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Visible light-induced diastereoselective semihydrogenation of alkynes to *cis*-alkenes over an organically modified titanium(IV) oxide photocatalyst having a metal co-catalyst

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ABSTRACT

Hydrogen (H_2)-free and poison (lead and quinoline)-free semihydrogenation of alkynes to *cis*-alkenes under gentle conditions is one of the challenges to be solved. In this study, a titanium(IV) oxide photocatalyst having two functions (visible light responsiveness and semihydrogenation activity) was prepared by modification with 2,3-dihydroxynaphthalene (DHN) and a copper (Cu) co-catalyst, respectively. The photocatalyst (DHN/TiO_2-Cu) showed high performance for diastereoselective semihydrogenation of alkynes to *cis*-alkenes in water-acetonitrile solution under visible light irradiation without the use of H_2 and poisons. Alkynes having reducible functional groups were converted to the corresponding alkenes with the functional groups being preserved. The addition of water to acetonitrile changed the amount of alkynes adsorbed on the photocatalyst, which was a decisive factor determining the rate of hydrogenation. A relatively large apparent activation energy, 27 kJ mol^{-1}, was obtained by a kinetic study, indicating that the rate-determining step of this reaction was not an electron production process but a thermal catalytic semihydrogenation process over the Cu co-catalyst. Semihydrogenation and hydrogen evolution occurred competitively on Cu metals and the former became predominant at slightly elevated temperatures, which is discussed on the basis of the kinetic parameters of two reactions.

1. Introduction

Hydrogenation of alkynes is one of the important reactions in the chemical industry. Semihydrogenation of alkynes to alkenes has been applied to syntheses of *cis*-alkenes, which are important building blocks for fine chemicals such as bioactive molecules, flavors and natural products [1,2]. The Lindlar catalyst consisting of palladium-loaded calcium carbonate (Pd/$CaCO_3$) treated by the addition of lead acetate ($Pb(OCOCH_3)_2$) and quinoline has been widely used for the semihydrogenation of alkynes [3,4]. The Lindlar catalyst shows high performance for semihydrogenation of internal alkynes to alkenes, whereas terminal alkynes are unfortunately completely hydrogenated to alkanes because of the high activity of a Pd catalyst. In addition, this catalyst has serious weak points including the requirements of undesirable additives such as a toxic Pb salt and a large amount of quinoline to suppress over-hydrogenation of alkenes. To avoid the use of undesirable additives, a number of alternative Pb-free catalytic semihydrogenations using metal catalysts such as copper (Cu) [5,6], Pd [7,8], ruthenium [9] and gold [10–12] have been reported. However, these catalytic systems require harsh reaction conditions such as high pressure of dihydrogen (H_2) and high temperature in a closed reactor. Therefore, milder catalytic reaction systems for semihydrogenation of alkynes are favored.

Aiming at the syntheses of organic compounds under mild reaction conditions, we have focused on the application of photocatalytic reactions over a semiconductor such as titanium(IV) oxide (TiO_2) to conversion of organic compounds. When TiO_2 powder is irradiated by UV light, charge separation occurs and thus-formed electrons in the conduction band (CB) and positive holes in the valence band (VB) cause reduction and oxidation, respectively. Since these photocatalytic reactions are driven by sunlight as the energy source at room temperature and under atmospheric pressure, in addition to mineralization of volatile organic compounds and water splitting, photocatalytic conversion of organic compounds has attracted much attention as the third application of TiO_2. Since irradiation of light is indispensable for a photocatalytic reaction, the reaction can be easily controlled by the intensity of light and finally can be stopped by turning the light source off. Furthermore, by simple filtration or centrifugation, a TiO_2 photocatalyst is easily separated from the reaction mixture after the

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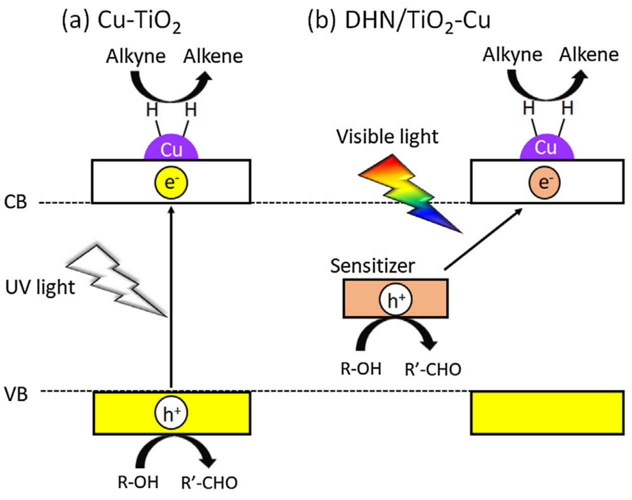
reaction and reused. The above-mentioned characteristics of photocatalysis satisfy almost all of the 12 proposed requirements for green chemistry [13]. We have found that a TiO_2 photocatalyst exhibited high performance for various conversions of organic compounds under irradiation of UV light. For example, a TiO_2 photocatalyst chemoselectively reduced nitrobenzenes [14] and benzaldehydes [15] having other functional groups such as a chlorine group to corresponding aminobenzenes and benzyl alcohols. We also showed that the combination of photocatalysis of TiO_2 and thermocatalysis of Pd nanoparticles drove difficult reductions, i.e., a TiO_2 photocatalyst having a Pd co-catalyst (Pd-TiO_2) successfully hydrogenated benzonitrile [16], styrene [17] and furan [18] to corresponding hydrogenation products. In other words, photogenerated electrons reduced protons to active hydrogen species (AHS) on the surface of Pd nanoparticles and formed AHS thermocatalytically hydrogenated target organic compounds. However, a Pd-TiO_2 photocatalyst is not suitable for semihydrogenation of alkynes to alkenes since it exhibits high performance in photocatalytic hydrogenation of unsaturated bonds such as vinyl and nitrile groups due to the strong catalytic activity of Pd. Recently, we developed an additive (Pb and quinoline)-free photocatalytic system for selective semihydrogenation of various alkynes to corresponding alkenes in an alcoholic suspension of a copper-loaded TiO_2 (Cu-TiO_2) photocatalyst (Scheme 1(a)) [19,20].

