Effective photocatalytic reduction of nitrate to ammonia in an aqueous suspension of metal-loaded titanium(IV) oxide particles in the presence of oxalic acid

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Photocatalytic reduction of nitrate ion (NO_3^-) in an aqueous suspension of metal-loaded titanium(IV) oxide (TiO_2) was examined in the presence of oxalic acid (OA) as a hole scavenger. Conversion of NO_3^- into ammonia (NH_3) competed with hydrogen liberation, and the NH_3 production selectivity increased with the order of loaded metal, (Pt, Pd, Co) < (Ni, Au) < (Ag, Cu), which was attributable to the efficiency of reduction of protons by photogenerated electrons at the loaded metal, *i.e.*, hydrogen overvoltage of the loaded metal. TiO_2 powder loaded with Cu showed higher NH_3 yield and selectivity as well as higher efficiency of OA consumption. TiO_2 with *in situ* deposited Cu gave results comparable to those of a Cu pre-loaded photocatalyst.

KEY WORDS: titanium oxide; photocatalyst; nitrate reduction; ammonia

1. Introduction

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. The World Health Organization has recommended a maximum NO_3^- concentration of 45 mg-nitrogen dm^{-3} in drinking water [1].

Photocatalytic reduction (or decomposition) of NO_3^- has been extensively studied by many researchers [2–7]. It has been found that titanium(IV) oxide (TiO_2) itself has no or almost no photocatalytic activity and that loading of metal is necessary for the photocatalytic reduction of NO_3^-. Recently, 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^- into ammonia (NH_3) or ammonium ion (NH_4^+). They have shown that the reaction proceeds according to the following equation [6]:

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

Oxalate anion is oxidized by two holes (h^+) to produce a twice molar amount of carbon dioxide (CO_2), whereas NO_3^- is reduced by eight photogenerated electrons (e^-) to form NH_3. Totally, an NO_3^- ion reacts with four oxalate anions to yield NH_3 and eight CO_2 molecules. Jentoft *et al.* [7] examined photocatalytic reduction of NO_3^- in the presence of humic acid as a hole scavenger. They reported that spontaneous reduction into nitrite (NO_2^-) of higher toxicity also occurs and that an effective catalytic system is required to reduce the NO_2^- production.

We examined the effect of metal loading onto TiO_2 on the photocatalytic reduction of NO_3^- into NH_3 in the presence of OA, and we briefly show here that the loading of copper or silver remarkably increased the activity and the selectivity for the NO_3^- reduction into NH_3 and, at the same time, the efficiency of OA consumption for NO_3^- reduction.

2. Experimental

Degussa P-25 TiO_2 was used in most of the experiments because it is known to be one of the most active photocatalysts. In the last part of the experiments, another TiO_2, HyCOM TiO_2, was also used to investigate the correlation between the physical properties and photocatalytic activity of TiO_2 in this reaction system. The HyCOM TiO_2 powder was synthesized by hydrothermal crystallization in organic media, as reported previously [8,9]. Loading of metals onto TiO_2 particles was performed by impregnation of adequate starting materials (mainly metal nitrates) onto TiO_2, drying, and hydrogen (H_2) reduction at 773 K. The bare or metal-loaded TiO_2 powder (50 mg) was suspended in a solution (5 cm^3) containing nitric acid (50 μmol) and oxalic acid (200 μmol) in a test tube. The tube was sealed with a rubber septum and then photoirradiated at a wavelength of >300 nm by a high-pressure mercury arc (400 W) under argon with magnetic stirring at 298 K. Concentrations of NO_3^-, NO_2^-,

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Table 1
Photocatalytic reduction of nitrate in an aqueous suspension of metal-loaded P-25 TiO_2 in the presence of oxalic acid (200 μmol; corresponding to 400 μmol of TOC).

Metal loaded	wt%	Time (h)	NO_3^- [a] (μmol)	NO_2^- (μmol)	NH_3 (μmol)	TOC (μmol)	CO_2 (μmol)	H_2 (μmol)	NH_3 selectivity[b] (%)	OA efficiency[c] (%)	Hydrogen overvoltage[d] (V)
–	–	3	4.9	0.03	2.1	374	45	0.2	98	37	–
Pt	0.5	3	3.2	0.04	<1	75	281	205	~0	~0	0.01–0.09
Pd	0.5	3	1.3	0.04	<1	67	315	209	~0	~0	0.04
Ni	1.0	6	10	0.03	10	ND[e]	260	169	21	34	0.29
Au	0.5	6	22	0.03	11	ND	260	151	22	35	0.18
Ag	0.5	3	43	ND	23	88	297	2.7	97	63	0.30
Cu	0.5	3	22	0.04	20	220	193	3.2	96	84	0.43
Cu[f]	0.5	3	21	0.03	18	233	168	0.6	99	86	0.43
Co	0.5	3	2.2	<0.02	<1	352	52	1.8	~0	~0	
(RuO_2)	2.0	6	8.6	0.03	2.9	ND	255	212	5.2	9.1	

[a] Nitrate reacted (initial amount 50 μmol).
[b] Calculated from the equation $100 \times 8NH_3/(8NH_3 + 2H_2)$.
[c] Oxalic acid efficiency calculated from the equation $100 \times 8NH_3/CO_2$.
[d] From [23–25].
[e] Not determined.
[f] Sodium nitrate (50 μmol) was used in place of nitric acid.

