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Photocatalytic Reactions of Azide Ions on Platinized Titanium Dioxide Powders in Solutions

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Ammonia was formed photocatalytically from an aqueous solution of azide ion by using illuminated Pt/TiO_2 semiconductor powder. The reaction products, NH_3, N_2, and small amounts of N_2O and NO_3^-, were detected. Hydrogen, O_2 and N_2H_4 were not formed in the primary reaction products. From these results, together with photoelectrochemical measurements, a mechanism of the ammonia formation from azide ion and water is presented.

From the viewpoint of the chemical conversion of solar energy, much attention has been paid to the synthesis of ammonia from molecular nitrogen and water with the aid of light energy. Photocatalytic synthesis of ammonia from N_2 on illuminated semiconductors has been reported by several researchers.[1-5] Schrauzer and Guth[1] first reported the ammonia synthesis on moist iron doped TiO_2 powders. Miyama *et al.*[2] described the synthesis of ammonia from N_2 saturated water by using various kinds of semiconductors as photocatalysts. Recently, $SrTiO_3$ doped with RuO_2 and NiO has been used by Tamaru and coworkers.[5] Yoneyama *et al.*[6] described the formation of a considerable amount of ammonia from nitrogen monoxide instead of N_2. Nitrogenase, which is a well known catalyst for ammonia synthesis, catalyzes the ammonia production from N_3^- and other nitrogen compounds as well as from N_2.[7] Since N_3^-, which is a halogen-like ion, has an oxidized state between N_2 and NH_3, it may be expected to have some connection with intermediate spieces of the NH_3 synthesis from N_2. However, there has been no report for the photocatalytic reaction of aqueous azide ions. Therefore, we studied the photocatalytic ammonia synthesis from N_3^- aqueous solution and examined the reaction mechanism.

Experimental

The platinized TiO_2 used in the present study was prepared by the following procedure. Titanium dioxide powder (anatase, 99.95%, Kojundo Kagaku Co., Ltd.) was mixed with a platinum tetrachloride aqueous solution, dried and fired at 600 °C in flowing argon. Then, the powder was reduced in flowing hydrogen at 600 °C for 4 h. The catalysts were washed thoroughly with pure water. The 5%-platinized TiO_2 was used, unless otherwise stated. In a typical experiment, 0.2 g of catalyst and 10 cm^3 of 0.1 mol/dm^3 sodium azide solution was placed in a Pyrex vessel of 30 mm diameter, and the mixture was vigorously stirred throughout the reaction. Irradiation was performed with a 500 W high pressure mercury lamp focused through two water-filled round flasks. The temperature of the reaction mixture was about 43 °C. The catalyst in the reaction tube was removed with a centrifuge before the quantitative analysis of the products in the solution. The amount of ammonia was determined by measuring the absorbance at 640 nm after the reaction with Indophenol Blue. Hydrazine and NO_3^- were analysed from the absorbance at 458 nm and 410 nm with *p*-dimethylaminobenzaldehyde and brucine, respectively. The amount of unreacted N_3^- was determined as FeN_3^{2+} with 460-nm absorbance, which was formed by passing N_3H gas evolved by heating the acidified sample solution through a $Fe(NO_3)_3$ solution. Gaseous products were analyzed by gas chromatography with a thermal conductivity detector. A molecular sieve 5A column was used for the analysis of H_2, O_2, and N_2. For N_2O an active carbon column was used. The carrier gases were argon and helium for the analysis of H_2 and the other gases, respectively. Ammonia could not be detected by the columns used in the present study.

The TiO_2 film electrodes used for electrochemical measurements were prepared by painting $TiCl_4$ solution on polished titanium plate and firing at 500 °C. The platinization on the electrode was performed by a similar method described above for TiO_2 powder. The method of the electrochemical measurements is the same as described previously.[8]

Results

Table 1 summarizes a part of experimental results. Platinization of TiO_2 caused marked ammonia formation from N_3^-. The effect of platinization could be observed for the catalyst made by mixing in an agate mortar. The activity of the catalysts prepared by the impregnation method was comparable to those by the photodeposition method.[9] Accordingly, the impregnation method was used in further experiments because of the simplicity of the preparation. The reproducibil-

