Selective photocatalytic reduction of nitrate to nitrogen molecules in an aqueous suspension of metal-loaded titanium(IV) oxide particles

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Nitrate was photocatalytically reduced to nitrogen molecules with a high selectivity in a basic aqueous suspension of palladium and copper-loaded titanium(IV) oxide powders in the presence of oxalate anion as a hole scavenger.

Nitrate (NO₃⁻) is a final product of nitrogen atom oxidation and is one of the most important components of fertilizer. However, NO₃⁻ is toxic in humans, and the recent gradual increase in the concentration of NO₃⁻ in ground water mainly due to agricultural effluents has became a serious problem. European Drinking Water Directive has set the maximum admissible concentration of NO₃⁻ in drinking water to 50 mg dm⁻³, and the World Health Organization has set the concentration to 25 mg dm⁻³ as a guide level.¹

There are several methods for reducing NO₃⁻ to other nitrogen compounds. Photocatalytic reduction (or decomposition) of NO₃⁻ by photogenerated electrons (e⁻) is one of the methods, and this method has been extensively studied by many researchers²⁻¹² because solar power can be used as an energy source for driving the reaction. However, it has been found that titanium(IV) oxide (TiO₂) itself has no or almost no photocatalytic activity. Li and Wasgestian⁶ reported that oxalic acid (OA) added to a suspension of bare TiO₂ containing NO₃⁻ acts as a hole (h⁺) scavenger and accelerates photocatalytic reduction of NO₃⁻ by e⁻ to ammonia (NH₃) or ammonium ions (NH₄⁺) (eqn. (1)). Reduction of NO₃⁻ by carbon dioxide anion radical (CO₂⁻⁻), which is an intermediate species formed by partial oxidation of OA by h⁺, has also been proposed.^{11,12}

$$NO_3^- + 4C_2O_4^{2-} + 10H^+ = NH_4^+ + 8CO_2 + 3H_2O$$
 (1)

From an environmental point of view, photocatalytic reduction of NO₃⁻ to non-toxic nitrogen molecules (N₂) is preferable because other nitrogen compounds such as nitrite (NO₂⁻) and NH₃ are more toxic than NO₃⁻. However, selective photocatalytic reduction of NO₃⁻ to N₂ under UV irradiation at a wavelength of >300 nm has not been reported, indicating that controlling the extent of NO₃⁻ reduction by photocatalysis is very difficult. Here we briefly show that NO₃⁻ is effectively and selectively reduced to N₂ in an aqueous suspension of both copper- and palladiumloaded TiO₂ particles under basic conditions in the presence of OA (eqn. (2)).

 $2NO_3^{-} + 5C_2O_4^{2-} + 8OH^{-} = N_2 + 10CO_3^{2-} + 4H_2O$ (2)

Degussa P-25 was used as a TiO₂ photocatalyst because it is known to be one of the most active photocatalysts. Bare TiO₂ powder (50 mg) was suspended in a solution (5 cm³) containing nitric acid (or sodium nitrate, 50 µmol), OA (or sodium oxalate, 200 µmol) and a metal source (mainly metal chloride) in a test tube. No effects of metal source (chloride or sulfate) were observed in this study. Using 5 M sodium hydroxide solution, pH of the suspension was adjusted to the desired value. The tube was sealed with a rubber septum and then photoirradiated at $\lambda > 300$ nm by a 400 W high-pressure mercury arc (Eiko-sha, Osaka, Japan) under argon with magnetic stirring. During photoirradiation, the test tube was set in a water bath kept at a continuous 298 K to avoid thermal reaction. In the early stage of irradiation, the metal source was reduced by photogenerated e⁻ and the metal was deposited on TiO₂ particles, resulting in the formation of metal-loaded TiO₂. Concentrations of NO_3^- , NO_2^- and NH_3 (in the form of NH_4^+) in the liquid phase were determined by absorption spectrophotometry (TOA Electronics LASA-20, Tokyo). The amounts of N₂, hydrogen and carbon dioxide in the gas phases of reaction mixtures were measured using a Shimadzu GC-8A gas chromatograph equipped with MS-5A (N_2 and H_2) and Porapak QS (CO₂) columns. Some blank experiments revealed that both TiO2 and photoirradiation were indispensable to drive all reactions observed in this study.

