Diastereoselective semi-hydrogenation of alkynes to *cis*-alkenes over visible-light responding organically modified titania photocatalyst

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Abstract: Hydrogenation of alkynes over organically modified titania under irradiation of visible light was investigated. Alkynes were selectively hydrogenated to *cis*-alkenes without the formation of *trans*-alkene or alkane which was obtained as a result of isomerization or sequential hydrogenation, respectively. Hydrogenation of alkynes were enhanced by increase in reaction temperature and apparent activation energy calculated by the Arrhenius plot was 27 kJ mol^{-1}, indicating that hydrogenation over copper nanoparticles was the rate-determining step.

Keywords: Semi-hydrogenation, Photocatalyst, Visible light

1. Introduction

Hydrogenation of alkynes is one of important reactions in chemical industry. Especially, semi-hydrogenation of alkynes to alkenes has been applied to syntheses of vitamin A, β-carotene and aromas. Alkenes produced from internal alkynes have *cis*-*trans* isomers. Lindlar's catalyst is currently used for the semi-hydrogenation of alkynes to alkenes.[1] However, toxic lead is used as catalyst poison and a large amount of quinoline should be added to the reaction system. Therefore, environmentally friendly catalytic system is keenly desired. We found that copper loaded titania (Cu-TiO_2) photocatalyst hydrogenated alkynes to *cis*-alkenes with high selectivity under additive- and hydrogen-free conditions.[2]

On the other hand, visible-light responding photocatalyst has been expected to utilize solar light efficiency. It was found that 2,3-dihydroxynaphthalene modified TiO_2 (DHN/TiO_2) having platinum exhibited photocatalytic activity for hydrogen production from aqueous triethanolamine solution and reduction of nitro group to amino group under visible-light irradiation.[3, 4] We reported that hydrogenation of alkenes and chemoselective reduction of aromatic aldehydes proceeded quantitatively using DHN/TiO_2 under irradiation of blue light.[5, 6]

Based on the above mentioned, we here reported diastereoselective semi-hydrogenation of alkynes to *cis*-alkenes over DHN/TiO_2 having Cu as a co-catalyst under irradiation of visible light.

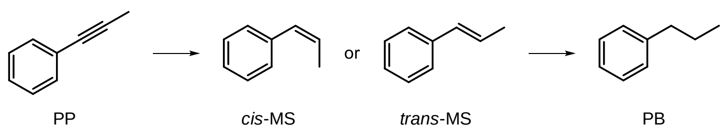
2. Experimental

DHN/TiO_2-Cu was prepared by impregnation (modification of DHN) and photodeposition (loading of Cu) method. In a typical run, prepared DHN/TiO_2-Cu (50 mg) was suspended in 10 vol% water-acetonitrile solution (5 cm^3) containing 1-phenyl-1-propyne (PP, *ca.* 50 μmol) as a substrate and triethanolamine (500 μmol) as a sacrificial reagent in a test tube. The tube was sealed with a rubber septum under argon, and then photoirradiated with visible light of the two sets of a blue LED (420-530 nm, 29.0 and 56.8 mW cm^{-2}) from two directions with magnetic stirring at 298 K.

3. Results and discussion

Fig. 1 shows time courses of hydrogenation of PP (Scheme) in 10 vol% water-acetonitrile suspension of DHN/TiO_2-Cu photocatalyst under irradiation of blue light. The amount of PP monotonically decreased with photoirradiation, while *cis*-β-methylstyrene (*cis*-MS) was formed corresponding to the conversion of PP. When PP had been completely consumed after 6-h photoirradiation, *cis*-MS was obtained with high yield (>99%). During the blue-light irradiation and even after consumption of PP, there was no formation of *trans*-β-methylstyrene (*trans*-MS) or propylbenzene (PB) obtained as a result of isomerization or sequential hydrogenation of *cis*-MS. These results indicated that hydrogenation of PP over DHN/TiO_2-Cu proceeded with high diastereoselectivity. When DHN/TiO_2-Cu was reused for the same reaction, *cis*-MS was obtained with high yield in four reuse tests, indicating that DHN/TiO_2-Cu had high stability and reusability. Moreover, the applicability of photocatalytic hydrogenation of alkynes to alkenes was investigated, various alkynes such as diphenylacetylene, 5-hexynenitrile, 6-chloro-1-hexyne and 3-hexyne-1-ol were hydrogenated to corresponding (*cis*-)alkenes with high yields. Therefore, we achieved the diastereoselective semi-hydrogenation of alkynes to *cis*-alkenes under visible-light irradiation.

