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Additive-free semihydrogenation of an alkynyl group to an alkenyl group over Pd-TiO2 photocatalyst utilizing temporary in-situ deactivation

Yasumi Kojima,[a] Makoto Fukui,[a] Atsuhiro Tanaka,[b] Keiji Hashimoto,[b] and Hiroshi Kominami[b],*

Abstract: Lindlar's catalyst, i.e., calcium carbonate-supported palladium (Pd) modified with lead, has been used for semihydrogenation of an alkynyl group in the presence of hydrogen gas (H_2). We examined hydrogenation of an alkynyl group in organosilane and hydrocarbon in methanolic suspensions of a Pd-loaded titanium(IV) oxide (Pd-TiO_2) photocatalyst without the use of additives and H_2. In the photocatalytic reaction, Pd particles worked as a co-catalyst for hydrogenation and alkyne hydrogenation had priority to alkene hydrogenation. Since the Pd co-catalyst was temporarily deactivated during the reaction due to accumlation of the oxidized product(s) of methnaol, the capacity of hydrogenation of the unsaturated C-C bond was limited. By optimizing the capacity and amount of alkynes, almost complete semihydrogenation of alkynes was achieved under a poison-free condition. Pd-TiO_2 can be regenerated by only very simple treatments, i.e., washing and drying at room temperature.

Introduction

Partial hydrogenation (semihydrogenation) of an alkynyl group to an alkenyl group is important and one of most difficult reactions.[1] Lindlar's catalyst, i.e., calcium carbonate-supported palladium (Pd) modified with lead (Pb), has been used for semihydrogenation of an alkynyl group;[2] however, this catalyst system requires undesirable additives, Pb salts and organic bases, to reduce the activity of Pd and increase the selectivity of hydrogenation of the alkynyl group to the alkenyl group. This means that semihydrogenation by using Lindlar's catalyst gives a large amount of undesirable waste. Since hydrogen (H_2) gas under a high pressure (1-10 MPa) is necessary as a hydrogen source, hydrogenation should be carried out in a pressure-tight reactor and should be monitored to avoid over-hydrogenation to an alkyl group.[3] Therefore, three key words, 1) additive-free, 2) hydrogen-free, and 3) highly selective, can be pointed out for an environmentally-friendly catalytic semihydrogenation system. We have reported that various hydrogenation reactions satisfying these three key words can be achieved by photocatalysis of titanium(IV) oxide (TiO_2) and metal-loaded TiO_2 in the presence of an appropriate hole scavenger and solvent. For example, 3-nitrostyrene was chemoselectively reduced to 3-aminostyrene without hydrogenation of a C=C double bond to 3-ethylaniline in a suspension of a TiO_2,[4,5] and benzonitrile was successfully hydrogenated to benzyl amine in an alcohol suspension of a palladium (Pd)-loaded TiO_2.[6] Recently, we have found that internal alkynes were semihydrogenated to the corresponding *cis*-alkenes in alcoholic suspensions of a copper (Cu)-loaded TiO_2 photocatalyst without the use of additives and a reducing gas.[7] Since the rate for semihydrogenation over a Cu-TiO_2 photocatalyst was small, a more active and still highly selective photocatalyst working under additive-free and hydrogen-free conditions is desired.

In this study, we explored a new photocatalytic system for rapid semihydrogenation of alkynes to alkenes without the use of additives and a reducing gas and we found that almost complete semihydrogenation was achieved in a methanolic suspension of a Pd-TiO_2 photocatalyst, in which the Pd-TiO_2 photocatalyst temporarily lost activity for hydrogenation during the reaction. Here we mainly used an organosilane having an alkynyl group to expand the possibility of the Pd-TiO_2 photocatalyst.

