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Photocatalytic hydrogenation of furan to tetrahydrofuran in alcoholic suspensions of metal-loaded titanium(IV) oxide without addition of hydrogen gas†

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The use of metal co-catalysts broadens the application of photocatalytic reduction without the use of dihydrogen (H_2) gas. We examined photocatalytic hydrogenation of furan, a representative heterocyclic compound and a compound derived from biomass, in alcoholic suspensions of metal-loaded titanium(IV) oxide (TiO_2) under a H_2-free condition and we found that furan was almost quantitatively hydrogenated to tetrahydrofuran with a high apparent quantum efficiency of 37% at 360 nm when palladium was used as a co-catalyst. Effects of different metal co-catalysts, different amounts of the co-catalyst, the type of TiO_2, the type of alcohol, light wavelength and reusability for furan hydrogenation were investigated. Based on the results, the functions of TiO_2 and the co-catalyst and the reaction process are discussed.

1. Introduction

Tetrahydrofurans (THFs) are important compounds as intermediates of chemical products, and they are produced by dehydration of diols and hydrogenation of corresponding furans.[1,2] Hydrogenation of furans to THFs is more attractive because furans can be produced from biomass. Hydrogenation of furans is achieved by catalytic hydrogenation using a metal catalyst such as nickel or palladium (Pd) supported on a suitable support.[2] However, these catalyst systems require the addition of an excess amount of dihydrogen (H_2) gas as a hydrogen source in a closed reactor. Therefore, a more environmentally friendly catalytic reaction system for hydrogenation of furans utilizing a "greener" hydrogen source is desired.

Since titanium(IV) oxide (TiO_2) is inexpensive and not toxic for humans and the environment, it has been used for a long time as an indispensable inorganic material such as a pigment and a UV absorber. Another important application of TiO_2 is the use as a photocatalyst. When TiO_2 is irradiated by UV light, charge separation occurs and thus-formed electrons in the conduction band and positive holes in the valence band cause reduction and oxidation, respectively. The photocatalytic reaction satisfies almost all of the 12 proposed requirements for green chemistry[3] because of its characteristics shown below. First, TiO_2 functions as a catalyst. The TiO_2-photocatalyzed reaction occurs at room temperature. Solar energy can be used to drive the reaction. Since TiO_2 is a typical solid catalyst, energy consumption for the separation of TiO_2 from the reaction mixture is much smaller than that for the separation of a homogeneous catalyst. In addition, a TiO_2 photocatalyst can be used repeatedly free from a special re-activation process because of its excellent chemical and physical stability. Therefore, photocatalytic material transformation has been studied by many researchers.[4–6] Recently, photocatalytic reduction of organic compounds has attracted the attention of researchers,[5,6] and much interest has been shown in the reduction of nitrobenzenes to aminobenzenes.[7–21] We recently found that benzonitrile and styrene were successfully hydrogenated in alcohol suspensions of a palladium-loaded TiO_2 (Pd-TiO_2) photocatalyst, although the reduction potentials of benzonitrile and styrene are believed to be much higher than the potential of the conduction band of TiO_2.[22,23] The reason why Pd-TiO_2 exhibited good performance in photocatalytic hydrogenation is the high "catalytic" activity for hydrogenation of unsaturated bonds such as C$=$C and C$\equiv$N bonds.[26,27] Two results have shown that (1) hydrogenation occurs without the use of H_2 because alcohol works as an electron and hydrogen source in the photocatalytic reaction, (2) the Pd co-catalyst strongly contributes to the reduction, and (3) the applicability of photocatalytic reduction is not limited by the conduction band position of semiconductor photocatalysts. We also reported other co-catalyst effects in chemoselective

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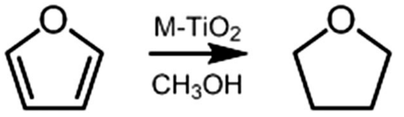

Scheme 1 Photocatalytic hydrogenation of furan to THF in a methanolic suspension of metal (M)-loaded TiO$_2$ under a H$_2$-free condition.

reduction of (2,3-epoxypropyl)benzene to allylbenzene (silver co-catalyst)[24] and semi hydrogenation of alkynes to alkenes (copper co-catalyst),[25] indicating that photocatalytic H$_2$-free reduction can be broadened by the use of metal co-catalysts. In this study, we examined photocatalytic hydrogenation of furan, a representative heterocyclic compound, to THF in an alcoholic suspension of metal-loaded TiO$_2$ (Scheme 1) to expand the possibility of photocatalytic hydrogenation. Here we report (1) the effects of metal co-catalysts and (2) the effects of various parameters on H$_2$-free hydrogenation of furan, and (3) details of the reaction.

