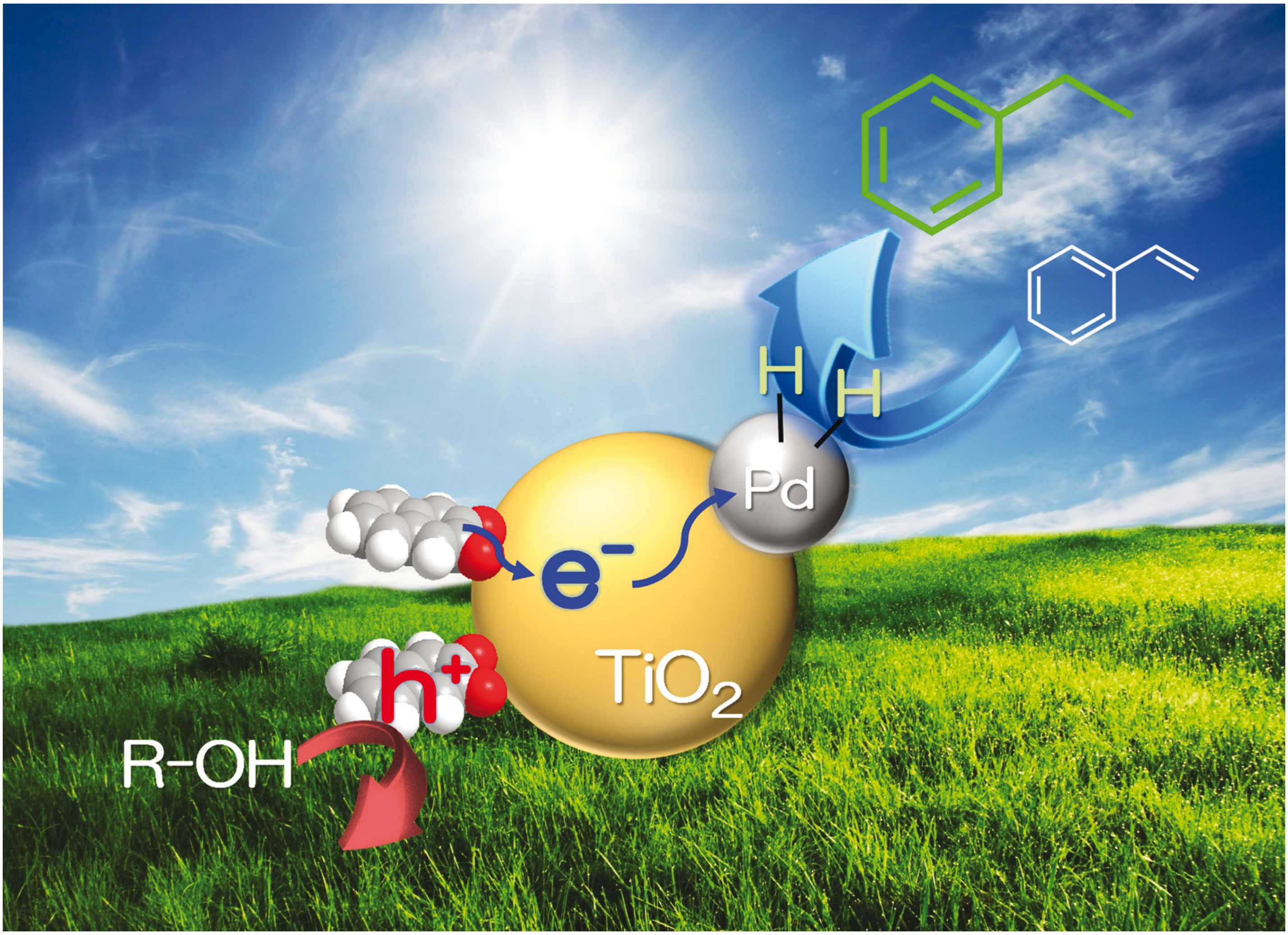

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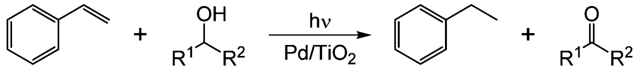
Organically modified titania having a metal catalyst: a new type of liquid-phase hydrogen-transfer photocatalyst working under visible light irradiation and H_2-free conditions†

Hiroshi Kominami,* Shin-ya Kitagawa, Yuki Okubo, Makoto Fukui, Keiji Hashimoto and Kazuya Imamura

Organically modified titania having a metal catalyst (OMTC), 2,3-dihydroxynaphthalene-modified titania having palladium metal, successfully worked as a hydrogen-transfer (C=C hydrogenation) photocatalyst in the presence of triethanolamine as the hydrogen source under visible light irradiation and hydrogen-free conditions.