The next strategy for photocatalytic conversion of organic compounds is efficient utilization of visible light since sunlight consists of 5% UV light, 50% visible light and 45% infrared light at the surface of the earth. Of course, no hydrogenation of alkynes occurs over a Cu-TiO_2 photocatalyst under irradiation of visible light because a TiO_2 photocatalyst shows no absorption in the region of visible light. Recently, we found that a 2,3-dihydroxynaphthalene-modified TiO_2 (DHN/TiO_2) photocatalyst exhibited an activity for chemoselective reduction of benzaldehyde having other functional groups to corresponding benzyl alcohols under irradiation of visible light [21], following the reduction of nitrobenzene over DHN/TiO_2 reported by Kamegawa et al. [22]. We chose DHN among various photosensitizers for TiO_2 because DHN is obtained easily and modification of TiO_2 with DHN is very easy without any special care. Therefore, the strategy for the design of a visible light-induced photocatalytic system for semihydrogenation of alkynes to alkenes is simple as shown in Scheme 1(b): (1) charge transfer from DHN to the CB of TiO_2 under visible light irradiation and (2) utilization of photogenerated electrons in the CB for production of AHS from H^+ and semihydrogenation of alkynes to alkenes with high selectivity.



Scheme 1. Semihydrogenation of alkyne to alkene over photocatalysts charge-separated by different systems: (a) band-gap excitation of TiO_2 and (b) charge transfer from a sensitizer to the conduction band of TiO_2.

Based on the above-described background, visible light-induced semihydrogenation of alkynes to *cis*-alkenes over DHN/TiO_2 having a Cu co-catalyst (DHN/TiO_2-Cu) without the use of toxic Pb at room temperature and under atmospheric pressure was investigated in this study. Here, we report (1) semihydrogenation of 1-phenyl-1-propyne (PP) over a DHN/TiO_2-Cu photocatalyst under irradiation of visible light, (2) expandability of DHN/TiO_2-Cu for semihydrogenation of various alkynes to corresponding alkenes, (3) the effect of water content of acetonitrile solutions on semihydrogenation and adsorption of PP and (4) the effect of reaction temperature on semihydrogenation of PP.

2. Experimental

2.1. Preparation of DHN/TiO_2-Cu by impregnation and photodeposition

TiO_2 (ST-01, 330 $m^2\ g^{-1}$, Ishihara, Osaka) powder was suspended in a methanol solution containing DHN (0.7 wt%) in an evaporating dish, and methanol was vapored over a water bath at 313 K until the powder dried, and DHN/TiO_2 was obtained. Then Cu (1.0 wt%) was loaded on DHN/TiO_2 using the photodeposition method. DHN/TiO_2 was suspended in 10 cm^3 of water-methanol (1:9) solution containing copper chloride ($CuCl_2$) in a test tube. The test tube was sealed with a rubber septum under argon (Ar) and then photoirradiated for 1 h 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 vaccuo*.

2.2. Characterization

Diffuse reflectance spectra of the samples were obtained with a UV–vis spectrometer (UV-2400, Shimadzu, Kyoto) equipped with a diffuse reflectance measurement unit (ISR-2000, Shimadzu) in which barium sulfate ($BaSO_4$) was used as a reference. Fourier transform infrared (FT-IR) spectra of TiO_2, DHN/TiO_2 and DHN/TiO_2-Cu were measured on an FT-IR spectrometer (FT-IR8300, Shimadzu) in which a potassium bromide (KBr) pellet method was used. X-ray photoelectron spectroscopy (XPS) spectra of TiO_2, DHN/TiO_2 and DHN/TiO_2-Cu were measured using a Shimadzu AXIS-NOVA ESCA in the Joint Research Center of Kindai University. Powder X-ray diffraction (XRD) was measured using CuKα radiation by a Rigaku MultiFlex equipped with a carbon monochromator. Morphology of sample was observed under a high-resolution transmission electron microscope (JEM-2100F, JEOL, Tokyo) operated at 200 kV in the Joint Research Center of Kindai University.