2. Experimental

2.1. Preparation of metal-loaded TiO$_2$

Various metals as co-catalysts (Au, Ag, Cu, Pd and Pt) were loaded on TiO$_2$ (MT-150A, Tayca, Osaka, Japan) using the photodeposition method. Some TiO$_2$ samples were selected from Japan Reference Catalysts (JRC-TIO series) registered at the Catalysis Society of Japan and used to examine the effects of different kinds of TiO$_2$. Metal-loaded TiO$_2$ powder and unloaded TiO$_2$ powder were each suspended in 10 cm^3 of an aqueous methanol solution (10 vol%) containing a metal source in a test tube. HAuCl$_4$, AgNO$_3$, CuCl$_2$, PdCl$_2$ and H$_2$PtCl$_6$ were used as metal sources. Each test tube was sealed with a rubber septum under argon (Ar) and then photoirradiated for 90 min at $\lambda > 300$ nm using a 400 W high-pressure mercury arc (Eiko-sha, Osaka) with magnetic stirring in a water bath continuously kept at 298 K. The resulting powder was washed repeatedly with distilled water and dried for 1 h *in vacuo*.

2.2. Characterization

The morphology of the Pd-TiO$_2$ particles was observed under a JEOL JEM-2100F transmission electron microscope (TEM) operated at 200 kV in the Joint Research Center of Kindai University.

2.3. Photocatalytic reaction

In a typical run, Pd-TiO$_2$ (50 mg) was suspended in 5 cm^3 of methanol containing furan (40 ± 4 μmol) in a test tube, which was sealed with a rubber septum and then photoirradiated under Ar at 298 K with the same high-pressure mercury lamp or a UV-LED (UV-LED, PJ-1505-2CA, CCS Inc., Kyoto, maximum energy at $\lambda = 365$ nm). The amounts of furan and THF were determined using an FID-type gas chromatograph (GC-2025, Shimadzu) equipped with a DB-1 column. Chlorobenzene was used as an internal standard sample. Chlorobenzene (7 mm^3) was added to the reaction solution (3 cm^3). After the mixture has been stirred for 7 min, furan and THF in the mixture solution were analyzed. The amounts of furan and THF were determined from the ratios of their peak areas to the peak area of chlorobenzene. The amount of H$_2$ as the reduction product of protons (H$^+$) was determined using a TCD-type gas chromatograph (GC-8A, Shimadzu) equipped with an MS-5A column. A multi-wavelength irradiation monochromator (MM-3, Bunkoukeiki Co., Ltd) was used to obtain apparent quantum efficiency (AQE), and light intensity was determined using a spectroradiometer (USR-45D, Ushio Inc.).

