

Supplementary information for

**Photocatalytic hydrogenation of alkenes to alkanes in alcoholic suspensions of  
palladium-loaded titanium(IV) oxide without use of hydrogen gas**

## Experimental

### *Preparation of metal-loaded TiO<sub>2</sub> samples*

All reagents were purchased from Wako Pure Chemical Industries, Ltd. and used without further purification. P 25 (Degussa) was used as a photocatalyst, and photodeposition was used to load metal co-catalysts (0.1 wt%). Metal chlorides were used as the starting metal sources (hexachloroplatinic(IV) acid, copper chloride, palladium(II) chloride and ruthenium(III) chloride). In a 10 vol% methanol aqueous solution (10 cm<sup>3</sup>) containing a metal source, TiO<sub>2</sub> particles were suspended, and the suspension was photoirradiated for 60 min with a 400 W high-pressure mercury arc ( $\lambda > 300$  nm, Eiko-sha) with magnetic stirring under argon (Ar) or the atmosphere at 298 K. Analysis of the liquid phase after photoirradiation revealed that the metal co-catalysts had been almost completely deposited on the TiO<sub>2</sub> particles. After photoirradiation, the metal-loaded TiO<sub>2</sub> particles were recovered, washed repeatedly with water by vigorous mixing and centrifuged (20 min at 3500 rpm) three times, and then dried at 293 K *in vacuo* for 60 min.

### *Characterization*

The morphology of Pd-TiO<sub>2</sub> particles was observed under a JEOL JEM-3010 transmission electron microscope (TEM) operated at 300 kV in the Joint Research Center of Kinki University.

### *Typical procedure of photocatalytic reaction*

Metal-loaded TiO<sub>2</sub> powder (50 mg) was suspended in methanol or 2-propanol (5 cm<sup>3</sup>) containing styrene (45  $\mu$ mol) in a test tube. The tube was sealed with a rubber septum and then photoirradiated by a 400 W high-pressure mercury arc ( $\lambda > 300$  nm, Eiko-sha) under Ar with magnetic stirring at 298 K. After the reaction, the gas phase was analyzed by a gas chromatograph (Shimadzu, GC-8A equipped with MS-5A columns for H<sub>2</sub>). After the suspension had been filtered to remove the particles, the amounts of styrene remaining and product(s) were determined by a gas chromatograph (Shimadzu GC-2025 equipped with DB-1 columns).

To obtain apparent quantum efficiency (AQE), a UV light-emitting diode (UV-LED, PJ-1505-2CA, CCS Inc., Kyoto, maximum energy at  $\lambda = 366$  nm) was used as the light source. Light intensity of the UV-LED was measured using a USR-45D spectroradiometer (Ushio, Tokyo).

## Results and Discussion

### *Effects of reaction conditions on ethylbenzene*

Effects of reaction conditions on hydrogenation of styrene to ethylbenzene are summarized in Table S1. No ethylbenzene was obtained without photoirradiation (entry 1) or a catalyst (entry 2). Both photoirradiation and a catalyst were indispensable for the formation of ethylbenzene, indicating that styrene in a methanolic suspension of 0.1 wt% Pd-TiO<sub>2</sub> under Ar was hydrogenated photocatalytically (entry 3). Entry 4 shows results photocatalytic hydrogenation of styrene under air instead of Ar. A very small amount of ethylbenzene was formed and material balance was almost unity, indicating that dioxygen (O<sub>2</sub>) trapped electrons and that thus-formed active oxygen species oxidized methanol.

Table S1 Effect of reaction conditions on ethylbenzene formed in methanol suspensions after 30-min photoirradiation.

Entries	Gas phase	Photoirradiation	Catalyst	Ethylbenzene yield /%
1	Ar	-	0.1 wt%Pd-TiO <sub>2</sub>	0
2	Ar	UV	-	0
3	Ar	UV	0.1 wt%Pd-TiO <sub>2</sub>	>99
4	Air	UV	0.1 wt%Pd-TiO <sub>2</sub>	1.3

### *Effect of Pd loading*

Figure S1 shows effects of the amounts of Pd loaded on the TiO<sub>2</sub> surface on yield of ethylbenzene formed by photocatalytic hydrogenation of styrene in methanolic suspensions after 5-min photoirradiation. No ethylbenzene formed over Pd-free TiO<sub>2</sub>. The yield of ethylbenzene increased with increase in the amount of Pd and reached a maximum at 0.5 wt%. The amounts of reduction sites for hydrogenation of styrene probably increased with increase in the Pd content. Further loading of Pd decreased the yield of ethylbenzene. The fact that excess loading of a co-catalyst often induces electron-hole recombination and shows a negative light-shading effect may explain the decrease in yield.

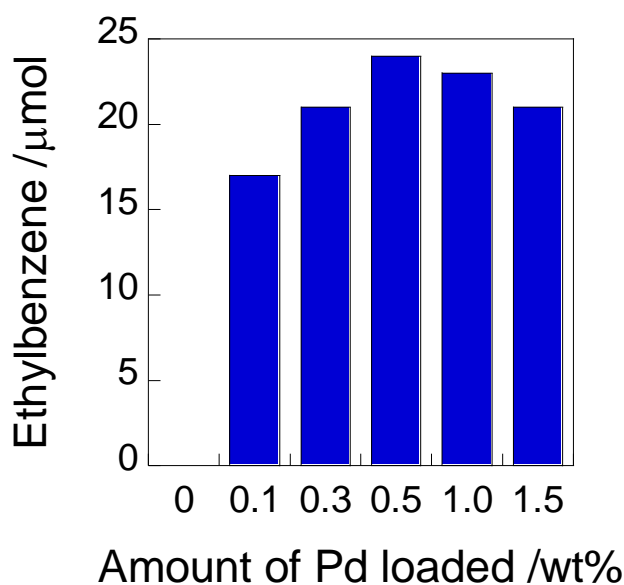


Figure S1 Effects of amounts of metal loaded on the TiO<sub>2</sub> surface on ethylbenzene yield in photocatalytic reductive hydrogenation of styrene in methanolic suspensions after 5-min photoirradiation.