2.3. Photocatalytic hydrogenation of alkynes in an aqueous acetonitrile suspension of DHN/TiO_2-Cu under visible light irradiation

In a typical run, prepared DHN/TiO_2-Cu (50 mg) was suspended in water-acetonitrile (1:9) solution (5 cm^3) containing alkyne (*ca.* 50 μmol) and triethanolamine (TEOA, 150 μmol) as a sacrificial reagent in a test tube, and the test tube was sealed with a rubber septum under argon and then photoirradiated with visible light of the two blue LEDs (420–530 nm, 29.0 and 56.8 mW cm^{-2}, Hayashi Watch Works, Tokyo) from two directions with magnetic stirring at 329 K. The emission spectra of light from two blue LEDs are shown in Fig. S1. The amount of H_2 was measured with an FID-type gas chromatograph (GC-8A, Shimadzu, Kyoto) equipped with an MS-5A column. After the suspension had been filtered to remove the catalyst, the amounts of PP unreacted and hydrogenation products (*cis*-alkene, *trans*-alkene and alkane) formed in the liquid phase were determined with an FID-type gas chromatograph (GC-2025, Shimadzu) equipped with a DB-1 column. Toluene was used as an internal standard substance. Toluene (5 mm^3), water (1 cm^3) and diethyl ether (3 cm^3) were added to the reaction solution (2 cm^3). After the mixture had been stirred for 10 min, the diethyl ether phase of the reaction solution was analyzed. The amounts of alkyne, alkene and alkane were determined from the ratios of the peak areas of these products to the peak area of toluene.

2.4. Adsorption experiment of PP on DHN/TiO_2-Cu in the dark

A DHN/TiO_2-Cu sample (300 mg) was suspended in 5 cm^3 of water-acetonitrile solution containing TEOA (150 μmol) in a test tube, and the test tube was sealed with a rubber septum under argon. To reduce partially oxidized Cu on the surface to the metal, the suspension was photoirradiated with visible light of the same blue LEDs with magnetic stirring at 298 K for 1 h. After water-acetonitrile solution (0.1 cm^3) containing PP (50 μmol) had been injected into the test tube, the test tube was magnetically stirred in a water bath continuously kept at 298 K for 20 h in the dark. After the suspension had been filtered to remove particles, the amount of PP in the liquid phase was determined with an FID-type gas chromatograph (GC-2025) equipped with a DB-1 column. Toluene (5 mm^3), water (1 cm^3) and diethyl ether (3 cm^3) were added to the reaction solution (2 cm^3). After the mixture had been stirred for 10 min, the diethyl ether phase of the reaction solution was analyzed. The amount of PP was determined from the ratio of the peak area of PP to the peak area of toluene.

3. Results and discussion

3.1. Characterization

Fig. S2 shows the FT-IR spectra of unmodified TiO_2, DHN/TiO_2 and DHN/TiO_2-Cu. A band attributable to DHN fixed on the surface of TiO_2 [23] was observed at 1284 cm^{-1} for the DHN modified samples. Fig. S3 shows the Cu 2p XPS spectra of unmodified TiO_2, DHN/TiO_2 and DHN/TiO_2-Cu. Peaks assignable to Cu $2p_{3/2}$ and Cu $2p_{1/2}$ [24] were observed at 954.9 and 934.5 eV. These results indicate that DHN and Cu are loaded on the surface of TiO_2 in DHN/TiO_2-Cu. Fig. S4 shows XRD patterns of unmodified TiO_2, DHN/TiO_2 and DHN/TiO_2-Cu. Peaks attributable to the anatase phase were observed in all samples, while other peaks were not observed, indicating that Cu particles were highly dispersed on the surface of TiO_2 having a large specific surface area of 330 $m^2\,g^{-1}$. Fig. S5 shows a TEM photograph of DHN/TiO_2-Cu. TEM observation revealed that fine Cu particles were loaded on TiO_2, which was in agreement with the result of XRD analysis.

3.2. Photocatalytic hydrogenation of PP in a water-acetonitrile (1:9) suspension of DHN/TiO_2-Cu

Fig. 1 shows the time courses of photocatalytic hydrogenation of PP in a water-acetonitrile (1:9) suspension of DHN/TiO_2-Cu with irradiation of light from a blue LED under deaerated conditions with magnetic stirring in a water bath continuously kept at 329 K. The amount of PP monotonically decreased with photoirradiation, while *cis*-1-phenyl-1-propene (*cis*-β-methylstyrene, *cis*-MS) was formed in an amount corresponding to consumption of the amount of PP. When PP had been completely consumed after 4-h photoirradiation, *cis*-MS was obtained in a high yield (>99%). During the blue light irradiation and even after consumption of PP, there was no formation of *trans*-1-phenyl-1-propene (*trans*-β-methylstyrene, *trans*-MS) or propylbenzene (PB) as a result of isomerization or sequential hydrogenation of *cis*-MS. These results indicate that semihydrogenation of PP over DHN/TiO_2-Cu proceeded with high diastereoselectivity. In order to reveal the selectivity for the target compound, an indicator, i.e., material balance (MB) calculated by using Equation (1) is also shown in Fig. 1.

