Application of Pt/TiO_2 photocatalyst to the treatment of aqueous ammonia-borane for H_2 production and water purification

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Abstract: Complete H_2 release from ammonia-borane (NH_3BH_3, AB) in water was achieved by using a platinum-loaded TiO_2 (Pt/TiO_2) *via* two consecutive reaction steps, *i.e.*, hydrolysis of AB and photocatalytic decomposition of thus formed NH_3 in water, under inert conditions at 298 K. Formation of H_2 through the hydrolysis of AB easily occurred on Pt-loaded catalysts, whereas the decomposition of thus formed NH_3 in water was not so easy. Photocatalytic reaction is one way for treatment of residual solution in hydrolysis of AB in water for H_2 production and water purification.

Keywords: TiO_2 photocatalyst, Hydrogen production, Ammonia-borane

1. Introduction

Recently, various types of photocatalysts are designed for solving the environmental concerns and energy related issues. Due to their unique properties, titania (TiO_2)-based photocatalysts have attracted considerable interests. These photocatalytic materials can be applicable for purification of air/water polluted with dilute organic compounds, solar energy conversion and production of clean energy resources.[1-3] TiO_2-based thin films are also well-known as multifunctional materials having fascinating properties, *i.e.*, photoinduced superhydrophilicity, anti-fogging and self-cleaning effect.[4,5]

On the other hand, H_2 storage materials and production systems have also attracted many attentions. Among the chemical H_2 storage materials, ammonia-borane (NH_3BH_3, AB) having the multiple advantages (e.g. the high hydrogen content, the high stability and the solubility in water) is a promising solid H_2 carrier. To release of H_2 gas from AB, thermal decomposition above 373 K and catalytic hydrolysis under moderate conditions are well investigated. The amount of H_2 generated is limited to a H_2/AB ratio up to 3 in conventional systems. There are also difficulties in the recycling and disposal of residual solution including ammonia after release of H_2 gas in catalytic hydrolysis. In the present study, complete H_2 release from AB in water was investigated by using a Pt/TiO_2 at 298 K under inert conditions, aimed at the treatment of the residual solution in hydrolysis of AB in water and water purification.

2. Experimental

The Pt-loaded TiO_2 (Pt/TiO_2) was prepared by a photo-deposition method. As a reference, Pt-loaded SiO_2 (Pt/SiO_2) was also prepared by an impregnation method. Prior to the characterization and reaction test, Pt/SiO_2 was treated with H_2 gas at 473 K. The Pt content of samples was adjusted to 0.2 wt%. The decomposition of AB was carried out in a suspension of each sample under inert conditions at 298 K. The fixed amount of sample (10 mg) was placed into a Pyrex reaction vessel under Ar atmosphere.[3] After bubbling of Ar gas, an aqueous AB solution (2 mmol/L, 5 mL) was charged into a Pyrex glass reaction vessel. The amount of H_2 and N_2 formed in the gas phase was measured by using a gas chromatograph. UV light irradiation was carried out using a 100 W high-pressure Hg lamp through a water filter.

3. Results and discussion

Figure 1(a-c) shows the time courses of H_2 formation in the decomposition of AB on TiO_2, Pt/SiO_2 and Pt/TiO_2 at 298 K under dark and UV light irradiation. In the dark conditions, no H_2 formation was observed on TiO_2. Catalytic hydrolysis of AB occurred on Pt/SiO_2 and Pt/TiO_2. The mainstream for hydrolysis of AB is noble metal-, non-noble metal- and alloy-loaded catalysts designed by using various catalysis supports. The formation of H_2 has ceased within 0.5 h under present conditions. The amount of H_2 formed showed good correspondences with the estimated value and the initial amount of AB in water, which was also almost same even after keeping for 2 h in the dark. The molar ratio (H_2/AB) was achieved about 3 on both Pt/SiO_2 and Pt/TiO_2. The H_2 formation was observed on Pt/TiO_2 in proportion to the reaction time, whereas the amount of H_2 was almost same in the case of Pt/SiO_2 under UV light irradiation (Fig. 1(b,c)). No catalytic activity of Pt/SiO_2 was observed in the release of H_2 from the residual solution in hydrolysis of AB. The formation of H_2 on Pt/TiO_2 was completed after UV light irradiation for 4 h. The amount of H_2 formed was equivalent to the 1.5 times of NH_4^+ exist in the residual solution in hydrolysis of AB. UV light irradiation was scarcely affected to hydrolysis of AB, and thus the total amount of H_2 formed was achieved to almost same value without the separation of two reactions (Fig. 1(d)). The small amount of H_2 formation was also observed in TiO_2 under UV light irradiation (Fig. 1(e)). Under UV light irradiation, stoichiometric production of H_2 and N_2 from NH_3 decomposition in the residual solution of hydrolysis of AB was successfully achieved by using a photocatalytic property of Pt/TiO_2 at 298 K. As a consequence, the molar ratio (H_2/AB) was finally achieved to be about 4.5 (Fig. 2).[3]

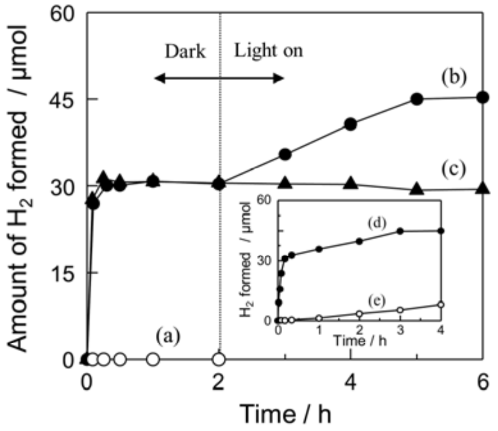

Figure 1. Time courses of H_2 formation in the decomposition of NH_3BH_3 in water on (a) TiO_2 (open circles), (b) Pt/TiO_2 and (c) Pt/SiO_2 at 298 K. Inset: time courses of H_2 formation on (d) Pt/TiO_2 and (e) TiO_2 under UV light irradiation.

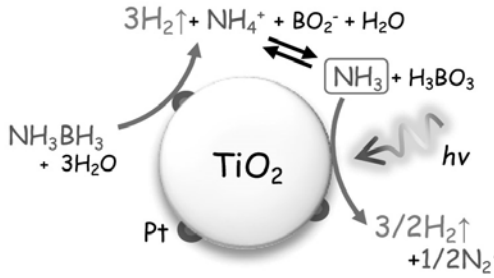

Figure 2. Schematic image in the complete hydrogen release from an aqueous solution of ammonia-borane on Pt/TiO_2 photocatalyst.

The photocatalytic performance was also dramatically affected by the pH of solution, depending on the kinds of reagents. The amount of H_2 formed decreased with decrease in the pH of a solution. The large increase in the number of NH_4^+ in water by the protonation of NH_3 results in the lower photocatalytic performance. The surface of TiO_2 also has a positive charge at low pH region, which is other reason for changing the photocatalytic performance. The residual solution in hydrolysis of AB has a relatively high pH (ca. 9.2) and is thus possible to release H_2 by photocatalytic reaction.

4. Conclusions

Pt/TiO_2 enables the complete H_2 release from an aqueous AB solution *via* two consecutive reactions under inert conditions at 298 K. Stoichiometric production of H_2 and N_2 from NH_3 in the residual solution of hydrolysis of AB was successfully achieved by using a photocatalytic property of Pt/TiO_2 under UV light irradiation. The utilization of photocatalytic reaction system is one way for the increases in the hydrogen storage density and use efficiency, as well as the treatment of the residual solution in the hydrolysis of AB for H_2 production and water purification.

References

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