



Short Communication

Dye-sensitized photo-hydrogenation of aromatic ketones on titanium dioxide under visible light irradiation



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ABSTRACT

Aromatic ketones were photocatalytically hydrogenated on P25 TiO₂ powder modified with metal free organic dyes under visible light irradiation. The suitable combination of dye-TiO₂ and triethylamine as a sacrificial electron donor successfully extended the photocatalytic UV response of TiO₂ toward visible light region in the photo-hydrogenation of acetophenone derivatives.

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1. Introduction

Dye-sensitization of semiconductor materials has developed in the application of photographs [1], solar cell devices [2–6], and photocatalysis [7–14] to extend UV light response of the materials toward visible light region. In particular, dye-sensitization of titanium dioxide (TiO₂) is receiving increased attention with respect to hydrogen production in water splitting [7,8] and CO₂ fixation [9–11] under visible light. However, less is known about synthetically useful organic reactions catalyzed by dye-sensitized TiO₂ [12–14], thus, the development of efficient dye-sensitized system has been a subject of current interest. In recent years, the utility of TiO₂ modified by Ru(II) complex as a transition metal dye in organic reactions was reported by König's and Jang's groups, respectively [12,13]. More recently, organocatalysis combining the metal-free organic dye-sensitized TiO₂ was studied by König's group [14]. In their study, the Texas-Red derived dye, which was covalently anchored on TiO₂ particle, was employed as an organic dye.

Photocatalytic hydrogenation on semiconductor particles has been reported as highly efficient and selective reductions of CH₃C≡CH to CH₃CH=CH₂ on Pt/TiO₂ (rutile) [15], carbonyl compounds to corresponding alcohols on the P25 TiO₂ [16–18] or on zinc sulfide nanocrystallite [19], nitroaromatics to corresponding amino-compounds on TiO₂ [12,20–25], and so on. These and other examples of photo-hydrogenation on semiconductor particles have been summarized in

our recent review [26]. We have recently demonstrated that P25 TiO₂ exhibited the excellent activity to hydrogenate aromatic ketones under UV light irradiation [17]. Furthermore, the study on adsorptive and kinetic behaviors shows that the accumulated conduction band (CB) electrons or those trapped at surface defect sites (Ti⁴⁺_{sd}) actually take part in the hydrogenation [18]. Therefore, we expect that electron injection from excited dyes into CB of TiO₂ will appear to a promising way to achieve the hydrogenation under visible light irradiation.

Here, we report the photo-hydrogenation of aromatic ketones using dye-sensitized P25 TiO₂ photocatalyst in the presence of triethylamine (TEA) as a sacrificial electron donor under visible light irradiation. In this study, fluorescein (Fl) and rhodamine B (RhB) dyes were employed as non-expensive and eco-friendly metal-free organics (Fig. 1). The merit using this system is to obtain the catalysts by a simple and easy mixing procedure as described in the Experimental section.

2. Experimental

Polycrystalline TiO₂ powder (Degussa P25, specific surface area: 50 m² g⁻¹) was purchased from Japan Aerosil and used as received. A ratio of anatase/rutile in TiO₂ was roughly estimated to be 9/1 by powder X-ray diffraction (Rigaku, Ultima IV, Cu K α). The TiO₂ powder was previously heated at 120 °C in air for 2 h to remove adsorbed water on the TiO₂ surface. The dyes were adsorbed onto the P25 TiO₂ powder, silica gel (SiO₂, Silicycle, F60, particle size: 40–63 μ m, 230–400 mesh), or alumina powder (Al₂O₃, Nacalai Tesque, Activated 200, ca. 200 mesh) by immersing 1.0 g of the powder into Fl in ethanol (13 mmol/dm³) or RhB in methanol (99 mmol/dm³) solution overnight at room temperature in the dark. After repeating the centrifugation and washing

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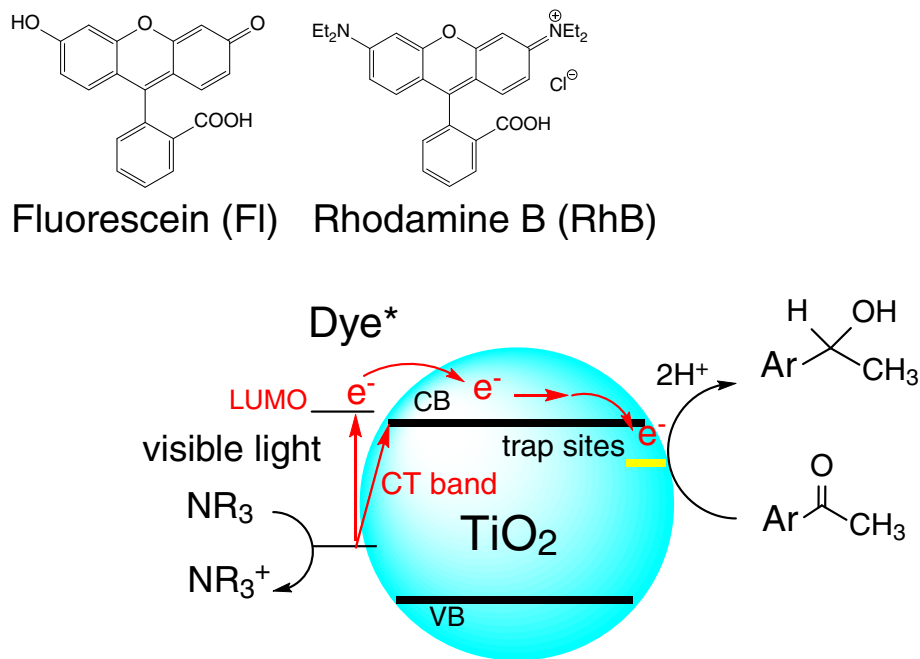