3. Results and discussion

3.1. Effects of different metal co-catalysts

In the hydrogenation of furan, H$_2$ may be formed as the product of reduction of H$^+$ by photogenerated electrons ($2H^+ + 2e^- \rightarrow H_2$). Therefore, hydrogenation of furan competes with the reduction of H$^+$, and the selectivity of two products (THF and H$_2$) is also an important indicator for evaluation of photocatalysts as well as the yields of THF and H$_2$. Fig. 1 shows the effects of metal co-catalysts (1.0 wt%) on the yields of THF and H$_2$ produced in photocatalytic hydrogenation of furan in methanolic suspensions of metal-loaded TiO$_2$ (MT-150A) for 10 min under Ar with irradiation of UV light from an LED. When bare TiO$_2$ was used as the photocatalyst, no THF or H$_2$ was formed. Just after photoirradiation, the color of TiO$_2$ became blue, indicating that Ti^{4+} in TiO$_2$ was reduced to Ti^{3+} by photogenerated electrons. These results mean that without the aid of a co-catalyst, photoirradiated TiO$_2$ has no ability to reduce (hydrogenate) a C=C double bond in a heterocyclic compound as well as a C=C double bond in hydrocarbons.[23] In the case of Au-, Ag- and Cu-loaded TiO$_2$ samples, no THF was formed, indicating that these metals were inactive as co-catalysts for furan hydrogenation. H$_2$ was evolved over Au- and Ag-loaded TiO$_2$ samples. Formation of H$_2$ will be discussed at the end of this section. In contrast to these metal-loaded TiO$_2$ samples, a small amount of THF was formed when Pt-loaded TiO$_2$ (Pt-TiO$_2$) was used, although a large amount of H$_2$ was simultaneously evolved. We noted that Pd-loaded TiO$_2$ (Pd-TiO$_2$) showed a distinctive photocatalytic activity for the largest production of THF and suppressed evolution of H$_2$. As clearly shown, Pd-TiO$_2$ possessed a favorable catalytic property in hydrogenation of furan in contrast to Pt-TiO$_2$. Bradley *et al.*[28] reported that Pd can readily adsorb a furan ring due to a strong interaction between the Pd

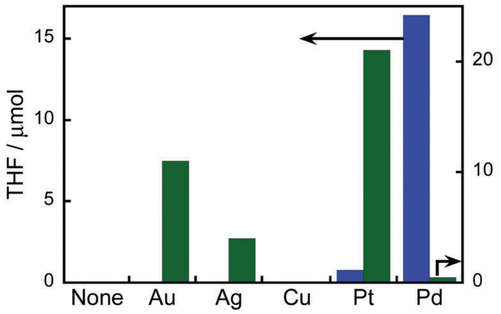

Fig. 1 Effects of different metal co-catalysts (1.0 wt%) on the yields of THF and H$_2$ produced in photocatalytic hydrogenation of furan (40 ± 4 μmol) in methanolic suspensions of metal-loaded TiO$_2$ (MT-150A) for 10 min under irradiation of UV light from an LED.

and π bonds in furan. The strong interaction between Pd and furan is attributed to the high activity of Pd-TiO_2.

As shown in Fig. 1, H_2 was formed when Au, Ag, Pt and Pd were used as co-catalysts. It is known that co-catalysts such as Pt loaded on a photocatalyst act as sites for storage of photogenerated electrons and as active sites for reaction, resulting in reduced activation energy of the reaction and formation of hydrogenated products.[29,30] In previous papers on photocatalytic NH_3 decomposition in aqueous suspensions of TiO_2 having co-catalysts, we reported that the rate of H_2 evolution was drastically changed depending on the type of co-catalyst and that the effect as a co-catalyst became smaller with an increase in hydrogen over-voltage of the co-catalyst metal when used as an electrode.[31,32] A similar tendency was observed in the evolution of H_2 from methanol in the presence of furan in this study as shown in Fig. 2. However, the use of a Pd co-catalyst resulted in a very small yield of H_2 that was much different from the value predicted from the hydrogen overvoltage. The second smallest value of hydrogen overvoltage means that the activation energy for H_2 evolution over Pd particles is rather small. The much smaller H_2 yield in furan hydrogenation indicates that the Pd co-catalyst provides an excellent route with very small activation energy for hydrogenation of furan to THF.

Supported Pd nanoparticles are often used for catalytic hydrogenation with H_2 as a hydrogen source. In thermocatalytic hydrogenation, H_2 molecules are adsorbed dissociatively on Pd particles, and thus-formed active hydrogen species are inserted into the C=C double bond.[33,34] Therefore, active hydrogen species formed reductively from H^+ in the photocatalytic process and formed dissociatively from H_2 gas would be essentially the same. It can be concluded that hydrogenation of furan to THF under the present conditions consists of two processes: (1) photocatalytic production of active hydrogen species and (2) thermocatalytic hydrogenation of furan over Pd particles. As can be seen in Fig. 1 and 2, only the thermocatalytic properties of metal particles decide whether hydrogenation of furan to THF occurs or not. Strictly speaking, the observed hydrogenation should be called a combination reaction by photocatalysis and thermocatalysis, although we call this reaction simply photocatalytic hydrogenation hereafter.

