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TiO_2-photocatalytic acceptorless dehydrogenation coupling of primary alkyl alcohols into acetals†

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Primary alkyl alcohols can be directly converted into acetals and H_2 *via* TiO_2-photocatalytic dehydrogenation coupling at room temperature, with no need for any hydrogen acceptors. The reaction follows a tandem process integrating photocatalytic alcohol dehydrogenation and H^+-catalytic acetalation, in which the H^+ ion catalysts are provided by the alcohol dehydrogenation in real time. This approach exhibits a very high reaction rate and product selectivity, and represents a novel green process for the conversion of primary alkyl alcohols, especially for bio-renewable ethanol and 1-butanol.

The serious environmental problems derived from fossil fuel-based chemical industries have triggered a growing demand in green chemistry, which is characterized by the employment of renewable feedstocks/energy, and more efficient and clean processes with good atom-economies and low energy consumption.[1–4] In this context, the efficient oxidation of ethanol and butanol into various chemicals such as aldehydes, ketones, esters, and acetals attracts great attention[5,6] because they can be readily produced from the fermentation of renewable biomass.[7–9] Acetals are not only a class of important chemical intermediate but they are also promising fuels or fuel additives due to their excellent combustion properties and water-insolubility.[10–14]

Conventional conversion of alcohols into acetals is a two-step process: alcohols are first oxidized to aldehydes, which are then condensed with alcohols into acetals using an acidic catalyst.[15–17] One-pot oxidation coupling of primary alcohols into acetals with molecular oxygen has been explored, with relatively high selectivity, using multielement catalysts consisting of palladium acetate, copper acetate, and *p*-toluenesulfonic acid (or perchloric acid).[18] In these processes, realization of the acetalation reaction requires environmentally malignant acidic catalysts. Stoichiometric or excess molar amounts of expensive and toxic oxidants such as chromate and permanganate are often required as sacrificial hydrogen acceptors for the oxidation of alcohols. Although great progress has been made on the selective oxidation of alcohols into aldehydes using O_2 as a cheap and clean hydrogen acceptor,[19–21] it is still difficult to use O_2 in the selective oxidation of ethanol/butanol-like primary alkyl alcohols.[22,23] Additionally, in the hydrogen acceptor-employed processes, a proportion of the energy-rich hydrogen atoms in alcohols are undesirably wasted, which is particularly emphasized in the conversion of inherently hydrogen-poor biomass sources. Recently, considerable attention has been paid to converting alcohols *via* acceptorless dehydrogenation (AD) reactions, in which alcohols are dehydrogenated to form aldehydes/ketones or successive reaction products, with the simultaneous liberation of a H_2 molecule as a high-energy clean fuel,[24–28] representing atom-economical green processes. However, the unfavorable thermodynamics of alcohol dehydrogenation make the AD processes highly challenging, requiring powerful selective catalysts to realize the reaction under mild conditions, especially for the direct acceptorless dehydrogenation coupling (ADC) of alcohols into acetals. Recently, Milstein *et al.*[24] found that an acridine-based ruthenium complex can catalyze the ADC reactions of 1-pentanol and 1-hexanol to the corresponding acetals and H_2, providing the possibility of converting alcohols into acetals directly. Unfortunately, since their homogenous catalytic reactions require higher temperatures and must be performed under reflux conditions, bio-renewable ethanol and butanol failed to react due to their low boiling points.[24] In addition, the high temperature conditions might be responsible for the relatively low selectivity, which was 53–88% for 1-hexanol.

On the other hand, photo-driven organic reactions have attracted growing interest due to the great potential of using renewable solar energy and its powerful abilities in the realization of thermodynamically unfavorable reactions at room temperature.[29–34] Highly selective oxidation of alcohols into aldehydes and ketones with O_2 was recently achieved by photo-

