

ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Journal Name

COMMUNICATION

Complete Hydrogen Release from Aqueous Ammonia-borane over Platinum-Loaded Titanium Dioxide Photocatalyst †

Received 00th January 20xx,
Accepted 00th January 20xx

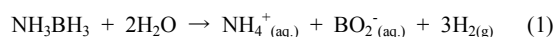
Takashi Kamegawa^{*a} and Takayuki Nakaue^{a,b}

DOI: 10.1039/x0xx00000x

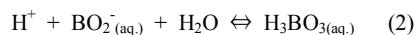
www.rsc.org/

Complete H₂ release from ammonia-borane (NH₃BH₃, AB) in water was achieved by using a platinum-loaded TiO₂ (Pt/TiO₂) via two consecutive reaction steps, i.e., hydrolysis of AB and photocatalytic decomposition of thus formed NH₃ in water, under inert conditions at 298 K.

Recently, H₂ storage materials and production systems have attracted many attentions in relation to the fuel cell systems.^{1,2} Among the chemical H₂ storage materials, ammonia-borane (NH₃BH₃, AB) having the multiple advantages (e.g. the high hydrogen content (19.6 wt%), the high stability as well as the solubility in water) is a promising solid H₂ carrier.³ To release of H₂ gas from AB, thermal decomposition above 373 K and catalytic hydrolysis under moderate conditions are well investigated.^{1d,3,4} The generation of H₂ gas through the hydrolysis of AB can be expressed as eq. (1) in the presence of a suitable catalyst at room temperature.



The amount of H₂ generated is limited to a H₂/NH₃BH₃ ratio up to 3 in catalytic hydrolysis. In water, equilibrium process of BO₂⁻ and H₃BO₃ (eq. (2)) as well as NH₄⁺ and NH₃ (eq. (3)) undergoes a rapid change between each other.⁵



The catalytic hydrolysis of AB under moderate conditions is intensively studied by many researchers for future applications in energy related issues, whereas there are difficulties in the recycling and disposal after release of H₂ gas (eq. (1)).⁶

On the other hand, TiO₂-based photocatalytic materials

have attracted many attentions for solving environmental and energy issues.^{7,8} These materials are able to promote the synthesis of chemicals and production of clean energies.⁹ The complete decomposition of diluted organic molecules such as dyes and endocrine disruptors in water occurs on these materials by using various light sources.^{9,10} Photocatalytic transformation of nitrogen-containing chemicals such as NH₃ and related compounds in water has also been investigated for treatment of waste water.^{11,12} In aerobic conditions, N₂, N₂O, NO₂⁻ and NO₃⁻ are predominantly formed by the decomposition of NH₃ in water.^{11,12} Meanwhile, the NH₃ in water is photocatalytically decomposed to N₂ and H₂ under inert conditions, which has been investigated as a more environmentally benign process.¹² In the present work, complete H₂ release from AB in water was investigated by using a platinum-loaded TiO₂ at 298 K under inert conditions, aimed at the treatment of the residual solution in hydrolysis of AB in water for H₂ production and water purification.

The Pt-loaded samples with different crystalline structure of TiO₂ were prepared by a photo-deposition method and denoted as Pt/TiO₂(R), Pt/TiO₂(A/R) and Pt/TiO₂(A). The Pt-loaded SiO₂ (Pt/SiO₂) was also prepared by an impregnation method. The Pt content of samples was adjusted to 0.2 wt%.

The specific surface area of samples and information about the deposited Pt was summarized in Table 1. Each commercially available oxide used as a Pt support was maintained its original surface area. Nano-sized Pt particles were formed on SiO₂ and each TiO₂, whereas there were some variations depending on the types of Pt supports. The average size of Pt was below 3.0 nm, indicating the formation of highly dispersed Pt particles.

