Hydrogen-free Ring Hydrogenation of Aromatic Compounds in Aqueous Suspensions of Rh-loaded TiO_2 Photocatalyst

Hiroshi Kominami,[a, *] **Kousuke Nakanishi,**[b] **Ryosuke Yagi,**[b] **Kazuya Imamura,**[a] **Atsuhiro Tanaka**[a]
[a]*Faculty of Science and Engineering, Kindai University, Higashiosaka, Osaka 577-8502, Japan*
[b]*Interdisciplinary Graduate School of Science and Engineering, Kindai University, Higashiosaka, Osaka 577-8502, Japan*
81-6-4307-3452, hiro@apch.kindai.ac.jp

Abstract: There are various possibilities of co-catalyst-assisted photocatalytic reduction (CPR) over a titanium(IV) oxide (TiO_2) photocatalyst, especially H_2-free and chemoselective CPR. We examined photoinduced ring hydrogenation of aromatics having a carboxyl group over metal-loaded TiO_2 under an H_2-free condition and found that the aromatics were almost quantitatively hydrogenated to corresponding cyclohexanes having a carboxyl group when rhodium, water and oxalic acid were used as a metal co-catalyst, solvent and hole scavenger, respectively. The effects of different metal co-catalysts, solvents and hole scavengers on the ring hydrogenation were also examined.

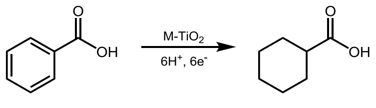
Keywords: Photocatalyst, Ring hydrogenation, TiO_2.

1. Introduction

Since a photocatalytic reaction satisfies almost all of the 12 proposed requirements for green chemistry,[1] photocatalytic conversion of various organic compounds has recently been studied by many researchers.[2] Our research group has explored new photocatalytic reduction systems under a hydrogen (H_2)-free condition with focus on a) selective and chemoselective photocatalytic reduction[3] and b) co-catalyst-assisted photocatalytic reduction (CPR).[4] As a case that satisfies both a) and b), *i.e.*, chemoselective CPR (CCPR), we reported chemoselective reduction.[5] We think that various possibilities are included in CCPR because many metal co-catalysts can be applied for photocatalytic reaction.

Ring hydrogenation of aromatics is an important method to produce compounds consisting of a cyclohexane structure. For example, cyclohexcanecarboxylic acid (CCA) which is an important intermediate of pharmaceutical and related compounds, is generally produced by ring hydrogenation of benzoic acid (BA).[6] In the case of substituted aromatics, hydrogenation (reduction) of the functional groups also occurs as a side-reaction and produces aromatic compounds of which the functional group is reduced. Ring hydrogenation of BA was achieved over metal catalysts supported on suitable supports.[7] However, these catalyst systems require the addition of an excess amount of H_2 gas as a hydrogen source in a closed reactor. Since special care should be paid during a reaction using H_2, a safer catalytic reaction system driving selective ring hydrogenation without the use of H_2 is desired. As described above, there are various possibilities of CCPR, and H_2-free CCPR can be applied for ring hydrogenation of aromatics having a carboxyl group to corresponding alicyclic compounds.

In this study, we chose BA as a model compound of aromatics having a carboxyl group and examined photoinduced H_2-free ring hydrogenation of BA over metal-loaded TiO_2, in the presence of a hole scavenger that works as an electron and hydrogen source (Scheme 1).



Scheme. Photoinduced ring hydrogenation of benzoic acid in an aqueous suspension of metal (M)-loaded TiO_2 under an H_2-free condition.

2. Experimental

Loading of co-catalyst on TiO_2 was performed by the photodeposition method. In a typical procedure of photocatalytic reaction, metal-loaded TiO_2 (50 mg) was suspended in 5 cm^3 of water containing BA and OA as a hole scavenger in a test tube, which was sealed with a rubber septum and then photoirradiated under Ar at 298 K with the high-pressure mercury lamp.

3. Results and discussion

Figure 1 shows time courses of BA remaining, CCA formed and H_2 evolved in an aqueous suspension of 1.0 wt% Rh-TiO_2 under irradiation of UV light. Just after irradiation, the amount of BA monotonously decreased, while CCA was formed. After 60 min, BA was almost completely consumed and CCA was obtained in a high yield (93%). To evaluate the selectivity of CCA and intermediates in the BA hydrogenation, an indicator, i.e., material balance (MB), was calculated by Equation (1):

$$MB = \frac{n(BA) + n(CCA)}{n_0(BA)}, \tag{1}$$

where n(BA) and n(CCA) are the amounts of BA and CCA during the photocatalytic reaction, respectively, and n_0(BA) is the amount of BA before the photocatalytic reaction. During the reaction, the value of MB was ca. 0.9. However, no other product such as benzaldehyde, benzyl alcohol or toluene was detected in the reaction mixture. As also shown in Figure 1, H_2 evolution was predominant under excessive photoirradiation after consumption of BA, indicating that active hydrogen species (AHS) over Rh were continuously formed by proton reduction over the Rh co-catalyst. We noted that the amount of CCA did not decrease after complete consumption of BA. Since an excess of OA used as a hole scavenger effectively consumes positive holes, the possibility of CCA re-oxidation and over-hydrogenation was eliminated.

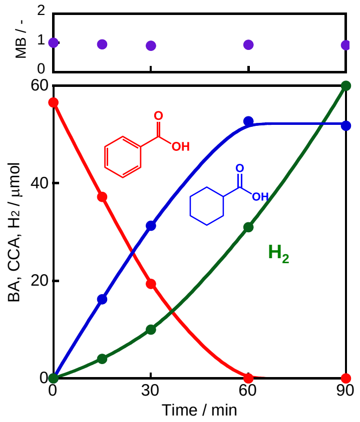


Figure 1. Time courses of BA remaining, CCA formed, and H_2, evolved in an aqueous suspension of 1.0 wt% Rh-TiO_2 under irradiation of UV light.

4. Conclusions

We examined photoinduced ring hydrogenation of BA in an aqueous suspension of metal-loaded TiO_2 in the presence of OA under an H_2-free condition. Rh-TiO_2 showed distinctive photocatalytic activity for the largest production of CCA, and apparent quantum efficiency reached 16% at 360 nm.

References

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