Catalytic Oxidation of Ammonium Ions with Nitrite Ions in Water over Metallic Platinum Supported on Titanium Dioxide at a Mild Reaction Temperature

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Titanium dioxide-supported platinum catalyst, which was pretreated with H_2 at 353 K in a reactor just before the reaction, exhibited extremely high activity toward the oxidation of ammonium ions with nitrite ions into nitrogen in water at 353 K.

In the biological process anaerobic ammonia oxidation (Anammox), which was discovered in 1995,[1] bacteria called *Candidatus* "Brocadia anammoxidans"[2] oxidizes $NH_4{}^+$ into N_2 with $NO_2{}^-$ (eq 1).[3] Anammox process is attractive as a means to remove ammonia from wastewater[1,4] but has some problems, including the difficulty in developing enrichment cultures of the bacteria and in immobilizing them in the reactor. Thus, if a reaction like that in eq 2, which is similar to the Anammox process, proceeds over a heterogeneous catalyst, it should be possible to remove ammonia from wastewater.

$$NH_4{}^+ + 1.32NO_2{}^- + 0.066HCO_3{}^- + 0.13H^+ \rightarrow$$
$$1.02N_2 + 0.26NO_3{}^- + 0.066CH_2O_{0.5}N_{0.15} + 2.03H_2O \quad (1)$$

$$NH_4{}^+ + NO_2{}^- \rightarrow N_2 + 2H_2O \quad (2)$$

In addition, the reaction in eq 2 can apply the decomposition of $NH_4{}^+$ produced during the catalytic hydrogenation of $NO_3{}^-$ in groundwater, because there are only few catalysts with acceptable selectivity for keeping the concentration of $NH_4{}^+$ below the allowable level (0.03 mmol dm^{-3}) in drinking water, although a number of investigations have been carried out on the catalytic hydrogenation of $NO_3{}^-$ over bimetallic catalysts.[5] Nitrite ions contributed for this can be produced by the selective hydrogenation of $NO_3{}^-$ to $NO_2{}^-$ over a Cu–Pd bimetallic cluster catalyst at alkaline pH conditions.[6]

Joko and Nakahara have reported the oxidation of $NH_4{}^+$ with $NO_2{}^-$ (eq 2) over a Pt/TiO_2 catalyst.[7] However, a high reaction temperature (433 K) is necessary for the reaction. If the reaction can proceed under mild reaction temperature (<373 K), the removal of $NH_4{}^+$ from water would become practical. We report here that metallic platinum supported on TiO_2 effectively catalyzed the oxidation of $NH_4{}^+$ with $NO_2{}^-$ into N_2 in water at 353 K when the catalyst was pretreated with H_2 in the reactor just before the reaction.

Platinum supported on TiO_2 (Aerosil P-25, 46 m^2 g^{-1}), Al_2O_3 (JRC-ALO-4, 166 m^2 g^{-1}) or on SiO_2 (Tosoh, 262 m^2 g^{-1}) was prepared by using incipient wetness impregnation with an aqueous solution of H_2PtCl_6 (Wako Pure Chem. Ind. Ltd., 96 mmol dm^{-3}). The loading amount of Pt was adjusted to 1 wt %. After drying overnight at 373 K, the catalysts were calcined in air at 523 K for 3 h and then were treated under a flow of H_2 at 723 K for 2 h.

The dispersion of Pt was estimated from the adsorbed amount of CO at 323 K by using an automatic apparatus (BEL-CAT, Bel Japan, Inc.). The CO/Pt stoichiometry was assumed to be 1. Before the measurement, the catalyst was reduced under a flow of H_2 at 353 K for 2 h.