Fig. 1(a-c) shows the time courses of H₂ formation in the decomposition of AB on TiO₂(A), Pt/SiO₂ and Pt/TiO₂(A) at 298 K under dark and UV light irradiation. In the dark conditions, no H₂ formation was observed on TiO₂(A). Catalytic hydrolysis of AB occurred on Pt/SiO₂ and Pt/TiO₂(A). The mainstream for hydrolysis of AB is noble metal-, non-noble metal- and alloy-loaded catalysts designed by using various catalysis supports.^{1d,3} The formation of H₂ has ceased within 0.5 h under

^a Nanoscience and Nanotechnology Research Center, Osaka Prefecture University, 1-2 Gakuencho, Nakaku, Sakai, Osaka 599-8570, Japan.

^b Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuencho, Nakaku, Sakai, Osaka 599-8531, Japan.

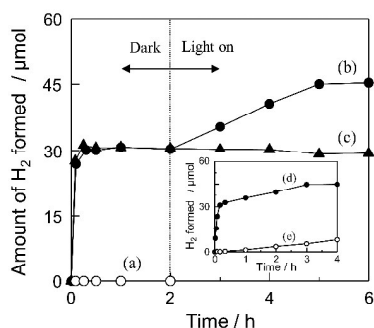
E-mail: t-kamegawa@21c.osakafu-u.ac.jp; Fax: +81-72-254-9709; Tel: +81-72-254-9709

† Electronic Supplementary Information (ESI) available: Material and Experimental procedure See DOI: 10.1039/x0xx00000x

Table 1. The specific surface area, as well as the dispersion, surface area and particle sizes of Pt metals.

Sample	S_{BET}^a / $\text{m}^2\cdot\text{g}^{-1}$	Pt dispersion ^b / %	Pt surface area ^b / $\text{m}^2\cdot\text{g}^{-1}$	Pt particle size ^b / nm
Pt/TiO ₂ (A)	279	57	139	2.0
Pt/TiO ₂ (A/R)	51	43	105	2.7
Pt/TiO ₂ (R)	49	39	94	3.0
Pt/SiO ₂ (A)	302	81	197	1.4

^a Specific surface area calculated by BET method. ^b Determined by pulsed CO adsorption.

**Fig. 1** Time courses of H₂ formation in the decomposition of AB in water on (a) TiO₂(A) (open circles), (b) Pt/TiO₂(A) and (c) Pt/SiO₂ at 298 K. Inset: time courses of H₂ formation on (d) Pt/TiO₂(A) and (e) TiO₂(A) under UV light irradiation.

present conditions. The amount of H₂ formed showed good correspondences with the estimated value from eq. (1) 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 (H₂/AB) was achieved about 3. The pH of this solution was ca. 9.2, which was similar to that of aqueous NH₃ solution (pH 9.8) and of the properly mixed solution of NH₃ and H₃BO₃ (pH 9.4).

Under UV light irradiation, the H₂ formation was observed on Pt/TiO₂(A) in proportion to the reaction time, whereas the amount of H₂ was almost same in the case of Pt/SiO₂ (Fig. 1(b,c)). No catalytic activity of Pt/SiO₂ was observed in the release of H₂ from the residual solution in hydrolysis of AB. The formation of H₂ on Pt/TiO₂(A) was completed after UV light irradiation for 4 h. The amount of H₂ formed was equivalent to the 1.5 times of NH₄⁺ (eq. (1)) 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 H₂ formed was achieved to almost same value without the separation of two reactions (Fig. 1(d)). The small amount of H₂ formation was also observed in TiO₂(A) under UV light irradiation (Fig. 1(e)).

As shown in eq. (3), NH₄⁺ and NH₃ exist in equilibrium. The photocatalytic decomposition of aqueous NH₃ to H₂ and N₂ has also been reported under inert conditions.^{11,12} Aqueous NH₃ is mainly decomposed to H₂ and N₂ in a nearly stoichiometric molar ratio (eq. (4)).