Table 1 shows effects of pH on the photocatalytic reduction (12 h irradiation) of NO_3^- in a suspension of Cu–TiO₂ in the presence of OA. When Cu–TiO₂ was used in this reaction system under acidic conditions, *i.e.*, without pH control (*ca.* pH 1), OA was oxidized by two holes to produce twofold greater molar amount of carbon dioxide, whereas NO_3^- was reduced by eight photogenerated electrons to form NH_3 (or NH_4^+) (eqn. 1).

$$2H^{+} + 2e^{-} = H_2$$
 (3)

Reduction of NO₃⁻ by e⁻ competes with that of H⁺ (eqn. (3)), and the selectivity was determined by hydrogen overvoltage (HOV) of metal loaded on the TiO₂ particles because metal works as a reduction center in this reaction.⁹ In the case of Cu–TiO₂, reduction of H⁺ to H₂ was completely inhibited due to the large HOV of Cu metal, and an NO₃⁻ ion reacted with four oxalate anions to yield NH₃ and eight CO₂ molecules (eqn. (1)).

$$NO_{3}^{-} + C_{2}O_{4}^{2-} + 2OH^{-} = NO_{2}^{-} + 2CO_{3}^{2-} + H_{2}O$$
(4)

At pH 5, NO_2^- , which was a two-electron reduction product, was formed as well as NH_3 (Table 1). Nitrogen balance after photoirradiation at pH 5 was 75%, suggesting that another

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Table 1 Photocatalytic reduction of nitrate in an aqueous suspension of 0.5 wt% metal-loaded P-25 TiO₂ in the presence of oxalic acid for 12 h

Metal loaded	pН	NO ₃ ^{-a} / µmol	NO2 ^{-/} μmol	NH3/ μmol	N ₂ / μmol	H ₂ / μmol	Nitrogen balance/%	NO ₂ ⁻ selectivity ^b /%	N ₂ selectivity ^c /%	Hydrogen overvoltage ^d /V
Cu	1	28	0	20	0	3	96	0	0	0.43
Cu	5	24	5	8	0	1	75	13	0	0.43
Cu	11	36	13	0	0	0	98	99	0	0.43
Pt	11	48	0	0	0	26	96	0	0	0.01-0.09
Pd	11	47	0	0	0	14	94	0	0	0.04
Au	11	42	6	0	0	6	96	50	0	0.18
Ag	11	38	13	0	0	0	102	100	0	0.30
Pd–Cu ^e	11	24	2.4	0	10	0	93	4.6	95	
Pd–Cu ^f	11	22	1.0	0	13	0	98	1.5	98	
^a Nitrate remaining after the reaction for 12 h (initial amount: 50 µmol). ^b Based on consumption of photogenerated electron. Calculated from										
the equation $100 \times 2NO_2^{-1}/(10N_2 + 2NO_2^{-1} + 8NH_3 + 2H_2)^c$ Based on consumption of photogenerated electron. Calculated from the equation										
$100 \times 10N_2/(10N_2 + 2NO_2^- + 8NH_3 + 2H_2)^{d}$ Ref. 18–20. ^e 0.5 wt% Pd-0.5 wt% Cu. ^f 1.0 wt% Pd-0.5 wt% Cu.										

intermediate species was produced, although the species was not identified. At pH 11, NO₂⁻ was the sole product with a high nitrogen balance, indicating that protonation of NO₃⁻, *i.e.*, production of NH₃, was suppressed in basic conditions. The oxidation product of oxalate anion, CO₂, did not evolve into the gas phase and remained in the suspension as carbonate (CO₃²⁻) due to the basicity of the suspension. Therefore, one NO₃⁻ ion reacted with one oxalate to yield one NO₂⁻ ion and two CO₃²⁻ anions (eqn. (4)). Two hydroxide anions are consumed in the reaction. In fact, a slight decrease in pH of the suspension was observed after photoirradiation. These results indicate that the extent of photocatalytic reduction of NO₃⁻ by e⁻ can be controlled by pH of the suspension of Cu–TiO₂.