Results and Discussion

Effects of metal co-catalysts

Figure 1 shows the effects of metal co-catalysts on photocatalytic hydrogenation of triethylsilylacethylene (TESA, 190 µmol) in methanol suspensions (5 cm^3) under Ar after 2 h. No product was formed in the case of bare TiO_2, indicating that neither hole scavenging by methanol nor electron scavenging by TESA and protons (H^+) occurred under the present conditions. When Au-, Cu- and Ag-TiO_2 were used as photocatalysts, TESA was recovered almost quantitatively within the experimental error and a large amount of H_2 was evolved. The latter result indicates that hole scavenging by methanol and electron scavenging by protons (H^+), i.e., dehydrogenation of methanol ($CH_3OH \rightarrow H_2 + HCHO$), occurred. In addition, production of H_2 means that active hydrogen species were formed and were then coupled to H_2 on these co-catalysts. Recovery of TESA in the cases of Au-, Cu-, Ag-TiO_2 means that active hydrogen species

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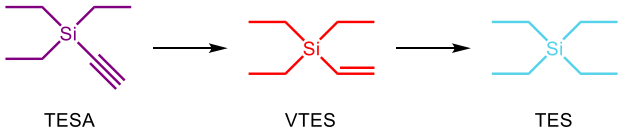
were not used for hydrogenation of TESA, probably due to the weak adsorption of the C≡C triple bond of TESA on these co-catalysts and/or the large activation energy for hydrogenation of the C≡C triple bond on these co-catalysts. When Pt was used as the co-catalyst, a very small amount of vinyltriethylsilane (VTES) was formed as the semihydrogenated product of TESA, accompanying evolution of a large amount of H_2. A very low hydrogen over-voltage of Pt is attributed to the large amount of H_2 production; however, the Pt co-catalyst had negligible activity for hydrogenation of TESA as did Au, Cu and Ag co-catalysts. The rhodium co-catalyst showed higher activity for TESA hydrogenation and lower activity for H_2 evolution than did the Pt co-catalyst. Unfortunately, hydrogenation was non-selective over the Rh co-catalyst, i.e., successive hydrogenation of VTES to tetraethylsilane (TES) also occurred, in which both C≡C triple and C=C double bonds were hydrogenated. In contrast to these metal-loaded TiO_2 samples, when the Pd-TiO_2 photocatalyst was used, most of the TESA was hydrogenated and a large amount of VTES was obtained.



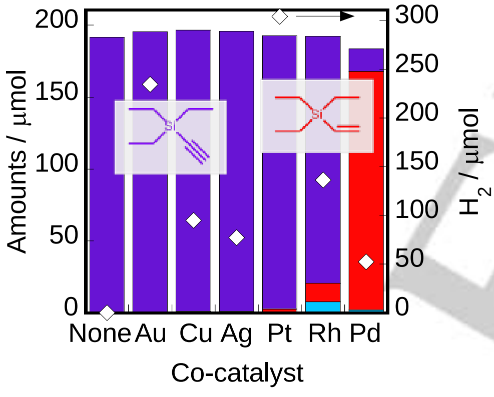


Figure 1. Effect of metal co-catalyst on photocatalytic hydrogenation of TESA (initially 190 μmol) in methanolic suspensions of bare and 0.5 wt% co-catalyst-loaded TiO_2 (50 mg) for 2 h (left axis for TESA, VTES and TES and right axis for H_2 (diamonds)).

The yield of TES was negligible in this case, indicating that semihydrogenation of TESA to VTES occurred very selectively over the Pd-TiO_2 photocatalyst. We also noted that H_2 yield was smallest over Pd-TiO_2 among the co-catalyst-loaded TiO_2 photocatalysts. A low H_2 yield means that photogenerated electrons are efficiently used for hydrogenation of TESA. From the results of all of the experiments, we concluded that Pd-TiO_2 showed distinguished performance for semihydrogenation of TESA to VTES among all of the co-catalyst-loaded TiO_2 photocatalysts prepared in this study. In the previous study, we reported that a small amount of phenylacetylene (50 μmol) having the C≡C triple bond was fully hydrogenated to ethylbenzene for 2 h in methanolic suspension of Pd-TiO_2 photocatalyst.[7] These results seem to be inconsistent with the result of Pd-TiO_2 shown in Figure 1 but did not. The reason will be clarified in latter section.

Table 1. Effect of reaction conditions on hydrogenation of TESA in methanol[a]

Entry	UV	Photo-catalyst[b]	Time / h	Gas Phase	VTES yield / %	TES yield / %
1	On	Pd-TiO_2	2	Ar	86	1.0
2	On	-	2	Ar	-	-
3	-	Pd-TiO_2	2	Ar	-	-
4	-	Pd-TiO_2	2	H_2 (1 atm)	1.9	91
5	-	Pd-TiO_2	0.5	Ar/H_2 (0.05 atm)[c]	5.9	-
6	-	Pd-TiO_2	1	Ar/H_2 (0.05 atm)[c]	11	-

[a] TESA: 190 μmol, methanol: 5 cm^3. [b] Pd(0.5)-TiO_2: 50 mg. [c] H_2: 83 μmol.