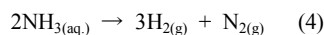
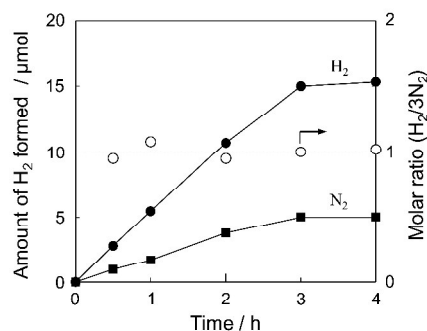


Fig. 2 shows the time courses of gases evolved from the residual solution in hydrolysis of AB on Pt/TiO₂(A) under UV light irradiation. The increases in the amount of H₂ and N₂ formed was directly proportion to irradiation time. The molar

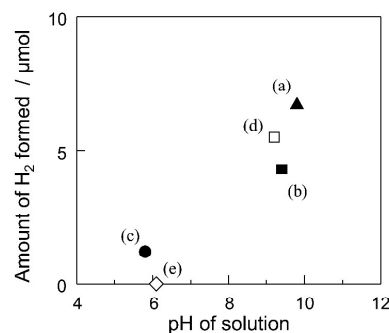
**Fig. 2** Time courses of gases (H₂ and N₂) evolved, as well as the molar ratio of them in the treatment of the residual solution in hydrolysis of AB on Pt/TiO₂(A) at 298 K under UV light irradiation.

ratio calculated by eq. (5) was determined to be ca. 1.0 at a certain time interval.

$$\text{Molar ratio} = (\text{Amount of H}_2 \text{ formed}) / 3(\text{Amount of N}_2 \text{ formed}) \quad (5)$$

These results clearly indicated that the H₂ and N₂ were stoichiometrically produced from the residual solution in hydrolysis of AB through the photocatalytic decomposition of NH₃ in water. The pH was gradually decreased during the formation of H₂ and N₂. These results clearly indicated that the complete H₂ release was successfully achieved *via* two consecutive reaction steps according to eq. (1)-(4).

Fig. 3 shows the pH of solution and amount of H₂ formed in the photocatalytic decomposition of NH₃ in water. The photocatalytic performance was dramatically affected by the pH of solution, depending on the kinds of reagents (Fig. 3(a,c)). The amount of H₂ formed decreased with decrease in the pH of a solution. The large increase in the number of NH₄⁺ in water by the protonation of NH₃ results in the lower photocatalytic performance. The surface of TiO₂ also has a positive charge at low pH region, which is other reason for changing the photocatalytic performance.^{12b,c} In the treatment of the residual solution in hydrolysis of AB, the amount of H₂ formed become slightly small as compared to that of pure NH₃ solution due to the co-existence of H₃BO₃ (Fig. 3(a,d)). The properly mixed solution of NH₃ and H₃BO₃ also showed slightly small amount of H₂ formed (Fig. 3(b)). This result corresponds to the changes in the pH of solution. The residual solution in hydrolysis of AB has a relatively high pH (ca. 9.2) and is thus

**Fig. 3** Relationship between pH of solution ((a) aqueous NH₃, (b) mixture of aqueous NH₃ and H₃BO₃, (c) aqueous (NH₄)₂SO₄, (d) residual solution in hydrolysis of AB, (e) aqueous H₃BO₃) and the amount of H₂ formed (reaction time: 1 h).

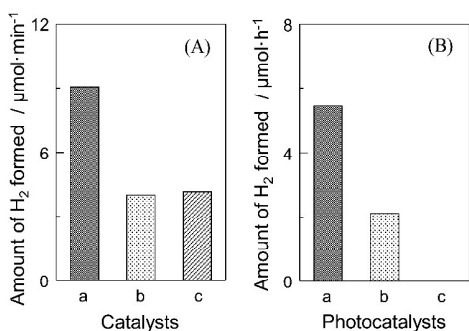


Fig. 4 Amount of H₂ formed in the hydrolysis of AB (A) and photocatalytic reaction for treatment of the residual solution in hydrolysis of AB under UV light irradiation (B) on each sample ((a) Pt/TiO₂(A), (b) Pt/TiO₂(A/R) and (c) Pt/TiO₂(R)).

possible to release H₂ by photocatalytic reaction. No formation of H₂ was also observed in the pure H₃BO₃ solution (Fig. 3(e)).

