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

Hiroshi Kominami,*[a] Takao Nakaseko,[a] Yumiko Shimada,[a] Akitoshi Furusho,[a] Hiroyuki Inoue,[a] Shin-ya Murakami,[a] Yoshiya Kera[a] and Bunsho Ohtani[b]

Received (in Cambridge, UK) 28th February 2005, Accepted 13th April 2005
First published as an Advance Article on the web 28th April 2005
DOI: 10.1039/b502909k

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 (NO_3^-) is a final product of nitrogen atom oxidation and is one of the most important components of fertilizer. However, NO_3^- is toxic in humans, and the recent gradual increase in the concentration of NO_3^- in ground water mainly due to agricultural effluents has became a serious problem. European Drinking Water Directive has set the maximum admissible concentration of NO_3^- 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 NO_3^- to other nitrogen compounds. Photocatalytic reduction (or decomposition) of NO_3^- by photogenerated electrons (e^-) is one of the methods, and this method has been extensively studied by many researchers[2–12] because solar power can be used as an energy source for driving the reaction. However, it has been found that titanium(IV) oxide (TiO_2) itself has no or almost no photocatalytic activity. Li and Wasgestian[6] reported that oxalic acid (OA) added to a suspension of bare TiO_2 containing NO_3^- acts as a hole (h^+) scavenger and accelerates photocatalytic reduction of NO_3^- by e^- to ammonia (NH_3) or ammonium ions (NH_4^+) (eqn. (1)). Reduction of NO_3^- by carbon dioxide anion radical ($CO_2^{\bullet -}$), which is an intermediate species formed by partial oxidation of OA by h^+, has also been proposed.[11,12]

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

From an environmental point of view, photocatalytic reduction of NO_3^- to non-toxic nitrogen molecules (N_2) is preferable because other nitrogen compounds such as nitrite (NO_2^-) and NH_3 are more toxic than NO_3^-. However, selective photocatalytic reduction of NO_3^- to N_2 under UV irradiation at a wavelength of >300 nm has not been reported, indicating that controlling the extent of NO_3^- reduction by photocatalysis is very difficult. Here we briefly show that NO_3^- is effectively and selectively reduced to N_2 in an aqueous suspension of both copper- and palladium-loaded TiO_2 particles under basic conditions in the presence of OA (eqn. (2)).

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

Degussa P-25 was used as a TiO_2 photocatalyst because it is known to be one of the most active photocatalysts. Bare TiO_2 powder (50 mg) was suspended in a solution (5 cm^3) 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 TiO_2 particles, resulting in the formation of metal-loaded TiO_2. 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 N_2, 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 (CO_2) columns. Some blank experiments revealed that both TiO_2 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–TiO_2 in the presence of OA. When Cu–TiO_2 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).

$$2H^+ + 2e^- = H_2 \quad (3)$$

Reduction of NO_3^- by e^- competes with that of H^+ (eqn. (3)), and the selectivity was determined by hydrogen overvoltage (HOV) of metal loaded on the TiO_2 particles because metal works as a reduction center in this reaction.[9] In the case of Cu–TiO_2, reduction of H^+ to H_2 was completely inhibited due to the large HOV of Cu metal, and an NO_3^- ion reacted with four oxalate anions to yield NH_3 and eight CO_2 molecules (eqn. (1)).

$$NO_3^- + C_2O_4^{2-} + 2OH^- = NO_2^- + 2CO_3^{2-} + H_2O \quad (4)$$

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

---

*hiro@apch.kindai.ac.jp

Table 1 Photocatalytic reduction of nitrate in an aqueous suspension of 0.5 wt% metal-loaded P-25 TiO_2 in the presence of oxalic acid for 12 h

Metal loaded	pH	NO_3^-[a]/ µmol	NO_2^-/ µmol	NH_3/ 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 $100 \times\ 2NO_2^-/(10N_2 + 2NO_2^- + 8NH_3 + 2H_2)$ [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, NO_2^- was the sole product with a high nitrogen balance, indicating that protonation of NO_3^-, *i.e.*, production of NH_3, was suppressed in basic conditions. The oxidation product of oxalate anion, CO_2, did not evolve into the gas phase and remained in the suspension as carbonate (CO_3^{2-}) due to the basicity of the suspension. Therefore, one NO_3^- ion reacted with one oxalate to yield one NO_2^- ion and two CO_3^{2-} 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 NO_3^- by e^- can be controlled by pH of the suspension of Cu–TiO_2.

$$C_2O_4^{2-} + 2OH^- = 2CO_3^{2-} + H_2 \tag{5}$$

The effects of type of metal on the photocatalytic reduction of NO_3^- 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 TiO_2 particles, only H_2 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 H_2 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–TiO_2 system.

