doi:10.1246/cl.2010.704

Photocatalytic Oxidation of Aqueous Ammonia in the Presence of Oxygen over Platinum-loaded TiO_2

Ikko Mikami,* Satoshi Aoki, and Yasuyuki Miura
Tokai University, 4-1-1 Kitakaname, Hiratsuka, Kanagawa 259-1292

(Received February 25, 2010; CL-100181; E-mail: ikmikami@keyaki.cc.u-tokai.ac.jp)

The oxidation of aqueous ammonia over a platinum-loaded TiO_2 photocatalyst was investigated for the purpose of purifying waste water. The reaction rate for the decomposition of aqueous ammonia was significantly increased by the addition of oxygen to the reaction system. Selectivity for nitrite and nitrate, which should be minimized, was reduced when oxygen was added at lower pressure or a higher concentration of ammonia was used.

Aqueous ammonia is a major nitrogen-containing pollutant in waste water from many sources, including fertilizer, metal-plating and semiconductor manufacturing facilities. As it is a source of nutrients that may accelerate the eutrophication of lake water and inland sea areas, the removal of ammonia from waste water is important from an environmental perspective. Several methods have been developed and applied to the treatment of ammonia contained in waste water, including biological processes, air stripping, ion exchange, breakpoint chlorination, and chemical oxidation,[1,2] among which the biological process is generally regarded as the most efficient method. However, the process has disadvantages, including handling difficulties and low reaction rates, and requires large equipment and long treatment times.

Photocatalytic reactions using TiO_2 are widely applied in water purification for the removal of inorganic ions (e.g., sulfide, cyanide) and organic pollutants (e.g., herbicides, fungicides).[3] There have been several studies of photocatalytic oxidation of ammonia using TiO_2 and/or Pt–TiO_2 for the purpose of purifying waste water.[4–9] Some of these mentioned the effect of pH—the photocatalytic oxidation of ammonia in water proceeds under alkaline conditions[4–8]—while others revealed the optimum concentration of TiO_2 in the reaction solution,[4,8] the effect of various levels of platinum loading on TiO_2,[7] or the effect of the presence of inorganic anions.[9] In these studies, the initial concentrations of ammonia in the reaction solution were of the order of ppm, and relatively long reaction times were required for the decomposition of ammonia. For these reasons, this method is difficult to apply to the treatment of waste water that contains higher concentrations of ammonia.

In the present study, we investigated the influence of the addition of oxygen to the reaction system on the rate of ammonia photodecomposition and also on selectivity for nitrite and nitrate, the formation of which must be minimized because they are also major nitrogen-containing pollutants. A better remediation process would be to convert ammonia into dinitrogen.

Platinum-loaded TiO_2 was used as a photocatalyst. The TiO_2 (ST-01, anatase, Ishihara Sangyo Co., Ltd.) used in the reaction had a BET surface area of $303\,m^2\,g^{-1}$ and an average particle size of 7 nm. Platinum (0.5 wt %) was loaded onto TiO_2 by photochemical reduction of tetrachloroplatinate in a TiO_2 suspension in the presence of 1.2 M methanol. The amount of platinum was confirmed by ICP measurement of the platinum left in solution.

The photocatalytic reactions were carried out in an inner irradiation reaction cell made of Pyrex glass. A high-pressure mercury lamp (Ushio UM-452, 450 W) was employed as the light source. Pt–TiO_2 (0.2 g) was suspended in 400 mL of aqueous ammonium sulfate solution. Sulfate ions did not affect to the decomposition rate. An initial pH was adjusted to 12.1 by the addition of an aqueous solution of sodium hydroxide in order to keep alkaline condition during the reaction, since the reaction proceeded under the alkaline condition and the pH of reaction solution was lowered by proceeding the reaction. Air or a nitrogen/oxygen mixture ($P_{O_2} = 0$–0.1 MPa) was fed into the reaction suspension using a mass flow controller (Kofloc Model 3200) at a flow rate of $100\,cm^3\,min^{-1}$. The concentrations of nitrate, nitrite, and ammonia in the aqueous phase were measured using a flow injection analysis system consisting of a JASCO UV-2070 detector and a UV-2075 detector equipped with a PU-2080 pump. Dissolved oxygen in the reaction mixture was measured using a dissolved oxygen meter (Lutron DO-5509).