The effect of types of TiO₂ was investigated in these reaction systems. In the hydrolysis of AB at 298 K, formation of H₂ was clearly observed in each sample (Fig. 4(A)). No induction period was observed, and H₂ was stoichiometrically formed during the reaction period in all samples. Pt/TiO₂(A/R) and Pt/TiO₂(R) had almost similar surface area of TiO₂ and Pt particle size, and showed comparable catalytic performance. The higher catalytic performance of Pt/TiO₂(A) might be attributed to a large surface area of TiO₂ and the small size of deposited Pt particle on TiO₂. Fig. 4(B) shows the amount of H₂ formed in the treatment of the residual solution in hydrolysis of AB at 298 K under UV light irradiation. Among the evaluated samples, Pt/TiO₂(A), having a relatively high surface area, exhibited a good photocatalytic performance. The crystalline structure, crystallinity and other properties of TiO₂ strongly affects the photocatalytic performance in reactions. In previous studies related to the photocatalytic decomposition of NH₃ in water, reaction rate is also mainly influenced by the surface area of TiO₂.^{12b,c} Adsorption of NH₃ on TiO₂ surface might be important for more efficient decomposition at relatively high pH region. On the other hand, negligible photocatalytic activity of Pt/TiO₂(R) was observed in this reaction system. The rutile phase of TiO₂ is insufficient for formation of H₂ due to the low level of conduction band position. It was also reported that the rutile phase of TiO₂ generally shows lower photocatalytic activity than anatase phase of TiO₂.¹³ As a consequence, a good catalytic and photocatalytic performance are realized on Pt/TiO₂(A) having a relatively large surface area and small Pt particles.

In summary, Pt/TiO₂(A) enables the complete H₂ release from an aqueous AB solution via two consecutive reactions under inert conditions at 298 K. Formation of H₂ through the hydrolysis of AB easily occurred on Pt-loaded catalysts, whereas the decomposition of thus formed NH₃ in water was not so easy. Stoichiometric production of H₂ and N₂ from NH₃ in the residual solution of hydrolysis of AB was successfully achieved by using a photocatalytic property of Pt/TiO₂(A) at 298 K under UV light irradiation. Photocatalytic reaction is one way for treatment of residual solution in hydrolysis of AB in water for H₂ production and water purification.

This study was partially supported by a Grant-in-Aid for Scientific Research (KAKENHI from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan (No. 26420786).