It should be noted that when both 0.5 wt% Pd and 0.5 wt% Cu were loaded on TiO_2 powder, five-electron reduction of NO_3^- to N_2 occurred (eqn. (2)) with a high nitrogen balance without formation of NO_2^- or NH_3 as shown in Table 1. An increase in Pd loading to 1 wt% resulted in an increase in N_2 yield. The yield of H_2 formed by reduction of H^+ by e^- was negligible as well as in the Cu–TiO_2 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–TiO_2 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 NO_3^- 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, CO_2 evolved from the suspension. The test tube was opened to release CO_2 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–TiO_2 and unreacted NO_3^- (18 µmol) and OA was photoirradiated again for 20 h. As shown in Fig. 1, 6.6 µmol of N_2 (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–TiO_2 system, photocatalytic reaction of NO_2^- in an aqueous suspension of Cu–TiO_2, Pd–TiO_2 or Pd–Cu–TiO_2 was carried out

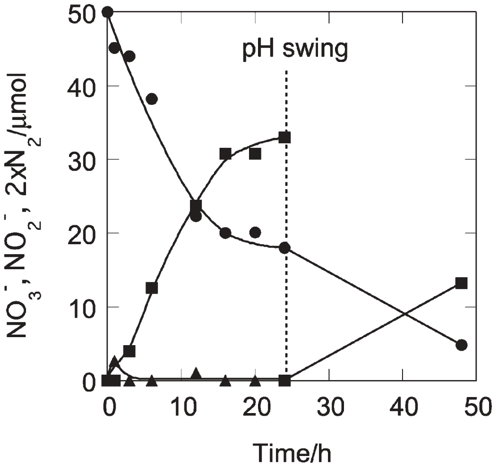

Fig. 1 Time course of photocatalytic reduction of nitrate (initially 50 µmol) in an aqueous suspension of Pd–Cu–TiO_2 powders in the presence of oxalate (200 µmol). At "pH swing", a small amount of sulfuric acid was added to remove CO_2 and then NaOH solution was added to increase the pH of the suspension 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–TiO_2 and Pd–Cu–TiO_2 systems but not for the Cu–TiO_2 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 H_2 as shown previously, Pd and Cu probably form an alloy on TiO_2 particles.

This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Areas (417) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government.

Hiroshi Kominami,*[a] Takao Nakaseko,[a] Yumiko Shimada,[a] Akitoshi Furusho,[a] Hiroyuki Inoue,[a] Shin-ya Murakami,[a] Yoshiya Kera[a] and Bunsho Ohtani[b]
[a] *Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University, Kowakae, Higashiosaka, Osaka, 577-8502, Japan. E-mail: hiro@apch.kindai.ac.jp; Fax: +81-6-6727-4301; Tel: +81-6-6721-2332*
[b] *Catalysis Research Center, Hokkaido University, Sapporo, Japan. E-mail: ohtani@cat.hokudai.ac.jp; Fax: +81-11-706-9133; Tel: +81-11-706-9132*

Notes and references

1 L. Bontoux, N. Bournis and D. Papameletiou, *IPTS Rep.*, 1997, **6**, 7.
2 A. Kudo, K. Domen, K. Maruya and T. Ohnishi, *Chem. Lett.*, 1987, 1019.
3 B. Ohtani, M. Kakimoto, H. Miyadzu, S.-i. Nishimoto and T. Kagiya, *J. Phys Chem.*, 1988, **92**, 5773.
4 A. Kudo, K. Domen, K. Maruya and T. Ohnishi, *J. Catal.*, 1992, **135**, 300.
5 K. T. Ranjit, T. K. Varadarajan and B. Viswanathan, *J. Photochem. Photobiol. A: Chem.*, 1995, **89**, 67.
6 Y. Li and F. Wasgestian, *J. Photochem. Photobiol. A: Chem.*, 1998, **112**, 255.
7 B. Bems, F. C. Jentoft and R. Schlogl, *Appl. Catal. B. Environ.*, 1999, **20**, 155.
8 T. Mori, J. Suzuki, K. Fujimoto, M. Watanabe and Y. Hasegawa, *J. Sol-Gel Sci. Technol.*, 2000, **19**, 505.
9 H. Kominami, A. Furusho, S.-y. Murakami, H. Inoue, Y. Kera and B. Ohtani, *Catal. Lett.*, 2001, **76**, 31.
10 H. Kato and A. Kudo, *Phys Chem. Chem. Phys.*, 2002, **4**, 2833.
11 R. Jin, W. Gao, J. Chen, H. Zeng, F. Zhang, Z. Liu and N. Guan, *J. Photochem. Photobiol., A: Chem.*, 2004, **162**, 585.
12 W. Gao, R. Jin, J. Chen, X. Guan, H. Zeng, F. Zhang and N. Guan, *Catal. Today*, 2004, **90**, 331.
13 J.-M. Herrmann, M.-N. Mozzanega and P. Pichat, *J. Photochem.*, 1983, **22**, 333.
14 A. Malinka and G. L. Kamalov, *React. Kinet. Catal. Lett.*, 1994, **52**, 13.
15 S.-i. Nishimoto, B. Ohtani and T. Kagiya, *J. Chem. Soc., Faraday Trans. 1*, 1985, **81**, 2467.
16 K. Domen, S. Naito, T. Ohnishi and K. Tamaru, *Chem. Lett.*, 1982, 555.
17 S. Teranishi, J. Nakamichi, K. Kaya and K. Tanaka, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 1688.
18 R. Ruetschi and P. Delahey, *J. Chem. Phys.*, 1995, **23**, 195.
19 B. E. Conway and J. O'M. Bockris, *J. Chem. Phys.*, 1957, **26**, 532.
20 H. Kita, *J. Electrochem. Soc.*, 1966, **113**, 1095.