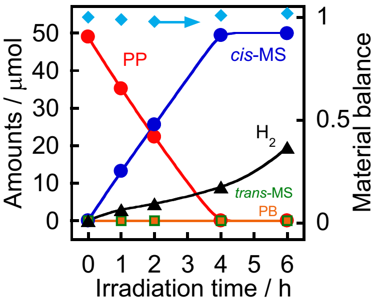


Fig. 1. Time courses of amounts of PP, *cis*-MS, *trans*-MS, PB and H_2 in photocatalytic hydrogenation of PP in a water-acetonitrile (1:9) suspension of DHN/TiO_2-Cu under visible light irradiation with magnetic stirring in a water bath continuously kept at 329 K.

$$\mathrm{MB} = \frac{\mathrm{n(PP)} + \mathrm{n(cis-MS)} + \mathrm{n(trans-MS)} + \mathrm{n(PB)}}{\mathrm{n_0(PP)}} \tag{1}$$

where n(PP), n(*cis*-MS), n(*trans*-MS) and n(PB) are the amounts of PP, *cis*-MS, *trans*-MS and PB during the photocatalytic reaction, respectively, and n_0(PP) is the amount of PP before the photocatalytic reaction. The values of MB close to unity before and after the complete consumption of PP indicate that only hydrogenation of an alkynyl group to an alkenyl group occurred. As also shown in Fig. 1, in addition to semihydrogenation of PP, AHS over Cu were coupled, resulting in H_2 evolution. This means that semihydrogenation and H_2 evolution are competitive reactions in utilization of photogenerated electrons.

The effects of various reaction conditions on the photocatalytic semihydrogenation of PP to *cis*-MS were investigated, and the results are summarized in Table 1. Photoirradiation for 4 h produced *cis*-MS almost quantitatively as shown in Fig. 1 (Entry 1). Entries 2–5 show the results of four blank reactions: (1) dark reaction (thermal catalytic reaction) over DHN/TiO_2-Cu (Entry 2), (2) photocatalytic reaction over DHN/TiO_2 (effect of a Cu co-catalyst, Entry 3), (3) photocatalytic reaction over Cu-TiO_2 (effect of DHN as a photoabsorption site, Entry 4) and (4) in the absence of DHN/TiO_2-Cu with irradiation of blue light (photochemical reaction, Entry 5). The results indicate that TiO_2, DHN, Cu co-catalyst and photoirradiation are indispensable for the semihydrogenation of PP under visible light irradiation. We also carried out thermal catalytic hydrogenation of PP over DHN/TiO_2-Cu under an H_2 atmosphere (1 atm) at various temperatures (Entries 6–9). Even at 323 K after 6 h, no *cis*-MS was formed, indicating that no PP was hydrogenated by AHS formed from H_2 over a Cu co-catalyst under these conditions and that more severe conditions are required for activation of H_2 to thermocatalytically hydrogenate PP over Cu [5,6].

It is important to confirm that an observed reaction was driven by photocatalysis. An action spectrum obtained by using monochromatic light is useful tool for determining whether an observed reaction occurs by a photoinduced or a thermal catalytic process. To obtain an action spectrum in this reaction system, hydrogenation of PP in a water-acetonitrile (1:9) suspension of DHN/TiO_2-Cu was carried out at 298 K under irradiation of monochromatic visible light from a Xe lamp with a light width of ±15 nm using a multi-wavelength irradiation monochromator

Table 1
Effects of various reaction conditions on photocatalytic production of *cis*-MS from PP in a water-acetonitrile (1:9) suspension of DHN/TiO_2-Cu.

Entry	Catalyst	Blue light	Gas phase	Temperature/K	Time/h	PP conv. /%	*cis*-MS yield /%
1	DHN/TiO_2-Cu	On	Ar	329	4	>99	>99
2	DHN/TiO_2-Cu	(Dark)	Ar	329	4	–	–
3	DHN/TiO_2	On	Ar	329	4	–	–
4	Cu-TiO_2	On	Ar	329	4	–	–
5	–	On	Ar	329	4	–	–
6	DHN/TiO_2-Cu	(Dark)	H_2	298	6	–	–
7	DHN/TiO_2-Cu	(Dark)	H_2	303	6	–	–
8	DHN/TiO_2-Cu	(Dark)	H_2	313	6	–	–
9	DHN/TiO_2-Cu	(Dark)	H_2	323	6	–	–

(MM-3PK, Bunkoukeiki, Tokyo). The light intensity determined with a spectroradiometer (USR-45D, Ushio, Tokyo) and the time course of the amount of *cis*-MS formed under irradiation of monochromatic light are shown in Fig. 2(a) and (b), respectively. *cis*-MS was formed linearly along with irradiation of light having wavelengths of 416, 437, 469, 492 and 521 nm, whereas no formation of *cis*-MS was observed under irradiation of light having wavelengths of 542 and 572 nm. These results indicate that DHN/TiO_2-Cu was induced by visible light having $\lambda < 521$ nm. The apparent quantum efficiency (AQE) at each centered wavelength of light was calculated from the ratio of the amount of *cis*-MS and the amount of incident photons by using Eq. (2).

$$AQE = \frac{2 \times the\ amount\ of\ cis-MS\ formed}{the\ amount\ of\ incident\ photons} \times 100 \tag{2}$$

The results are shown in Fig. 2(c). Values of AQE measured at 416, 437, 469, 492 and 521 nm were determined to be 2.3%, 1.4%, 0.52%, 0.32% and 0.11%, respectively. Wavelength-dependency of AQE was similar to the photoabsorption of DHN/TiO_2-Cu (Fig. 2 (d)), indicating that hydrogenation of PP in a water-acetonitrile (1:9) suspension was induced by visible-light absorption of DHN/TiO_2-Cu.