When titania (titanium(IV) oxide, TiO_2) is irradiated by UV light, electrons in the valence band (VB) are excited to the conduction band (CB), leaving a positive hole in the VB. The photogenerated electrons are captured by a species adsorbed on the surface of TiO_2, resulting in the formation of a reduced species, whereas positive holes directly or indirectly cause oxidation of another species. Since photocatalytic reactions proceed at room temperature under atmospheric pressure and since light is indispensable, the reactions can be operated safely and can be easily controlled by the light intensity. Therefore, conversion of various substances over a TiO_2 photocatalyst has been extensively studied.[1] However, applications of photocatalytic reduction have been less frequently reported than photocatalytic oxidation because most of the organic substrates are easily oxidized or decomposed by positive holes. Another reason is that reduction potentials of many organic compounds are more negative than the potential of the CB of TiO_2. Therefore, target compounds in photocatalytic reduction are basically limited to those having a carbonyl group[2] and a nitro group,[3] and other photocatalytic reductions of organic compounds have scarcely been reported. On the other hand, we recently reported that introduction of potential metal catalysts into TiO_2 changes the reduction properties and greatly widens the applicability of a TiO_2 photocatalyst. For example, a cyano group (benzonitrile) was converted to an amino group (benzylamine)[4] over palladium-loaded TiO_2 (Pd/TiO_2). Over silver-loaded TiO_2, epoxides were chemoselectively deoxygenated to alkenes.[5] We also found photocatalytic hydrogenation of a vinyl group (styrene) to an ethyl group (ethylbenzene)[6] in an alcoholic suspension of Pd/TiO_2 (Scheme 1). Alcohols used as solvents were oxidized to give carbonyl compounds, and these reactions proceeded with both material balance and redox balance close to unity.



Scheme 1 Photocatalytic hydrogen-transfer reaction between alkenes and alcohols over Pd/TiO_2.

Of course, no reaction occurred over bare (Pd-free) TiO_2, indicating that Pd is an indispensable component driving the hydrogenation after receiving electrons from the TiO_2 photocatalyst. This reaction is regarded as a hydrogen-transfer reaction between alkenes and alcohols, giving alkanes and carbonyl compounds, and the combination of TiO_2 and a potential metal catalyst will therefore provide various possibilities of photocatalytic reaction. However, TiO_2 does not work as a photocatalyst under irradiation of visible light, which is largely contained in solar light.

Various types of photocatalysts that work under irradiation of visible light have been reported.[7] Most of the photocatalysts were developed for decolorization of dyes or degradation of contaminants dissolved in water, and only a few of them were active in water splitting ($H_2O \rightarrow H_2 + 1/2O_2$) or hydrogen ($H_2$) evolution by proton reduction ($2H^+ + 2e^- \rightarrow H_2$). For example, Ikeda *et al.*[8] reported H_2 evolution over TiO_2 modified with a 1,1′-binaphthalene-2,2′-diol and platinum (Pt) co-catalyst in the presence of triethanolamine as an electron donor. On the other hand, application of visible-light-responding photocatalysts for substance conversion, especially reductive conversion, has been less frequently studied[9] probably because target reactions are limited and strategies for efficient conversion are still unknown. We have focused on organically modified TiO_2 (OMT) as a photocatalyst responding to visible light. Since the use of a combination of TiO_2 and a metal catalyst is regarded as a new strategy to expand the possibility of photocatalytic reactions, OMT can be applied for substance conversion by combining it

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with a metal catalyst. We prepared organically modified TiO_2 having catalysts (OMTCs) and found that OMTC works as a new type of photocatalyst for liquid-phase hydrogen transfer under visible light irradiation and H_2-free conditions. We show here the high potential of 2,3-dihydroxynaphthalene (DHN)-modified TiO_2 having a palladium catalyst, one of the OMTCs, and a new application of a visible light-responding photocatalyst for substance conversion other than water splitting and dye decolorization.