$$C_2 O_4^{2-} + 2OH^- = 2CO_3^{2-} + H_2$$
 (5)

The effects of type of metal on the photocatalytic reduction of NO₃⁻ at pH 11 are also summarized in Table 1. The effects of gold and silver were almost the same as the effect of Cu. When palladium (Pd) and platinum (Pt) were loaded on TiO₂ particles, only H₂ formation was observed. In this case, photogenerated e⁻ was captured only by H⁺, *i.e.*, photocatalytic decomposition of oxalate^{13,14} (eqn. (5)) proceeded. The promotive effect of loading of noble metals having a small HOV on H₂ liberation from aqueous alcohol solutions has been observed in previous studies and has been attributed to the efficient reduction of H⁺ by e⁻ on the metal surface.^{15–17} The same mechanism accounts for the results observed in the Pd– and Pt–TiO₂ system.

It should be noted that when both 0.5 wt% Pd and 0.5 wt% Cu were loaded on TiO₂ powder, five-electron reduction of NO₃⁻ to N₂ occurred (eqn. (2)) with a high nitrogen balance without formation of NO₂⁻ or NH₃ as shown in Table 1. An increase in Pd loading to 1 wt% resulted in an increase in N₂ yield. The yield of H₂ formed by reduction of H⁺ by e⁻ was negligible as well as in the Cu–TiO₂ system.

Fig. 1 shows the time courses of yields of N_2 and NO_2^- and the amount of NO_3^- in the aqueous suspension of Pd–Cu–TiO₂ powders. The amount of NO_3^- remaining in the suspension decreased monotonously with photoirradiation. A small amount of NO_2^- was observed in the early stage of photoirradiation, but the yield of NO_2^- was decreased with prolongation of photoirradiation. The yield of N_2 increased with photoirradiation with a good nitrogen balance, and finally 16.5 µmol of N_2 (corresponding to 33.0 µmol of nitrogen atoms) was formed after photoirradiation for 24 h. Fig. 1 also shows that the reaction rate (both N_2 evolution and NO₃⁻ reduction) gradually decreased, especially after 16 h. When sodium carbonate was added to the suspension before photoirradiation, the reaction rate was suppressed. Therefore, the gradual decrease in the reaction rate was attributed to adsorption of dissolved CO_3^{2-} arising from OA. When a small amount of sulfuric acid (5 M) was injected into the suspension after 24 h irradiation, CO2 evolved from the suspension. The test tube was opened to release CO2 and sealed again after Ar bubbling, and then NaOH solution was injected to maintain the pH of the suspension at 11. This process of removing CO_3^{2-} from the suspension is hereafter called "pH swing". After pH swing, the suspension containing Pd-Cu-TiO₂ and unreacted NO₃ (18 µmol) and OA was photoirradiated again for 20 h. As shown in Fig. 1, 6.6 µmol of N₂ (corresponding of 13.2 µmol for nitrogen atoms) evolved after this second photoirradiation, indicating that subsequent photocatalytic reduction of NO_3^- to N_2 is possible if CO_3^{2-} is removed from the suspension.

To investigate the formation of N_2 from NO_3^- in the Pd–Cu–TiO₂ system, photocatalytic reaction of NO_2^- in an aqueous suspension of Cu–TiO₂, Pd–TiO₂ or Pd–Cu–TiO₂ was carried out



Fig. 1 Time course of photocatalytic reduction of nitrate (initially 50 μ mol) in an aqueous suspension of Pd–Cu–TiO₂ powders in the presence of oxalate (200 μ mol). At "pH swing", a small amount of sulfuric acid was added to remove CO₂ and then NaOH solution was added to increase the pH of the suspension to 11. Circles: nitrate, triangles: nitrite, squares: nitrogen molecules.

at pH 11 in the presence of OA. Evolution of N_2 was observed for the Pd–TiO₂ and Pd–Cu–TiO₂ systems but not for the Cu–TiO₂ system, indicating that Pd is indispensable for reduction of $NO_2^$ to N_2 in the photocatalytic reaction. Since Pd alone promoted reduction of H⁺ producing H₂ as shown previously, Pd and Cu probably form an alloy on TiO₂ particles.

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