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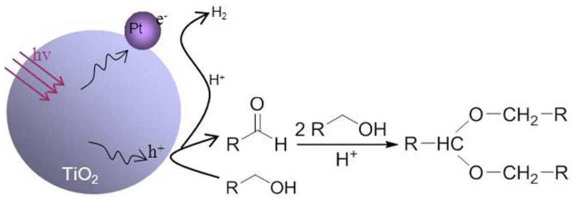

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COMMUNICATION

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 a TiO_2-photocatalytic dehydrogenation coupling at room temperature, with no need for any hydrogen acceptors. The reaction follows a tandem process integrated with 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 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 heavy environmental problems derived from fossil fuel-based chemical industries have triggered a growing demand in green chemistry, which is characterized as the employments of renewable feedstock/energy and more efficient and clean processes with atom-economy 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 draws great attention [5, 6] because they can be readily produced from the fermentation of renewable biomass.[7-9] Acetals is not only a class of important chemical intermediate but also promising fuels or fuel additives due to their excellent combustion property and water-insolubility.[10-14]

The conventional conversion of alcohols into acetals is the two-step process: alcohols first are oxidized as aldehydes which then condense with alcohols into acetals catalyzed by acidic catalyst.[15-17] One-pot oxidation coupling of primary alcohols into acetals with molecule 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, the realization of the acetalation reaction requires environmentally malignant acidic catalysts. Particularly, 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 the selective oxidation of alcohols into aldehydes using O_2 as a cheap and clean hydrogen acceptor have got great progress,[19-21] it is still difficult in the selective oxidation of ethanol/butanol-like primary alkyl alcohols.[22, 23] Additionally, in the hydrogen acceptor-employed processes, a part of energy-rich hydrogen atoms involved in alcohols are undesirably wasted, which should be emphasized particularly for the conversion of the inherently hydrogen-poor biomass sources. Recently, considerable attentions have been paid to convert alcohols with acceptorless dehydrogenation (AD) reactions, in which alcohols are dehydrogenated as aldehydes/ketones or successive reaction products, with the simultaneous liberation of molecule H_2 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 challenged, requiring powerful selective catalysts to realize 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 reaction of 1-pentanol and 1-hexanol to corresponding acetals and H_2, providing the possibility of converting alcohols into acetals directly. Unfortunately, since their homogenous catalytic reactions require higher temperatures, performed under refluxing conditions, the bio-renewable ethanol and butanol failed to react due to their low boiling points.[24] In addition, the high temperature condition might be also responsible for the relatively low selectivity, 53-88% for 1-hexanol.

On the other hand, photo-driving organic reactions have catch growing interests due to the great potential of using renewable solar energy and its powerful ability of realizing the thermodynamically unfavorable reaction at room temperature.[29-34] Highly selective oxidation of alcohols with O_2 into aldehydes and ketones was recently achieved by photocatalysis process.[35-39] The oxidation coupling 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 O_2 over the employed photocatalysts and the aerobic condition made the reaction quite complicated and leaded to the formation of considerable amounts of by-products such as acetaldehyde, acetate acid, and ethene. Actually, the photocatalytic anaerobic dehydrogenation (oxidation) of alcohols in aqueous solution has been extensively studied for the purposes

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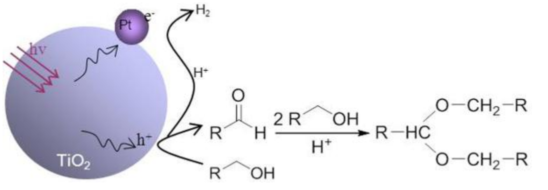
of H_2 generation from water and alcohols,[42-44] in which alcohols serve as sacrificed active reagents or hydrogen donors and are degraded as CO_2. We recently intrigued by the idea of selectively converting the "sacrificed" alcohols synchronously into valuable products during the photohydrogen production. We found that over TiO_2 photocatalysts, ethanol could perform 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, lower reactive TiO_2 photocatalysts such as rutile TiO_2 are favorable for the selective coupling, while the highly reactive photocatalysts such as the commercial TiO_2 (Degussa P25) tends to over-oxidize ethanol as acetic acid and CO_2.



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

Herein we report that in organic medium 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, in which aldehydes first form by a 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.

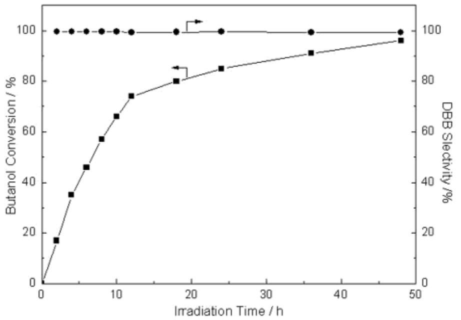
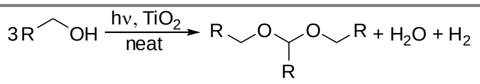


Fig. 1 Photocatalytic conversion of butanol into DBB in cyclohexane. Conditions: butanol, 10 mmol; solution volume, 20 ml; catalyst, Pt-P25, 0.1 g with 1 wt% of platinum; atmosphere, argon; temperature, 20 °C; Light source, 300 W high-pressure Hg-lamp.