Ishihara ST-01 particles were used as TiO_2. Preparation of 2,3-dihydroxynaphthalene-modified TiO_2 (TiO_2–DHN) and Pd-loaded TiO_2–DHN (Pd/TiO_2–DHN) and the procedure of photocatalytic reactions is provided in the ESI.†

Fig. 1(a) shows absorption spectra of TiO_2, TiO_2–DHN and Pd/TiO_2–DHN. Bare TiO_2 exhibited strong photoabsorption at $\lambda < 390$ nm due to the band-gap excitation. A large increase in photoabsorption in the range of visible light was observed in the spectrum of TiO_2–DHN. A transmission spectrum of DHN dissolved in methanol is shown in Fig. 1(b), indicating that DHN itself did not absorb visible light. Ikeda *et al.* reported that strong interaction between TiO_2 and 1,1′-binaphthalene-2,2′-diol resulted in absorption in the visible light region.[8] Based on the results of this study and the previous study, it can be concluded that strong absorption observed in TiO_2–DHN was caused by interaction between DHN and TiO_2. In the spectrum of Pd/TiO_2–DHN, a slight increase in photoabsorption in the range of visible light was caused by light scattering by Pd fine particles fixed on TiO_2–DHN.

Fig. 2(a) shows time courses of the amount of styrene remaining and the amounts of ethylbenzene and H_2 formed in photocatalytic hydrogen-transfer reaction between styrene and triethanolamine over Pd/TiO_2–DHN under irradiation of blue light. The emission spectrum of light from a blue LED is shown in Fig. 1(a). Just after photoirradiation, styrene monotonously decreased, while ethylbenzene was formed as the hydrogenated product of styrene, indicating that Pd/TiO_2–DHN works as a photocatalyst for styrene hydrogenation under irradiation of visible light. After 60 min of photoirradiation, styrene was almost completely consumed and ethylbenzene was obtained in a high yield (98%). It should be noted that H_2 was formed only after consumption of styrene. Formation of H_2 means that protons were reduced by photogenerated electrons. These results indicate that photocatalytic reduction (hydrogenation) of styrene occurred selectively over Pd/TiO_2–DHN under irradiation of visible light.

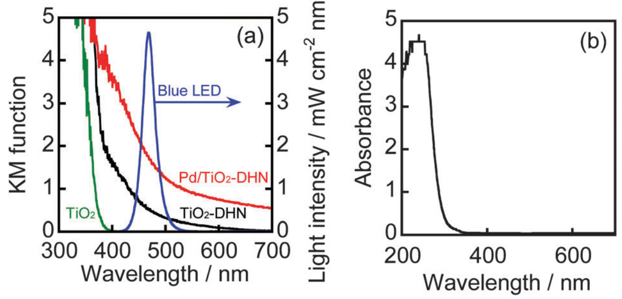


Fig. 1 (a) Diffuse reflectance spectra of TiO_2, TiO_2–DHN and Pd/TiO_2–DHN (left axis) and emission spectrum of blue LED used as the light source for photocatalytic reactions (right axis) and (b) transmission spectrum of DHN dissolved in methanol.

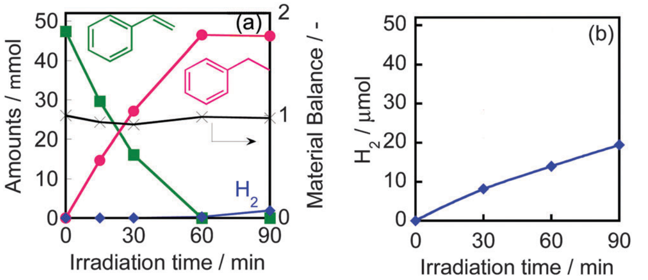


Fig. 2 Time courses of (a) amounts of styrene remaining (squares), ethylbenzene formed (circles) and H_2 formed (diamonds), and MB (right axis, crosses) in photocatalytic hydrogen-transfer reaction over Pd/TiO_2–DHN under visible light irradiation at 298 K and (b) amount of H_2 formed in the absence of styrene under the same conditions.

Material balance (MB) calculated by using eqn (1) is also shown in Fig. 2(a).

$$\text{Material balance} = \frac{n(\text{styrene}) + n(\text{ethylbenzene})}{n_0(\text{styrene})}, \qquad (1)$$

where n(styrene) and n(ethylbenzene) are the amounts of styrene and ethylbenzene after photoirradiation, respectively, and n_0(styrene) is the initial amount of styrene. The high yield of ethylbenzene and the value of MB close to unity indicate that only hydrogenation of styrene to ethylbenzene occurred, *i.e.*, polymerization of styrene, cracking of ethylbenzene and hydrogenation of the aromatic ring did not occur. Fig. 2(b) shows the result of reaction in the absence of styrene. In this case, only reduction of protons occurred, resulting in H_2 evolution. It should be noted that the reaction rate was much smaller than that of hydrogenation shown in Fig. 2(a). The large difference in the reaction rates of ethylbenzene production and H_2 production indicates that the activation energy for styrene hydrogenation is much smaller than that for H_2 evolution (hydrogen coupling) over Pd metal.