Notes and references

- (a) L. Schlapbach, A. Züttel, *Nature*, 2001, **414**, 353; (b) A. W. C. van den Berg, C. O. Areán, *Chem. Commun.*, 2008, 668; (c) J. Yang, A. Sudik, C. Wolverton, D. J. Siegel, *Chem. Soc. Rev.*, 2010, **39**, 656; (d) M. Yadav, Q. Xu, *Energy Environ. Sci.*, 2012, **5**, 9698.
- (a) B. C. H. Steele, A. Heinzl, *Nature*, 2001, **414**, 345; (b) P. Costamagna, S. Srinivasan, *J. Power Sources*, 2001, **102**, 242.
- (a) A. Staubitz, A. P. M. Robertson, I. Manners, *Chem. Rev.*, 2010, **110**, 4079; (b) M. Chandra, Q. Xu, *J. Power Sources*, 2006, **156**, 190; (c) T. J. Clark, G. R. Whittell, I. Manners, *Inorg. Chem.*, 2007, **46**, 7522; (d) F. Durap, M. Zahmakiran, S. Özkar, *Appl. Catal., A: Gen.*, 2009, **369**, 53.
- (a) G. Wolf, J. Baumann, F. Baitalow, F. P. Hoffmann, *Thermochim. Acta*, 2000, **343**, 19; (b) A. Gutowska, L. Li, Y. Shin, C. M. Wang, X. S. Li, J. C. Linehan, R. S. Smith, B. D. Kay, B. Schmid, W. Shaw, M. Gutowski, T. Autrey, *Angew. Chem. Int. Ed.*, 2005, **44**, 3578.
- M. Chandra, Q. Xu, *J. Power Sources*, 2006, **159**, 855.
- (a) S. Hausdorf, F. Baitalow, G. Wolf, F. O. R. L. Mertens, *Int. J. Hydrogen Energy*, 2008, **33**, 608; (b) B. L. Davis, D. A. Dixon, E. B. Garner, J. C. Gordon, M. H. Matus, B. Scott, F. H. Stephens, *Angew. Chem. Int. Ed.*, 2009, **48**, 6812; (c) A. D. Sutton, A. K. Burrell, D. A. Dixon, E. B. Garner III, J. C. Gordon, T. Nakagawa, K. C. Ott, J. P. Robinson, M. Vasiliu, *Science*, 2011, **331**, 1426.
- (a) A. Fujishima, T. N. Rao, D. A. Tryk, *J. Photochem. Photobiol. C: Photochem. Rev.*, 2000, **1**, 1; (b) X. Chen, S. S. Mao, *Chem. Rev.*, 2007, **107**, 2891; (c) X. Qian, K. Fuku, Y. Kuwahara, T. Kamegawa, K. Mori, H. Yamashita, *ChemSusChem*, 2014, **7**, 1528.
- (a) R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi, T. Watanabe, *Nature*, 1997, **388**, 431; (b) T. Kamegawa, Y. Shimizu, H. Yamashita, *Adv. Mater.*, 2012, **24**, 3697.
- (a) F. Amano, O. O. Prieto-Mahaney, Y. Terada, T. Yasumoto, T. Shibayama, B. Ohtani, *Chem. Mater.*, 2009, **21**, 2601; (b) H. Kominami, S. Yamamoto, K. Imamura, A. Tanaka, K. Hashimoto, *Chem. Commun.*, 2014, **50**, 4558; (c) T. Kamegawa, S. Matsuura, H. Seto, H. Yamashita, *Angew. Chem. Int. Ed.*, 2013, **52**, 916.
- (a) K. Inumaru, T. Kasahara, M. Yasui, S. Yamanaka, *Chem. Commun.*, 2005, 2131; (b) T. Kamegawa, D. Yamahana, H. Yamashita, *J. Phys. Chem. C*, 2010, **114**, 15049; (c) T. Kamegawa, Y. Ishiguro, H. Seto, H. Yamashita, *J. Mater. Chem. A*, 2015, **3**, 2323.
- (a) J. Nemoto, N. Gokan, H. Ueno, M. Kaneko, *J. Photochem. Photobiol. A: Chem.*, 2007, **185**, 295; (b) J. Lee, H. Park, W. Choi, *Environ. Sci. Technol.*, 2002, **36**, 5462; (c) I. Mikami, S. Aoki, Y. Miura, *Chem. Lett.*, 2010, **39**, 704; (d) H. Kominami, K. Kitsui, Y. Ishiyama, K. Hashimoto, *RSC Adv.*, 2014, **4**, 51576.
- (a) K. Fuku, T. Kamegawa, K. Mori, H. Yamashita, *Chem.-Asian J.*, 2012, **7**, 1366; (b) H. Yuzawa, T. Mori, H. Itoh, H. Yoshida, *J. Phys. Chem. C*, 2012, **116**, 4126; (c) H. Kominami, H. Nishimura, Y. Ohta, Y. Arakawa, T. Inaba, *Appl. Catal. B: Environ.*, 2012, **111-112**, 297; (d) K. Obata, K. Kishishita, A. Okemoto, K. Taniya, Y. Ichihashi, S. Nishiyama, *Appl. Catal. B: Environ.*, 2014, **160-161**, 200.
- O. O. Prieto-Mahaney, N. Murakami, R. Abe, B. Ohtani, *Chem. Lett.*, 2009, **38**, 238.