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Supplementary Information

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

Takashi Kamegawa*[,a] and Takayuki Nakaue[a,b]

[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

Material. Ammonia-borane (NH_3BH_3, AB) was obtained from Sigma-Aldrich Co. Hydrogen hexachloroplatinate (IV) hexahydrate ($H_2PtCl_6 \cdot 6H_2O$), aqueous ammonia solution (5 mmol/l), ammonium sulfate ($(NH_4)_2SO_4$), and methanol were purchased from Nacalai Tesque Inc. Boron trioxide (B_2O_3) was obtained from Kishida Chemical Co. Ltd. All chemicals were used without further purification.

Sample preparation. The different types of TiO_2 such as JRC-TiO-3 (crystalline phase: rutile (R), Surface area: 51 m^2/g), JRC-TiO-4 (anatase/rutile (A/R), 50 ± 15 m^2/g) and JRC-TiO-8 (anatase (A), 338 m^2/g) were supplied from the Catalysis Society of Japan as a reference catalyst. The photo-deposition of Pt nanoparticles on each TiO_2 was conducted using a de-aerated aqueous methanol solution of $H_2PtCl_6 \cdot 6H_2O$ under UV light irradiation ($\lambda > 290$ nm). Samples were denoted as Pt/TiO_2(R), Pt/TiO_2(A/R) and Pt/TiO_2(A), respectively. As a reference, Pt-loaded SiO_2 (Pt/SiO_2) was also prepared by an impregnation method using a SiO_2 (Aerosil 300, 300 ± 30 m^2/g) and aqueous $H_2PtCl_6 \cdot 6H_2O$ solution. After an impregnation, Pt/SiO_2 was calcined at 773 K for 5 h in air. Prior to the characterization and reaction test, Pt/SiO_2 was treated with H_2 gas (flow rate: 20 ml/min) at 473 K for 1 h.

Characterization. The surface area of samples was obtained by measurement of N_2 adsorption isotherms using a BEL-SORP max (BEL Japan, Inc.) at 77 K after degassing of samples under vacuum at 393 K for 2 h. CO pulse adsorption was carried out to evaluate the Pt surface area and Pt particle size in each sample by using a BEL-METAL-1 instrument (BEL Japan, Inc.) at 323 K. The Pt-loaded TiO_2 was pre-treated by a H_2 flow at 323 K for 1 h.

Catalytic reaction. In a typical experiment, 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. 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 (Shimadzu GC-8A (Ar-carrier gas) and GC-2014 (He-carrier gas)) equipped with a MS-5A column and TCD detector. UV light irradiation was carried out using a 100 W high-pressure Hg lamp through a water filter (UV light intensity ($\lambda = 360$ nm), 10 mW/cm^2). Photocatalytic reactions were carried out by using the same equipment. The solution of H_3BO_3 was prepared by dissolving a B_2O_3 in water. The aqueous solution (5 mL) with appropriate concentration of NH_3 (2 mmol/L), $(NH_4)_2SO_4$ (1 mmol/L) and H_3BO_3 (2 mmol/L) was used in the comparative studies. The mixture of aqueous NH_3 and H_3BO_3 was also obtained by mixing a predetermined quantity of them (aqueous NH_3 and H_3BO_3: 4 mmol/L, 2.5 ml). These chemicals and AB showed no typical light absorption in the wavelength longer than 220 nm.