The time course of dissolved oxygen (DO) and ammonia concentrations during the photooxidation of ammonia over 0.5 wt % Pt–TiO_2 under air or nitrogen gas is shown in Figure 1. When the reaction was conducted under a flow of nitrogen, the concentration of ammonia decreased slowly with reaction time. Although the concentration of DO was 0.24 mM at the beginning of the reaction, it decreased immediately to less than 0.1 mM, indicating that oxygen was consumed during the reaction. When the reaction was performed under a flow of air, in contrast, the decrease in the concentration of ammonia was much faster. The concentration of DO was maintained at about 0.24 mM during the reaction by the addition of air. The selectivity for nitrite and nitrate (total) under air was higher than under nitrogen (96% vs. 41%) after 240 min.

It is well known that ammonia volatilizes when bubbling is carried out in alkaline solution.[10] However, in the present study, the decrease in the ammonia concentration in solution was small under a flow rate of $100\,cm^3\,min^{-1}$ of air and with an ammonia concentration of 5–100 mM (adjusted pH 12), under UV irradiation and in the absence of a photocatalyst. This indicates that volatilization of ammonia into the atmosphere would be negligible under the reaction conditions used in this study. An experiment performed without UV irradiation and in the presence of 0.2 g of Pt–TiO_2 confirmed that the extent of ammonia adsorption onto the Pt–TiO_2 surface was negligible. Furthermore, a reduction of the ammonia concentration and an increase in nitrate/nitrite concentration were not observed under UV irradiation in the absence of Pt–TiO_2, indicating that the decomposition of aqueous ammonia by UV light does not occur under these reaction conditions. Therefore, the decrease in ammonia concentration shown in Figure 1 must arise through

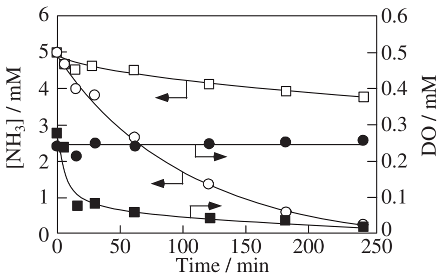

Figure 1. Time course of DO and NH_3 concentrations during the reactions under air and under N_2. Circular symbol: air; square symbol: N_2.

photocatalytic decomposition and not through volatilization, adsorption to the surface of the photocatalyst, or photodecomposition in the absence of a photocatalyst.

These results indicate that the presence of oxygen has a strong effect on the rate of photocatalytic decomposition of ammonia in aqueous solution. It may be considered that one cause of the increase in the ammonia decomposition rate with the addition of oxygen is enhancement of the charge separation efficiency. It is known that oxygen is a good electron acceptor in aqueous solution, and an electron generated by UV irradiation of TiO_2 would easily react with O_2 to give O_2^-, with the resulting electron generated by UV irradiation of TiO_2 consumed efficiently to prevent the accumulation of negative charge on the surface of photocatalyst.[11] Recombination of the photoinduced electrons and holes would be suppressed due to the consumption of the electrons by O_2, enhancing the rate of ammonia oxidation by the holes. A similar observation—that the addition of oxygen increased the photooxidation rate of organic compounds in the aqueous phase using a TiO_2 photocatalyst—was reported by Hirakawa et al.[12] To confirm whether charge separation efficiency affects the rate of ammonia decomposition, the reaction was conducted with the addition of silver nitrate, which acts as a sacrificial reagent for electrons, instead of oxygen (Figure 2). The reaction was carried out under the condition of $[NH_3]_i = 0.5$ mM and $[AgNO_3]_i = 5$ mM, because silver was loaded too much on the surface of the catalyst by photodeposition under the condition of $[NH_3]_i = 5$ mM and $[AgNO_3]_i = 50$ mM. An increase in the ammonia decomposition rate was observed by addition of silver nitrate, and silver loaded on Pt–TiO_2 did not accelate the decomposition rate; thus an increase in charge separation efficiency was concluded to be a contributor to the reaction.

The concentration of DO is summarized in Table 1, the conversion of ammonia and the selectivity for nitrite and nitrate after 240 min of the photocatalytic reaction under various partial pressures of oxygen. Although the concentrations of DO remained constant over time during the reaction, they varied depending on the oxygen partial pressure: from 0.07 mM at $P_{O_2} = 0.001$ MPa to 0.92 mM at $P_{O_2} = 0.1$ MPa. The ammonia conversions after 240 min increased with increasing partial pressure of oxygen up to 0.01 MPa, although they did not continue to rise significantly at greater pressures. Selectivity toward nitrite and nitrate was decreased at lower partial pressures of oxygen (51% at $P_{O_2} = 0.001$ MPa, 93% at $P_{O_2} = 0.1$ MPa); however, selectivity for nitrite was higher under all conditions.