In addition, we examined the effect of temperature on hydrogenation of PP using water bath controlled at various temperatures. As shown in Fig. 2, the formed amount of *cis*-MS increased with increase of reaction temperature, indicating that hydrogenation of PP was accelerated at higher temperature. A linear Arrhenius plot (logarithm of rate constants vs reciprocals of temperature) was obtained. Apparent activation energy (E_a) for the formation of *cis*-MS calculated by the Arrhenius plot was 27 kJ mol^{-1}, whereas E_a for the simple dehydrogenation from triethanolamine calculated by the Arrhenius plot was 15 kJ mol^{-1} which was the close value as a typical photocatalytic reaction (*ca.* 10 kJ mol^{-1}). Therefore, we concluded that hydrogenation of alkynes over Cu nanoparticles was the rate-determining step in this photocatalytic system.



Scheme Hydrogenation of PP.

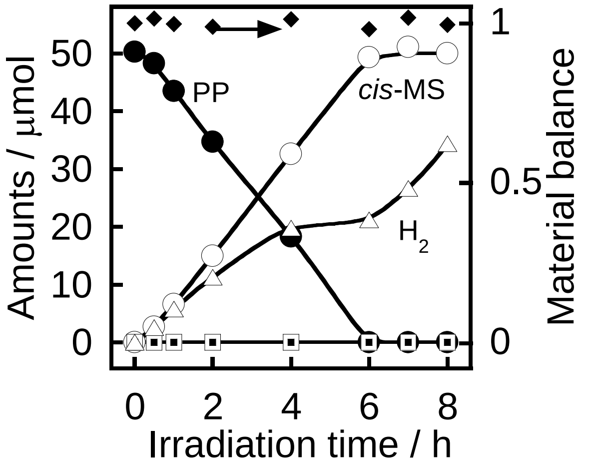


Fig. 1 Time courses of amounts of PP (●), *cis*-MS (○), *trans*-MS (■), PB (□), H_2 (△) and material balance (◆) in photocatalytic hydrogenation of PP.

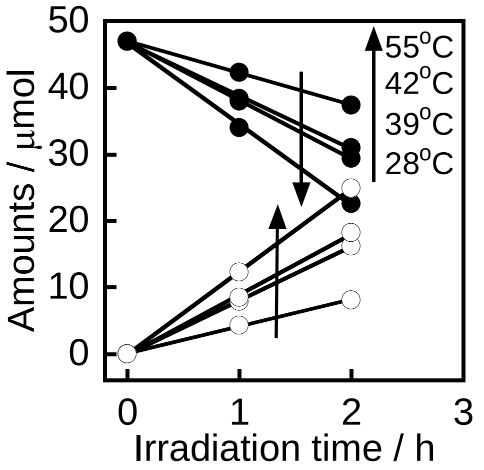


Fig. 2 Effect of temperature on photocatalytic hydrogenation of PP (●) to *cis*-MS (○).

4. Conclusions

We succeeded in the visible-light induced diastereoselective semi-hydrogenation of alkynes to *cis*-alkenes over organically modified titania photocatalyst under additive- and hydrogen-free conditions. From the kinetic study using the Arrhenius plot, in this photocatalytic system, hydrogenation of alkynes over Cu nanoparticles loaded on organically modified titania was the rate-determining step.

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