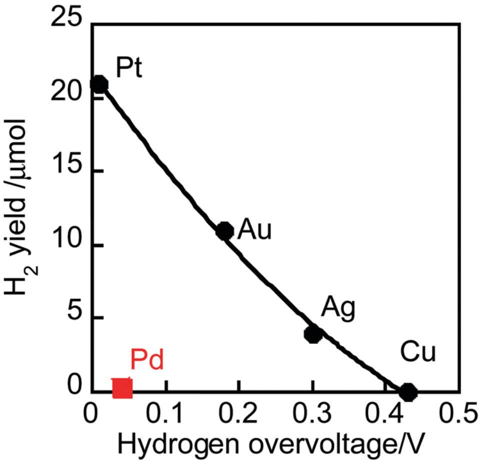

Fig. 2 Correlation between yield of H_2 produced in photocatalytic hydrogenation of furan and hydrogen overvoltage of metal electrodes. Reaction conditions are shown in Fig. 1.

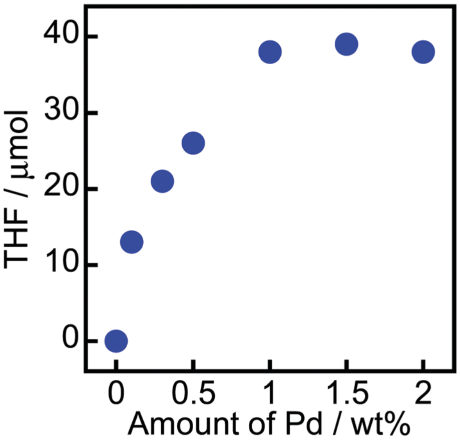

Fig. 3 Effects of amounts of Pd loading on TiO_2 in photocatalytic hydrogenation of furan (40 ± 4 μmol) in methanolic suspensions for 5 min under irradiation of UV light from a high-pressure mercury lamp.

Fig. 3 shows effects of the Pd loadings on the yield of THF formed by photocatalytic hydrogenation of furan in methanolic suspensions after 5 min photoirradiation from a high-pressure mercury lamp. The yield of THF increased with an increase in the amount of Pd up to 1.0 wt% probably because the number of reduction sites for hydrogenation of furan increased with an increase in the Pd content. However, the yield was saturated over 1.0 wt%. There are some possible reasons for the saturation: (1) dispersion of Pd on the TiO_2 surface was saturated, (2) the rate-determining step changed from the reduction process to the oxidation process, and (3) the overall reaction was limited by photon flux.

TEM photographs of bare TiO_2 (MT-150A) and 1.0 wt% Pd-TiO_2 and the distribution of Pd particles in 1.0 wt% Pd-TiO_2 are shown in Fig. 4a–c, respectively. Fine Pd particles can be seen in the TEM photograph (Fig. 4b), and the average diameter was determined to be 3.4 nm, indicating that Pd nanoparticles were deposited on the TiO_2 surface using the photodeposition method. The amount of THF (40 μmol) after photoirradiation for 5 min was larger than the amount of Pd (4.7 μmol) loaded on TiO_2, indicating that Pd metal works as a catalyst for the hydrogenation of furan.

3.2. Effects of reaction conditions on photocatalytic hydrogenation of furan

The effects of various reaction conditions on photocatalytic hydrogenation of furan to THF were investigated, and the results are summarized in Table 1. First, the effects of different kinds of commercial TiO_2 were examined (entries 1–7). In addition to MT-150A TiO_2, six samples were selected from Japan Reference Catalysts (JRC-TIO series) registered at the Catalysis Society of Japan. Rutile TiO_2 (R, entries 6 and 7) showed THF yields higher than those by anatase TiO_2 (A, entries 1–3) and those of TiO_2 consisting of two phases (A/R, entries 4 and 5). In the case of