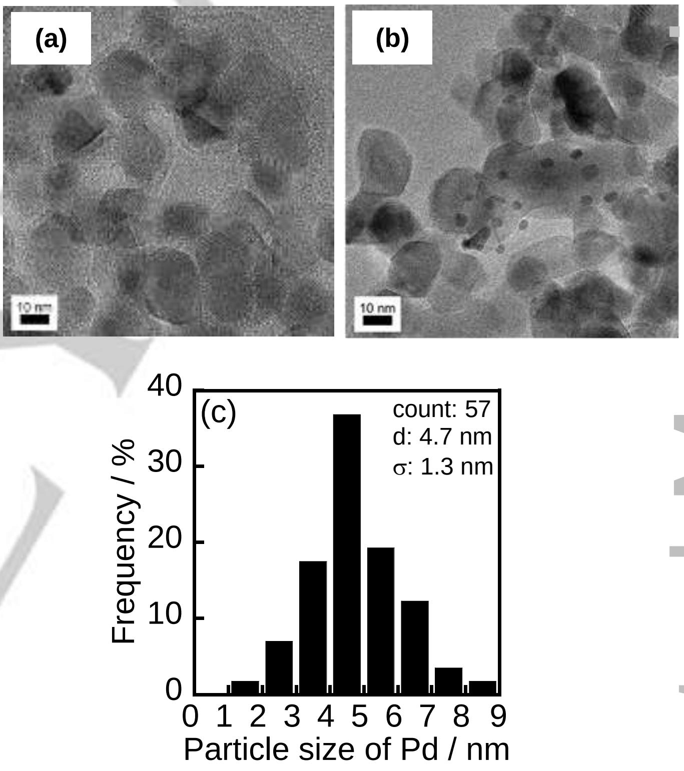


Figure 2. TEM images of (a) TiO_2 and (b) Pd(0.5)-TiO_2 and (c) size distribution of Pd nanoparticles of Pd(0.5)-TiO_2.

Blank tests

Effects of various reaction conditions on hydrogenation of TESA to VTES were investigated, and the results are summarized in Table 1. Two blank reactions of TESA at 298 K, (1) photochemical reaction in the absence of Pd-TiO_2 (Entry 2) and (2) dark reaction in the presence of Pd-TiO_2 (Entry 3) gave no or only a trace amount of VTES. From the results of the two blank tests, it can be concluded that Pd-TiO_2 and UV light are indispensable for hydrogenation of TESA to VTES. Three control experiments in the presence of H_2 were also carried out to examine the effect of H_2 in gas phase on hydrogenation of TESA over Pd-TiO_2 in the dark at 298 K (Entries 4-6). Under 1 atm H_2, TES was formed as the main product for 2 h, indicating that deep hydrogenation of TESA occurred (Entry 4). When the partial pressure of H_2 was reduced to 0.05 atm (Ar balance), only a small amount of VTES was obtained for 0.5 h and 1 h (Entries 5 and 6). These control experiments show the difficulty of thermocatalytic semihydrogenation of TESA over Pd-TiO_2 using H_2 gas.

Characterization of Pd(0.5)-TiO_2

We observed TiO_2 and Pd-TiO_2 samples by using a transmission electron microscope (TEM) (Figures 2(a) and 2(b)). The two TEM images clearly show that fine Pd nanoparticles were deposited on the TiO_2 particles by the photodeposition method without a change in the morphology of TiO_2 particles. TEM observation of Pd-TiO_2 revealed that Pd nanoparticles have an average diameter (D_{Pd}) of 4.7 nm (Figure 2(c)). The number density of Pd nanoparticles (N_{Pd}) was calculated to be 7.7×10^{15} (g-Pd-TiO_2)$^{-1}$ from D_{Pd}, the density of Pd metal (r= 12.02 g cm^{-3}) and the amount of Pd loaded on TiO_2 with the assumption that all of the Pd nanoparticles were spherical (Table 2). From D_{Pd} and N_{Pd}, the external surface area (S_{Pd}) of Pd-TiO_2 was calculated to be 0.53 m^2 (g-Pd-TiO_2)$^{-1}$ (Table 2).