Table 1. Rate of ammonia formation[a)]

Pt content	Atmosphere	NH_3/(μmol/h)		Remarks
wt%		light	dark	
0	air	<0.01	<0.01	
1.0[b)]	air	0.76	—	
3.0[b)]	air	5.5	—	
5.0[b)]	air	11.7	0.10	
5.0	air	0.17	—	Pt mixed
5.0	air	10.5	<0.01	Pt photodeposited
3.6	He	15.5	—	
5.0	He	31.0	—	
5.0	air	0.61	—	N_3^-: 100 μmol
5.0	air	<0.01		N_3^-: 10 μmol

a) Unless otherwise remarked, platinization of TiO_2 powder was done by the impregnation method, and 1 mmol N_3^-, 10 cm^3 water, and 0.2 g of catalysts were used. b) These catalysts were prepared in the same process.

ity in the activity measurements was within ±5% for the same catalysts. However, the activity of catalysts was different from preparation to preparation up to about 3 times. The maximum quantum yield obtained for the ammonia production was estimated to be about 0.5%. The effect of different compounded metals on the catalytic activity has been described already.[10] The activity of 1.0% platinized TiO_2 is much smaller than that of 3.0% or 5.0% platinized TiO_2. Sakata *et al.*[11] reported the effect of the platinum content on the photocatalytic activity for hydrogen evolution from alcohol and water. They have shown that the activity increases rapidly with the amount of platinum up to 0.05%, and the increase becomes gradual above this content. The difference in the dependence of the platinum content on the catalytic activity may be attributed to the difference in platinization method. The dependence on the platinum content is similar to that of the photoconductivity of Pt/TiO_2 powders prepared by the impregnation method.[12] One of the factors controlling the photoconductivity is the rate of recombination of photoinduced electron-hole pairs. Therefore, the present result suggests that the rate of the decomposition of N_3^- is determined by the separation of the photoinduced electron-hole pairs, as has been proposed in the previous paper.[10]

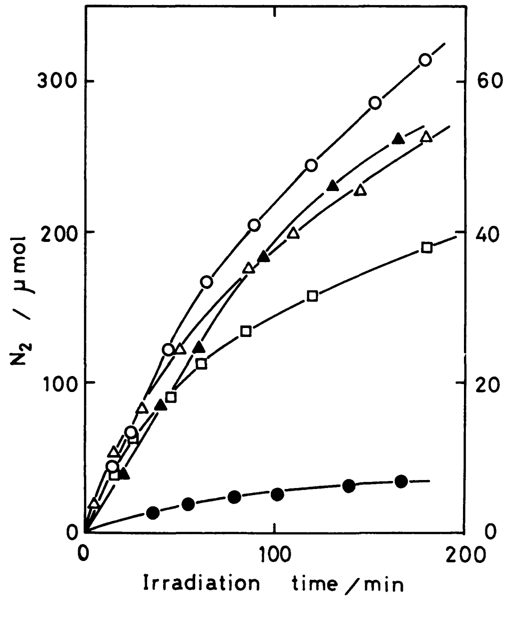

Fig. 1. The formation of N_2 (○, △, and □) and N_2O (● and ▲) as a function of the irradiation time in various atmospheric conditions; He (○ and ●), O_2 (△ and ▲), and N_2O (□).

When the reaction mixture had been deaerated, the rate of ammonia formation increased to three times that for the aerated conditions. This indicates that reduction of N_3^- competes with that of O_2 in the air. In order to clarify this observation, photocatalytic reaction was performed in various atmospheres with the same Pt/TiO_2 catalyst. The product yields are shown in Table 2 and the growth features of gaseous products are shown in Fig. 1. In the He atmosphere, N_2O was formed gradually with irradiation time. When the reactant mixture was bubbled with O_2 gas thoroughly, the amount of ammonia formed was very low. In this case, a large amount of N_2O was formed. In a N_2O atmosphere, the N_2 yield did not increase, although the ammonia yield was greater than that in the O_2 atmosphere, indicating that N_2O formed in the reaction with O_2 was not responsible for the decrease in the ammonia yield. Under any reaction conditions, O_2 and H_2 were not detected as a primary product. After the mitigation of the evolution of N_2, molecular hydrogen was observed in the He atmosphere. Since aqueous ammonia is known to be decomposed into N_2 and H_2 with photocatalysts,[5] the delayed formation of H_2 is attributed to the decomposition of the ammonia produced. The amount of remaining N_3^- was measured at the end of the growth of N_2 in the reaction under He atmosphere. The amount of N_3^- was 100 μmol when 1240 μmol of N_2 and 180 μmol of ammonia had been