Fig. 1. Schematic illustration of dye-sensitized photo-hydrogenation of AP derivatives on TiO_2 .

with methanol at least five times, the TiO_2 powders modified with the dyes (dye- TiO_2) were dried overnight at 40 °C and kept in the dark. Diffuse reflectance spectra of the dye- TiO_2 samples were measured before and after irradiation experiments by using a UV–vis spectrophotometer (JASCO, V-650-IRM) equipped with an integrating sphere unit (JASCO, SIV-767). The amount of adsorbed dyes was estimated by measuring the concentration of the dyes desorbed from the TiO_2 powder, which was attained by immersing 0.20 g of the dye- TiO_2 samples into 2.0 cm^3 of 0.1 mol/dm^3 NaOH solution as reported by Jang et al. [13]. After centrifugation, the absorbance of supernatants was measured at maximum wavelength of 490 nm (FI) or 554 nm (RhB) using a UV–vis spectrophotometer (Shimadzu, UV-2550) and compared with reference solutions (dye concentrations: 1, 2, and 4 $\mu\text{mol/dm}^3$ in 0.1 mol/dm^3 NaOH solutions).

Irradiation experiments were carried out for a mixture of aromatic ketone and the photocatalyst powder in the presence or absence of TEA in deaerated acetonitrile solution at 32 °C. The suspended solution was irradiated with visible light (wavelength > 400 nm) from a 300 W xenon arc lamp (ILC Technology, CERMAX LX300) through a dichroic mirror and a cut-off filter (Toshiba L42). After appropriate irradiation times, 0.2 cm^3 of sample solution was withdrawn and centrifuged to

remove the catalyst powders. Concentration of the substrate and product in supernatant was determined by GC. The details of the irradiation experiment and GC analysis have been described in our previous report [17] and in electronic Supplementary information (ESI) of this paper.

3. Results and discussion

The amount of adsorbed dyes per unit gram of the TiO_2 powders were estimated to be 0.10 $\mu\text{mol g}^{-1}$ for FI and 0.27 $\mu\text{mol g}^{-1}$ for RhB. Color of FI- TiO_2 and RhB- TiO_2 powders indicated light brown and pale pink, respectively (see Fig. S1 in ESI). Fig. 2 shows the diffuse reflectance spectra of TiO_2 , FI- TiO_2 , and RhB- TiO_2 powders. FI- TiO_2 and RhB- TiO_2 exhibited broad absorption bands in visible light region (400–700 nm) with a maximum wavelength at 500 and 520 nm, respectively, while the non-modified TiO_2 powder mainly absorbed UV light. Interestingly, the

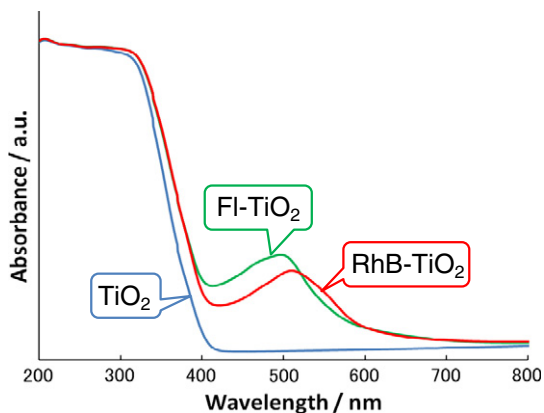


Fig. 2. Diffuse reflectance spectra of TiO_2 , FI- TiO_2 , and RhB- TiO_2 powders.

Table 1
Photocatalytic hydrogenation of AP.^a

AP		AP-OH			
Catalyst	Time (h)	TEA (vol.%)	Conv. (%) ^b	Yield (%) ^b	Reaction rate (mol dm ⁻³ h ⁻¹)
TiO_2	96	10	39	32	0.10 ^d (0.032) ^e
FI- TiO_2	96	10	100	99	0.44 ^d (0.043) ^e
FI- TiO_2	8	0	NR ^c	–	–
RhB- TiO_2	96	10	100	99	0.70 ^d (0.046) ^e
RhB- TiO_2	8	0	NR ^c	–	–
FI- SiO_2	8	10	NR ^c	–	–
FI- Al_2O_3	8	10	NR ^c	–	–
RhB- SiO_2	8	10	NR ^c	–	–
RhB- Al_2O_3	8	10	NR ^c	–	–

^a Carried out for a mixture of AP (1.5 mmol) and photocatalyst powder (30 mg) in deaerated acetonitrile solution (total volume: 15 cm^3) under visible light (>400 nm) at 32 °C.

^b Determined by GC analysis.

^c No reaction.

^d Initial reaction rate.

^e Reaction rate after 48 h.

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