Table 2. Various properties of Pd(0.5)-TiO_2 prepared by photodeposition method.

$^aD_{Pd}$ / nm	$^bN_{Pd}\times10^{-15}$ / (g-Pd-TiO_2)	$^cS_{Pd}$ / m^2 (g-Pd-TiO_2)
4.7	7.7	0.53

$^aD_{Pd}$: average size of Pd nanoparticles calculated from the values of 57 particles observed by TEM. $^bN_{Pd}$: number density of Pd nanoparticles in g-Pd/TiO_2. This value was calculated from D_{Pd}, density of metal (12.02 g cm^{-3}), and the amount of Pd loaded on TiO_2 on the assumption that all of the particles were spheres. $^cS_{Pd}$: external surface area of supported Pd nanoparticles. This value was calculated from the average size of Pd nanoparticles and N_{Pd}.

Photocatalytic hydrogenation of TESA (initially 190 µmol) in a methanolic suspension of Pd-TiO_2

Figure 3 shows time courses of the amounts of VTES and TES in a photocatalytic reaction of TESA (190 µmol) in methanol suspensions of Pd-TiO_2 (50 mg) without the use of additives and H_2 gas. The amount of TESA remaining in the reaction mixture is also plotted in Figure 3. The amount of TESA decreased just after irradiation of UV light, while only VTES was formed with decrease in the amount of TESA. The material balance (MB) calculated by using Equation (1) is also shown in Figure 3.

$$MB = \frac{n(TESA) + n(VTES) + n(TES)}{n_0(TESA)}, (1)$$

where n(TESA), n(VTES) and n(TES) are the amounts of TESA, VTES and TES after photoirradiation, respectively, and n_0(TESA) is the initial amount of TESA. A value of MB close to unity indicates that only hydrogenation of TESA to VTES occurred. After irradiation for 4 h, TESA was almost completely consumed and 190 µmol of VTES was formed without the formation of TES. Turnover number was calculated to be 81 based on the total number of Pd atoms. Longer photoirradiation did not alter the yield of VTES, indicating that almost quantitative conversion of TESA to VTES was achieved. The following is an expected working mechanism for hydrogenation of TESA in methanol suspensions of Pd-TiO_2 photocatalysts under irradiation of UV light. Surface hydrogen species are formed on Pd (Pd-H) by the reduction of protons by photogenerated electrons, while methanol is oxidized by holes. Two processes consuming thus-formed Pd-H would occur: (1) TESA is hydrogenated by the surface hydrogen species with the aid of Pd, resulting in the formation of VTES and in regeneration of the photocatalyst and (2) H_2 formation also occurs as a result of coupling of the surface hydrogen species. In the case of Pd-TiO_2, the reaction rate of (1) is much larger than that of (2) probably because of strong interaction between Pd and the C≡C bond of TESA.

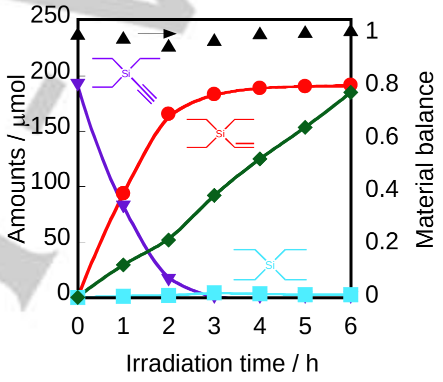


Figure 3. Time courses of the amounts of TESA (▼), VTES (●), TES (■) and H_2 (◆) in photocatalytic hydrogenation of TESA (initially 190 µmol) in methanolic suspensions of Pd-TiO_2.

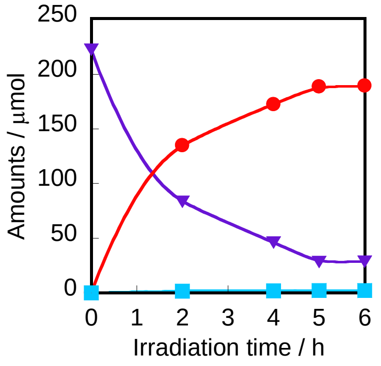


Figure 4. Time courses of the amounts of TESA (▼), VTES (●) and TES (■) in photocatalytic hydrogenation of TESA (initially 220 µmol) in a methanolic suspension of Pd-TiO_2.