At the start of our investigations, we performed the dehydrogenation of butanol in cyclohexane solution in argon atmosphere, using a commercial TiO_2 photocatalyst (Degussa P25) under a UV irradiation at room temperature. Pure TiO_2-P25 showed no any detectable reaction after a long irradiation (52 hours). When 1 wt% of platinum co-catalyst was loaded on P25 surfaces (Pt-P25), hydrogen was immediately generated. The analyses of the liquid products by GC-MS showed that butanol is successfully converted into the coupling product, dibutoxybutane (DBB). The conversion of butanol is more rapid initially, reaching 75% within 12 h, and then increases slowly to 96% after 50 h reaction (Fig. 1). The reacted butanol is near completely converted into DBB, with a selectivity of 99.6%, although trace amounts of other products, such as 1-butyraldehyde, butyric acid, butyl butyrate, CO, and CO_2 were also detected. We additionally evaluated the reaction using Pt-P25 within 12 h under neat butanol condition (butanol serves as both reactant and solvent). It showed that the formation of DBB still exhibits a very high selectivity (99.2%) and a butanol conversion of 22. 2 % (Table 1, entry 1). Obviously, the reaction displays a higher reaction rate under the neat condition, reaching 40.4 $mmol \cdot g^{-1} \cdot h^{-1}$ (vs. 2.2 $mmol \cdot g^{-1} \cdot h^{-1}$ in cyclohexane).

We also inspected the effect of TiO_2 structure on catalyst performance. The P25-TiO_2 photocatalyst exhibits much higher activity than rutile and brookite TiO_2, likely due to its anatase-rutile-mixed phase structure that facilitates the separation of electron-hole pairs.[45-47] However, the product selectivity seems not dependent on the structure, always at a very high level, above 99% (Table 1, entries 2, 3). This event is quite different from the situation reported previously in the photocatalytic hydrogen generation from an aqueous solution of alcohols,[48, 49] where over-oxidation of ethanol into acetic acid and CO_2 is dominant for the P25-TiO_2 photocatalyst due to its high reactivity. Under the neat conditions, over-oxidation of alcohols 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 extent and show no obvious loss in reaction selectivity (Table 1, entries 1, 4-6).

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



Entry	Alcohol	Catalyst	Conv. (%)	Sel. (%)	Rate[b] ($mmol \cdot g^{-1} \cdot h^{-1}$)
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 corresponding ketones or aromatic aldehydes, showing no coupling reaction.

We further explored the ADC reaction of other alcohols under a neat condition. The results are presented in Table 1. Similar to the situation of butanol, primary alcohols such as ethanol, 1-

propanol, 1-pentanol and 1-hexanol exhibit a highly selective conversion towards corresponding acetals, with selectivities of 99.3, 99.5, 99.3 and 97.2, respectively (Table 1, entries 7-10). Differently, the secondary and aromatic alcohols (such as 2-propanol, 2-butanol, and benzyl alcohol) fail to display the coupling behavior, only dehydrogenated slowly into corresponding ketones or aromatic aldehydes (Table 1, entries 11-13). These data indicate that primary alcohols can generally behave as a dehydrogenation coupling reaction under photocatalytic conditions and readily produce acetals. Notably, the rates of the ADC of primary alcohols are several times higher than the rates of the 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. Deducted the chemical stoichiometric effect in the ADC reaction (the dehydrogenation of one alcohol molecule induce additional two molecules condensing into acetals), the rate of the ADC reaction is still higher, suggesting that there is an acceleration effect involved in the ADC reaction. In comparison with the 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 present approach are 27.4 and 16.2 mmol·h^{-1}·g^{-1}, respectively, with higher product selectivity of 99.3 and 97.2%. While, the conversion rates for pentanol and hexanol in the previously reported thermo-catalysis process[24] are 21.7 and 21.3 mmol·h^{-1}·g^{-1}, respectively, with lower product selectivity of 98 and 88.6%. Particularly, the direct synthesis of acetals from bio-renewable ethanol and butanol is permitted in this photocatalysis approach but not in the thermo-catalysis method.

