Selective Catalytic Oxidation of Ammonia over Au/Nb_2O_5 at Room Temperature

Mingyue Lin,[a] **Baoxiang An,**[a] **Nao Niimi,**[b] **Yohei Jikihara,**[b] **Tsuruo Nakayama,**[b] **Tamao Ishida,**[a] **Masatake Haruta**[a] , **Toru Murayama**[a,]*
[a]*Research Center for Gold Chemistry, Tokyo Metropolitan University, Minami-Osawa, Hachioji, Tokyo, 192-0397, Japan*
[b]*NBC Meshtec Inc., NBC Meshtec Inc., 2-50-3 Toyoda, Hino, Tokyo, 191-0053, Japan*
**Corresponding author: murayama@tmu.ac.jp*

Abstract: Au/Nb_2O_5 catalysts with three different Nb_2O_5 crystal structures (layered-structure-type, orthorhombic and amorphous) and gold loading amount were synthesized and evaluated for selective catalytic oxidation of NH_3. The structure of Nb_2O_5 and gold loading amount would greatly influence the catalytic activity. This study reported a 60% conversion of NH_3 with 100% selectivity to N_2 at 25°C on Au/Nb_2O_5 which is the highest activity of NH_3 oxidation at low temperatures reported to date.

Keywords: Gold catalyst, Niobium oxide, Ammonia oxidation.

1. Introduction

Ammonia is a well-known pollutant with the characteristic pungent smell which has adverse effects on human health and environment. Selective catalytic oxidation (SCO) of NH_3 with O_2 to harmless N_2, H_2O is a potentially efficient method to remove NH_3. Previous studies showed that noble metals such as Pt, Pd, Rh, Ir, Ru, Ag were active for NH_3-SCO at temperatures around 300°C but less selective to N_2 with byproducts of nitrogen oxides. Most metal oxide catalysts such as Fe_2O_3-TiO_2, V_2O_5-TiO_2, MnO_2 were found to give a good N_2 selectivity but their activities were not sufficient below 300°C. On the aspect of developing air purification system in a living environment, it is essential to develop efficient catalysts for NH_3-SCO at low temperatures. The properties of metal oxide supports and the ability of desorption of surface oxygen atoms are critically important since the formation of active atomic oxygen species is the crucial reaction step after the first step of NH_3 adsorption.

Gold catalysts are well known for their high catalytic activities in ambient air at low temperatures, especially for low-temperature oxidation of CO even at -70°C in which the active site is perimeter interface between Au and metal oxide support.[1] It has been reported that the addition of Au can lead to a significant enhancement in NH_3-SCO because Au can enhance the band intensity of imide-like adspecies. Besides, acidic metal oxides can adsorb NH_3. Therefore, acidic metal oxides supported gold catalysts are the promising candidates for realizing NH_3-SCO at low temperatures. Niobium oxides (Nb_2O_5), which is a solid acid with a low isoelectric point, is attractive as an acidic support, but it is very difficult to prepare nanoparticulate gold catalysts if the support's isoelectric point is below 5. However, our group has recently developed a method[2] to deposit gold nanoparticle (smaller than 3 nm in diameter) on Nb_2O_5 which will provide a new possibility for NH_3-SCO.

2. Experimental

Layered-structure-type Nb_2O_5 (Nb_2O_5-L) and orthorhombic Nb_2O_5 (Nb_2O_5-T) were synthesized by a hydrothermal method from ammonium niobium oxalate ($NH_4[NbO(C_2O_4)_2(H_2O)_2]\cdot nH_2O$, Aldrich). Hydrothermal reaction was carried out at 175°C for 24 h. The obtained solid was filtered, washed thoroughly with deionized water and dried at 80°C overnight. The dried solid was heat-treated for 2 h at 400°C and 650°C in the air to get Nb_2O_5-L and Nb_2O_5-T, respectively. Amorphous Nb_2O_5 (Nb_2O_5-A) was provided from Catalysis Society of Japan. Nb_2O_5-A was calcined at 400°C for 2 h under air before being used as the support. Au/Nb_2O_5 catalysts were prepared by a sol immobilization method according to the previous report[2].

The catalytic activity measurement was carried out by using a continuous fixed-bed reactor system. The reactant gas containing 50 ppm NH_3 and 20% O_2 balanced with Ar was passed through the catalytic bed.

The amount of catalyst was 0.15 g. NH_3 conversion and N_2 selectivity were estimated at a steady state to exclude the adsorption of ammonia on the support.