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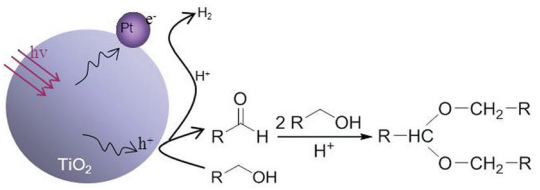
catalytic processes.[35–39] The oxidation coupling reaction of ethanol into diethoxyethane (DEE) was also studied by Yoshida *et al.*,[40,41] using silica-supported Ta_2O_5 and Nb_2O_5 photocatalysts. However, the reaction did not occur without the presence of O_2 over the employed photocatalysts, and the aerobic conditions made the reaction quite complicated, leading to the formation of considerable amounts of by-products such as acetaldehyde, acetate acid, and ethene. The photocatalytic anaerobic dehydrogenation (oxidation) of alcohols in aqueous solution has been extensively studied for the purposes of H_2 generation from water and alcohols,[42–44] in which alcohols serve as sacrificial active reagents or hydrogen donors and are degraded to CO_2. We were recently intrigued by the idea of selectively converting the "sacrificed" alcohols synchronously into valuable products during photohydrogen production. We found that over TiO_2 photocatalysts, ethanol could undergo an acceptorless dehydrogenation C–C coupling reaction in aqueous solution and selectively produce 2,3-butanediol during the H_2 liberation.[45] In this water-mediated process TiO_2 photocatalysts with lower reactivities, such as rutile TiO_2, are favorable for selective coupling, while highly reactive photocatalysts, such as commercial TiO_2 (Degussa P25), tend to over-oxidize ethanol into acetic acid and CO_2.

Herein we report that in organic media or neat reagents, primary alcohols (including bio-renewable ethanol and butanol) can undergo the ADC reaction under UV irradiation with the highly active P25-TiO_2 photocatalyst, selectively producing acetals; aldehydes first form *via* hole-induced dehydrogenation of alcohols and then condense *in situ* with unreacted alcohols into acetals. Simultaneously, the formed H^+ ions are reduced by photo-generated electrons into H_2, as shown in Scheme 1.

At the start of our investigation, we performed dehydrogenation of butanol in cyclohexane solution in an argon atmosphere, using a commercial TiO_2 photocatalyst (Degussa P25) under UV irradiation at room temperature. Pure TiO_2-P25 did not show any detectable reaction after a long irradiation time (52 hours). When 1 wt% of platinum co-catalyst was loaded onto the P25 surfaces (Pt-P25), hydrogen was immediately generated. Analyses of the liquid products by GC-MS showed that butanol was successfully converted into the coupling product, dibutoxybutane (DBB). The conversion of butanol is more rapid initially, reaching 75% within 12 h, and then it increases slowly to 96% after 50 h (Fig. 1). The reacted butanol was nearly completely converted into DBB, with a selectivity of 99.6%, although trace amounts of other products,



Scheme 1 Schematic illustration of the TiO_2-photocatalytic ADC reaction for the direct conversion of primary alcohols into acetals.

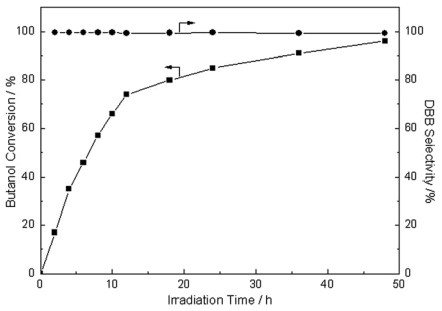
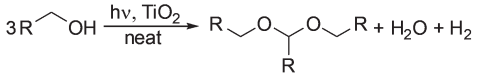


Fig. 1 Photocatalytic conversion of butanol into DBB in cyclohexane. Conditions: butanol, 10 mmol; solution volume, 20 ml; catalyst, Pt-P25, 0.1 g with 1 wt% of platinum; atmosphere, argon; temperature, 20 °C; light source, 300 W high-pressure Hg-lamp.

Table 1 Experimental data for the TiO_2-photocatalytic ADC reaction for the direct conversion of primary alcohols into acetals[a]



Entry	Alcohol	Catalyst	Conv. (%)	Sel. (%)	Rate[b] (mmol g^{-1} h^{-1})
1	1-Butanol	Pt-P25	22.2	99.2	40.4
2	1-Butanol	Pt-rutile	2.5	99.5	4.6
3	1-Butanol	Pt-Brookite	0.9	99.5	1.6
4	1-Butanol	Pd-P25	21.3	99.3	38.8
5	1-Butanol	Au-P25	16.1	99.5	29.3
6	1-Butanol	Rh-P25	8.6	99.6	15.7
7	Ethanol	Pt-P25	27.7	99.3	79.2
8	1-Propanol	Pt-P25	24.8	99.5	55.3
9	1-Pentanol	Pt-P25	17.9	99.3	27.4
10	1-Hexanol	Pt-P25	12.1	97.2	16.2
11	2-Propanol[c]	Pt-P25	5.1	0	11.1
12	2-Butanol[c]	Pt-P25	4.0	0	7.3
13	Benzyl alcohol[c]	Pt-P25	3	0	4.8