NH_3 (in the form of NH_4^+) and total organic carbon (TOC) in the liquid phase were determined with a TOA Electronics LASA-20 spectrophotometer using kits specified for measurement of each component. The amounts of CO_2 and H_2 in the gas phase were measured using a Shimadzu GC-8A gas chromatograph equipped with Porapak QS and MS-5A columns, respectively.

3. Results and discussion

In the presence of OA, NO_3^- was reduced into NH_3, together with H_2 liberation, as reported previously [6], while the NO_3^- reduction was negligible in the absence of OA. Table 1 summarizes the results. Since e^- can be used for the reduction of NO_3^- and proton (H^+), selectivity of the reduction of NO_3^- into NH_3 was calculated as $100 \times 8NH_3/(8NH_3 + 2H_2)$ and is also listed in table 1. In the case of bare TiO_2, formation of NO_2^- was negligible and the NH_3 yield (2.1 μmol) was much smaller than that of reacted NO_3^- (4.9 μmol), suggesting that another intermediate species was produced. The yield of CO_2 (45 μmol) was *ca.* three times larger than that expected from the NH_3 yield (16.8 μmol $= 2.1 \times 8$). As a result, OA efficiency, the proportion of OA consumed for the NH_3 production ($100 \times 8NH_3/CO_2$), was low (37.3%). However, the high NH_3 selectivity (97.6%) indicated that most of e^- was used for reduction of NO_3^- rather than H^+ on the bare TiO_2 surface in the presence of OA.

Loading of platinum or palladium on TiO_2 particles decreased the NH_3 yield a little but increased the H_2 yield, showing that photocatalytic decomposition (dehydrogenation) of OA [14,15] (equation (2)) was accelerated.

$$H_2C_2O_4 \rightleftharpoons 2CO_2 + H_2 \qquad (2)$$

The promotive effect of loading of noble metals 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 [10–13]. The same mechanism accounts for the results observed in the present system. A high H_2 yield was also observed in the case of ruthenium(IV) oxide–TiO_2. When nickel or gold was loaded on TiO_2, a relatively high NH_3 yield was obtained, though a large amount of H_2 was also liberated and the NH_3 selectivity was still low. On the other hand, TiO_2 loaded with copper (Cu) or silver gave a higher NH_3 yield (23.2 and 20.3 μmol-NH_3 by 3 h irradiation) and suppressed H_2 formation (2.7 and 3.2 μmol), leading to higher NH_3 selectivity (97.2 and 96.2%). Cu–TiO_2 showed the highest OA efficiency (84.1%) among the metal-loaded photocatalysts, *i.e.*, Cu–TiO_2 drives the photocatalytic reaction of equation (1) selectively and efficiently. This was also the case for the reaction operated under neutral conditions (table 1).

These metals loaded on TiO_2 particles seem to act as reduction sites. Since equal numbers of e^- and h^+ must be consumed in the photocatalytic systems, the acceleration of reduction with e^- at the metal surface enhances the overall reaction as observed by the CO_2 liberation. Except for cobalt, the loaded metal showed this enhancing effect in the same order of magnitude. On the other hand, the selectivity of the reaction product depended strongly on the kind of loaded metal. Comparison of the NH_3 selectivity with hydrogen overvoltage (HOV, table 1) of electrodes composed of each metal suggested that the higher HOV is, the more difficult it is to reduce H^+ by e^-, in other words, the more efficiently e^- reduces NO_3^- to give higher NH_3 selectivity and OA efficiency. Other metals having high HOV such as lead (0.67 V), tin (0.85 V) and zinc (0.72 V), however, exhibited no activity. These metals are unstable (or dissolved) in solution of nitric acid or NH_3 and might not act as reduction sites.

The process of metal loading onto TiO_2 particles includes impregnation of a starting salt, drying, and reduction by

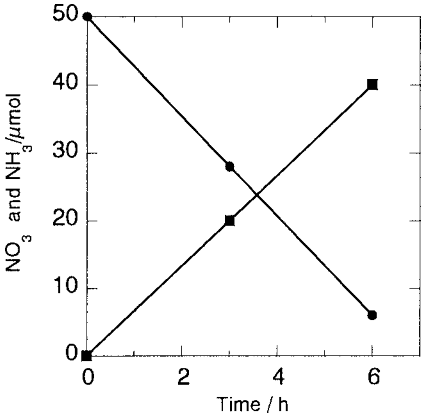

Figure 1. Time courses of changes in concentrations of NO_3^- (●) and NH_3 (■) in a photoirradiated (>300 nm) aqueous suspension (5 cm^3) of P-25 TiO_2 (50 mg) in the presence of oxalic acid (200 μmol) and copper sulfate (3.9 μmol).