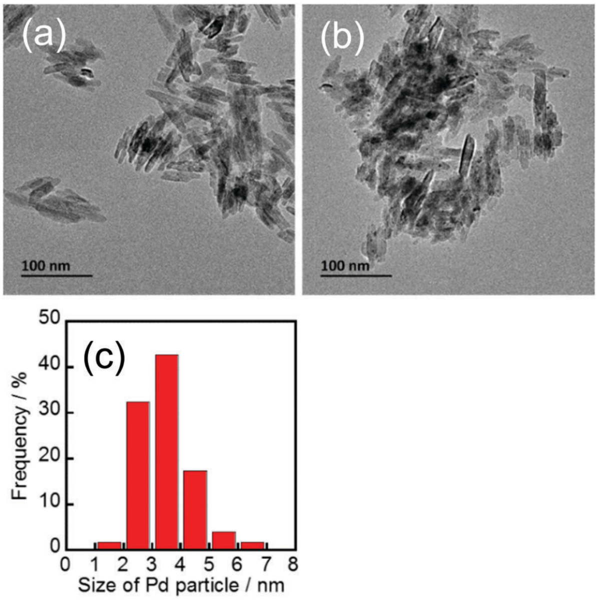

Fig. 4 TEM photographs of (a) TiO_2 (MT-150A) and (b) 1.0 wt% Pd-TiO_2, and (c) distribution of Pd particles in 1.0wt% Pd-TiO_2.

photocatalytic hydrogenation of nitro compounds, rutile phase TiO_2 was active, though the reason is not clear.[20,35] An increase in Pd loading up to 1.0 wt% resulted in an increase in THF yield (entry 8) as has already been shown in Fig. 3. Prolonging the reaction time increased the yield as expected (entry 9). To examine the durability of the Pd-TiO_2 photocatalyst in this reaction system, Pd-TiO_2 was used repeatedly. After reaction for 10 min (entry 9), Pd-TiO_2 particles were recovered by simple filtration from the reaction mixture and were re-used. Entries 10 and 11 show that Pd-TiO_2 photocatalysts were reusable at least twice without notable loss of activity. Entries 12–14 show the results of three blank reactions: (1) in the absence of Pd-TiO_2 in the dark (non-catalytic thermal reaction between furan and methanol, entry 12), (2) in the absence of Pd-TiO_2 with irradiation of light (photochemical reaction, entry 13), and (3) in the presence of Pd-TiO_2 in the dark (thermo-catalytic reaction over Pd-TiO_2, entry 14). These results indicate that the Pd-TiO_2 photocatalyst and photoirradiation were indispensable for the hydrogenation of furan. In the dark at 298 K, THF was formed in the presence of Pd-TiO_2 and H_2 (1 atm) (entry 15), indicating that H_2 was used for hydrogenation of furan over Pd-TiO_2. In other words, Pd particles loaded on TiO_2 showed thermo-catalytic activity for hydrogenation of furan as discussed earlier. When the amount of H_2 added in the reactor was reduced to 50 μmol, THF was not formed in the dark at 298 K (entry 16). Results of the dark reactions under H_2 (entries 15 and 16) mean that a large excess of H_2 is necessary to obtain a sufficient rate of THF production at 298 K.

Dark reactions over metal-free TiO_2 and TiO_2 modified with other metal co-catalysts under H_2 (1 atm) were negligible (entries 17–21). To examine the effects of different kinds of alcohol, ethanol, 2-propanol, 2-butanol, 2-pentanol and glycerol were chosen (entries 22–26). Ethanol and glycerol have attracted much attention as typical biomasses and by-products in biomass utilization

Table 1 Effects of various reaction conditions on photocatalytic production of THF from furan in alcoholic suspensions of Pd-TiO_2 at 298 K[a]