3. Results and discussion

Fig.1 shows the effect of reaction temperature on NH_3 conversion over different catalysts. Nb_2O_5-L showed no catalytic activity for NH_3 oxidation even at 250°C. In contrast, the catalytic activities of Au/Nb_2O_5 for NH_3 oxidation were greatly enhanced. Table 1 summarizes the physical properties and catalytic activities of different Au/Nb_2O_5 catalysts. Au/Nb_2O_5-L showed a lower $T_{1/2}$ than Au/Nb_2O_5-T and Au/Nb_2O_5-A despite no large difference in gold loading amount of 1wt%. In previous studies, Au/Nb_2O_5-L which is a deformed orthorhombic structure with a large BET surface area has been reported to be favorable for the deposition of Au as nanoparticles and for their CO oxidation's activity based on the TOF comparison with Au/Nb_2O_5-T which is an orthorhombic structure with a small BET surface area. Moreover, the lattice oxygen species on Au/Nb_2O_5-L is good for the formation of active atomic oxygen species which may give an explanation of its high catalytic activity for NH_3 oxidation. In addition, the gold loading amount would greatly influence the catalytic activity of Au/Nb_2O_5-L for NH_3 oxidation. The catalytic activity increased with the increase of gold loading amount from 1wt% to 5wt% while the size of gold nanoparticles remaining the same. Au(5wt%)/Nb_2O_5-L showed a 60% conversion of NH_3 at 25°C which is the highest conversion of NH_3 oxidation reported yet at room temperature. This result indicated the periphery interface between gold and Nb_2O_5 may be the active sites.

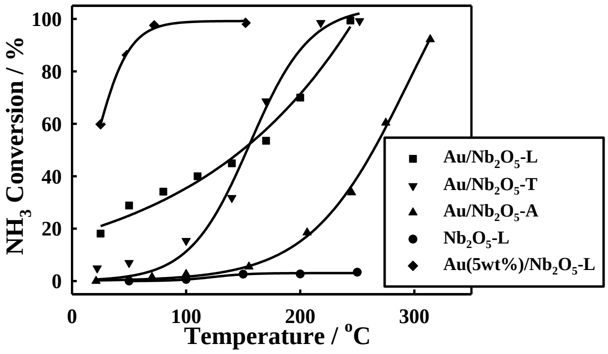

Figure 1. Effects of reaction temperature on NH_3 conversion over different Nb_2O_5 supported gold catalysts. The gold loading amount is 1wt%.

Table 1. Physical properties of supported gold catalysts and their catalytic activity for NH_3 conversion.

Catalyst	BET (m^2/g)	Au loading (wt%)[a]	Au Particle Size (nm)[b]	$T_{1/2}$ (°C)[c]	N_2 selectivity at $T_{1/2}$ / %
Au(1wt%)/Nb_2O_5-L	208	1.1	2.8 ± 0.5	149	100
Au(3wt%)/Nb_2O_5-L	208	2.8	2.7 ± 0.7	81	100
Au(5wt%)/Nb_2O_5-L	208	5.2	2.9 ± 0.8	16	100
Au(7wt%)/Nb_2O_5-L	208	6.2	2.7 ± 0.7	28	100
Au(1wt%)/Nb_2O_5-T	24	0.89	2.7 ± 0.7	154	100
Au(1wt%)/Nb_2O_5-A	116	0.91	2.9 ± 1.6	264	65.8

[a] Determined by AAS. [b] Measured by TEM. [c] Temperature for 50% NH_3 conversion.

4. Conclusions

Different kinds of Nb_2O_5 were used as supports for the preparation of Au/Nb_2O_5 catalysts. The Nb_2O_5-L was inactive for NH_3 oxidation. However, the catalytic activity was significantly enhanced by the deposition of gold nanoparticles. Moreover, the catalytic activity of Au/Nb_2O_5-L was much higher than other two kinds of Nb_2O_5 supported gold catalysts because of its large surface area and surface's lattice oxygen species. The effect of gold loading amount on the catalytic activity of Au/Nb_2O_5-L indicated that the periphery interface between gold and Nb_2O_5-L may be the active sites for NH_3 oxidation.

References

1. M. Haruta, T. Kobayashi, H. Sano H, N. Yamada. Chem. Lett. 16 (1987) 405.
2. T. Murayama, W. Ueda, M. Haruta, ChemCatChem 8 (2016) 2620.