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photo-hydrogenation of acetophenone derivatives.

Short Communication

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



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ABSTRACT

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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 (TiO_2) 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 TiO_2 [12–14], thus, the development of efficient dye-sensitized system has been a subject of current interest. In recent years, the utility of TiO_2 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 TiO_2 was studied by König's group [14]. In their study, the Texas-Red derived dye, which was covalently anchored on TiO_2 particle, was employed as an organic dye.

Photocatalytic hydrogenation on semiconductor particles has been reported as highly efficient and selective reductions of $CH_3C \equiv CH$ to $CH_3CH = CH_2$ on Pt/TiO_2 (rutile) [15], carbonyl compounds to corresponding alcohols on the P25 TiO_2 [16–18] or on zinc sulfide nanocrystallite [19], nitroaromatics to corresponding amino-compounds on TiO_2 [12,20–25], and so on. These and other examples of photohydrogenation 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 (Ti_{sd}^{4+}) 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.

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 elec-

tron donor successfully extended the photocatalytic UV response of TiO₂ toward visible light region in the

Here, we report the photo-hydrogenation of aromatic ketones using dye-sensitized P25 TiO_2 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: $50 \text{ m}^2 \text{ g}^{-1}$) 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 *Ka*). 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 µm, 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 TiO₂.

with methanol at least five times, the TiO₂ powders modified with the dyes (dye-TiO₂) were dried overnight at 40 °C and kept in the dark. Diffuse reflectance spectra of the dye-TiO₂ 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 TiO₂ powder, which was attained by immersing 0.20 g of the dye-TiO₂ samples into 2.0 cm³ of 0.1 mol/dm³ 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 µmol/dm³ in 0.1 mol/dm³ 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 cm³ of sample solution was withdrawn and centrifuged to



Fig. 2. Diffuse reflectance spectra of TiO₂, Fl-TiO₂, and RhB-TiO₂ powders.

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 TiO₂ powders were estimated to be 0.10 μ mol g⁻¹ for Fl and 0.27 μ mol g⁻¹ for RhB. Color of Fl-TiO₂ and RhB-TiO₂ powders indicated light brown and pale pink, respectively (see Fig. S1 in ESI). Fig. 2 shows the diffuse reflectance spectra of TiO₂, Fl-TiO₂, and RhB-TiO₂ powders. Fl-TiO₂ and RhB-TiO₂ 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 TiO₂ powder mainly absorbed UV light. Interestingly, the

Table 1

Photocatalytic hydrogenation of AP.^a

	CH ₃ + 2e	- +2H ⁺	> 400 nm photocataly	/st	CH ₃ .
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
Fl-TiO ₂	96	10	100	99	0.44 ^d (0.043) ^e
Fl-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	-	-
Fl-SiO ₂	8	10	NR ^c	-	-
Fl-Al ₂ O ₃	8	10	NR ^c	-	-
RhB-SiO ₂	8	10	NR ^c	-	-
RhB-Al ₂ O ₃	8	10	NR ^c	-	-

 $^{\rm a}$ Carried out for a mixture of AP (1.5 mmol) and photocatalyst powder (30 mg) in deaerated acetonitrile solution (total volume: 15 cm³) 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.



Fig. 3. Time courses of production yields of AP-OH from AP upon visible light irradiated FI-TiO₂ (\odot) and RhB-TiO₂ (\odot), and TiO₂ (\triangle) photocatalysts. The irradiation experiments were carried out for a mixture of AP (1.5 mmol) and photocatalyst powder (30 mg) in the presence of TEA (1.5 cm³) in deaerated acetonitrile solution (total volume: 15 cm³) under visible light (>400 nm) at 32 °C.

maximum wavelength of Fl–TiO₂ (500 nm) became the remarkable redshift compared to that of free Fl in acetonitrile solution (438 nm), whereas that of RhB–TiO₂ (520 nm) slightly shifted toward the reverse direction (blue-shift) from the maximum wavelength of RhB in acetonitrile (555 nm). Similar red-shift was observed by Ramakrishna and Ghosh in Fl adsorbed on TiO₂ nanoparticles [27]. They also observed an increase of molar extinction coefficient of Fl on adsorption onto the TiO₂ nanoparticles along with the red shift in the absorption maximum from 440 to 485 nm. This can explain the comparable absorbance between Fl– TiO₂ (500 nm) and RhB–TiO₂ (520 nm) in Fig. 2, even though the amount of adsorbed Fl was about third times smaller than that of RhB. They suggested that a charge transfer complex $(TiO_2^{\delta-..}Fl^{\delta+})$ would form on the TiO₂ surface where the carboxyl group of Fl (R–COO⁻) can interact with surface hydroxyl groups on TiO₂ (Ti–OH₂⁺), thus R–COO⁻ + Ti–OH₂⁺ \rightarrow Ti–OOC–R + H₂O, and exhibit the intense charge transfer absorption band (CT band) at around 485 nm [27]. In a similar manner, the absorption band of Fl–TiO₂ at around 500 nm in Fig. 2 may be assigned to the CT band formed on the P25 TiO₂ surface. Further, Hidaka et al. proposed that RhB also tends to adsorb on the TiO₂ surface through the negatively charged carboxyl group [28], though the characteristic CT band was not observed for RhB.

