Photocatalytic oxidation of aqueous ammonia over titanium dioxide loaded on various supports

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Abstract:

The effect of the use of various supports for TiO_2 photocatalyst on decomposition of ammonia in water was was investigated. The highest ammonia decomposition rate was obtained when TiO_2 was loaded on mordenite that can adsorb a large amount of ammonia. In the case of TiO_2/mordenite, the formation of undesirable nitrate and nitrite were suppressed significantly. The influence of TiO_2 content on activity and selectivity was investigated with TiO_2/mordenite. As a result, the high activity per weight of TiO_2 and low selectivity for nitrate and nitrite were obtained at low loading amount of TiO_2.

Keywords: Photocatalysis, ammonia, water treatment.

1. Introduction

Aqueous ammonia is a major nitrogen-containing pollutant in waste water from many sources, including fertilizer, metal plating and semiconductor manufacturing facilities. As ammonia is a source of nutrients for the eutrophication of lake water and inland sea areas, the removal of ammonia from waste water is important from an environmental perspective. There have been several studies on the photocatalytic oxidation of ammonia using TiO_2 and/or Pt-TiO_2 as a method of purifying wastewater[1-2]. We have found that the reaction rate increases significantly by the addition of oxygen into the reaction system,[3] and the adsorption amount of ammonia on TiO_2 strongly affect the decomposition rate and selectivity[4]. It has been reported that the photocatalytic decomposition rate of the organic substance (propionaldehyde) increased as the adsorption amount increased by the loading of TiO_2 on supports with medium adsorption constant for the substrate [5]. Therefore, it is expected that decomposition rate and selectivity for nitrogen in photocatalytic oxidation of ammonia can be improved by loading of TiO_2 on supports that can adsorb a large amount of ammonia. In this study, effect of TiO_2 loading on various supports on the photocatalytic oxidation of ammonia was investigated by measuring the amount of ammonia adsorbed on the supports and conducting decomposition reactions.

2. Experimental

The loading of TiO_2 on various supports (mordenite, ferrilite, zeolite A-4, zeolite F-9, silica, alumina, activated carbon(AC)) was carried out as follows. Titanium tetraisopropoxide (TTIP) in acetylacetone solvent was impregnated into a dried support by incipient wetness method. After drying overnight at 100°C, the solid was calcined at 723 K for 4 h (TiO_2/AC was calcined at 673 K for 2 h). Prior to the reaction, platinum was loaded by photo-deposition method. The photocatalytic reactions were carried out in an inner irradiation reaction cell made of Pyrex glass. A high-pressure mercury lamp (450 W) was employed as the light source. The photocatalyst (0.4 g) was suspended in 400 mL of $(NH_4)_2SO_4$ aqueous solution. The initial concentration of ammonia was set at 5.0 mM. The initial pH was adjusted to 10 by the addition of NaOH(aq). Air was fed into the reaction suspension at a flow rate of 100 cm^3 min^{-1}. The reaction selectivity was evaluated based on the sum of the amounts of nitrate and nitrite formed. The amount of ammonia adsorbed on the samples was measured as follows: the sample (0.10 g) was placed in 25 mL aqueous $(NH_4)_2SO_4$, and the pH was adjusted to 10 using NaOH(aq). The suspension was stirred for 24 h at 298 K and filtered. The concentration of ammonia in the filtrate was measured using a flow injection analysis system.

3. Results and discussion

The amount of ammonia adsorption and catalytic performance for ammonia decomposition were evaluated with 50 wt%TiO_2/support samples (Table 1). TiO_2/mordenite and TiO_2/ferrierite showed higher initial decomposition rate than that of unsupported TiO_2, whereas the loading of TiO_2 on the other supports lead to decline in activity. The formation of undesirable nitrate and nitrite suppressed considerably when TiO_2/mordenite was used. The amount of ammonia adsorbed at the initial concentration of 5 mM, which is the same as the initial concentration of the reaction, was high on TiO_2/mordenite and TiO_2/ferrierite. The adsorption equilibrium constant (K_{ad}) obtained from Langmuir adsorption isotherm was 0.32, 0.27, 0.61, 0.32 (dm^3/mmol) for mordenite, ferrierite, AC, and TiO_2, respectively. Thus, in the case of TiO_2/Mordenite, a large amount of adsorbed ammonia that can be supplied to TiO_2 particle due to relatively moderate K_{ad} of mordenite is available, resulting in enhancement of the activity. The formation of dinitrogen or nitrous oxide preferentially proceeds when there is a high density of N-species on the photocatalyst surface, because the formation of these products requires the combination of two N-containing species that result from the oxidation of ammonia. Therefore, high density of ammonia on TiO_2/mordenite surface would also lead to increase in selectivity for dinitrogen or nitrous oxide.

Table 1. The amount of ammonia adsorption and catalytic performance for ammonia decomposition of 50%TiO_2/support and TiO_2.

support	Ads. amount of NH_3^{*1}/ mmol g^{-1}	Initial decomp. rate*^{2}/μM min^{-1}	Selectivity for NO_2^-+NO_3^-(%)^{*3}
Mordenite	0.41	95	52
Ferierite	0.30	92	67
Zeolite A-4	0.22	26	61
Zeolite F-9	0.16	31	63
Al_2O_3	0.17	39	66
AC	0.16	36	74
unsupported TiO_2	0.12	71	82

* Initial concentration of NH_3 was set at 5 mM. *2,3: 0.25 wt% Pt/50 wt%TiO_2/support, *3: at 50%NH_3 conversion.

Subsequently, the influence of TiO_2 content in TiO_2/mordenite on decomposition rate and selectivity were investigated (Figure 1). At low TiO_2 content, high decomposition rate per weight of TiO_2 and low selectivity for nitrate and nitrite was obtained. The SEM-EDX observation revealed that TiO_2 particles in 5%TiO_2/mordenite were dispersed on the mordenite, whereas that in 50%TiO_2 mordenite covered on surface of mordenite. These results suggest that the amount of the interface between TiO_2 and mordenite affects the decomposition rate per weight of TiO_2 and selectivity.

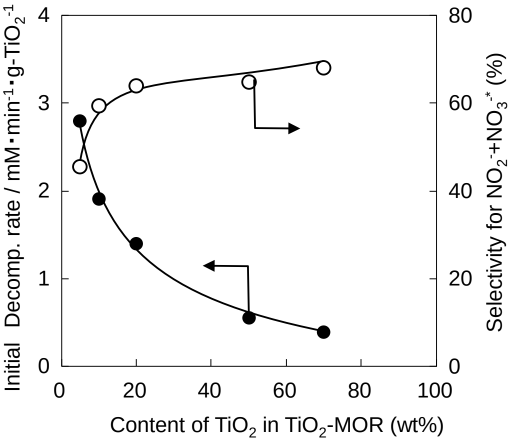

Figure 1. Influence of TiO_2 content in TiO_2/mordenite on decomposition rate and selectivity for nitrate and nitrite
*:at 50% NH_3 conversion

4. Conclusions

By loading TiO_2 on mordenite, the effects of improving the ammonia decomposition activity and decline in selectivity for undesirable nitrate and nitrite were obtained. The large amount of ammonia adsorbed on TiO_2/mondenite affords to enhance the photocatalytic oxidation of ammonia and the formation of dinitrogen or nitrous oxide.

References

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