Photocatalytic lactonization of diols over platinum-loaded titanium oxide

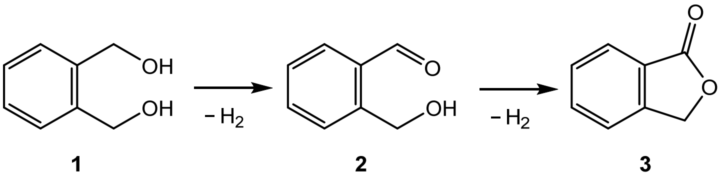
Hisao Yoshida,[a,b,*] **Emiko Wada,**[a] **Akanksha Tyagi,**[a] **Akira Yamamoto**[a,b]
[a] *Graduate School of Human and Environmental Studies, Kyoto University, Kyoto, 606-8501, Japan*
[b] *ESICB, Kyoto University, Kyotodaigaku-Katsura, Kyoto, 615-8520, Japan*
**Corresponding author: FAX +81-75-753-2988, E-mail, yoshida.hisao.2a@kyoto-u.ac.jp*

Abstract: A new catalytic route for lactonization of diols was developed by using metal-loaded TiO_2 photocatalyst. Especially, Pt-loaded rutile TiO_2 exhibited high photocatalytic activity with high selectivity. In addition, it was found that heterogeneous acid catalyst can accelerate this photocatalytic lactonization.

Keywords: Photocatalytic organic synthesis, Rutile, Lactonization of diols.

1. Introduction

Lactones, which is cyclic esters, are important chemical intermediates or solvents in organic syntheses. The dehydrogenative oxidation of diols is a promising synthesis route for lactones. While several heterogeneous catalysts for the lactonization have been reported,[1] we have examined dehydrogenative lactonization of diols at a mild condition without consuming any other reagents by using photocatalyst as a new methodology. In the present study, we found that Pt-loaded rutile TiO_2 photocatalyst can promote the lactonization for the dehydrogenative lactonization of 1,2-benzenedimethanol to phthalide (eq. 1) with high yield and selectivity, which can be also applied to various diols for producing lactones.[2] To our best knowledge, this is the first report for the photocatalytic dehydrogenative lactonization of diols with hydrogen evolution around room temperature.



(1)

2. Experimental

Three kinds of TiO_2 powders supplied from Catalysis Society of Japan (JRC-TIO-8, anatase, 338 m^2/g; JRC-TIO-6, rutile, 100 m^2/g; and JRC-TIO-4, anatase and rutile, 50 m^2/g) were employed as the photocatalysts, where rutile and anatase are referred to as (R) and (A), respectively. Metal loaded TiO_2 (M/TiO_2) samples were prepared by a conventional photodeposition method.[3] The Pt loading amount was 0.1 wt%. The average particle size of the loaded Pt nanoparticles was determined to be 2.1 nm by a CO adsorption method.[3] For each catalytic reaction test, 0.1 g of the M/TiO_2 sample was used. Before the reaction, the sample was photoirradiated for 20 min by a xenon lamp (PE300BUV) with an optical long pass filter (λ>350 nm), where the light intensity measured at 360 nm±15 nm in wavelength was 27 mW cm^{-2}. After an argon purge, the reaction mixture, 200 or 400 μmol of diol dissolved in 4 mL of a solvent, was introduced into a quartz reactor (46 cm^3). The reaction tests were carried out for 1 h or more under photoirradiation. Products in gas phase were analyzed by GC-TCD (Shimadzu, GC-8A) and those in liquid phase were analyzed by GC-MS (Shimadzu, GCMS-QP2020). The product amounts were determined by each calibration curves, although only the amount of 2-(hydroxymethyl)benzaldehyde was determined by using the calibration curve of phthalide. As the amount of hydrogen produced was large, it could not be determined precisely.

3. Results and discussion

Figure 1 shows the time courses of the product yields in the lactonization of 1,2-benzenedimethanol (**1**) over the Pt/TiO_2 samples consisting of anatase or rutile TiO_2 photocatalyst in an acetonitrile solution. In the initial period of the reaction over the Pt/TIO-8(A) photocatalyst, 2-(hydroxymethyl)-benzaldehyde (**2**) was preferably formed and the yield of phthalide (**3**) gradually increased (Fig. 1a). Then, phthalide became the major product after 2 h with a decrease of 2-(hydroxymethyl)benzaldehyde yield. The yield of phthalide reached to 60 % in 3 h. This result indicates that 2-(hydroxymethyl)benzaldehyde is formed as an intermediate, and phthalide is produced by further oxidation. As for the gaseous product, only hydrogen was detected. Therefore, the lactonization of benzenedimethanol to form phthalide proceeds via two-step dehydrogenative oxidation (eq. 1). However, the reaction over the Pt/TIO-8(A) photocatalyst provided low selectivity to phthalide such as 60% after 3 h, but only 25 % after 1 h. The carbon balance was also low such as 60 % after 3 h, which means that formation of other byproducts or decomposition of the substrate and products would also take place. On the other hand, the Pt/TIO-6(R) photocatalyst produced phthalide in the yield of 90 % even at initial 1 h with high selectivity such as 90% (Fig. 1b), where the intermediate 2-(hydroxymethyl)benzaldehyde was not detected. That is, the Pt/TIO-6(R) sample consisting of rutile TiO_2 showed 3.5 times higher yield of phthalide than the Pt/TIO-8(A) sample consisting of anatase TiO_2, although the BET surface area of TIO-6(R) (100 m^2/g) is smaller than that of TIO-8(A) (338 m^2/g). The Pt/TIO-4(A, R) photocatalyst consisting of both anatase and rutile phases with low specific surface area did not afford much phthalide. These results suggest that pure rutile phase is suitable for this lactonization.