The oxidation of $NH_4{}^+$ with $NO_2{}^-$ in water was performed using a continuous fixed-bed reactor at 353 K. The reaction mixture was an aqueous solution of $NaNO_2$ (Wako Pure Chem. Ind. Ltd., 4.30 mmol dm^{-3}) and $(NH_4)_2CO_3$ (Wako Pure Chem. Ind. Ltd., 2.15 mmol dm^{-3}). The catalyst powder (2 g) was fixed in the reactor, and H_2 gas was fed into the reactor at 353 K. After stopping the flow of H_2 gas, the aqueous reaction mixture was fed into the reactor. The liquid at the reactor outlet was intermittently collected, and the concentrations of $NO_3{}^-$, $NO_2{}^-$, and $NH_4{}^+$ were determined using a flow injection analysis (FIA) system. Gas products (N_2 and N_2O) at the reactor outlet were analyzed by using a gas chromatography equipped with a thermal conductivity detector (Shimadzu GC-8A). Prior to use, the water was deoxygenated by bubbling dry N_2 (ca. 500 cm^3 min^{-1}) into the water, and just before the reaction, the reaction solution was deoxygenated also by bubbling dry N_2. The concentration of dissolved oxygen in the reaction solution was measured by using an oxygen analyzer (YSI, Model DO200 DO). The amount of dissolved Pt during the reaction was measured by using inductively coupled plasma atomic emission spectroscopy (Shimadzu, ICPS-7000) on the aqueous solution at the reactor outlet.

Figure 1 shows time courses for the oxidation of $NH_4{}^+$ with $NO_2{}^-$ over Pt/TiO_2. The catalyst, which was not reduced under the H_2 flow at 353 K just before the reaction, showed only a very low activity (Figure 1, □). In contrast, when the catalyst was reduced under a H_2 flow at 353 K and a deoxygenated reaction solution (concentration of O_2 was 0.003 mmol dm^{-3}) was utilized, Pt/TiO_2 showed a high activity (Figure 1, ○), and the initial conversion was almost 100%. However, when a reaction solution with an O_2 concentration of 0.1 mmol dm^{-3} was utilized with Pt/TiO_2, only a moderate conversion even at the initial stage of the reaction was achieved, and pronounced deactivation occurred, even if the catalyst was reduced with H_2 just before the reaction (Figure 1, △). Joko and Nakahara have reported that, in order to perform the reaction in eq 2 over Pt/TiO_2, a high temperature of about 473 K is needed.[7] However, our results clearly show that $NH_4{}^+$ could be effectively oxidized with $NO_2{}^-$ even at low reaction temperature (353 K) when Pt/TiO_2 was treated with H_2 in the reactor just before the reaction and a deoxygenated reaction solution was used.

Using GC analysis of the gas at the reactor outlet, it was confirmed that the main gas product was N_2 (>95%), although a small amount of N_2O (<5%) formed. NO and NO_2 were not detected by using GC analysis. In addition, the conversion of $NH_4{}^+$ was almost equal to that of $NO_2{}^-$ (data not shown). $NO_3{}^-$ in the aqueous phase was not detected by using FIA. These results indicate that the reaction proceeds basically according

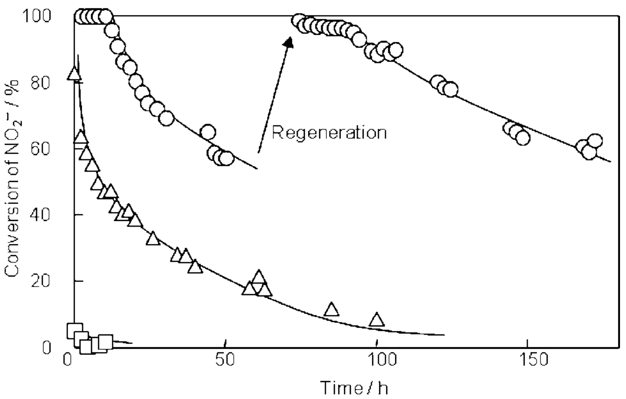

Figure 1. Time courses of the oxidation of NH_4^+ with NO_2^- (NH_4^+:NO_2^- = 1.0:1.0) over 1.0 wt % Pt/TiO_2. (○) The catalyst was reduced with H_2 in the reactor just before the reaction, and a deoxygenated reaction solution was used; (△) the catalyst was reduced with H_2 in the reactor just before the reaction, and the reaction solution was not deoxygenated; (□) the deoxygenated reaction solution was used, but the catalyst was not reduced with H_2 just before the reaction. Reaction conditions: temperature, 353 K; concn of NO_2^- from $NaNO_2$, 4.3 mmol dm^{-3}; concn of NH_4^+ from $(NH_4)_2CO_3$, 4.3 mmol dm^{-3}; WHSV = 15 h^{-1}. Regeneration of the catalyst was carried out by treating Pt/TiO_2 with H_2 in the reactor at 353 K for 20 h.