At first, we tested the viability of Fl-TiO₂ and RhB-TiO₂ in the hydrogenation of acetophenone (AP) giving 1-phenylethanol (AP-OH) under visible light irradiation (>400 nm). The reactions using both Fl-TiO₂ and RhB-TiO₂ proceeded almost quantitatively in the presence of TEA and completed after 96 h to give AP-OH in 99% yields (Table 1). Fig. 3 depicts the growths of production yields of AP-OH upon visible light irradiated Fl-TiO₂, RhB-TiO₂, and non-modified TiO₂ photocatalysts. The photo-hydrogenation using Fl-TiO₂ or RhB-TiO₂ did not take place in the absence of TEA (Table 1). Further, the reaction did not occur on dve modified silica gel (Fl-SiO₂ and RhB-SiO₂) and alumina (Fl-Al₂O₃ and RhB-Al₂O₃) powders as well as free Fl or RhB (1 mmol/dm³) in acetonitrile solution containing TEA. It is thus concluded that the reductive hydrogenation is never induced by the direct electron transfer from the excited dyes to AP. On the other hand, AP-OH was obtained in 32% yield even when the non-modified TiO₂ was employed in the presence of TEA. This can be due to the band edge absorption (3.0 eV) of the rutile phase at around 400 nm [26], followed by electron transfer from the rutile TiO₂ to AP adsorbed on the same TiO₂ particles. Recently, Shiraishi et al. reported that the rutile TiO₂ catalyzed a highly efficient photohydrogenation of nitroaromatics to the corresponding aniline derivatives in 2-propanol [25]. They demonstrated that the Ti³⁺ atoms located at the oxygen vacancies on the rutile surface behave as the adsorption site for nitroaromatics and the trapping site for photo-generated CB



Fig. 4. Time profiles of AP-OH production from AP on (a) Fl–TiO₂ and (b) RhB–TiO₂ as well as changes in diffuse reflectance spectra of (c) Fl–TiO₂ and (d) RhB–TiO₂. The repeating irradiation experiments were carried out for a mixture of AP (3 mmol) and photocatalyst powder (0.1 g) in the presence of TEA (3 cm³) in deaerated acetonitrile solution (total volume: 30 cm³) under visible light (>400 nm) at 32 °C.

Table 2

Photocatalytic hydrogenation of acetophenone derivatives.^a



Substrate		Reduction potential (V vs. SCE) ^b	Catalyst	Conv. (%) ^c	Yield (%) ^c	Yield/conv.
AP	CH ₃	-2.13	TiO ₂ Fl-TiO ₂ RhB-TiO ₂	15 59 65	12 56 63	0.80 0.95 0.97
o-F-AP	CH ₃	-1.86	TiO ₂ FI-TiO ₂ RhB-TiO ₂	12 78 78	12 74 73	1 0.95 0.94
m-F-AP	CH ₃	-2.04	TiO ₂ FI-TiO ₂ RhB-TiO ₂	22 69 69	22 69 67	1 1 0.97
p-F-AP	F F Q	-2.15	TiO ₂ Fl-TiO ₂ RhB-TiO ₂	8 52 37	7 48 35	– 0.92 0.95
PFAP	F F F	-1.83	TiO ₂ FI–TiO ₂ RhB–TiO ₂	17 ^d 29 ^d 32 ^d	Trace 7 ^d 10 ^d	- 0.24 0.31

^a Carried out for a mixture of the substrate (3 mmol) and photocatalyst powder (0.1 g) in the presence of TEA (3 cm³) in deaerated acetonitrile solution (total volume: 30 cm³) under visible light (>400 nm) at 32 °C.

^b Reduction potential vs. SCE determined by cyclic voltammetry in CH₃CN containing Bu₄NClO₄ supporting electrolyte [17].

^c Determined by GC analysis.

d For 8 h.

electrons. In a similar manner, the photo-hydrogenation of AP may occur on Ti_{sd}^{4+} site on the rutile TiO₂ surface [18].

A comparison of the reaction rates between dye-TiO₂ and nonmodified TiO₂ showed that the initial rates using Fl–TiO₂ (0.44 mol dm⁻³ h⁻¹) and RhB–TiO₂ (0.70 mol dm⁻³ h⁻¹) were much faster than those using non-modified TiO₂ (0.10 mol dm⁻³ h⁻¹), while the rates after 48 h became comparable between the three samples as summarized in Table 1. These results clearly indicate that the dye-sensitized photo-hydrogenation of AP proceeded upon the TiO₂ surface and a prolonged irradiation gradually led to the decomposition of Fl and RhB on TiO₂. In this dye-sensitized system, electron injection from dye into TiO₂ can take place in two different ways: (1) injection via a LUMO level of the excited dye to CB of TiO₂ and (2) direct injection to CB of TiO₂ on excitation of the charge transfer complex ($TiO_2^{8-...}Fl^{8+}$) as illustrated in Fig. 1 [27]. The electrons thus injected should be then trapped and distributed to Ti_{sd}^{4+} formed on the P25 TiO₂ surface. The accumulated electrons (Ti_{sd}^{3+}) were actually observed as the blue-gray color for both Fl–TiO₂ and RhB–TiO₂ powders during the visible light irradiation (see Fig. S2 in ESI) [18]. The oxidized dyes on TiO₂ can be reduced and recovered by electron transfer from the sacrificial electron donor, TEA, since the reduction potential of TEA⁺/TEA (+0.96 V vs. SCE in acetonitrile [29]) is sufficiently positive compared to the HOMO level of Fl and RhB [30]. The sacrificial reagent of TEA may also act as a hydrogen source giving AP-OH, in which an oxidative dealkylation of TEA would proceed as reported in the literature [31,32].

