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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.

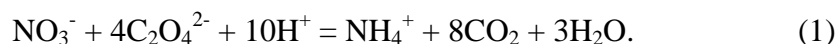
Keywords: titanium oxide, photocatalyst, nitrate reduction, ammonia

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 become 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]:



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. Experiment

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 TiO₂, HyCOM TiO₂, was also used to investigate the correlation between the physical properties and photocatalytic activity of TiO₂ in this reaction system. The HyCOM TiO₂ powder was synthesized by hydrothermal crystallization in organic media as reported previously [8, 9]. Loading of metals onto TiO₂ particles was performed by impregnation of adequate starting materials (mainly metal nitrates) onto TiO₂, drying, and hydrogen (H₂) reduction at 773 K. The bare or metal-loaded TiO₂ powder (50 mg) was suspended in a solution (5 cm³) 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 NO₃⁻, NO₂⁻, NH₃ (in the form of NH₄⁺) 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 CO₂ and H₂ 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, NO₃⁻ was reduced into NH₃, together with H₂ liberation, as reported previously [6], while the NO₃⁻ reduction was negligible in the absence of OA. Table 1 summarizes the results. Since e⁻ can be used for the reduction of NO₃⁻ and proton (H⁺), selectivity of the reduction of NO₃⁻ into NH₃ was calculated as $100 \times 8\text{NH}_3 / (8\text{NH}_3 + 2\text{H}_2)$ and is also listed in table 1. In the case of bare TiO₂, formation of NO₂⁻ was negligible and the NH₃ yield (2.1 μmol) was much smaller than that of reacted NO₃⁻ (4.9 μmol), suggesting that another intermediate species was produced. The yield of CO₂ (45 μmol) was ca. 3-times larger than that expected from the NH₃ yield (16.8 μmol = 2.1 × 8). As a result, OA efficiency, the proportion of OA consumed for the NH₃ production ($100 \times 8\text{NH}_3 / \text{CO}_2$), was low (37.3%). However, the high NH₃ 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.



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 $\mu\text{mol-NH}_3$ 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 eq. 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 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 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 μ mol, corresponding to 0.5 wt% Cu metal) solution was injected into a suspension of bare TiO_2 containing NO_3^- (50 μ mol) and OA (200 μ mol), 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 TiO₂ gradually decreased, while the crystallite size increased; i.e., crystallinity of TiO₂ was improved. Dependence of NH₃ yield on S_{BET} is shown in figure 2. HyCOM TiO₂'s except the rutile sample of small S_{BET} (HyCOM-D) showed much higher NH₃ yields than that by P-25. The superior activity of HyCOM TiO₂ could also be seen for H₂ formation [19], oxygen evolution [19, 20] or mineralization of acetic acid [22]. Among HyCOM TiO₂'s, the NH₃ yield increased with S_{BET}, but samples having S_{BET} > 95 m²g⁻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 TiO₂ particles. Since the adsorption of OA on TiO₂ was reported to be much stronger than that of NO₃⁻ [6], the adsorption of OA is predominant in the latter factor.

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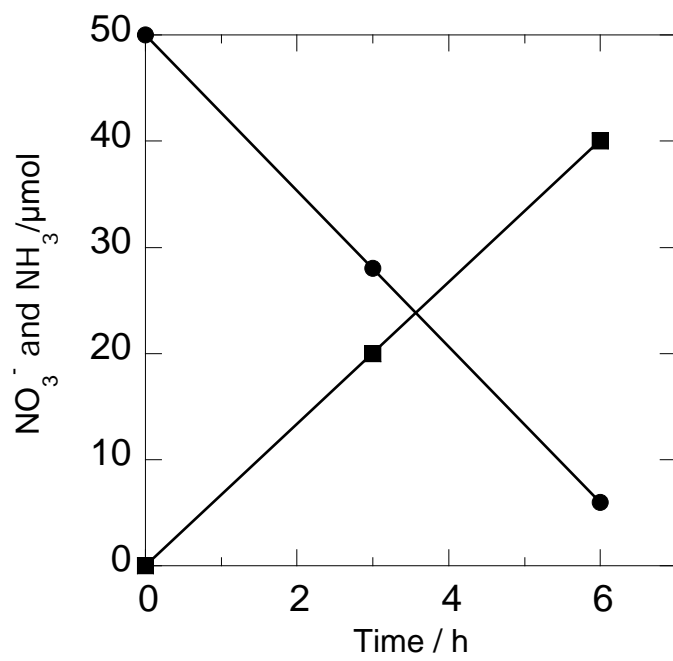
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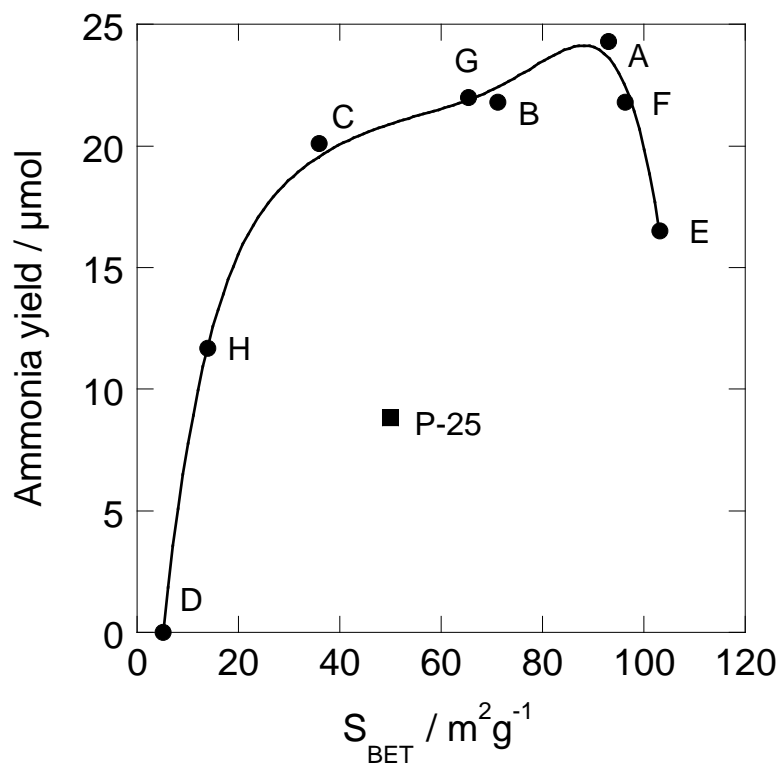
Figure captions

Figure 1. Time courses of changes in concentrations of NO_3^- (circles) and NH_3 (squares) 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).

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.



Kominami et al., Fig. 1



Kominami et al., Fig. 2

Table 1

Photocatalytic reduction of nitrate in an aqueous suspension of metal-loaded P-25 TiO₂ 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 ^f	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 ^e	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	

^aNitrate reacted (initial amount: 50 μmol).

^bCalculated from the equation, $100 \times 8\text{NH}_3 / (8\text{NH}_3 + 2\text{H}_2)$.

^cOxalic acid efficiency calculated from the equation, $100 \times 8\text{NH}_3 / \text{CO}_2$.

^dRef. [23-25]

^eSodium nitrate (50 μmol) was used in place of nitric acid.

^fNot determined.

Table 2
Bare HyCOM TiO₂ 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

^aThe amount of water used for synthesis of HyCOM TiO₂ at 573 K.

^bAs-synthesized TiO₂ was calcined at T_{cal} for 1 h.

^cA: anatase, R: rutile

^dCrystallite size calculated from the 101 diffraction peak of anatase.

^eBET surface area.