Photocatalytic hydrogenation of TESA (initially 220 µmol) in a methanolic suspension of Pd-TiO_2

To understand the sharp selectivity for semihydrogenation of TESA to VTES, photocatalytic hydrogenation of a slightly larger amount of TESA (220 µmol) was examined (Figure 4). The amount of VTES reached 190 µmol at 5 h and further irradiation to the reaction mixture did not alter the amount of VTES even in the presence of unreacted TESA and a large excess of methanol. This result indicates that semihydrogenation of TESA to VTES had priority to the subsequent hydrogenation of VTES to TES and that Pd-TiO_2 somehow lost the activity for hydrogenation after 190 µmol of VTES had been produced. The results shown in Figures 3 and 4 indicate two important and interesting features of photocatalytic hydrogenation in a methanolic suspension of Pd-TiO_2. The first one is that the amount of the hydrogenation product was same for the case of 190 µmol of TESA, and the second one is that the limitation is caused by in-situ deactivation of Pd-TiO_2. Deactivation of a TiO_2 photocatalyst due to deposition of intermediates is often observed when TiO_2 is used for degradation of gaseous organic pollutants in a flow-type reactor and oxidation of aromatics in a batch-type reactor.[8] On the other hand, as far as we know, there had been no report of deactivation of a Pd-TiO_2 photocatalyst suspended in methanol and the present work is the first work showing that Pd-TiO_2 suspended in methanol is deactivated during a photocatalytic reaction.

When VTES (80 µmol) having an alkenyl group was used as the starting substrate in place of TESA, VTES was hydrogenated to TES for 0.5 h. This result is consistent with the result of alkene hydrogenation over Pd-TiO_2 photocatalyst,[9] i.e., Pd-TiO_2 photocatalyst has a sufficient ability for hydrogenation of the C=C double bond if the photocatalyst is not deactivated. Full hydrogenation of the C≡C triple bond of phenylacetylene observed over Pd-TiO_2[7] indicates that Pd-TiO_2 was not deactivated due to the small amount of phenylacetylene (50 µmol).

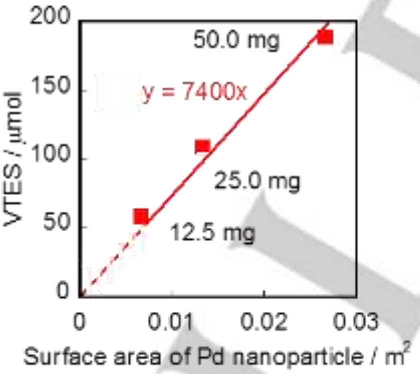


Figure 5. Effects of the surface area of Pd particles on maximum yields of VTES in photocatalytic semihydrogenation of TESA (initially 190 µmol) in methanol suspensions of Pd(0.5)-TiO_2. Values in the figure mean the weights of Pd(0.5)-TiO_2 used in the reaction.

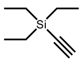
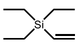
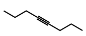
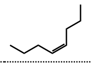
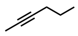
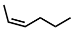
Effect of the amount of photocatalyst

To further understand the high selectivity for semihydrogenation of TESA over the Pd-TiO_2 photocatalyst and deactivation of the Pd-TiO_2 photocatalyst during the reaction, we examined photocatalytic hydrogenation of TESA (190 µmol) in methanol suspensions (5 cm^3) of different amounts of the Pd(0.5)-TiO_2 photocatalyst (12.5, 25.0 and 50.0 mg) under irradiation of UV light. Figure 5 shows effects of the external surface area of Pd nanoparticles (Table 1) on the yields of VTES after sufficient photoirradiation for more than 5 h. The yields mean the maximum values that Pd(0.5)-TiO_2 with different amounts produced until its deactivation. The result shown in Figure 3 (50 mg of Pd(0.5)-TiO_2) corresponds to the plot at 0.0265 m^2 in Figure 5. The maximum yield over Pd(0.5)-TiO_2 decreased with decrease in the amount of catalyst. Interestingly, a linear correlation was observed between the surface area of Pd and the maximum amount of VTES produced. The clear surface area dependency suggests that the Pd surface was inactivated by some species simultaneously formed during the photocatalytic reaction.