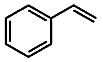
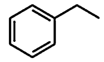
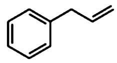
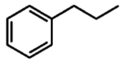
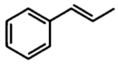
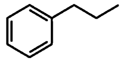
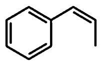
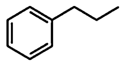
Table 1 shows effects of catalyst components (Pd and DHN) and blue light on ethylbenzene production in photocatalytic hydrogenation of styrene after 90 min at 298 K. Hydrogenation of styrene to ethylbenzene almost quantitatively occurred (high selectivity at high conversion) over Pd/TiO_2–DHN under irradiation of blue light (entry 1), whereas no ethylbenzene was produced over Pd/TiO_2 and TiO_2–DHN under irradiation of blue light (entries 2 and 3) and over Pd/TiO_2–DHN in the dark (entry 4). These control experiments indicate that (1) introduction of both a Pd catalyst and DHN into TiO_2 is indispensable for hydrogenation of styrene, (2) light from a blue LED does not induce band-gap excitation of TiO_2, (3) neither photochemical nor thermal reaction occurs under visible light irradiation, and (4) this reaction is induced by photoabsorption by TiO_2–DHN, *i.e.*, hydrogenation of styrene is a photocatalytic reaction occurring over Pd/TiO_2–DHN. Hydrogenation occurred under H_2 (1 atm) over Pd/TiO_2–DHN and Pd/TiO_2 at 298 K in the dark (entries 5 and 6). In this case, styrene was hydrogenated by hydrogen species formed by

Table 1 Results of hydrogenation of styrene to ethylbenzene under various conditions

Entry	Catalyst[a]	Blue light[b]	Gas phase[c]	Yield[d]/%
1	Pd/TiO_2–DHN	Yes	Ar	>98
2	TiO_2–DHN	Yes	Ar	ND
3	Pd/TiO_2	Yes	Ar	ND
4	Pd/TiO_2–DHN	No	Ar	ND
5	Pd/TiO_2–DHN	No	H_2	>98
6	Pd/TiO_2	No	H_2	98
7[e]	Pd/TiO_2–DHN	Yes	Ar	>98
8[f]	Pd/TiO_2–DHN	Yes	Ar	>98

[a] Each catalyst (50 mg) was suspended in acetonitrile (5 cm^3) containing styrene (50 μmol) in the presence of triethanolamine (80 μmol). [b] Irradiated by two sets of blue LEDs (420–530 nm, 137 ± 4 mW cm^{-2}). [c] Space in a test tube (30 cm^3). [d] Determined by GC. [e] Second use. [f] Third use.

Table 2 Photocatalytic hydrogenation of various alkenes to alkanes in an acetonitrile suspension of Pd/TiO_2–DHN under irradiation of light from a blue LED at 298 K for 30 min

Entry	Substrate	Product	Yield/%
1			98
2			94
3			87
4			92
5			98

dissociative adsorption of H_2 over Pd metal. The result obtained under an H_2 atmosphere is helpful to understand photocatalytic hydrogenation of styrene over Pd/TiO_2–DHN under irradiation of blue light, and the reaction mechanism will be discussed later.

An action spectrum is a strong tool for determining whether an observed reaction occurs *via* a photoinduced process or a thermocatalytic process. To obtain an action spectrum in this reaction system, hydrogenation of styrene in an acetonitrile suspension of Pd/TiO_2–DHN was carried out at 298 K under irradiation with monochromated visible light from a Xe lamp with a light width of ±5 nm. The apparent quantum efficiency (AQE) at each centered wavelength of light was calculated from the ratio of the amount of ethylbenzene and the amount of photons irradiated using eqn (2), and the results are shown in Fig. 3 together with a subtraction spectrum obtained from spectra of Pd/TiO_2–DHN and Pd–TiO_2. The value of AQE showed the same tendency as that of the subtraction spectrum, indicating that the observed reaction is caused by photoabsorption of TiO_2–DHN. However, photoabsorption at a longer wavelength (>550 nm) did not contribute to hydrogenation of styrene (discussed later).

$$\mathrm{AQE} = \frac{2 \times \text{Amount of ethylbenzene formed}}{\text{Number of incident photons}}. \tag{2}$$

To evaluate the durability of the Pd/TiO_2–DHN photocatalyst in this reaction system, the reaction was repeated. As shown in Table 1, the Pd/TiO_2–DHN photocatalyst was reusable at least three times without loss of activity (entries 7 and 8). In total, 149 μmol of ethylbenzene was formed by using Pd/TiO_2–DHN three times and, based on eqn (3), the turnover number (TON) of Pd for styrene hydrogenation was calculated to be 316, indicating that Pd worked as a catalyst.