[a] Reaction conditions: alcohol, 20 ml; TiO_2, 0.1 g; noble metal co-catalyst, 1 wt%; atmosphere, argon; temperature, 20 °C; light source, 300 W high-pressure Hg-lamp; irradiation time, 12 h. [b] The rates were calculated on the basis of the converted alcohols. [c] These alcohols are only dehydrogenated into the corresponding ketones or aromatic aldehydes, showing no coupling reaction.

such as 1-butyraldehyde, butyric acid, butyl butyrate, CO, and CO_2 were also detected. We additionally evaluated the reaction using Pt-P25 over 12 h using neat butanol (butanol serves as both a reactant and solvent). It showed that the reaction still exhibited a very high selectivity for the formation of DBB (99.2%) and a butanol conversion of 22. 2% (Table 1, entry 1). Obviously, the reaction displays a higher reaction rate when using the neat alcohol, reaching 40.4 mmol g^{-1} h^{-1} (*vs.* 2.2 mmol g^{-1} h^{-1} in cyclohexane).

We also investigated the effect of the TiO_2 structure on the catalytic performance. The P25-TiO_2 photocatalyst exhibits a much higher activity than rutile and brookite TiO_2, which is likely to be due to its anatase–rutile-mixed phase structure that facilitates the separation of electron–hole pairs.[45–47] However, the product selectivity does not seem to be dependent on the

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structure, and is always at a very high level, above 99% (Table 1, entries 2, 3). This is quite different from the situation reported previously for photocatalytic hydrogen generation from an aqueous solution of alcohols,[48,49] where over-oxidation of ethanol into acetic acid and CO_2 was dominant for the P25-TiO_2 photocatalyst due to its high reactivity. When using neat alcohol, over-oxidation of the alcohol is intrinsically avoided due to the absence of external oxygen sources in the reaction system. Other noble metal co-catalysts such as palladium, gold, and rhodium were also evaluated, and the results showed that all of these co-catalysts, like platinum, can promote the ADC reaction to different extents and show no obvious loss in reaction selectivity (Table 1, entries 1, 4–6).

We further explored the ADC reaction of other neat alcohols. The results are presented in Table 1. Similar to the situation with butanol, primary alcohols such as ethanol, 1-propanol, 1-pentanol and 1-hexanol exhibit highly selective conversion towards the corresponding acetals, with selectivities of 99.3, 99.5, 99.3 and 97.2, respectively (Table 1, entries 7–10). In contrast, secondary and aromatic alcohols (such as 2-propanol, 2-butanol, and benzyl alcohol) failed to display the coupling behavior, and only dehydrogenated slowly into the corresponding ketones or aromatic aldehydes (Table 1, entries 11–13). These data indicate that primary alcohols can generally undergo a dehydrogenation coupling reaction under photocatalytic conditions and readily produce acetals. Notably, the rates of the ADC reactions of primary alcohols are several times higher than the rates of sole dehydrogenation of secondary and aromatic alcohols, for instance, 40.4 mmol g^{-1} h^{-1} for 1-butanol *vs.* 7.3 mmol g^{-1} h^{-1} for 2-butanol. Deducting the chemical stoichiometric effect in the ADC reaction (the dehydrogenation of one alcohol molecule induces the condensation of an additional two molecules into acetals), the rate of the ADC reaction is still higher, suggesting that there is an acceleration effect involved in the ADC reaction. On comparison with a previously reported thermo-catalytic homogenous process,[24] the present photocatalytic ADC reaction is comparable in reaction rate and exhibits higher product selectivity. For instance, the conversion rates for pentanol and hexanol in the present approach are 27.4 and 16.2 mmol h^{-1} g^{-1}, respectively, with high product selectivities of 99.3 and 97.2%. While the conversion rates for pentanol and hexanol in the previously reported thermo-catalytic process[24] are 21.7 and 21.3 mmol h^{-1} g^{-1}, respectively, with lower product selectivities of 98 and 88.6%. Additionally, the direct synthesis of acetals from biorenewable ethanol and butanol is permitted in this photocatalytic approach but not in the thermo-catalytic method.