Reusability and expandability tests

Various experiments revealed that the *in-situ* deactivation of Pd-TiO_2 is the most important reason for the almost quantitative conversion of TESA to VTES. After photocatalytic semihydrogenation of TESA in a methanol suspension of Pd-TiO_2 for 6 h, the deactivated Pd-TiO_2 was recovered, washed with methanol, dried in air at room temperature, and then used for the same reaction. Table 3 shows the results of re-using tests of photocatalytic semihydrogenation of TESA to VTES (Entries 1-3). Interestingly, Pd-TiO_2 could be used repeatedly for photocatalytic semihydrogenation of TESA to VTES, although Pd-TiO_2 was actually deactivated in each reaction. In the liquid phase after the photocatalytic reactions, Pd species was not detected in atomic absorption analysis. The reusability of Pd-TiO_2 indicates that *in-situ* deactivation of Pd-TiO_2 is temporary, and Pd-TiO_2 can be regenerated by only very simple treatments, i.e., washing and drying at room temperature. At the same time, the reusability and no leaching of Pd means high stability of Pd-TiO_2. Advantages of this photocatalytic semihydrogenation of TESA utilizing *in-situ* deactivation of Pd-TiO_2 can be summarized as follows: 1) no additives or toxic materials are required to control the activity of Pd, 2) no careful operation and observation are necessary to avoid overhydrogenation and 3) Pd-TiO_2 works repeatedly.

Table 3. Reusability and expandability tests of Pd-TiO_2 photocatalyst for semihydrogenation of alkynl group in methanolic suspensions^a.

Entry	Substrate	Product	Pd /wt%	Time / h	Conv. / %	Select. / %
1 $^{b, c}$			0.5	6	>99	99
2 $^{b, d}$			0.5	6	>99	93
3 $^{b, e}$			0.5	6	>99	96
4^f			0.5	2	>99	>99
5^g			0.1	4	>99	81

^{a}Methanol: 5 cm^3, Pd-TiO_2: 50 mg. ^{b}TESA: 190 µmol. ^{c}First use. ^{d}Second use. ^{e}Third use. ^{f}4-octyne: 140 µmol. ^{g}2-hexyne: 400 µmol.

Two other hydrocarbon alkynes were used to examine the expandability of semihydrogenation of the alkynyl group over a Pd-TiO_2 photocatalyst in methanol, and the results are also shown in Table 3. 4-Octyne was almost quantitatively converted to 4-octene with almost complete *cis* selectivity after irradiation for 2 h (Entry 4). This result means that chemoselective hydrogenation of alkyne to the corresponding *cis*-alkene was achieved without any additives or careful observation. In our previous paper, we reported that a Cu-TiO_2 photocatalyst showed almost complete selectivity for hydrogenation of alkynes to corresponding *cis*-alkenes.[7] We noted that the reaction rate over Pd-TiO_2 (190 µmol for 2 h) was much larger than that over Cu-TiO_2 (50 µmol for 6 h) (ca. eleven times). 2-Hexyne was also hydrogenated to *cis*-2-hexene, although the selectivity was slightly low probably due to a side-reaction reducing the selectivity (Entry 5). From these results, the following advantage of this photocatalytic semihydrogenation over Pd-TiO_2 can be added: 4) Pd-TiO_2 can be used for semihydrogenation of hydrocarbon alkynes. From the four advantages, it is apparent that the present photocatalytic method using Pd-TiO_2 and methanol is superior to the thermocatalytic method using the Lindlar's catalyst in which additives, H_2 gas and continuous monitoring are required.[10]

