pulse adsorption measurement. As a result, catalytic activity were in the order of Pt/TiO_2(HS) ≒ Pt/TiO_2(MS) > Pt/TiO_2(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 NH_3 even at 150°C.

References

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