

Photocatalytic hydrogenation of furan over palladium-loaded titanium dioxide without addition of H₂ gas

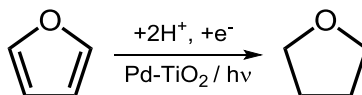
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Hydrogenation of furan is one of methods for preparation of tetrahydrofuran (THF). THF is an important compound as solvent and intermediate of chemical product. The catalytic hydrogenation of furans requires an addition of hydrogen (H₂) gas.^[1, 2] H₂ gas is green reducing agent. However, it is difficult to store and transport H₂ gas. Therefore, a method for hydrogenation of furan without addition of H₂ gas is required. Photocatalytic reaction proceeds at room temperature and under atmospheric pressure, and the titanium dioxide (TiO₂) photocatalyst is easily separated from the reaction mixture after the reaction. In the previous studies, we found that the unsaturated C-C bond was hydrogenated to saturated bond over palladium-loaded TiO₂ (Pd-TiO₂) without addition of H₂ gas^[3,4,5]. In this study, we investigated photocatalytic hydrogenation of furan to THF in a methanolic suspension of Pd-TiO₂.



Scheme Photocatalytic hydrogenation of furan to THF over Pd-TiO₂.

Loading of Pd as co-catalyst on TiO₂ was performed by the photodeposition method. Figure (a) shows time courses of the amounts of furan remaining and THF and H₂ formed in methanolic suspensions of Pd-TiO₂ photocatalyst without addition of H₂ gas. The amount of furan decreased with photoirradiation, while THF as the hydrogenation product of furan was formed corresponding to the decrease in the amount of furan. After 25 min, furan was almost completely consumed and THF was obtained in a high yield (97%). The amount of THF (42 μmol) after photoirradiation for 25 min was larger than the amounts of Pd (4.7 μmol) loaded on TiO₂, indicating that Pd metal works as the catalyst for the hydrogenation of furan. Material balance (M. B.) calculated by using eqn (1) is shown in figure (a).

$$\text{M. B.} = \frac{n(\text{furan}) + n(\text{THF})}{n_0(\text{furan})} \quad (1),$$

where $n(\text{furan})$ and $n(\text{THF})$ are the amounts of furan and THF during the photocatalytic reaction, respectively, and $n_0(\text{furan})$ is the amount of furan before the photocatalytic reaction. The values of M. B. were almost unity during the reaction, indicating that only the reaction shown in scheme occurred with a high selectivity. After consumption of furan, H₂ evolution was predominant because only protons were reducible species in the reaction system. When H₂ is present, catalytic hydrogenolysis of THF may occur over Pd-TiO₂. However, this was

not the case. Since the activation energy of catalytic hydrogenolysis of THF over Pd-TiO₂ is probably large, catalytic hydrogenolysis of THF was suppressed almost completely at 298 K. The kinetic selectivity is effectively utilized in this case because the photocatalytic reaction occurred at room temperature.

An action spectrum is a strong tool for determining whether a reaction observed occurs via a photoinduced process or a thermocatalytic process. To obtain an action spectrum in this reaction system, hydrogenation of furan in methanolic suspensions of Pd-TiO₂ 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 the following eqn (2):

$$\text{AQE} = \frac{4 \times \text{the amount of THF formed}}{\text{amount of incident photons}} \times 100 \quad (2).$$

AQE was in agreement with the absorption spectrum of TiO₂. Therefore, it can be concluded that hydrogenation of furan in a methanolic suspension was induced by photoabsorption of TiO₂. As also shown in Figure (b), AQE reached 37% at 360 nm, indicating that photocatalytic hydrogenation of furan proceeded with high efficiency of photon utilization as well as chemical aspects such as selectivity and M. B..

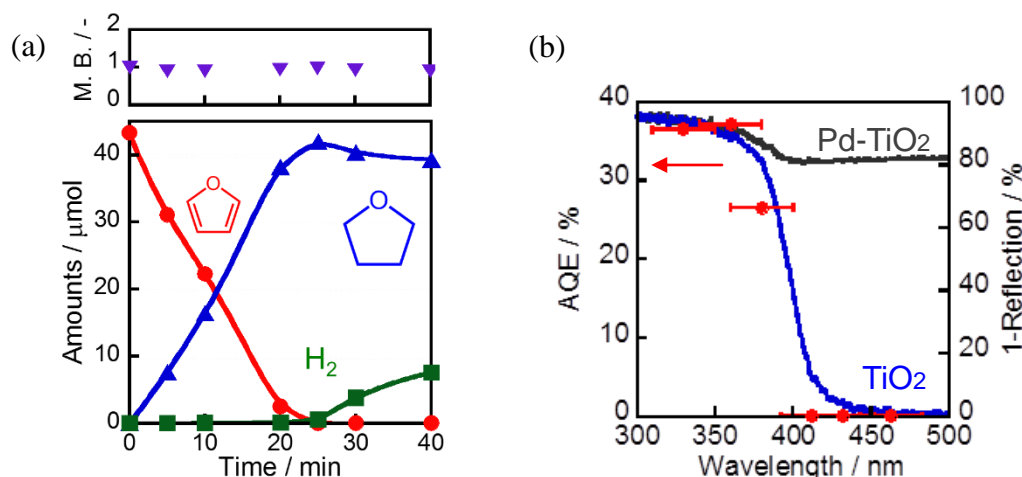


Figure (a) Time courses of amounts of furan (●), THF (▲), H₂ (■) and material balance (M. B., ▼) on photocatalytic hydrogenation in methanolic suspensions of Pd-TiO₂ under irradiation of UV light from LED. (b) Absorption spectrum (right axis) and action spectrum of TiO₂ and Pd-TiO₂ in the hydrogenation of furan (left axis).

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