One-pot synthesis of imines from alcohols and amines with TiO_2 loading Pt nanoparticles under UV irradiation

Yasuhiro Shiraishi,[a]* Makoto Ikeda,[a] Daijiro Tsukamoto,[a] Shunsuke Tanaka[b] and Takayuki Hirai[a]

[a] Research Center for Solar Energy Chemistry, and Division of Chemical Engineering, Graduate School of Engineering Science, Osaka University, Toyonaka 560-8531, Japan;

[b] Department of Chemical, Energy and Environmental Engineering, Kansai University, Suita 564-8680, Japan.

E-mail: shiraish@cheng.es.osaka-u.ac.jp

Electronic Supplementary Information (ESI†)

Catalyst preparation

Pt(x)@TiO_2 [x = 0.05, 0.1, 0.2, 0.3, 0.5, 1.0] were prepared as follows: TiO_2 (1.0 g) and H_2PtCl_6 (1.1, 2.1, 4.2, 6.4, 10.6, 21.2 mg) were added to water (10 mL) and evaporated under stirring at 353 K for 12 h. The obtained powders were calcined at 673 K for 3 h under air flow and then reduced under H_2 at 473 K for 3 h. The Pt amounts on the catalysts were determined by X-ray fluorescence analysis.

Photoreaction procedure

Photoreaction was performed within a Pyrex glass tube (capacity, 20 mL) using a 2 kW Xe lamp (>300 nm; Ushio Inc.; light intensity, 18.2 W m^{-2} at 300−400 nm) with magnetic stirring at 298 K. The reactant and product concentrations were determined by GC-FID or -TCD.

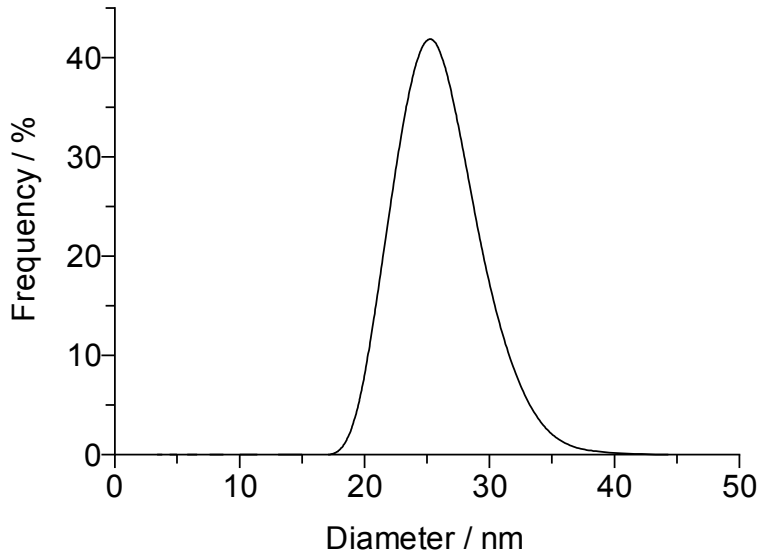

Fig. S1 Size distribution of TiO_2 particles used for catalyst synthesis, which was measured by a laser dynamic light scattering analysis in EtOH.