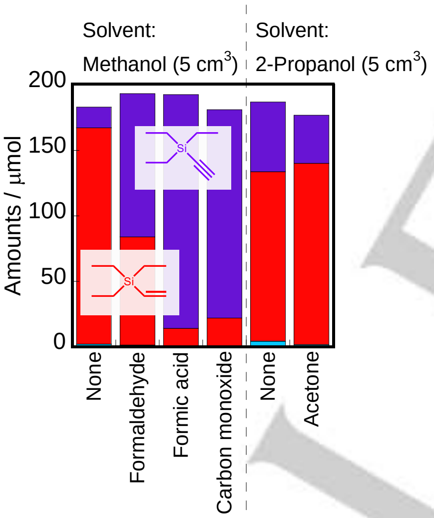


Figure 6. Effects of the addition of formaldehyde (400 µmol), formic acid (10 µmol), carbon monoxide (400 µmol) and acetone (400 µmol) on photocatalytic hydrogenation of TESA (initially 190 µmol) in methanol or 2-propanol suspensions of Pd(0.5)-TiO_2 (50 mg) for 2 h.

Effects of oxidized products

The results described in the previous paragraphs suggest that products derived from methanol, i.e., formaldehyde (FAD), formic acid (FA) and carbon monoxide (CO), are responsible for deactivation of the Pd-TiO_2 photocatalyst. Formation of these compounds is shown below.

$$CH_3OH + 2h^+ \rightarrow HCHO + 2H^+$$
$$HCHO + H_2O + 2h^+ \rightarrow HCOOH + 2H^+$$
$$HCOOH \rightarrow CO + H_2O$$

The results of re-using tests (Table 3), which revealed that Pd-TiO_2 can be regenerated only by washing and drying at room temperature, also indicate that deactivation of the Pd-TiO_2 photocatalyst is temporary and is caused by a soluble and/or volatile product(s). To examine the effects of the three oxidized products on the photocatalytic semihydrogenation of TESA, several experiments were carried out in which one of the oxidized products was intentionally added before the photoirradiation.

Figure 6 shows the results of photocatalytic hydrogenation of TESA (190 µmol) in methanol suspensions of Pd-TiO_2 (50 mg) for 2 h in the presence of FAD (400 µmol), FA (10 µmol) and CO (400 µmol). Yields of VTES in the presence of FAD, FA and CO were much smaller than the yield in the absence of additives, indicating that the activity of the Pd-TiO_2 photocatalyst was drastically suppressed by these products of methanol oxidation. To understand the effects of products from methanol, additional control experiments were carried out using 2-propanol in place of methanol for photocatalytic hydrogenation of TESA (190 µmol) under the same conditions except for the alcohol (Figure 6). The yield of VTES in 2-propanol was smaller than that of VTES in methanol. There are two possibilities for the smaller yield of VTES when 2-propanol was used: 1) the efficiency of hole scavenging by 2-propanol was less than that of hole scavenging by methanol and 2) the activity of the Pd-TiO_2 photocatalyst was suppressed by a product of 2-propanol oxidation. To clarify the exact reason, photocatalytic hydrogenation of TESA in 2-propanol in the presence of acetone (400 µmol) was examined (Figure 6). The result indicates that the effect of acetone addition was negligible and the results of the reaction using 2-propanol further support the possibility that the activity of the Pd-TiO_2 photocatalyst was suppressed by a product(s) of methanol oxidation.

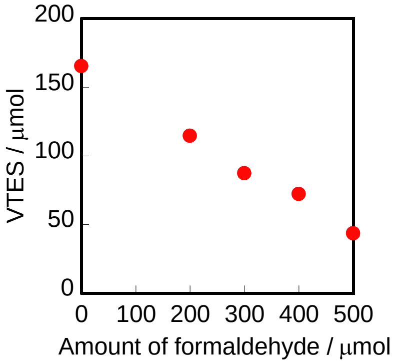


Figure 7. Effect of the amount of formaldehyde intentionally added on maximum yields of VTES in photocatalytic semihydrogenation of TESA (initially 190 µmol) in methanol suspensions of Pd(0.5)-TiO_2 (50 mg) for 2 h.

Since a large amount of methanol was used as the solvent for photocatalytic hydrogenation of TESA, it is expected that FAD was formed as the main product of methanol oxidation. In addition to the type of oxidized products, the effect of the amount of FAD on photocatalytic hydrogenation of TESA was investigated by intentionally adding FAD to a suspension of Pd(0.5)-TiO_2 in methanol. The results after 2 h are shown in

Figure 7. Although VTES was obtained in a high yield (166 µmol) with no FAD being added to the system, the yield of VTES linearly decreased with an increase in the amount of FAD added. The results indicate that FAD directly suppresses photocatalytic hydrogenation of TESA.