Regarding the mechanism, we are almost certain that the total reaction is mediated by aldehydes because they are the initial products of alcohol dehydrogenation, although aldehydes were detected only in a trace amount during the conversion of primary alcohols. What is more interesting is how aldehydes condense with alcohols to form acetals so efficiently, so that they are converted almost completely after their formation. As proposed by Milstein *et al.*, enol ethers might be the intermediates in their thermo-catalytic process,[24] but these types of compounds were not observed in our reaction systems, suggesting that the mechanism for the formation of acetals in our photocatalytic process might be different. In investigations into photocatalytic H_2 generation from water, alcohols were frequently employed as sacrificial reagents and oxidized by photo-generated holes to produce H^+ ions for subsequent H_2 generation from the reduction of H^+ ions by photo-generated electrons.[43,45] In view of the similarities between this oxidation process and the present process (except the waterless medium here), we detected H^+ ions throughout the duration of the reactions for both ethanol and butanol. It was found that H^+ ions are generated in the liquid bulk phase and exhibit a quick increase in concentration within the initial 40 min of the reaction, after which the concentrations stay at constant values, $1 \times 10^{-3.4}$ and $1 \times 10^{-3.0}$ mol L^{-1} for ethanol and butanol, respectively (Fig. 2a). The H^+ ions generated afterwards are continually reduced to H_2 by photo-generated electrons. Based on this information, we estimated that condensation of the aldehydes and alcohols into acetals was likely to be realized by a catalytic function of the H^+ ions formed in real time, following the traditional acid-catalyzed acetalation pathway.[15–17] This estimation is strongly supported by the following additional observations. (1) As tested, a H^+ ion concentration of 1×10^{-3} mol L^{-1} (externally fed with HCl) is high enough to promote an acetalation reaction for both ethanol–acetaldehyde and butanol–butyraldehyde pairs. The reactions are quite fast, reaching the equilibrium stage within

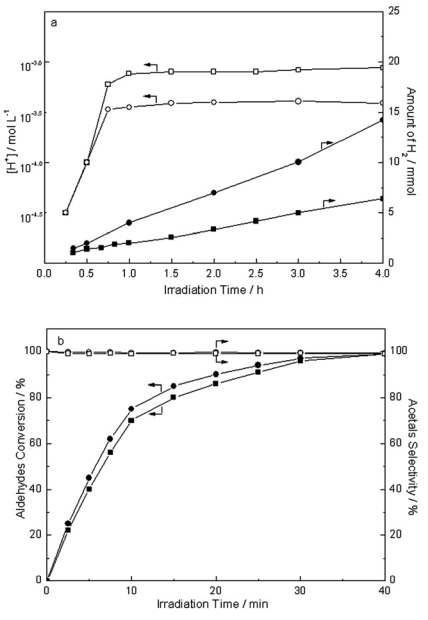

Fig. 2 (a) The evolution profiles for H^+ ions and H_2 during the photocatalytic ADC reactions of ethanol (circle) and butanol (square). The reaction conditions are the same as those shown in Table 1 (entries 7 and 1). (b) Photocatalytic condensation of acetaldehyde–ethanol (circle) and butyraldehyde–butanol (square) pairs into DEE and DBB, respectively, with no acid catalysts fed externally. Conditions: ethanol/butanol, 20 ml; acetaldehyde/butyraldehyde, 1 ml; others are the same as those shown in Table 1.

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41 min. (2) The acetaldehyde–ethanol and butyraldehyde–butanol reactant pairs show no reaction in the dark without acid catalysts fed externally, but display a very fast acetalation reaction under photocatalytic conditions. Fed aldehydes (one-twentieth of the amount of the corresponding alcohols) are completely converted into acetals within 30 minutes (Fig. 2b), catalyzed by the H^+ ions generated from the photocatalytic dehydrogenation of ethanol/butanol. These observations reveal that the present dehydrogenation coupling of primary alcohols into acetals follows a photocatalysis and H^+-catalysis tandem reaction mechanism, as shown in Scheme 1. Alcohols are first dehydrogenated by photo-generated holes into aldehydes, which then undergo an *in situ* H^+-catalytic acetalation reaction with unreacted alcohols. This mechanism gives a good explanation for the failed attempts for secondary and aromatic alcohols in the photocatalytic ADC reaction. As tested, they are incapable of reacting with the corresponding ketones and aromatic aldehydes, even if a higher concentration of acid catalyst (HCl) is fed externally.