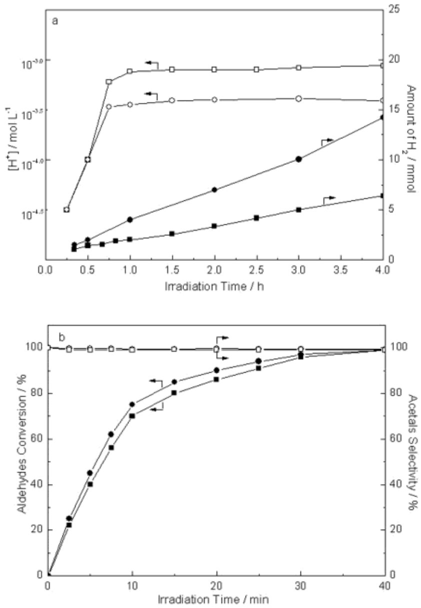


Fig. 2 a) The evolution profiles of H^+ ions and H_2 during photocatalytic ADC reaction of ethanol (circle) and butanol (square). The reaction conditions are the same as shown in Table 1 (entries 7 and 1). b) Photocatalytic condensation of acetaldehyde-ethanol (circle) and butyraldehyde-butanol (square) 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 shown in Table 1.

In mechanism, it is nearly doubtless 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 as acetals such efficiently so that they are converted near completely after their formation. As proposed by Milstein et al., enol ethers might be the intermediates in their thermo-catalytic process,[24] but this type of compounds were not observed in our reaction systems, suggesting that the mechanism for the formation of acetals in our photocatalysis process might be different. In the fully studied photocatalytic H_2 generation from water, alcohols were frequently employed as sacrificed reagents and oxidized by photo-generated holes to produce H^+ ions for the subsequent H_2 generation from a reduction of H^+ ions by photo-generated electrons.[43, 45] In view of the similarity between this oxidation process and the present process (excepting the waterless medium here), we detected H^+ ions along reaction duration for both ethanol and butanol. It was found that H^+ ion are really generated in the liquid bulk phase and exhibit a quick increase in concentration within initial 40 min reaction, after which its concentration stays at constant values, $1\times10^{-3.4}$ and $1\times10^{-3.0}$ mol·L^{-1} for ethanol and butanol, respectively (Fig. 2a). The H^+ ions generated afterwards are continually reduced as H_2 by photo-generated electrons. Based on this information, we estimated that the condensation of the aldehydes and alcohols into acetals is likely 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 following additional observations. (1) As tested, the H^+ ions with a 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 41 min. (2) Acetaldehyde-ethanol and butyraldehyde-butanol reactant pairs show no reaction in dark, without acid catalysts fed externally, but display a very fast acetalation reaction under photocatalysis conditions. The fed aldehydes (one-twentieth of the amount of 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 perform an in-situ H^+-catalytic acetalation reaction with unreacted alcohols. This mechanism can give a well explanation for the fails of the secondary and aromatic alcohols in the photocatalytic ADC reaction. As tested, they are incapable of reacting with corresponding ketones and aromatic aldehydes even if at higher concentration of acid catalyst (HCl) 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 considerable fast. (Fig. 2b) It is further confirmed by special light-on-off switch experiments on ethanol/butanol reaction system showed that DBB is readily

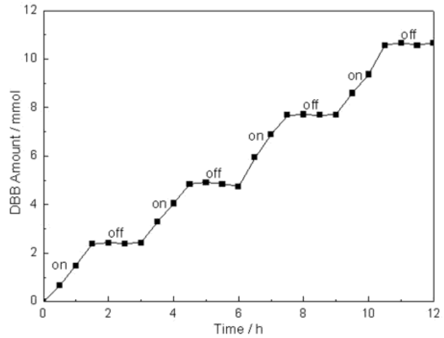


Fig. 3 A light-on-off responses to the DBB production in the photocatalytic ADC reaction of butanol. Conditions are the same as shown in Table 1 (entry 1).

produced upon light irradiation but shows no change in its amount upon light turning off (Fig. 3). This kinetic characteristic gives a foundational 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 would effectively consume the dehydrogenation products, aldehydes, which is significantly responsible for the high selectivity. Unlike other alcohol oxidation processes,[18, 24] which generated many by-products such as aldehydes and esters especially for the oxidation cases with O_2, the fast H^+-catalytic acetalation moiety in the present process totally eliminate intermediate aldehydes and kinetically prevail over the dehydrogenation of intermediate hemiacetals that was considered responsible for the formation of esters.[26]

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 undergoes via a tandem process containing a photocatalytic dehydrogenation reaction of alcohols and a H^+-catalytic acetalation reaction and displays 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 of integrating photocatalysis, acid-catalysis, and the feeding and cleaning-up of acidic catalyst (H^+) in a single reaction unit, which makes the reaction system more efficient and clean.

Experimental section

The 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 light source and was cooled by 20°C water circulation. Liquid products were analyzed by GC (GC-950 with a FID detector and Rtx-5 column from Alltech) and GC-MS (Shimadzu GCMS-QP2010 with a mass spectrometer and DB-5ms column from Alltech). Identification of compounds was carried out by comparison mass spectrum and/or retention time of pure chemicals. The concentrations of alcohol and acetals were determined with GC system and cyclohexane was used as internal standard. A GC-9790 (equipped with TCD and FID detector) was used to detect CO, CO_2 and H_2. Concentration of H^+ ion in liquid solution was detected from a water-diluted reaction solution by a Leici PHSJ-3F pH meter.

Acknowledgements

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