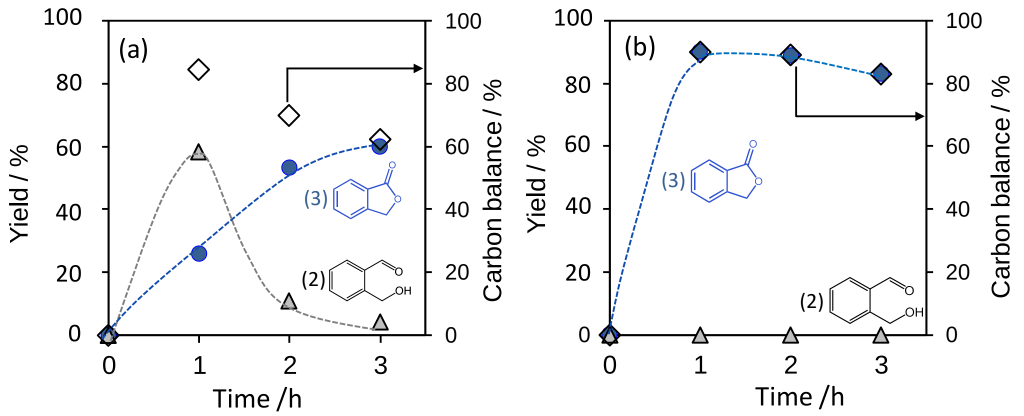


Figure 1. Time courses of products yields in lactonization of 1,2-benzenedimethanol (**1**) over the Pt/TIO-8(A) photocatalyst (a) and the Pt/TIO-6(R) photocatalyst (b). Products were 2-(hydroxymethyl)-benzaldehyde (**2**) and phthalide (**3**). Reaction conditions: 200 µmol of 1,2-benzenedimethanol, 4 mL of acetonitrile, 0.1 g of the Pt/TiO_2 photocatalyst. The wavelength of the irradiation light was longer than 350 nm, and the light intensity was 27 mW cm^{-2} measured at 360±15 nm.

It was also confirmed that the photocatalytic lactonization can be applied to various diols such as 1,2-cyclohexanedimethanol, 1,4-butanediol and 1,5-pentanediol. For these reactions, the Pt/TIO-6(R) photocatalyst exhibited higher activity than the Pt/TIO-8(A) photocatalyst.

Further, the addition of heterogeneous acid catalyst to the reaction system was examined. The yield of phthalide increased when the Al_2O_3 powder sample was introduced to the photocatalytic reaction mixture in the coexistence of the Pt/TIO-6(R) photocatalyst. The acid catalyst having weak acid sites such as Al_2O_3 would selectively accelerate the photocatalytic reaction rate without promoting the side reactions. Separate experiment evidenced that the acid catalysts itself did not promote the reaction without photocatalyst, confirming that the acid catalysis accelerates at least one step during the photocatalytic reaction, which might be the second cyclization step.

References

1. N. Ichikawa, *et al.*, J. Mol. Catal. A Chem. 212 (2004) 197; T. Hu, *et al.*, Catal. Commun. 8 (2007) 193; J. Huang, *et al.*, J. Catal. 252 (2007) 69; T. Akashi, *et al.*, Catal. Commun. 4 (2003) 411; T. Mitsudome, *et al.*, Green Chem. 11 (2009) 793; A. S. Touchy and K. Shimizu, RSC Advances 5 (2015) 29072; Q. Zhu, *et al.*, Green Chem. 12 (2010) 205; Q. Zhu, *et al.*, Appl. Catal. A 435 (2012) 141.
2. E. Wada, A. Tyagi, A. Yamamoto, H. Yoshida, Photochem. Photobio. Sci. , *accepted*. DOI: 10.1039/c7pp00258k
3. E. Wada, T. Takeuchi, Y. Fujimura, A. Tyagi, T. Kato and H. Yoshida, Catal. Sci. Technol. 7 (2017) 2457.