Entries	TiO_2[b]	Phase[c]	S_{BET}[d]/$m^2\ g^{-1}$	Pd/wt%	Alcohol	UV	Time/min	Gas phase	Yield/mmol
1	JRC-TIO-1	A	72	0.5	MeOH	On	5	Ar	17
2	JRC-TIO-8	A	313	0.5	MeOH	On	5	Ar	16
3	JRC-TIO-13	A	59	0.5	MeOH	On	5	Ar	18
4	JRC-TIO-4	A, (R)	54	0.5	MeOH	On	5	Ar	9
5	JRC-TIO-11	A, (R)	97	0.5	MeOH	On	5	Ar	20
6	JRC-TIO-3	R	48	0.5	MeOH	On	5	Ar	21
7	MT-150A	R	93	0.5	MeOH	On	5	Ar	26
8	MT-150A	R	93	1.0	MeOH	On	5	Ar	38
9	MT-150A	R	93	1.0	MeOH	On	10	Ar	40
10[e]	MT-150A	R	93	1.0	MeOH	On	5	Ar	33
11[f]	MT-150A	R	93	1.0	MeOH	On	5	Ar	36
12	—	—	—	—	MeOH	(Dark)	10	Ar	—
13	—	—	—	—	MeOH	On	5	Ar	—
14	MT-150A	R	93	1.0	MeOH	(Dark)	5	Ar	—
15	MT-150A	R	93	1.0	MeOH	(Dark)	5	H_2	39
16	MT-150A	R	93	1.0	MeOH	(Dark)	5	H_2[g]/Ar	—
17	MT-150A	R	93	—	MeOH	(Dark)	5	H_2	—
18	MT-150A	R	93	1.0 (Au)	MeOH	(Dark)	5	H_2	—
19	MT-150A	R	93	1.0 (Ag)	MeOH	(Dark)	5	H_2	—
20	MT-150A	R	93	1.0 (Cu)	MeOH	(Dark)	5	H_2	—
21	MT-150A	R	93	1.0 (Pt)	MeOH	(Dark)	5	H_2	0.6
22	MT-150A	R	93	1.0	EtOH	On	10	Ar	19
23	MT-150A	R	93	1.0	2-PrOH	On	10	Ar	22
24	MT-150A	R	93	1.0	2-BuOH	On	10	Ar	29
25	MT-150A	R	93	1.0	2-PnOH	On	10	Ar	13[h]
26	MT-150A	R	93	1.0	Glycerol	On	10	Ar	35

[a] Alcohol solution (5 cm^3) of furan (40 ± 4 μmol) and 50 mg of the photocatalyst under irradiation of UV light from a high-pressure mercury lamp. [b] JRC-TIO series registered at the Catalysis Society of Japan as Japan Reference Catalysts. MT-150A was supplied from Tayca. [c] A: Anatase, R: Rutile, minor form in bi-phase samples is shown in parentheses. [d] Determined using the BET method. [e] Second use. [f] Third use. [g] H_2: 50 μmol. [h] H_2 formed: 6 μmol, 2-pentanone formed: 33 μmol.

(saponification and transesterification of fats and oils). When these alcohols were used, THF was formed, indicating that various alcohols can be used as solvents and electron sources for hydrogenation of furan. The results for ethanol and glycerol indicate another important possibility of two alcohols: biomass alcohols can be used as hydrogen sources without another H_2-producing process for upgrading of another biomass (hydrogenation of furan to THF in this study). In the reaction in 2-pentanol, the oxidation product was analyzed as well as THF and H_2 (entry 25). 2-Pentanone was formed and the redox balance (RB) was calculated to be 0.97 from eqn (1):

$$\mathrm{RB} = \frac{2 \times n(\mathrm{THF}) + n(\mathrm{H_2})}{n(\text{2-pentanone})} \tag{1}$$

where n(THF), $n(H_2)$ and n(2-pentanone) are the amounts of THF, H_2 and 2-pentanone formed. The value indicates that photogenerated electrons and positive holes were equally used in the photocatalytic reaction.

3.3. Photocatalytic hydrogenation of furan

Fig. 5 shows time courses of furan remaining and THF and H_2 formed in a methanolic suspension of 1.0 wt% Pd-TiO_2 (MT-150A) under deaerated conditions. The amount of furan decreased almost linearly with photoirradiation, while THF as the hydrogenation product of furan was formed with a decrease in the amount of furan. After 25 min, furan was almost completely consumed and THF was obtained in a high yield (97%). To evaluate the selectivity of THF and intermediates in the furan hydrogenation, an indicator, *i.e.*, material balance (MB), was calculated by eqn (2):