$$\mathrm{TON} = \frac{\text{Amount of ethylbenzene formed}}{\text{Amount of Pd catalyst}}. \tag{3}$$

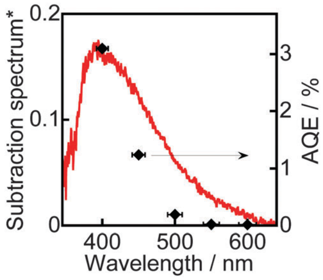
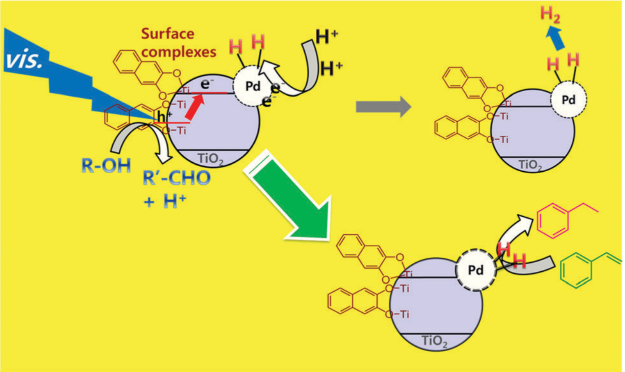


Fig. 3 Subtraction spectrum obtained from spectra of Pd/TiO_2–DHN and Pd–TiO_2 (left) and action spectrum in ethylbenzene formation over Pd/TiO_2–DHN under visible light irradiation.

Applicability of the photocatalytic hydrogenation of alkenes to alkanes was investigated using various aromatic alkenes (entries 1–4) and aliphatic alkenes (entry 5). Table 2 shows the results of photocatalytic hydrogenation over Pd/TiO_2–DHN under irradiation of visible light. Hydrogenation reaction proceeded in all cases, and high yield was obtained, indicating that Pd/TiO_2–DHN is applicable for hydrogenation of various alkenes. We also examined the effect of the type of sacrificial reagent on hydrogenation of styrene. Very small reaction rates were obtained when methanol, formic acid and oxalic acid were used, indicating that the oxidation power of TiO_2–DHN is relatively weak and sacrificial reagents applicable to TiO_2–DHN are limited.

Photocatalytic hydrogen evolution over TiO_2 modified with a 1,1′-binaphthalene-2,2′-diol and a platinum (Pt) co-catalyst in the presence of triethanolamine under irradiation of visible light has been reported, and the reaction mechanism has been proposed.[8] Our group reported photocatalytic hydrogen-transfer reaction between alkenes and alcohols over Pd–TiO_2 under irradiation of UV light and proposed the reaction mechanism.[5] Based on the proposed mechanisms of the two different reaction systems and results of blank experiments shown in Table 1, the mechanism of the present photocatalytic hydrogen-transfer reaction can be considered as follows (Scheme 2): (1) excitation of the surface complex by visible light followed by electron injection into the conduction band of TiO_2, (2) migration of the injected electrons in the TiO_2 particles to the Pd catalyst followed by reduction of H^+ to give active H species (probably H-Pd), (3) insertion of H species into a C=C double bond on Pd, resulting in the formation of ethylbenzene, and (4) reduction of the oxidized form of the surface complex by triethanolamine as a sacrificial electron donor, resulting in the formation of aldehyde and H^+. In the absence of alkenes in the system, H_2 was formed as a coupling product of the active H species, although the reaction rate is small probably due to the large activation energy



Scheme 2 Proposed mechanism for photocatalytic hydrogen-transfer reaction between alkenes and alcohols over Pd/TiO$_2$–DHN under visible light irradiation.

compared with that for hydrogenation. Photoabsorption (>550 nm) (Fig. 1) is probably caused by electron transfer from the surface complex into trap sites locating below the CB of TiO$_2$. These trapped electrons cannot be used for reduction of protons resulting in negligible values of AQE at >550 nm (Fig. 3).

Conclusions

A new type of hydrogen-transfer photocatalyst working under visible light irradiation and hydrogen-free conditions, *i.e.*, organically modified titania with catalysts (OMTCs), was reported. 2,3-Dihydroxynaphthalene (DHN)-modified titania with a palladium catalyst was active toward various alkenes, and the reaction rate was larger than that of simple hydrogen evolution. OMTCs can be applied for another liquid-phase reaction by using an appropriate catalyst for the reaction.

Acknowledgements

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