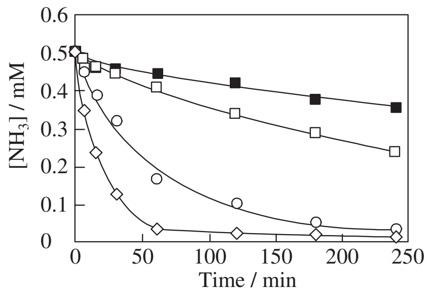

Figure 2. Effect of additon of air or silver nitrate. Catayst: 0.5 wt % Pt–TiO_2 (○, ◇, □), 1 wt % Ag–0.5 wt % Pt–TiO_2 (■). (◇): Silver nitrate was added (5 mM). The reactions were conducted under air (○) or N_2 (◇, □, ■).

Table 1. Effect of partial pressure of oxygen on activity and selectivity in NH_3 photooxidation reaction over Pt–TiO_2

P_{O_2} /MPa[a]	DO /mM	Conv. /%[b]	Selectivity/%		
			NO_2^-	NO_3^-	$NO_2^- + NO_3^-$[c]
0.001	0.07	42	48	3	51
0.003	0.09	84	54	13	67
0.005	0.10	88	62	13	75
0.01	0.16	92	62	20	82
0.02	0.24	95	63	34	97
0.05	0.48	94	60	34	94
0.1	0.92	94	57	36	93

[a] N_2 balance. [b] Reaction time: 240 min. [c] Sum of selectivity for NO_2^- and NO_3^-. $[NH_3]_i$: 5.0 mM.

The influence of the initial concentration of ammonia on selectivity was also investigated under a flow of air. The selectivity for nitrite and nitrate was found to be lower for higher concentrations of ammonia: 44% for 1.0×10^{-2} M $[NH_3]_i$ and 87% for 5.0×10^{-4} M $[NH_3]_i$ at NH_3 conversion of 100%. Although the nitrite/nitrate selectivities obtained in the present study are not yet suitable for application to the purification of waste water, it is expected that they could be minimized by the use of a highly concentrated ammonia solution and a low partial pressure of oxygen.

References

1 C. C. Delwiche, *Denitrification, Nitrification, and Atmosphere Nitrous Oxide*, John Wiley & Sons, New York, **1981**, p. 107.
2 G. Tchobanoglous, F. L. Burton, *Wastewater Engineering Treatment, Disposal and Reuse*, McGraw-Hill, New York, **1991**.
3 J.-M. Herrmann, C. Duchamp, M. Karkmaz, B. T. Hoai, H. Lachheb, E. Puzenat, C. Guillard, *J. Hazard. Mater.* **2007**, *146*, 624.
4 A. Bravo, J. Garcia, X. Demenech, J. Peral, *J. Chem. Res.* **1993**, 376.
5 A. Wang, J. G. Edwards, J. A. Davies, *Sol. Energy* **1994**, *52*, 459.
6 E.-M. Bonsen, S. Schroeter, H. Jacobs, J. A. C. Broekaert, *Chemosphere* **1997**, *35*, 1431.
7 J. Lee, H. Park, W. Choi, *Environ. Sci. Technol.* **2002**, *36*, 5462.
8 X. Zhu, S. R. Castleberry, M. A. Nanny, E. C. Butler, *Environ. Sci. Technol.* **2005**, *39*, 3784.
9 X. Zhu, M. A. Nanny, E. C. Butler, *J. Photochem. Photobiol., A* **2007**, *185*, 289.
10 P. H. Liao, A. Chen, K. V. Lo, *Bioresour. Technol.* **1995**, *54*, 17.
11 H. Gerischer, A. Heller, *J. Phys. Chem.* **1991**, *95*, 5261.
12 T. Hirakawa, T. Daimon, M. Kitazawa, N. Ohguri, C. Koga, N. Negishi, S. Matsuzawa, Y. Nosaka, *J. Photochem. Photobiol., A* **2007**, *190*, 58.