to eq 2. Since the turnover number (TON) from 0 to 13 h for the reaction over Pt/TiO_2 was 17, it is obvious that the reaction is catalytic.

The conversion gradually decreased over time; however, no Pt was detected in the aqueous phase at the reactor outlet by using ICP-AES analysis. When the catalyst was reduced under the H_2 flow again in the reactor at 353 K for 20 h (Figure 1, at 75 h), the catalytic activity was completely recovered; 100% conversion was obtained. The catalyst could be regenerated at least three times. The XRD pattern of the deactivated catalyst was the same as that of the initial one (data not shown). From these results, it was concluded that metallic Pt showed a high activity for the reaction, and the Pt surface was deactivated owing to oxidation or adsorption of oxygen during the reaction. Actually, when the reaction was performed using a reaction solution containing excess NH_4^+ (NH_4^+:NO_2^- = 1.5:1.0), deactivation was remarkably suppressed, and 100% conversion was maintained over 100 h.[8] When the reaction was conducted in the presence of H_2, NO_2^- was reacted with H_2, only low conversion of NH_4^+ was obtained.

Figure 2 shows time courses for the oxidation of NH_4^+ with NO_2^- over Pt/TiO_2, Pt/Al_2O_3, and Pt/SiO_2. Contrary to Pt/TiO_2, Pt/Al_2O_3, and Pt/SiO_2 showed only low activity. The dispersions of Pt, estimated from the amount of CO adsorbed on the catalyst, were 12%, 25%, and 10% for Pt/TiO_2, Pt/Al_2O_3, and Pt/SiO_2, respectively, which do not correlate with the activities, suggesting that the electronic state of Pt controls the catalytic activity, but further investigations are needed.

In conclusion, Pt/TiO_2, which was reduced with H_2 in a reactor just before the reaction, effectively catalyzed the oxidation of NH_4^+ with NO_2^- in water at a mild reaction temperature (353 K). The activity of Pt/TiO_2 gradually decreased because of oxidation of the Pt surface or adsorption of oxygen onto it. However, the activity was fully recovered by reduction of the Pt/TiO_2 with H_2 in the reactor.

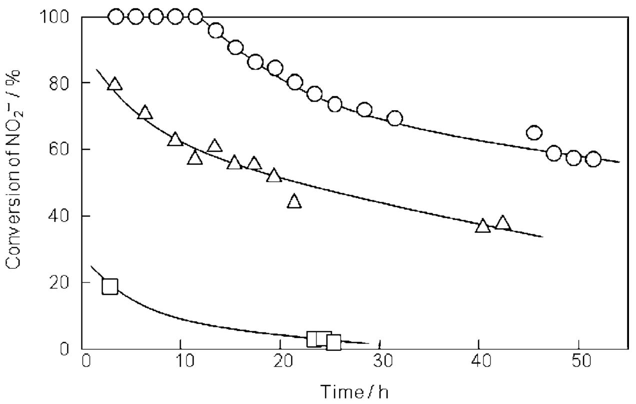

Figure 2. Time courses of the oxidation of NH_4^+ with NO_2^- (NH_4^+:NO_2^- = 1.0:1.0) over various Pt catalysts. (○) 1.0 wt % Pt/TiO_2, (△) 1.0 wt % Pt/Al_2O_3, and (□) 1.0 wt % Pt/SiO_2. Reaction conditions: temperature, 353 K; concn of NO_2^- from $NaNO_2$, 4.3 mmol dm^{-3}; concn of NH_4^+ from $(NH_4)_2CO_3$, 4.3 mmol dm^{-3}; WHSV = 15 h^{-1}.

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