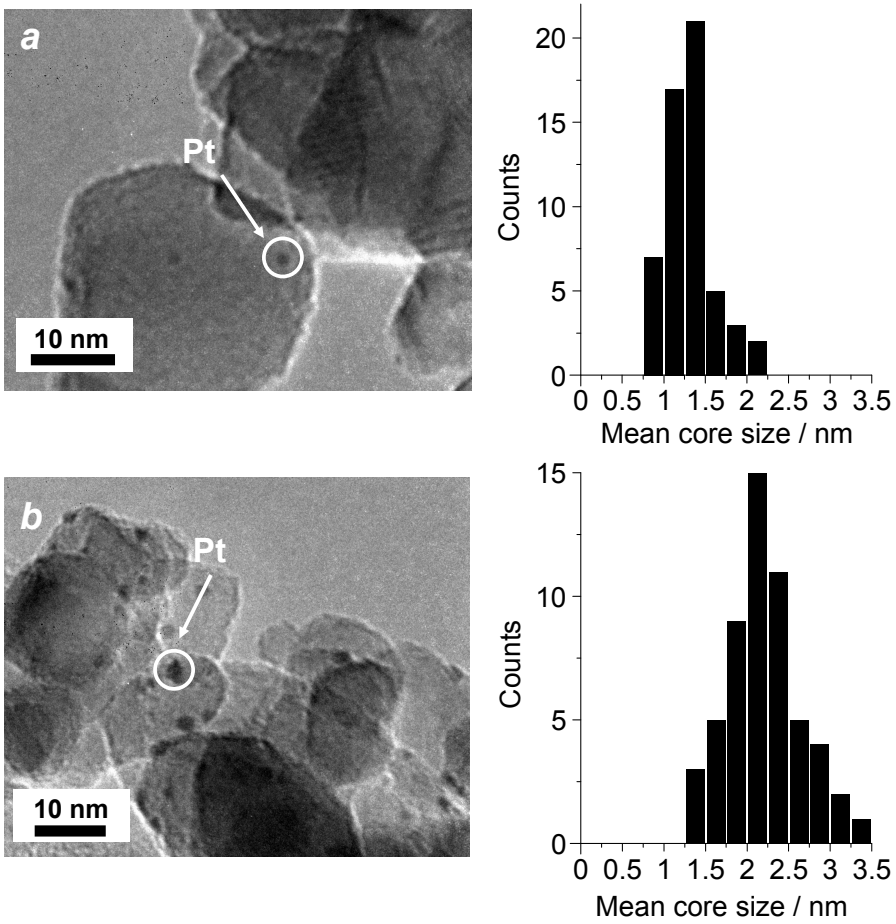

Fig. S2 TEM images and size distributions of Pt particles on (a) Pt(0.1)@TiO_2 and (b) Pt(1.0)@TiO_2 catalysts.

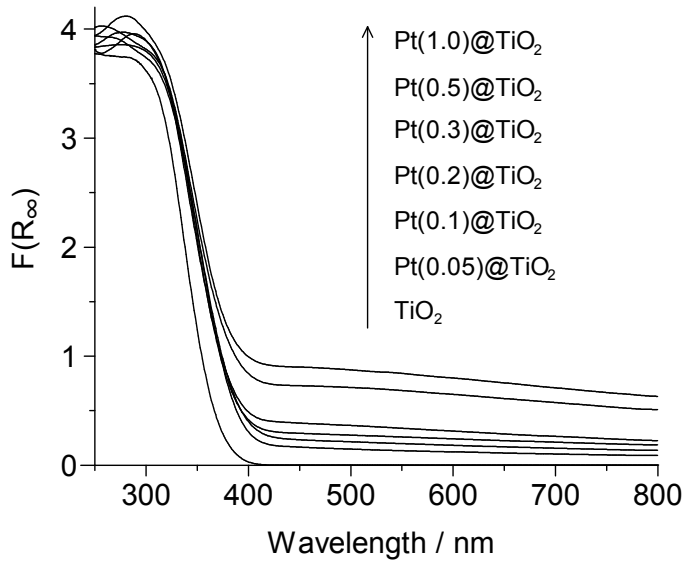

Fig. S3 Diffuse reflectance UV-vis spectra of catalysts.