H_2, and the process is time-consuming and requires careful control of the preparation conditions. A physical mixture of fine metal particles and TiO_2 particles needs a much larger amount of metal compared with the above deposition–reduction process. To avoid a tedious loading process and to reduce the amount of loaded metals, copper(II) sulfate (3.9 μmol, corresponding to 0.5 wt% Cu metal) solution was injected into a suspension of bare TiO_2 containing NO_3^- (50 μmol) and OA (200 μmol), and then the suspension was photoirradiated under the same conditions to induce the photocatalytic deposition of Cu [16–18]. As figure 1 shows, NO_3^- and NH_3 decreased and increased linearly, respectively, with irradiation time. The amount of unreacted Cu^{2+} in the liquid phase decreased with time, and most of the Cu^{2+} (99.0%) was removed after 6 h. This clearly shows that Cu^{2+} in the starting suspension was reduced by e^- to form copper metal on TiO_2 particles and acted as a reduction site for NO_3^-.

We have shown that TiO_2 of a large surface area and high crystallinity can be synthesized by hydrothermal crystallization in organic media (HyCOM) [8,9] and exhibited activity *ca.* twice higher than that of P-25 for photocatalytic reactions under both deaerated and aerated conditions [19–22]. Physical properties of HyCOM TiO_2 can be controlled in a wide range by changing synthesis conditions and post-calcination temperature, and the post-calcination had various effects depending on the type of reaction [20]. HyCOM samples were synthesized, calcined at various temperatures, and used in this reaction. The preparation conditions, BET surface area (S_{BET}), and crystallite size of these HyCOM samples (not metal-loaded) are summarized in table 2. With elevation in calcination temperature, S_{BET} of TiO_2 gradually decreased, while the crystallite size increased; *i.e.*, crystallinity of TiO_2 was improved. Dependence of NH_3 yield on S_{BET} is shown in figure 2. HyCOM TiO_2's except the rutile sample of small S_{BET} (HyCOM-D) showed much higher NH_3 yields than that by P-25. The superior activity of HyCOM TiO_2 could also be seen for H_2 formation [19], oxygen evolution [19,20] or mineralization of acetic acid [22]. Among HyCOM TiO_2's, the NH_3 yield increased with S_{BET}, but samples having S_{BET} > 95 $m^2\,g^{-1}$ showed smaller yields. These results suggested that both crystallinity and surface area affect the activity; *i.e.*, the former determines the probability of recombination of e^-–h^+ and the latter controls the amount of substrate(s) adsorbed on the TiO_2 particles. Since the adsorption of OA on TiO_2 was reported to be much stronger than that of NO_3^- [6], the adsorption of OA is predominant in the latter factor.

Table 2
Bare HyCOM TiO_2 samples.

HyCOM TiO_2	Water[a] (cm^3)	T_{cal}[b] (K)	TiO_2 phase[c]	d_{101}[d] (nm)	S_{BET}[e] ($m^2\,g^{-1}$)
A	10	–	A	13	93
B	10	823	A	16	71
C	10	973	A	23	36
D	10	1173	A,R	55	5
E	25	–	A	12	103
F	25	823	A	14	96
G	25	973	A	21	65
H	25	1173	A	38	18

[a] The amount of water used for synthesis of HyCOM TiO_2 at 573 K.
[b] As-synthesized TiO_2 was calcined at T_{cal} for 1 h.
[c] A = anatase, R = rutile.
[d] Crystallite size calculated from the 101 diffraction peak of anatase.
[e] BET surface area.

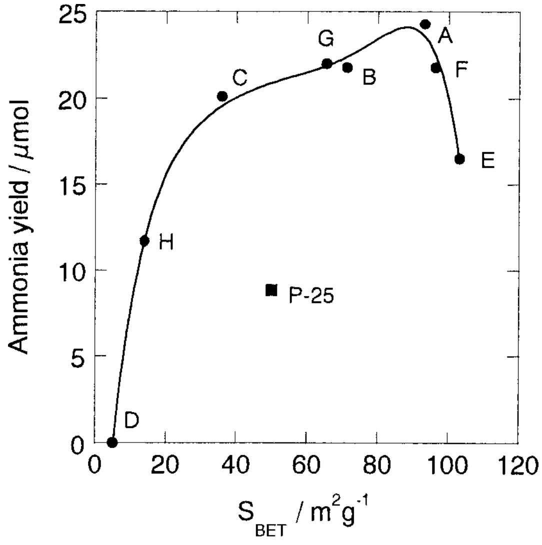

Figure 2. Dependence of NH_3 yield on S_{BET} of HyCOM TiO_2. The reaction conditions were the same as those described in the legend to figure 1. Irradiation was performed for 1.5 h.

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