Conclusions

We achieved almost complete semihydrogenation of an alkynyl group to an alkenyl group in oragnosilane and hydrocarbon in methanolic suspensions of a Pd-TiO_2 photocatalyst. Pd particles worked as a co-catalyst for semihydrogenation and, in the case of 4-octyne, the reaction rate over Pd-TiO_2 was 11 times larger than that over Cu-TiO_2. Over the Pd co-catalyst, alkyne hydrogenation had priority to alkene hydrogenation. The Pd co-catalyst was temporarily deactivated during the reaction and the capacity of hydrogenation of the unsaturated C-C bond is limited, which greatly contributed to semihydrogenation of an alkynyl group. This process provides environmentally friendly, i.e., 1) additive-free, 2) hydrogen-free, and 3) highly selective, hydrogenation. In semihydrogenation, a Pd-TiO_2 works as a photocatalyst because the Pd-TiO_2 can be re-generated and re-used.

Experimental Section

Loading of a co-catalyst on TiO_2

Various metals (0.5 wt%) as co-catalysts were loaded on TiO_2 by using the photodeposition method. As metal sources, $HAuCl_4$, $AgNO_3$, $CuCl_2$, $PdCl_2$, H_2PtCl_6 and $RhCl_3$ were used. In 10 cm^3 of an aqueous methanol solution (10 vol%) containing a metal source in a test tube, TiO_2 powder (P 25 supplied by Nippon Aerosil Co., Ltd.) was suspended. The tube was sealed with a rubber septum and then photoirradiated at a wavelength $\lambda > 300$ nm by a 400 W high-pressure mercury arc (Eiko-sha, Osaka) under argon (Ar) with magnetic stirring at 298 K. The co-catalyst source was reduced by photogenerated electrons, and metal was deposited on the surface of the TiO_2 particles. Analysis of the liquid phase after photodeposition revealed that the co-catalyst source had been almost completely (>99.9%) deposited on the TiO_2 particles. The resultant powder was washed repeatedly with distilled water and then dried at 293 K *in vacuo* for 60 min. Hereafter, TiO_2 having 0.5 wt% of co-catalyst (M) is designated as M(0.5)-TiO_2.

Hydrogenation of an alkynyl group to an alkenyl group in organosilane over M(0.5)-TiO_2 photocatalyst

M(0.5)-TiO_2 powder was suspended in a methanol suspension (5 cm^3) containing triethylsilylacethylene (Tokyo Chemical Industry (TCI), TESA) (190 µmol) in a Pyrex test tube. The tube was sealed with a rubber septum and then photoirradiated at a wavelength $\lambda > 300$ nm by a 400 W high-pressure mercury arc (Eiko-sha, Osaka) under Ar with magnetic stirring at 298 K. After the reaction, the gas phase (H_2) was analyzed using a gas chromatograph (Shimadzu, GC-8A equipped with MS-5A). After the suspension had been filtered to remove the particles, toluene (5 µL) as an internal standard was added. The amounts of TESA and the products, vinyltriethylsilane (VTES) and tetraethylsilane (TES), were determined using a gas chromatograph (Shimadzu, GC-2025 equipped with a DB-1 column).

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Keywords: hydrogenation • photocatalysis • alkynes • TiO_2 • palladium

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Entry for the Table of Contents

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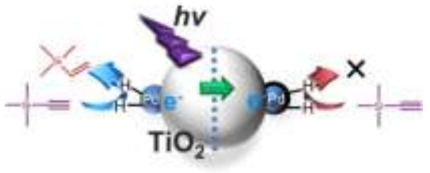

Alkyne hydrogenation had priority to alkene hydrogenation over Pd-TiO$_2$ photocatalyst and the Pd co-catalyst was temporarily deactivated during the reaction, resulting in almost complete semihydrogenation of alkynes by optimizing the amount of alkynes under an additive-free condition.

*Y. Kojima, M. Fukui· A. Tanaka, K. Hashimoto, and H. Kominami**

Page No. – Page No.

Additive-free semihydrogenation of an alkynyl group to an alkenyl group over Pd-TiO$_2$ photocatalyst utilizing temporary in-situ deactivation