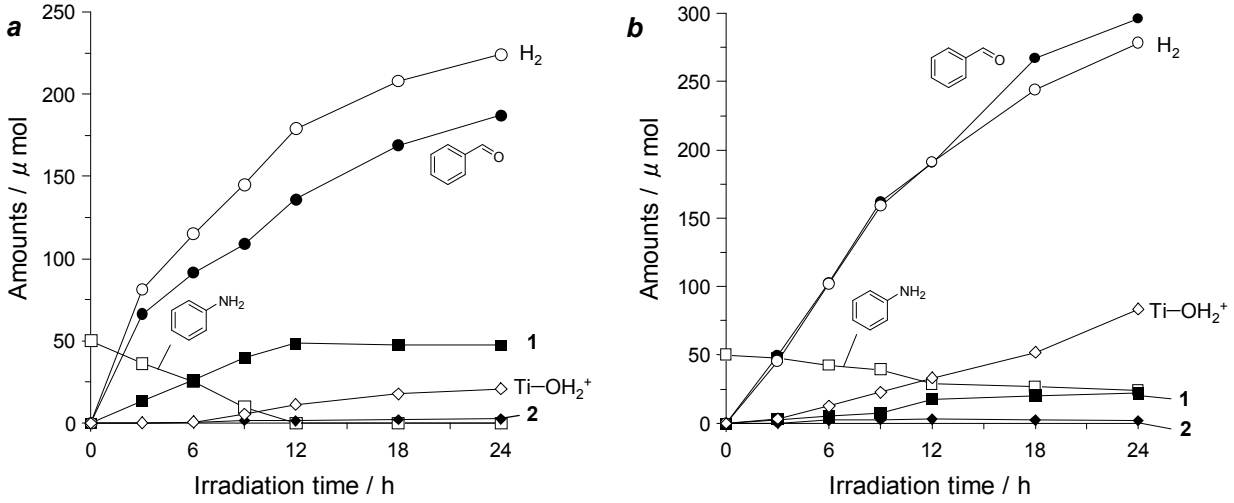

Fig. S4 Time-dependent change in the amounts of substrate and products during photoirradiation of benzyl alcohol solution containing aniline with (a) Pt(0.3)@TiO_2 and (b) Pt(1.0)@TiO_2. Reaction conditions: catalyst (5 mg), aniline (50 μmol), benzyl alcohol (5 mL), N_2 (1 atm), λ >300 nm, 298 K.

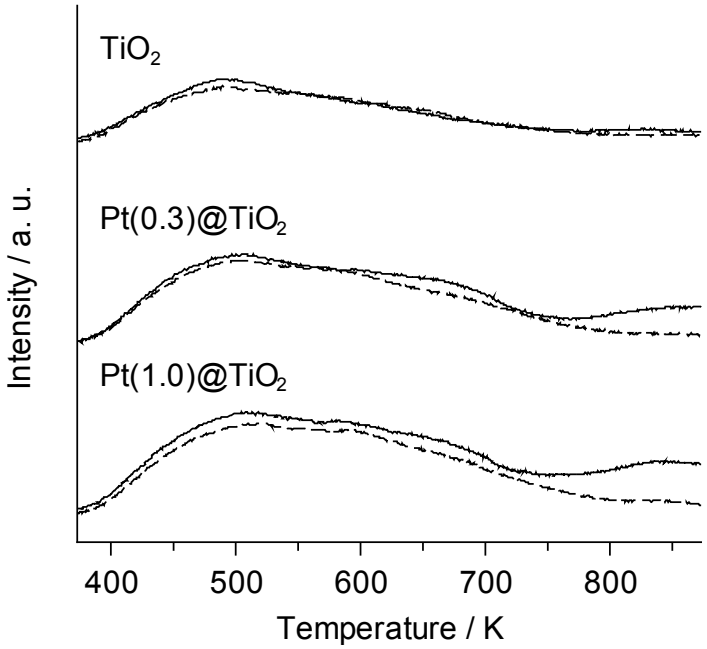

Fig. S5 NH_3-TPD profiles for (dotted line) fresh catalysts and (solid lines) the catalysts used after UV irradiation. The catalysts are TiO_2, Pt(0.3)@TiO_2, and Pt(1.0)@TiO_2, respectively.

The measurements were carried out as follows:
The NH_3-TPD profiles were obtained using an AUTOSORB-1-C/TCD analyzer (Yuasa Ionics Co., Ltd.). The respective sample (0.1 g) was added to the Pyrex sample tube and treated in a He flow at 723 K for 1 h. The tube was saturated with NH_3 at 373 K and settled for 10 min. After purging the tube with He for 1 h, the TPD measurement was started in He flow with the heating rate 10 K/min.
The photoirradiation of the catalyst samples was carried out as follows:
The respective catalysts (5 mg) were added to benzyl alcohol (5 mL) in a Pyrex glass tube. The tube was purged with N_2 and photoirradiated by a Xe lamp for 3 h under magnetic stirring at 298 K. The catalysts were washed with MeCN, recovered by centrifugation, and dried at 353 K for 12 h. The required amounts of catalysts (0.1 g) were collected by the photoirradiation of 25 samples and used for the above TPD measurement.