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Simultaneous production of aromatic aldehydes and dihydrogen by photocatalytic dehydrogenation of liquid alcohols over metal-loaded titanium(IV) oxide under oxidant- and solvent-free conditions

Kazuya Imamura, Hikaru Tsukahara, Kenta Hamamichi, Naoko Seto, Keiji Hashimoto, Hiroshi Kominami*

Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University, Higashiosaka, Osaka 577-8502, Japan

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ABSTRACT

Photocatalytic conversion of aromatic alcohols in acetonitrile (CH_3CN) suspensions of metal-loaded titanium(IV) oxide under various conditions was examined. Benzaldehyde (PhCHO) and hydrogen (H_2) were simultaneously produced with a molar ratio of 1:1 from benzyl alcohol (BnOH) in CH_3CN suspensions of platinum-loaded titanium(IV) oxide (Pt–TiO_2) under deaerated conditions and BnOH was converted quantitatively with high apparent quantum efficiency of 38% at 366 nm. The yield of PhCHO in dehydrogenation under deaerated conditions (>99%) was much higher than that (53%) obtained by dehydrogenation of BnOH in the presence of oxygen accompanying the formation of water instead of H_2. When a small amount of water was intentionally added to the CH_3CN suspension of Pt–TiO_2, reaction rates of hydrogenation drastically decreased. Control experiments carried out under air and in the presence of water indicated that an oxygen-free condition was important for quantitative conversion of BnOH to PhCHO in two points, i.e., the reaction under oxygen-free conditions yields no water and active oxygen, that caused drastic decrease in the reaction rate and undesired oxidation of BnOH and PhCHO, respectively. Photocatalytic dehydrogenation of BnOH to PhCHO occurred even in a solvent-free condition in which Pt–TiO_2 particles were suspended in BnOH. Photocatalytic hydrogenation under deaerated conditions was applied for conversions of various aromatic alcohols to corresponding aldehydes.

1. Introduction

Since carbonyl compounds such as aldehydes and ketones are precursors for many drugs, vitamins and fragrances, selective oxidation of alcohols to carbonyl compounds is one of the most important transformations in industrial chemistry. In particular, the oxidation of primary alcohols to aldehydes is a fundamentally important laboratory and commercial procedure [1–6]. Aromatic aldehydes are valuable as intermediates for both perfumes and medicines [5–7]. Although there are many methods for oxidation of alcohols to aldehydes, these methods are generally carried out at a high temperature and high pressure by employing stoichiometric oxygen donors (such as chromate and permanganate) [7–10]. Since large amounts of wastes containing heavy metal are formed along with the products, atom efficiency [11], which is defined as Eq. (1), of these methods is very low.

$$\text{Atom efficiency}\,(\%) = \frac{\text{molecular weight of the desired product}}{\text{sum total of molecular weights of all substances produced}} \times 100 \quad (1)$$

A catalytic process is favorable especially in an oxidation of alcohols to corresponding carbonyl groups using molecular oxygen (O_2) as oxidant instead of stoichiometric oxygen donors. Since only water (H_2O) is formed as the by-product when O_2 is used, atom efficiency is much higher than that of oxidations using stoichiometric oxygen donors. A catalytic process for selective oxidation of various alcohols to corresponding aldehydes under mild conditions, i.e., low temperature and nearly atmospheric pressure, has recently been reported [12]. Since a photocatalytic reaction proceeds at room temperature and under atmospheric pressure, application of photocatalytic reactions to organic synthesis has attracted attention in terms of green chemistry. Recently, photocatalytic partial oxidations of benzyl alcohol with O_2 have been reported [13–17]. However, atom efficiency in these photocatalytic methods never reaches 100% because a stoichiometric amount of H_2O is formed as a by-product. Formation of aldehydes by simple dehydrogenation

* Corresponding author. Tel.: +81 6 6721 2332; fax: +81 6 6727 2024.
E-mail address: hiro@apch.kindai.ac (H. Kominami).

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