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Photocatalytic Reduction of NO_3^- to Form NH_3 over $Pt-TiO_2$

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Photocatalytic reduction of NO_3^- to form NH_3 and the simultaneous evolution of O_2 were observed over $Pt-TiO_2$ in aqueous nitric acid and sodium nitrate solutions.

Photocatalytic decomposition of water into H_2 and O_2 ($\Delta G^o{}_{298}$ = 237 kJ) has been accomplished in several systems.$^{1-6)}$ In the case of $Pt-TiO_2$, however, only a small amount of H_2 evolves from distilled water and aqueous alkaline solutions and no O_2 evolution takes place.$^{7-9)}$ Here, a new photoinduced energy conversion reaction is reported on $Pt-TiO_2$ powder, i.e.

$$2HNO_{3(aq)} + H_2O_{(l)} \longrightarrow NH_4NO_{3(aq)} + 2O_{2(g)} \qquad \Delta G^o{}_{298} = 269\ \text{kJ} \qquad (1)$$

TiO_2 (BET surface area; 23.2 m^2/g, anatase) was prepared by pyrolysis of $Ti(SO_4)_2$ (Kanto Chemical Co., INC.) at 1000 K for 2 h in air. Pt, Rh, and Pd(0.3 wt%) were supported on TiO_2 from H_2PtCl_6, $RhCl_3$, and $PdCl_2$ respectively by photodeposition. The photocatalytic reactions were carried out in a closed gas circulation system with a vacuum line. The catalyst (0.2 g) was suspended in solution (250 - 300 ml) by magnetically stirring in a Pyrex reaction cell with a flat window, and it was irradiated by an Xe short arc lamp (USHIO, UXL 500D-O, 500 W). The amounts of evolved H_2, O_2, and N_2 were determined by gas chromatography (Ar carrier, molecular sieve-5A column). NH_3, which existed in a supernatant liquid of a reactant, was analyzed by absorptiometry (BECKMAN, ACTA C-III) at 430 nm by means of Nessler's reagent (Kanto Chemical Co., INC.), and NO_2^- at 520 nm using Griess-Romijin Nitrite reagent (Kanto Chemical Co., INC.). On the reaction of aqueous HNO_3 and CH_3OH mixed solution, NH_3 was determined as NH_4NO_3 obtained by drying up the supernatant solution at ca. 330 K in a vacuum line.

Time courses of NH_3 and O_2 formations from aqueous nitric acid and sodium nitrate solutions with the Pt(0.3 wt%)-TiO_2 photocatalyst are shown in Fig. 1. The amounts of produced NH_3 and O_2 increased proportionally to the irradiation time. The quantum yield for NH_3 formation was ca. 2% at 330 nm in 1 M HNO_3 (1 M = 1 $mol\cdot dm^{-3}$). Negligible amounts of H_2 and N_2 were observed. The amount of evolved O_2 should be twice of that of NH_3 according to the Eq. 1. However, it was less than the stoichiometric amount as shown in Fig. 1. Similar phenomena were reported in the cases of photodecomposition of water on Pt-TiO_2, and they were attributed to the peroxide formation.7-9)

When aqueous nitric acid solution without any catalysts was irradiated, only a little amount of NO_2^- was detected as shown in Table 1. Furthermore, over the TiO_2 photocatalyst, a little amount of NO_2^- and a trace of NH_3 were observed in aqueous nitric acid solution. The amounts of NO_2^- were similar in both cases. It seems that NO_2^- is formed under the UV irradiation by the photochemical reaction of NO_3^- in the solution. The reduction of NO_3^- to NO_2^- over ZnO photocatalyst was also reported previously.10) On the contrary, NH_3 and O_2 evolved over the Pt(0.3 wt%)-TiO_2 photocatalyst and the rate of NH_3 formation increased with the increase of the concentration of HNO_3. The reaction also occured over TiO_2 loaded with other noble metals such as Rh and Pd. A small amount of H_2 (0.05 μmol/h) was evolved over the Pd(0.3 wt%)-TiO_2 photocatalyst. When methanol as a reducing agent was added to HNO_3 (1 M) / Pt(0.3 wt%)-TiO_2, the rate of NH_3 formation increased by more than 5 times, and the H_2 evolution was also observed as shown in

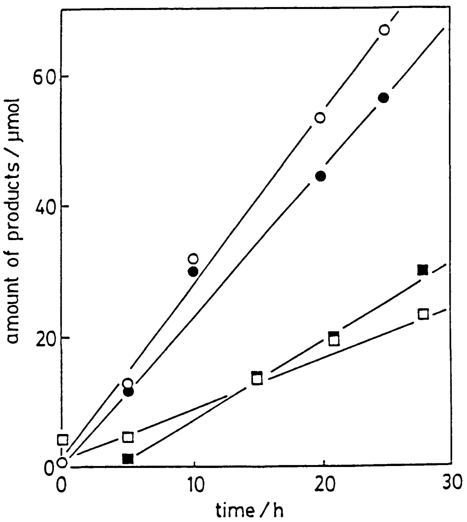

Fig. 1. NH_3 and O_2 formations from aqueous HNO_3 and $NaNO_3$ solutions over Pt(0.3 wt%)-TiO_2 photocatalyst.