$$\mathrm{MB} = \frac{n(\mathrm{furan}) + n(\mathrm{THF})}{n_0(\mathrm{furan})} \tag{2}$$

where n(furan) and n(THF) are the amounts of furan and THF during the photocatalytic reaction, respectively, and n_0(furan) is the amount of furan before the photocatalytic reaction. In the initial stage of the reaction, the value of MB was *ca.* 0.9. We examined furan adsorption on TiO_2 and metal-loaded TiO_2 in the dark (Fig. S1, ESI†). The results indicated that furan was adsorbed on both TiO_2 and some metals (Pd, Pt and Au) and Pd-TiO_2 showed the highest amount of adsorption. The value of MB in the early stage can be attributed to the adsorption of furan on Pd-TiO_2. Formation of an intermediate(s) may also be one of the reasons for the value of MB. Since species other than furan and THF were not detected in GC, we cannot discuss the possibility of adsorption of an intermediate(s). As also shown in Fig. 5, H_2 evolution was predominant under excessive photoirradiation after consumption of furan, indicating that active hydrogen species were continuously formed over the Pd co-catalyst. We noted that the amount of THF slightly decreased after complete consumption of furan. Since a large excess of methanol used as a solvent effectively consumes positive holes, the possibility of THF re-oxidation can be eliminated. The results after consumption of furan suggest the occurrence of a reductive process of THF in which a part of the active hydrogen species was probably used for catalytic hydrogenolysis of THF, resulting in consumption of THF. Mizugaki *et al.* reported the formation of butanol in the ring opening reaction of furfural that has a furan ring.[36] Since butanol was not detected in GC, butanol was probably adsorbed on Pd-TiO_2. The high yield of THF at 25 min indicates that the activation energy of catalytic hydrogenolysis of THF over Pd is larger than that of catalytic hydrogenation of furan. Therefore, furan hydrogenation predominantly occurred at 298 K when furan was present in the reaction system.

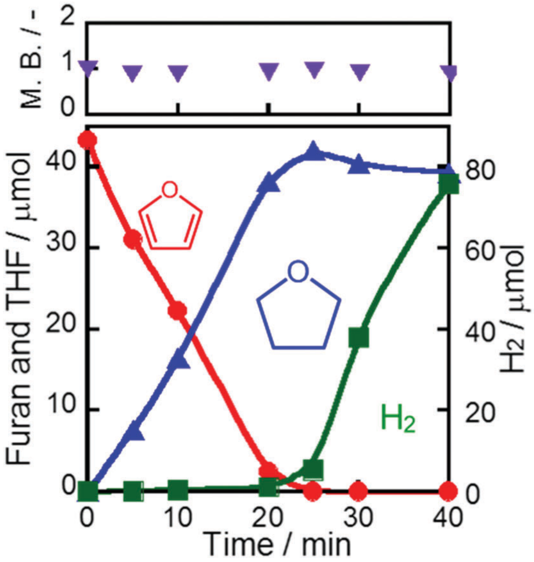

Fig. 5 Time courses of furan remaining, THF formed and material balance of furan and THF in a methanolic suspension of 1.0 wt% Pd-TiO_2 under irradiation of UV light from an LED.

3.4. Action spectrum and the reaction process

An action spectrum is a strong tool for determining whether a photoinduced process is the rate-determining step in the reaction observed. To obtain an action spectrum in this reaction system, hydrogenation of furan in methanolic suspensions of 1.0 wt% Pd-TiO_2 (MT-150A) was carried out at 298 K under irradiation of monochromated light from a Xe lamp. Apparent quantum efficiency (AQE) at each centered wavelength of light was calculated from the ratio of quadruple the amount of THF formed and the amount of photons irradiated using eqn (3):

$$\mathrm{AQE} = \frac{4 \times \text{the amount of THF formed}}{\text{amount of incident photons}} \times 100 \tag{3}$$

As shown in Fig. 6, AQE was in agreement with the absorption spectrum of TiO_2. Therefore, it can be concluded that hydrogenation of furan in a methanolic suspension was induced by photoabsorption of TiO_2. As also shown in Fig. 6, AQE reached 37% at 360 nm, indicating that photocatalytic hydrogenation of furan to THF occurred with a high efficiency of photon utilization in addition to high selectivity and MB close to unity. This result indicates that photoabsorption at 410 nm does not contribute to the reaction, in other words, this photoabsorption does not induce the band-gap excitation of TiO_2. Electrons in the trap site below the bottom of the conduction band of TiO_2 have no potential to reduce protons to H_2.