Furthermore, in the photocatalysis and H^+-catalysis tandem reaction, the rate-determining step is estimated to be the photocatalytic dehydrogenation because the acid-catalytic acetalation reaction is considerably fast (Fig. 2b). It is further confirmed by special light on–off switch experiments on the ethanol–butanol reaction system, which showed that DBB is readily produced upon light irradiation but there is no change in its amount upon the light turning off (Fig. 3). These kinetics characteristics provide an initial perspective for the further understanding of the high selectivity and the acceleration effect shown in the ADC of primary alcohols. The high efficiency and rapid kinetics of the H^+-catalytic acetalation reaction mean that the dehydrogenation products (aldehydes) are effectively consumed, which is largely responsible for the high selectivity. Unlike other alcohol oxidation processes,[18,24] which generated many by-products such as aldehydes and esters, especially the oxidation cases using O_2, the fast H^+-catalytic acetalation moiety in the present process totally eliminates intermediate aldehydes and kinetically prevails over the dehydrogenation of intermediate hemiacetals, which was considered responsible for the formation of esters.[26]

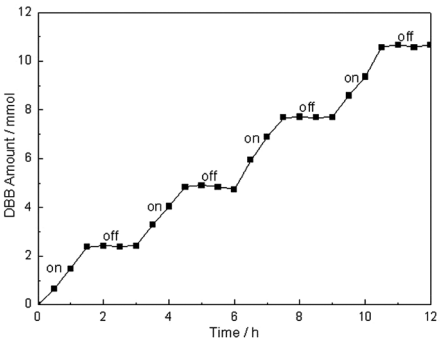

Fig. 3 Light on–off responses of DBB production in the photocatalytic ADC reaction of butanol. Conditions are the same as those shown in Table 1 (entry 1).

Conclusions

We find that primary alcohols can be directly converted into acetals and H_2 by a TiO_2-photocatalytic process at room temperature with no need of any externally added reagents including hydrogen acceptors. Notably, this reaction occurs *via* a tandem process consisting of a photocatalytic dehydrogenation reaction of alcohols and a H^+-catalytic acetalation reaction, and displays a very high selectivity (>99%). This result not only represents a green, highly selective process for the acceptorless dehydrogenation of alcohols into acetals, especially for bio-renewable ethanol and butanol, but also provides a paradigm for integrating photocatalysis, acid-catalysis, and the feeding and cleaning-up of an acidic catalyst (H^+) in a single reaction unit, which makes the reaction system more efficient and clean.

Experimental section

TiO_2-P25 photocatalyst was purchased from Degussa Company. Rutile and brookite TiO_2 photocatalysts were prepared by a hydrothermal process referring to the methods reported previously.[50,51] Noble metal co-catalysts were loaded on the TiO_2 by an *in situ* photodeposition method.[44] $H_2PtCl_6{\cdot}6H_2O$, $PdCl_2$, $RhCl_3{\cdot}3H_2O$, and $HAuCl_4{\cdot}3H_2O$ were used as precursors. The photocatalytic reactions were performed in a quartz photoreactor, containing 20 ml solution (alcohol in cyclohexane or neat alcohol) and 0.1 g catalyst (loading 1 wt% noble metal), with pure Ar continuously bubbling. A 300 W high-pressure Hg lamp was used as a light source and was cooled by 20 °C water circulation. Liquid products were analyzed by GC (GC-950 using a flame ionization detector (FID) and Rtx-5 column from Alltech) and GC-MS (Shimadzu GCMS-QP2010 using a mass spectrometer and DB-5 ms column from Alltech). Identification of compounds was carried out by comparing mass spectra and/or retention times of pure chemicals. The concentrations of alcohols and acetals were determined using a GC system and cyclohexane was used as an internal standard. A GC-9790 (equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID)) was used to detect CO, CO_2 and H_2. Concentrations of H^+ ions in liquid solution were detected in a water-diluted reaction solution using a Leici PHSJ-3F pH meter.

Acknowledgements

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