○; NH_3, ●; O_2 in 1 M HNO_3

□; NH_3, ■; O_2 in 1 M $NaNO_3$

Catalyst; 0.2 g, Light source, Xe lamp (500 W), Solution, 300 ml (initial).

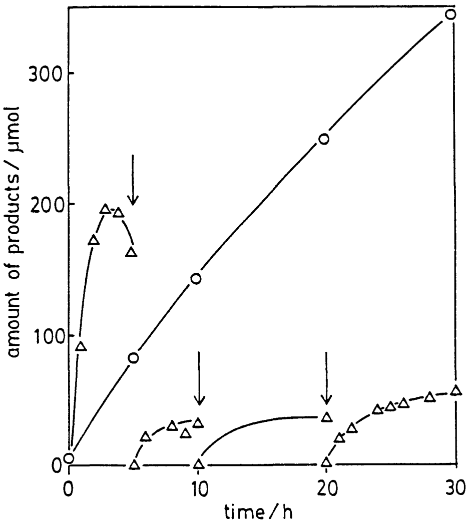

Fig. 2. NH_3 and H_2 formations from aqueous HNO_3 and MeOH mixed solution over Pt(0.3 wt%)-TiO_2 photocatalyst.

○; NH_3, △; H_2

Catalyst; 0.2 g, Solution;

1 M HNO_3 (200 ml)+MeOH (50 ml), Arrows indicate that the gas phase was evacuaued.

Table 1. Photocatalytic reactions of aqueous nitric acid solutions over TiO_2 and TiO_2 loaded with some noble metals[a)]

Photocatalysts	Concentration of HNO_3/M	NH_3 μmol·h^{-1}	O_2 μmol·h^{-1}	NO_2^- μmol·h^{-1}
none	0.1	0	0	0.3
TiO_2	0.1	trace	0	0.2
$Pt\text{-}TiO_2$[b)]	0.1	0	0	-
$Pt\text{-}TiO_2$[c)]	0.1	19	0	-
$Pt\text{-}TiO_2$	0.01	0.4	0.8	-
$Pt\text{-}TiO_2$	0.1	2.1	1.6	0
$Pt\text{-}TiO_2$	1	2.4	2.2	0
$Pt\text{-}TiO_2$[d)]	1	15.2	0	-
$Rh\text{-}TiO_2$	0.1	0.7	0.4	0
$Pd\text{-}TiO_2$	0.1	0.2	0.1	0

a) Catalyst: 0.2 g, light source: Xe lamp (500 W). b) Dark reaction. c) H_2 (ca. 7 kPa) was introduced into the gas phase and the reaction was carried out in dark. d) MeOH was added. (1 M HNO_3 : MeOH = 4 : 1 v/v)

Fig. 2. Interestingly, the rate of H_2 evolution decreased with the reaction time, which was not the case in aqueous methanol solution without HNO_3. When the gas phase was evacuated a small amount of H_2 was accumulated again. It seems that the evolved H_2 was exhausted by the reduction of NO_3^-. Actually, the NH_3 formation proceeded from aqueous HNO_3 solution (0.1 M) and gaseous H_2 over Pt(1 wt%)-TiO_2 in dark. This means that the reduction of NO_3^- into NH_3 by hydrogen occurs on Pt without any assistance of photon. It is inferred that NO_3^- is reduced by the adsorbed hydrogen on Pt produced by the photoreduction of water. The similar phenomenon that photocatalytically evolved H_2 and/or H is concerned with a successive reaction was reported on N-alkylation of amine over the $Pt\text{-}TiO_2$ photocatalyst.[11,12)]

Thus, the follwing reaction schemes are proposed for the reduction of NO_3^- on $Pt\text{-}TiO_2$ under the irradiation condition;

$$NO_3^- + 9H^+ + 8e^- \longrightarrow NH_3 + 3H_2O \quad \text{on Pt} \qquad (2)$$

$$4OH^- + 4h^+ \longrightarrow O_2 + 2H_2O \qquad \text{on } TiO_2 \qquad (3)$$

Photochemically produced NO_2^- also seems to be reduced on Pt in a manner similar to that of Eq. 2. Recently Halmann et al. reported the reduction of nitrite ion to ammonia in the presence of the Na_2S as a reducing agent over various semiconductors without noble metals in aqueous KOH solution.$^{13)}$ However, Pt supported on TiO_2 was indispensable for the photoreduction of NO_3^- and/or NO_2^- to NH_3 in our system which contained no reducing agent in acidic or neutral solution. It is noteworthy that NH_3 was predominantly produced as a reduced product over the Pt-TiO_2 photocatalyst in spite of the low overpotential for the H_2 evolution on Pt.

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