

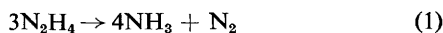
Photocatalytic Hydrogen Evolution from an Aqueous Hydrazine Solution

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Hydrogen is evolved easily from an acidic aqueous solution of hydrazine on irradiation using an Hg-lamp in the presence of Pt-TiO₂ around room temperature.

In recent years, photocatalytic hydrogen evolution from semiconductor-photocatalyst-water-organic compound systems has been widely investigated.¹ However, few systems containing only inorganic compounds have been reported to produce hydrazine photocatalytically.² In an acidic aqueous solution hydrazine can react with protons producing hydrogen thermodynamically. However, the catalytic decomposition of the same solution over platinum black proceeds according to equation (1), and no hydrogen is evolved.³



Hydrogen is evolved easily from an aqueous solution of hydrazine dihydrochloride on irradiation (300–420 nm) in the presence of Pt-TiO₂ (anatase or rutile) around room temperature. Pt-anatase (1 wt %) and Pt-rutile (1 wt %) were prepared by an impregnation-calcination (H₂, 200 °C, 4 h) method from anatase (Fuji Titan, 1.5 μm), rutile (Fuji Titan, 1.4 μm), and H₂PtCl₆·6H₂O. Anatase was treated with hydrogen (200 °C, 4 h) before use. The reaction was performed in a Pyrex Schlenk tube (108 ml) with a rectangular parallelepiped lower part (35 × 35 × height 60 mm) and a septum.

The reaction mixture, consisting of photocatalyst (Pt-anatase, Pt-rutile, or anatase, 10 mg), hydrazine dihydrochloride (3 mmol), and deionized water (30 ml) in an argon atmosphere, was stirred and irradiated using a 500 W ultra-high-pressure Hg-lamp (Ushio), at ca. 40 °C in the stationary

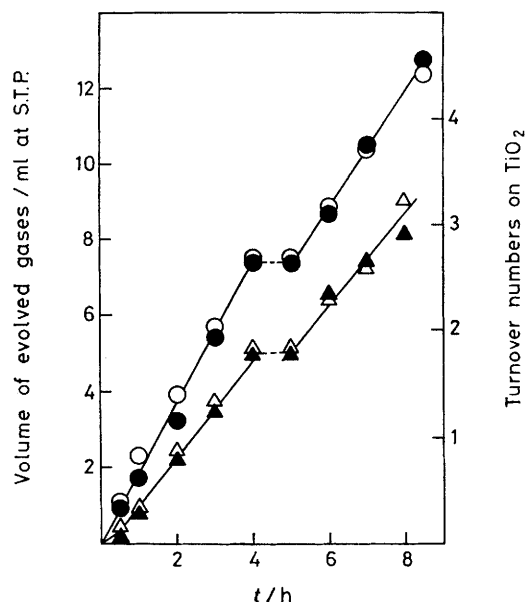


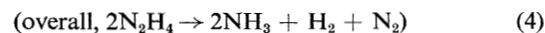
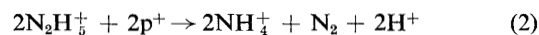
Figure 1. Evolution of H₂ and N₂ from an aqueous solution of hydrazine dihydrochloride in the presence of Pt-TiO₂ on irradiation with a 500 W Hg-lamp: Pt-anatase, ○ H₂, ● N₂; Pt-rutile, △ H₂, ▲ N₂; - - - cut-off filter.

state under irradiation. The concentrations of hydrogen and nitrogen in the reaction vessel were measured by gas chromatography.

The turnover numbers of hydrogen and nitrogen on TiO_2 (moles of H_2 and N_2 evolved/moles of TiO_2) indicate that the reaction proceeds catalytically. The reaction stopped when the mixture was irradiated through a cut-off filter (Toshiba Glass, L-42, transparent at $\lambda > 420$ nm). Since TiO_2 absorbs light whose wavelength is shorter than 390 nm, it is assumed that the reaction occurred *via* the electrons in the conduction band and the holes in the valence band generated by photo-excitation of the TiO_2 . No hydrogen and little nitrogen evolved when anatase was used in place of the Pt-anatase. This fact indicates that the presence of platinum on anatase markedly promotes the reaction. Neither hydrogen nor nitrogen were evolved in the presence of the Pt-anatase or Pt-rutile in the dark (50 °C).

As the amount of hydrogen evolved was almost equal to that of nitrogen (Figure 1), it was assumed that ammonia was also formed. The amount of ammonia formed at the end of the reaction over Pt-anatase, shown in Figure 1, was determined to be 0.94 mmol. Therefore, the reaction was assumed to proceed according to the reaction scheme given by equations (2), (3), and (4).

It is known that the methanol-water (1:1 v/v) system exhibits a fairly high quantum efficiency.⁴ The amount of hydrogen evolved from the Pt-anatase (10 mg)-methanol (3 mmol)-water (30 ml) system on irradiation for 5 h was



6.7 ml (S.T.P.) under the same conditions as those used for the present Pt-anatase- $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$ -water system. The hydrogen evolution rate of the former system is rather lower than that obtained for the latter. Therefore, it is expected that the present $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$ -water system will show a similarly high quantum efficiency with concentrated solutions.

The activities of the photocatalysts depended on the conditions used for the reduction of the supported H_2PtCl_6 by hydrogen. It has been found that Pt- SrTiO_3 also photocatalyses the evolution of hydrogen from an acidic aqueous solution of hydrazine.

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