*TEM observation*

A TEM photograph of 0.5 wt%Pd-TiO<sub>2</sub> and distribution of Pd particles in 0.5 wt%Pd-TiO<sub>2</sub> are shown in Figure S2. Fine Pd particles were fixed on TiO<sub>2</sub> and the average diameter was determined to be 4.8 nm.

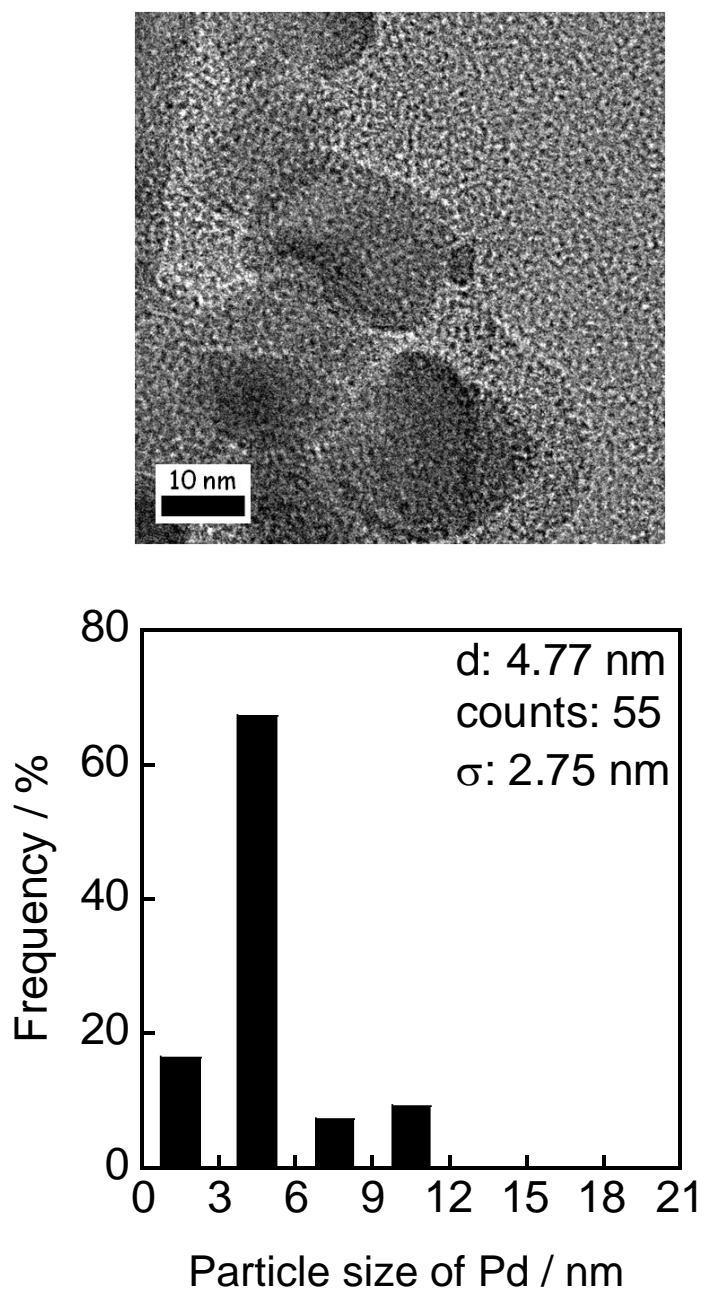


Figure S2 TEM photograph of 0.5 wt%Pd-TiO<sub>2</sub> and distribution of Pd particles in 0.5 wt%Pd-TiO<sub>2</sub>.

### *Durability test*

To examine the durability of the Pd-TiO<sub>2</sub> photocatalyst in this reaction system, the reaction was repeated. After reaction for 30 min, Pd-TiO<sub>2</sub> particles were recovered by simple filtration from the reaction mixture and were re-used. As shown in Figure S3, Pd-TiO<sub>2</sub> photocatalysts were reusable without loss of activity. Totally, 141 μmol of ethylbenzene was formed by three-time reuse of Pd-TiO<sub>2</sub> and, based on Equation 4, the turnover number (TON) of Pd for styrene hydrogenation was calculated to be 300, indicating that Pd worked as a co-catalyst.

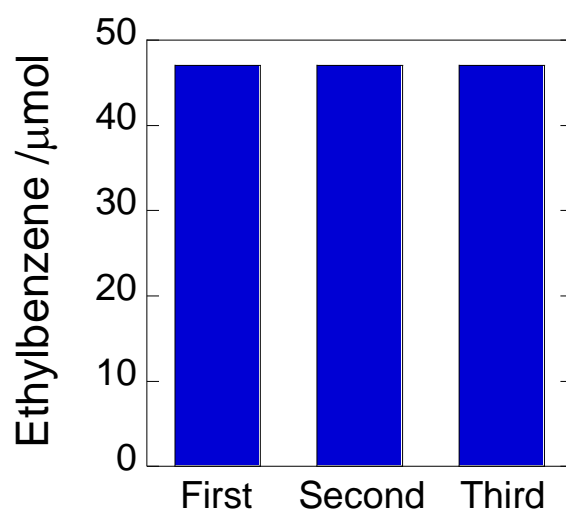


Figure S3 Durability of 0.1 wt% Pd-TiO<sub>2</sub> in photocatalytic hydrogenation of styrene to ethylbenzene for 30-min photoirradiation.