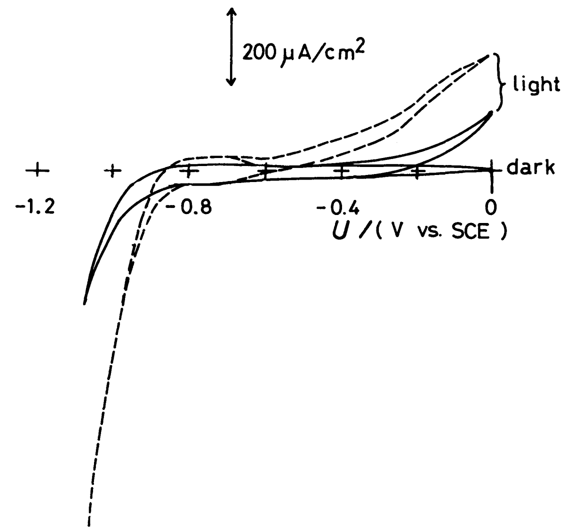

Fig. 2. Current-potential curves obtained for a Pt/TiO_2 polycrystalline electrode with and without illumination. Electrolyte; ----: 0.1 mol/dm³ NaN_3, ——: 0.05 mol/dm³ Na_2SO_4+KOH (pH 8.4).

Table 2. Yield of products for the reactions in various atmospheres[a)]

Atmosphere[b)]	NH_3/μmol	N_2/μmol	N_2O/μmol	O_2/μmol	H_2/μmol
He	80	324	6.7	0.0	0.0
O_2	2.0	278	53	—	0.0
N_2O	12	190	—	0.0	0.0

a) Solutions containing 1 mmol of N_3^- and 0.2 g of 5%-platinized TiO_2 powder in 10 cm³ of water were irradiated for 3 h. b) Thoroughly bubbled and saturated with these gases.

produced. Since the initial amount of N_3^- has been 1 mmol, this result suggests that all of the consumed N_3^- turned into ammonia or N_2. For confirmation, the by-products possibly formed in the solutions were analyzed. Hydrazine was not detected to a sensitivity of about 0.01 μmol, and the amount of NO_3^- was less than 0.5 μmol. Under the aerated conditions, these nitrogen compounds were not increased.

In order to clarify the mechanism of the photocatalytic reaction, electrode reactions were measured with a platinized TiO_2 polycrystalline film electrode. For aqueous solutions of 0.1 mol/dm³ NaN_3 and 0.05 mol/dm³ Na_2SO_4, current-potential curves were measured and some of them are shown in Fig. 2. The pH value of sulfate solution had been adjusted to that of azide solution (pH 8.4) by the addition of a small amount of KOH. A reduction current accompanied by the evolution of a gas was observed at less cathodic potential in the presence of N_3^-. After the reduction with the Pt/TiO_2 electrode, ammonia was detected in the solution. The gas evolved was determined to be nitrogen by a separate experiment using a platinum electrode. By the irradiation on the Pt/TiO_2 electrode, the feature of the reduction current was almost unchanged. On the other hand, at anodic potentials photoinduced oxidation currents were observed for both of the solutions. In the presence of N_3^-, the photocurrent appeared at less anodic potential, indicating that N_3^- is more easily oxidized than OH^- at TiO_2 surface. This experimental result is consistent with the report for the oxidation of N_3^- on platinum electrodes.[13]

Discussion

Bard has pointed out that an illuminated platinized TiO_2 powder works as a microelectrode.[14] Consequently, the surface reactions on the photocatalyst are predicted by those of cathodic and anodic processes observed in the photoelectrochemical measurements. In the present study, the current-potential curves in Fig. 2 show that N_3^- is oxidized before the oxidation of OH^-. The oxidation potential of N_3^- on a platinum electrode is 0.78 V (*vs.* SCE).[13] The azide radical, $N_3\cdot$, formed by the oxidation of N_3^- becomes, instantly, the dimer, $(N_3)_2$, followed by the evolution of N_2.[13] Therefore, at the oxidation site on the photocatalysts the following reaction is expected to occur.