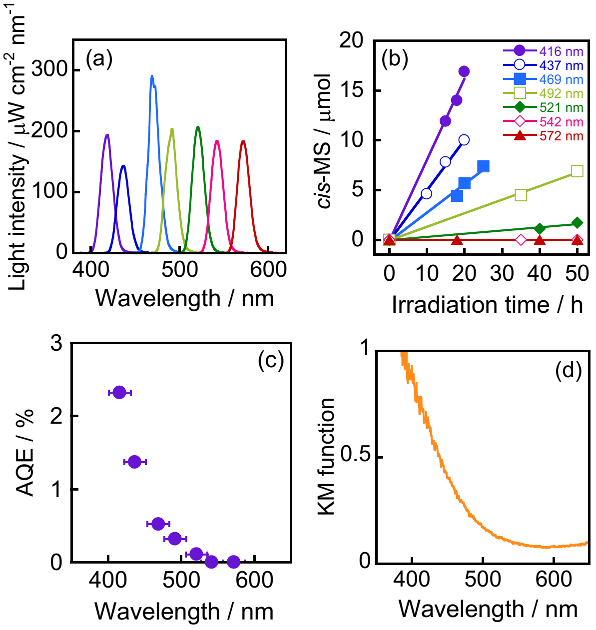


Fig. 2. (a) Light intensity of visible light from a multi-wavelength irradiation monochromator (MM-3PK, Bunkoukeiki Co., Ltd), (b) time course of the amount of *cis*-MS formed in a water-acetonitrile (1:9) suspension of DHN/TiO_2-Cu under irradiation of each monochromatic light, (c) action spectrum in the hydrogenation of PP (*ca.* 50 µmol) to *cis*-MS over DHN/TiO_2-Cu and (d) absorption spectrum of DHN/TiO_2-Cu.

A durability test of a (photo)catalyst is very important for its practical applications of (photo)catalyst. To evaluate the durability of DHN/TiO_2-Cu, after photocatalytic hydrogenation of PP to *cis*-MS, DHN/TiO_2-Cu was recovered from the reaction mixture by simple filtration and washed with distilled water and used repeatedly for the same reaction. Conversion and selectivity were maintained at *ca.* 100% in the second, third and fourth reactions (Fig. 3(a)), and light absorption spectra of DHN/TiO_2-Cu after the repeated reactions were almost the same as the spectrum before the reaction (Fig. 3(b)). These results indicate that DHN/TiO_2-Cu worked as a reusable photocatalyst at least 4 times without losing its activity and diastereoselectivity.

In addition, to evaluate the possibility of practical use of diastereoselective semihydrogenation of alkynes to *cis*-alkenes under visible light irradiation, we carried out photocatalytic hydrogenation of a large amount of PP (550 µmol) with the volume of the reaction mixture being unchanged (5 cm^3). The results are shown in Fig. S6. After photoirradiation for 80 h, PP was almost quantitatively hydrogenated to *cis*-MS over the DHN/TiO_2-Cu photocatalyst even in the presence of a large amount of PP. Under this condition, the turnover numbers (TON) of *cis*-MS formation based on the amounts of DHN (0.7 wt%, 2.2 µmol) and Cu (1.0 wt%, 7.9 µmol) after 80-h photoirradiation were calculated to be 250 and 70, respectively. These values indicate that DHN/TiO_2-Cu works as a catalytic material for semihydrogenation of alkynes to *cis*-alkenes.

3.3. Effect of water content in an acetonitrile suspension of DHN/TiO_2-Cu on photocatalytic hydrogenation of PP

In a catalytic reaction, a reaction solvent, not appearing in the chemical reaction formula, often affects the reaction rate, product selectivity, adsorption of the substrate and product and so on. Previously, we reported that various types of solvents such as water, methanol and acetonitrile have positive and negative effects on

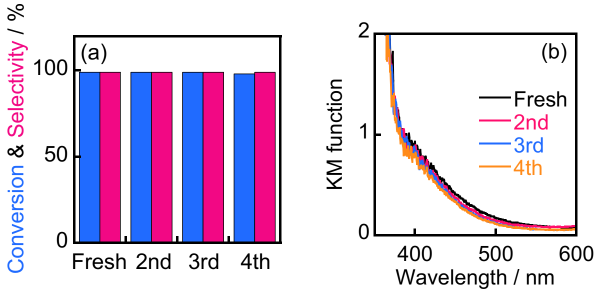


Fig. 3. (a) Durability test of DHN/TiO_2-Cu in photocatalytic hydrogenation of PP to *cis*-MS in a water-acetonitrile (1:9) suspension of DHN/TiO_2-Cu for 6-h photoirradiation of visible light and (b) light absorption spectra of DHN/TiO_2-Cu before and after hydrogenation of PP.

photocatalytic ring hydrogenation of aromatics over a rhodium (Rh)-loaded TiO_2 photocatalyst [25]. Here, we investigated effects of the water content of water-acetonitrile solution on the production of *cis*-MS over DHN/TiO_2-Cu and adsorption of PP and TEOA on DHN/TiO_2-Cu (Fig. 4). The addition of a small amount of water to acetonitrile drastically increased the yield of *cis*-MS as shown in Fig. 4(a). The maximum yield of *cis*-MS (15 μmol) was obtained in water-acetonitrile (1:9) solution, and that yield was about 6-times larger than that obtained in water-free acetonitrile (2.4 μmol). Positive effects of the addition of water to acetonitrile have been observed in various photocatalytic reductions [14,26–28], photocatalytic hydroxylation of aromatic compounds [29,30] and hydration of alkenes [31] in the presence of water over metal-loaded TiO_2 have recently been reported. On the other hand, hydroxylated and hydrated compounds were not observed in the present system, i.e., the addition of water to acetonitrile did not affect the selectivity of *cis*-MS but affected the rate of the reaction. Similar results were obtained in the case of water-2-propanol solution (Fig. S7).