The expected reaction process of photocatalytic hydrogenation of furan to THF over Pd-TiO_2 is shown in Fig. 7: (1) by

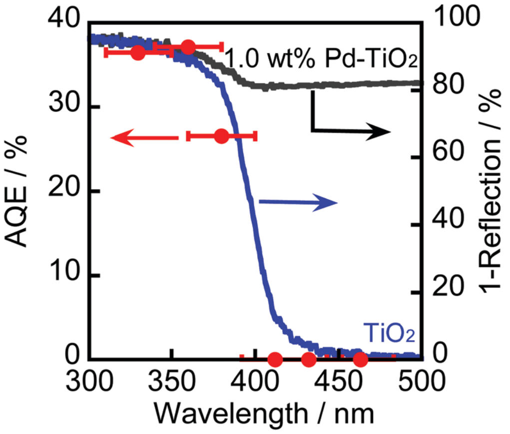

Fig. 6 Absorption spectrum (right axis) and the action spectrum of TiO_2 and 1.0 wt% Pd-TiO_2 in the hydrogenation of furan (left axis).

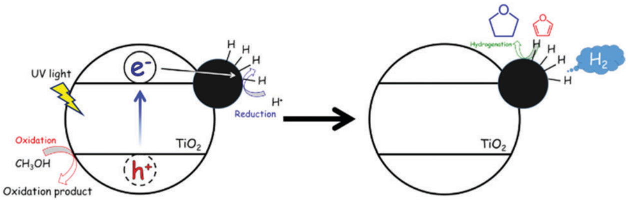

Fig. 7 Expected reaction process of photocatalytic hydrogenation of furan to THF over Pd-TiO_2.

irradiation of UV light, photogenerated electrons (e^-) and positive holes (h^+) are formed in the conduction and valence bands of TiO_2, and methanol is oxidized by h^+, (2) H^+ is reduced by e^-, resulting in the formation of active hydrogen species over Pd particles and (3) two C=C double bonds of furan are successively hydrogenated by the active hydrogen species over Pd particles, resulting in the formation of THF. Higher adsorption ability of Pd is one of the most important reasons for the large yield of THF in the photocatalytic hydrogenation of furan. Since THF was formed in the presence of H_2 in the dark at 298 K, the active hydrogen species would be essentially the same as those formed in the photocatalytic process. Active hydrogen species also induce other reactions, *i.e.*, H_2 evolution by self-coupling and hydrogenolysis of THF; however, these reactions are negligible as long as furan to be reacted with active hydrogen species is present in the reaction system. The negligible production of H_2 in the photocatalytic hydrogenation of furan means that the active species formed on Pd are very active for hydrogenation of furan, and the equilibrium between the active species formed on Pd and H_2 in the gas phase greatly shifts toward the left side (formation of the active species).

4. Conclusions

We examined the photocatalytic hydrogenation of furan, a representative heterocyclic compound and a compound derived from biomass, in an alcoholic suspension of metal-loaded TiO_2 under a H_2-free condition, in which alcohol worked as a solvent, electron donor and hydrogen source. Among the metal-loaded TiO_2 samples examined in this study, Pd-loaded TiO_2 (Pd-TiO_2) showed a distinctive photocatalytic activity for the largest production of THF and suppressed evolution of H_2, with apparent quantum efficiency reaching 37% at 360 nm. Hydrogenation of furan to THF under the present condition consisted of two processes: (1) photocatalytic production of active hydrogen species and (2) thermocatalytic hydrogenation of furan over Pd particles. Biomass-related alcohols (ethanol, butanol and glycerol) can also be used for hydrogenation of furan. The results obtained in this study show that photocatalytic hydrogenation is not limited to hydrocarbons and can be applied to heterocyclic compounds.

Conflict of interest

There are no conflicts to declare.

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