$$2N_3^- \longrightarrow 3N_2 + 2e^- \tag{1}$$

On the other hand, the reduction of N_3^- aqueous solution on solid electrodes has not been reported. However, Fig. 2 shows that N_3^- is reduced before the formation of H_2. Since the formation of adsorbed hydrogen atoms precedes the evolution of H_2, the hydrogen atoms seem to react with N_3^-. The reductive decomposition may occur in succession as indicated by the current-potential curve having no shoulder. As mentioned above, the evolution of N_2 gas was observed during the electrode reduction, then the reduction of N_3^- accompanied by the reaction with water may be expressed by Eq. 2;

$$N_3^- + 3H_2O + 2e^- \rightarrow NH_3 + N_2 + 3OH^-. \tag{2}$$

The standard potential for the electrode reduction of N_3H was reported to be 1.82 V (*vs.* NHE) in acidic solution,[15] so that of Eq. 2 can be estimated as 0.97 V at pH 8.4. At this pH, the standard potential for the reduction of water is −0.50 V. Therefore, from a thermodynamical view point, Eq. 2 is more likely to occur than the reduction of water.

The total stoichiometric equation for the photocatalytic reaction of N_3^- and water should be expressed by the combination of Eqs. 1 and 2; *viz.*,

$$3N_3^- + 3H_2O \longrightarrow NH_3 + 4N_2 + 3OH^-. \tag{3}$$

This equation is consistent with the present experimental results that the formation of ammonia involves N_2 gas evolution and that N_2 has not been detected for the undoped TiO_2 photocatlyst which did not yield ammonia. This stoichiometric equation implies that the ratio of the products N_2 : NH_3 is to be 4:1. The experimental result in Table 2 shows that the amount of ammonia formed was really about a quarter of that of N_2 in the early stage of the reaction. However, in the later stage, the amount of ammonia was smaller than that of stoichiometry. This may be attributed to the decomposition of produced ammonia into N_2 and H_2, as mentioned above.

In the helium atmosphere, N_2O was the major by-product. The formation of N_2O from N_3^- aqueous solution was studied by the method of radiolysis.[16] As a reaction intermediate, the presence of HNO, which gives $H_2N_2O_2$ followed by the formation of N_2O, has been assumed. When this assumption is adopted in the present system, the intermediate HNO may arise from N_3OH^- which is formed from $N_3\cdot$ and OH^-. The formation of N_3OH^- is probable,[17] because N_3^- is known to behave in chemical properties like halogen ions.[15] Since the yield of N_2O was very low, it is also probable that the oxygen of N_2O may originate from the possible absorbed oxygen on the catalysts.

In the oxygen atmopsphere, the NH_3 yield was very low while N_2O was formed largely. This indicates that at the reduction site the reactions of Eqs. 4 and 5 may happen instead of Eq. 2.

$$O_2 + H^+ + e^- \longrightarrow HO_2\cdot \tag{4}$$

$$2HO_2\cdot \longrightarrow H_2O_2 + O_2 \tag{5}$$

The hydrogen peroxide may produce N_2O by the following exothermic reactions[16];

$$H_2O_2 + N_3^- \longrightarrow HNO + N_2 + OH^- \tag{6}$$

$$2HNO \longrightarrow N_2O + H_2O. \tag{7}$$

Since N_2O is considered to be formed through some intermediates, there must be a delay for the formation of N_2O. Fig. 1 shows that the formation of N_2O delays from that of N_2. This reaction mechanism for N_2O formation predicts that the product ratio of N_2:N_2O is 8:1. The observed ratio was, however, nearly equal to 5:1. Then, another process such as the reaction of $N_3\cdot$ radical with O_2 at the oxidation site may be taken into account.

Since the standard free energy change for Eq. 3 is negative, the photocatalytic ammonia production *via* azide ion is not suitable for storage of solar energy. Further investigation concerning the mechanism of the formation of ammonia may provide a clue to improving the yield of ammonia synthesis from N_2 and water.

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