In photocatalytic ring hydrogenation of aromatics over Rh-TiO_2, solvents greatly influenced the behavior of adsorption of aromatics and hole scavengers, which resulted in a large change in the photocatalytic performance [25]. Hence, we observed the effect of the water content on adsorption of the substrate and hole scavenger in the dark for 24 h in this system. Fig. 4(b) and (c) show the amounts of PP and TEOA adsorbed on the surface of the DHN/TiO_2-Cu photocatalyst in aqueous acetonitrile solutions having various water contents. The addition of a small amount of water greatly increased the amount of PP adsorbed on DHN/TiO_2-Cu. This result is probably caused by the change in solubility of PP in the solvents, i.e., PP was concentrated on the surface of the photocatalyst due to the slightly decreased solubility in acetonitrile having a small amount of water. On the other hand, the amount of TEOA adsorbed on DHN/TiO_2-Cu decreased with an increase in the water content due to the increase in solubility in solvents containing water. Since a similar tendency was observed in yields of *cis*-MS and the amount of PP adsorbed in the dark, the yields of *cis*-MS were plotted against the amounts of PP adsorbed on DHN/TiO_2-Cu (Fig. 4(d)). An almost linear correlation between them was obtained, indicating that adsorption of the substrate controlled the rate of the photocatalytic reaction and that the amount of adsorption can be easily increased only by the addition of a small amount of water to acetonitrile.

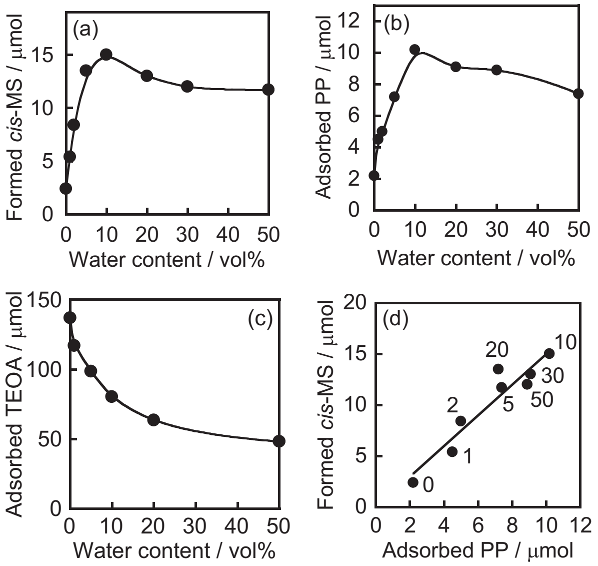
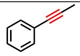
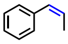
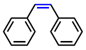
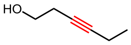
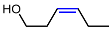
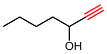
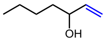
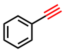
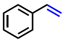
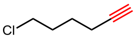
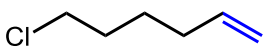
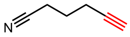
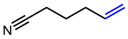


Fig. 4. Effect of water content of water-acetonitrile solution on (a) *cis*-MS yield in photocatalytic hydrogenation of PP over DHN/TiO_2-Cu under visible light irradiation, (b) amount of PP adsorbed on the surface of DHN/TiO_2-Cu in the dark and (c) amount of TEOA adsorbed on the surface of DHN/TiO_2-Cu in the dark. (d) Correlation between the yield of *cis*-MS and amount of PP adsorbed. The values mean water content.

3.4. Applicability of photocatalytic hydrogenation of alkynes in a water-acetonitrile (1:9) suspension of DHN/TiO_2-Cu

In order to evaluate the applicability of a DHN/TiO_2-Cu photocatalyst in semihydrogenation under visible light irradiation, various alkynes were used as substrates and the results are shown in Table 2. Three internal alkynes including PP were converted to the corresponding *cis*-alkenes in high yields (Entries 1–3). In these reactions, no *trans*-alkenes and alkanes were produced, indicating that the DHN/TiO_2-Cu photocatalyst has wide applicability for diastereoselective hydrogenation of alkynes to the corresponding *cis*-alkenes. Terminal alkynes were also hydrogenated to the corresponding terminal alkenes in high yields (Entries 4–7). In addition, this photocatalytic system exhibited high chemoselectivity for an alkynyl group because other functional groups such as phenyl, hydroxy, chloro and cyano groups were not influenced. There were possibilities that a hydroxy group is oxidized to a carbonyl group by positive holes and that chloro and cyano groups are reductively eliminated or hydrogenated by excited electrons in the CB of the

Table 2
Photocatalytic hydrogenation of various alkynes in water-acetonitrile (1:9) suspensions of DHN(0.7)/TiO_2-Cu(1.0) under visible-light irradiation.