Stability and durability of Fl–TiO₂ and RhB–TiO₂ photocatalysts were evaluated by repeating the irradiation experiments. Fig. 4 indicates the growth of AP-OH on reused catalyst after the recovery of dye–TiO₂ by



Scheme 1. Photo-defluorination of PFAP.

centrifugation as well as the spectral changes in diffuse reflectance spectra of dye-TiO₂ powders after 24 and 48 h irradiation. The photocatalytic activity of recycling Fl–TiO₂ (Fig. 4(a)) slightly decreased but maintained in a certain extent after the recovery of Fl–TiO₂, though the shapes of diffuse reflectance spectra considerably varied with irradiation time (Fig. 4(c)). On the other hand, the activity of RhB–TiO₂ greatly reduced during 24 h and 48 h irradiation (Fig. 4(b)), which was consistent with the drastic spectral changes in the RhB–TiO₂ powder (Fig. 4(d)). It is thus concluded that Fl is a better photosensitizer for coexisting with TiO₂ in the photocatalytic hydrogenation. In contrast, RhB adsorbed on TiO₂ was more quickly deactivated because of the oxidative deethylation of RhB, followed by the destruction of chromophore [28].

Next, the reaction of other AP derivatives having fluorine atom on aromatic ring was investigated. Conversion and yields in the reactions using non-modified TiO₂, Fl–TiO₂, and RhB–TiO₂ were evaluated after being irradiated for 24 h (Table 2). It should be noted that conversions and yields were almost the same except for PFAP possessing pentafluorobenzene ring. Both *o*-F-AP and *m*-F-AP showed better reactivity than AP because of the positive reduction potential, while *p*-F-AP was less reactive due to its negative one (Table 2). A rate-determining step for the dye-sensitized photo-hydrogenation of AP derivatives may be ascribed to the electron transfer step from Ti_{sd}^{3+} to the adsorbed substrates on the TiO₂ surface [18]. This is supported by the fact that the yields mostly depend on the reduction potential of AP derivatives as reported in our recent paper except for PFAP (Table 2) [17].

The hydrogenation of PFAP was accompanied by a side reaction, causing the erosion of chemical efficiency. A considerable amount of the side product with a molecular ion (M^+) of m/z = 192 and fragment ions of m/z = 177 and 149 was detected on a gas chromatographymass spectroscopy. The mass peak at $m/z = 192 (M^+)$ can be explained by the loss of one fluorine atom and the addition of one hydrogen atom on PFAP (PFAP: $C_8H_3OF_5$, m/z = 210 (M⁺)). In addition, the appearance of fragment ions of $m/z = 177 (M^+ - 15)$ and 149 $(M^+ - 43)$ strongly suggests that the product possesses an acetyl group. Consequently, the photoreductive defluorination reaction concurrently occurred on both Fl-TiO₂ and RhB-TiO₂ catalysts (Scheme 1) [31,32]. The side reaction was also observed on dye modified silica gel (Fl-SiO₂ and RhB-SiO₂) as well as on alumina (Fl-Al₂O₃ and RhB-Al₂O₃) powders under visible light irradiation. However, the defluorination reaction did not take place on the non-modified P25 TiO₂ powder under UV irradiation [18]. Therefore, this side reaction is probably induced by the direct electron transfer from the excited dyes into PFAP, and should not proceed on the P25 TiO₂ surface.

4. Conclusions

The use of dye-TiO₂ (P25) in the presence of TEA successfully extended the photocatalytic UV response of TiO₂ toward visible light region in the photo-hydrogenation of AP derivatives. Almost quantitative conversions were achieved on both Fl-TiO₂ and RhB-TiO₂ catalysts in the photo-hydrogenation of AP. Stability and durability of the dye-TiO₂ systems were also examined, and concluded that Fl-TiO₂ was superior to RhB-TiO₂. The advantages using such metal-free organic dyes are non-expensive, eco-friendly, and non-toxic in comparison with the use of transition metal dyes (e.g. Ru complexes). Although the stability and durability were unsatisfactory as yet, experimental endeavors are now in

progress in our laboratory to find out stable and highly efficient organic dyes for improving durability, chemical efficiency, and reaction rate in the dye-TiO₂ catalyzed photo-hydrogenation.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.catcom.2013.09.006.

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