Entry	Substrate	Product	Time / h	Conv. / %	Yield / %	MB / %
1			4	>99	>99	>99
2			24	>99	>99	>99
3	 HO	 HO	20	>99	93	93
4	 OH	 OH	4	>99	86	86
5			18	>99	70	70
6	 Cl	 Cl	7	>99	85	85
7	 N	 N	5	>99	90	90

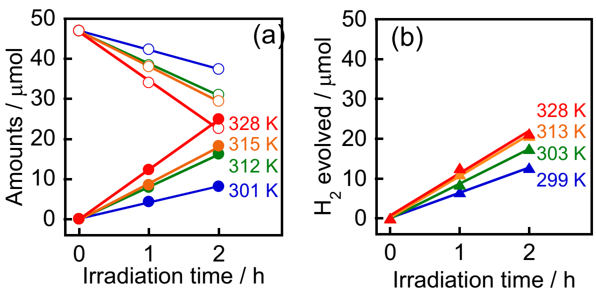


Fig. 5. Effects of reaction temperature on (a) hydrogenation of PP (○) to *cis*-MS (●) in a water-acetonitrile (1:9) suspension of a DHN/TiO_2-Cu photocatalyst in the presence of TEOA under visible light irradiation and (b) evolution of H_2 from TEOA in a water-acetonitrile (1:9) suspension of a DHN/TiO_2-Cu photocatalyst in the absence of PP under visible light irradiation.

photocatalyst. For example, we have reported that Pd-TiO_2 photocatalytically hydrogenated benzonitrile to benzyl amine [16] and that DHN/TiO_2 having Pd as a co-catalyst eliminated a chloro group in chlorobenzaldehyde to form benzaldehyde [21]. As far as we know, this is the first report showing the achievement of diastereoselective semihydrogenation of alkynes to *cis*-alkenes under visible light irradiation without the use of H_2 and undesirable additives.

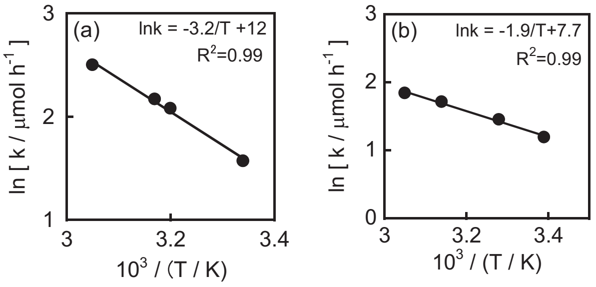


Fig. 6. Arrhenius plots (logarithm of *k* vs reciprocal of T) for (a) hydrogenation of PP to *cis*-MS and (b) H_2 evolution. The reaction conditions are shown in Fig. 5.

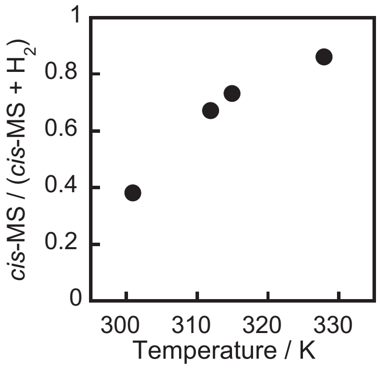


Fig. 7. Ratio of *cis*-MS and H_2 in hydrogenation of PP in a water-acetonitrile (1:9) suspension of DHN/TiO_2-Cu under irradiation of blue light for 2 h at various temperatures.

3.5. Effect of reaction temperature on photocatalytic hydrogenation of PP over DHN/TiO_2-Cu

In recent years, we have reported several selective hydrogenations of organic compounds having various functional groups such as a vinyl group [17], cyano group [16] and aromatic ring [18,25] using a TiO_2 photocatalyst having a metal co-catalyst such as Pd or Rh. In this photocatalytic process, photogenerated electrons reduced protons to form AHS on the surface of the metal co-catalyst, and AHS hydrogenated organic compounds selectively. After the formation of electrons by photocatalysis, the reaction proceeded by thermal catalysis of the metal co-catalyst. In fact, we have reported that semihydrogenation over a Cu-TiO_2 photocatalyst under UV light irradiation was greatly accelerated by a slight increase in the reaction temperature [20]. Based on the above finding, we expected that the reaction rate of photocatalytic semihydrogenation of alkynes to alkenes over DHN/TiO_2-Cu can be increased at elevated temperatures. In order to examine the effect of reaction temperature on hydrogenation over a DHN/TiO_2-Cu photocatalyst, the reaction was carried out at various temperatures (301–328 K), and the results are shown in Fig. 5(a). At any temperature, semihydrogenation of PP to *cis*-MS proceeded linearly with maintenance of high selectivity. As expected, the rate of *cis*-MS production increased with increase in the reaction temperature and the reaction rate at 328 K was three-times larger than the rate at 301 K, indicating that catalytic hydrogenation of PP over Cu metals was the rate-determining step of this reaction. For comparison, we also examined simple H_2 evolution from TEOA over DHN/TiO_2-Cu in the absence of PP (Fig. 5(b)). The rate of H_2 evolution increased with an increase in the reaction temperature as did PP hydrogenation. Assuming these reactions were zero-order reactions, rate constants (k) at these temperatures were determined from the slopes in Fig. 5, and Arrhenius plots (logarithm of k vs reciprocal of T) for both reactions are shown in Fig. 6. Two linear correlations were observed in the Arrhenius plots. From the slope of the Arrhenius plot (Fig. 6(a)), the apparent activation energy (E_a) for *cis*-MS formation was determined to be 27 kJ mol^{-1}. The value of E_a for H_2 evolution from TEOA was calculated to be 15 kJ mol^{-1}, which is close to values (*ca.* 10 kJ mol^{-1}) previously reported [32–36], indicating that H_2 evolution over Cu nanoparticles was also the rate-determining step in the latter reaction. From a comparison of Figs. 1 and 5(b) at 328 K, we noted that the yield of H_2 in the presence of PP (Fig. 1) was much smaller than that in the absence of PP (Fig. 5(b)). This fact suggests that both *cis*-MS

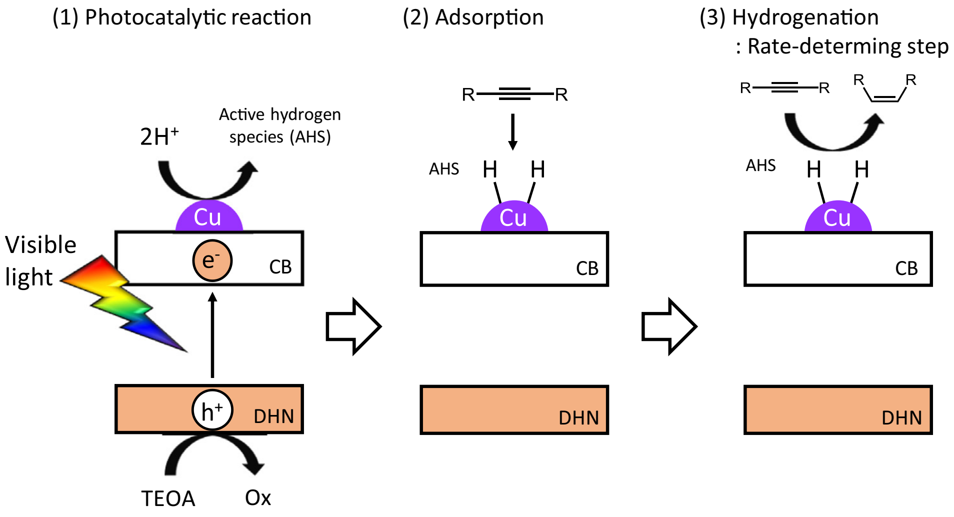


Fig. 8. Expected photocatalytic mechanism over DHN/TiO_2-Cu for semihydrogenation of alkynes under visible light irradiation.

formation (hydrogenation of PP with AHS) and H_2 evolution (coupling of AHS) occurred competitively on the same active sites, i.e., Cu metals. In other words, the selectivity of *cis*-MS formation (PP hydrogenation) can be controlled by the reaction temperature because the reaction rate was dependent on E_a, frequency factor (A) and temperature. To examine the effect of the reaction temperature on the selectivity of *cis*-MS formation (PP hydrogenation), semihydrogenation of PP over DHN/TiO_2-Cu was carried out under blue light irradiation at various temperatures, and the selectivity of *cis*-MS formation is shown in Fig. 7. At around room temperature, *cis*-MS formation was inferior to H_2 evolution due to the larger E_a. However, *cis*-MS formation became predominant at elevated temperatures and the selectivity reached 86% at 328 K. The increase in selectivity can be explained as follows: elevation of the reaction temperature decreased the negative effect of the large activation energy on the reaction rate, while the effect of A on the rate became larger at high temperatures. In fact, the value of A for *cis*-MS formation ($2.2 \times 10^{5}\ \mu\text{mol h}^{-1}$) was much larger than that of A for H_2 evolution ($2.2 \times 10^{3}\ \mu\text{mol h}^{-1}$).

3.6. Possible photocatalytic mechanism over DHN/TiO_2-Cu for semihydrogenation of alkynes

Based on the above-described results, the expected reaction mechanism of semihydrogenation of alkynes to *cis*-alkenes over DHN/TiO_2-Cu is shown in Fig. 8: (1) by irradiation with visible light, photogenerated electrons (e^-) and positive charges (h^+) are formed in DHN/TiO_2-Cu, and TEOA is oxidized by h^+, (2) H^+ is reduced by e^-, resulting in the formation of AHS over Cu particles and (3) adsorbed alkynes are successively hydrogenated by AHS over Cu particles, resulting in the formation of *cis*-alkenes. Relatively large values of E_a for PP hydrogenation and H_2 evolution indicate that the third process is the rate-determining step in this photocatalytic system.

4. Conclusions

We succeeded in H_2-free and Pb-free semihydrogenation of alkynes to the corresponding *cis*-alkenes in water-acetonitrile suspensions of an organically modified TiO_2 photocatalyst having a Cu co-catalyst under visible light irradiation. The addition of water (10 vol%) to acetonitrile is important for increasing the reaction rate and yield of *cis*-alkenes because alkynes were concentrated on the surface of the photocatalyst due to the slightly decreased solubility in acetonitrile having a small amount of water. This system was applied to hydrogenation of alkynes having a halogen atom, cyano group, hydroxy group and aromatic ring, producing corresponding alkenes. Formation of *cis*-MS (semihydrogenation of PP with AHS) and H_2 evolution (coupling of AHS) occurred competitively on Cu metals, and *cis*-MS formation was inferior to H_2 evolution at around room temperature due to the larger E_a for hydrogenation ($27\ \text{kJ mol}^{-1}$). However, *cis*-MS formation became predominant at slightly elevated temperatures and the selectivity reached 86% at 328 K because the frequency factor (A) for *cis*-MS formation was much larger than A for H_2 evolution and the negative effect of the larger E_a on the reaction rate became small at higher temperatures.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2019.04.022.

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