ACS Catalysis
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Photocatalytic Oxidation of Benzyl Alcohol by Homogeneous $CuCl_2$/Solvent: A Model System to Explore the Role of Molecular Oxygen

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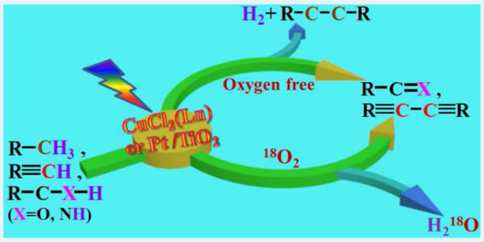
Ⓢ *Supporting Information*



ABSTRACT: The oxidation of alcohols to the corresponding carbonyl compounds is a pivotal reaction in organic synthesis. Under visible light irradiation, the homogeneous $CuCl_2$ and cheap solvent oxidized benzyl alcohol into benzaldehyde with a selectivity higher than 95% using molecular oxygen as an oxidant. The formation of a visible light responsive complex between Cu(II) and solvent is responsible for the occurrence of the oxidation of benzyl alcohol. During the photocatalytic process, molecular oxygen was not incorporated into the final benzaldehyde and only involved in the oxidation of Cu(I) into Cu(II) in which it served as a terminal hydrogen acceptor to form H_2O. A similar role of molecular oxygen has also been observed in the heterogeneous TiO_2 photocatalytic system. The understanding of the role of molecular oxygen helps us to further design new classes of synthetic organic reactions by photocatalytic processes.

KEYWORDS: *photocatalysis, benzyl alcohol, copper complex, selective oxidation, molecular oxygen, isotopic labeling*

1. INTRODUCTION

The selective oxidation of alcohols to carbonyl compounds is one of the fundamental transformations both in laboratory synthesis and industrial production since aldehydes and ketones are ubiquitous intermediates in the synthesis of pharmaceuticals and fine chemicals. Conventional alcohol oxidation not only requires the use of heavy-metal and corrosive stoichiometric oxidants but also produces large amounts of heavy metal waste. This gives rise to the development of environmentally friendly catalytic processes utilizing molecular oxygen as an oxidant that is available at virtually no cost and produces water as only a byproduct.[1,2] The aerobic oxidation of benzyl alcohol has been performed by using noble-metal or transition-metal complexes as catalysts in thermal catalysis system.[3] Recently, heterogeneous TiO_2-based photocatalysis has also emerged as a good candidate for selective oxidation of aromatic alcohols due to the using of sustainable solar energy.[4−8]

Undoubtedly, molecular oxygen is indispensable and plays a pivotal role in all these aerobic transformations of alcohols. Although many researchers have reported the aerobic oxidation of benzyl alcohol to benzaldehyde using a variety of catalytic materials,[9] there are only few investigations about the role of O_2 in the reaction process and most are speculative in nature. In the widely used Pd catalysis,[2,10−13] molecular oxygen is not incorporated into the products and only involved in the catalyst regeneration. In the P450-catalyzed oxidation of alcohols,[14] molecular oxygen is generally incorporated into the oxidized product, but there are also some exceptions that partial or complete lack of incorporation of molecular oxygen into the carbonyl product has been observed. In heterogeneous TiO_2-based photocatalysis, Zhang's group found that the oxygen atom in the product aldehyde completely came from molecular oxygen by isotopic tracer technique.[7,8] The differences in the role of molecular oxygen in different catalytic systems prompt us to approach this question by investigating homogeneous and heterogeneous photocatalytic systems.

In addition to palladium-based catalysts, copper-based catalysts[15−24] have also been employed for the aerobic oxidization of alcohols into aldehydes and ketones under mild conditions, such as copper-DEAD/DBAD,[15] copper-phenanthroline,[20] and recently developed copper(I)/TEMPO catalysts.[22−24] Although the copper counterion is critical to the success of the reaction, it is also necessary to add an additive as the ligand in these reactions. Herein, we found a photocatalytic system consisting of common copper ions and cheap organic solvent that can be used repeatedly for the selective oxidation of benzyl alcohol into benzaldehyde without the necessity of other organic additives. As a model system, detailed isotopic labeling studies were performed to identify the role of molecular oxygen that is significant for designing various synthetic reactions by phtotocatalysis.

2. RESULTS AND DISCUSSION

Photocatalytic Oxidation of Alochols. The photocatalytic oxidation of benzyl alcohol by homogeneous $CuCl_2$ in different solvents is shown in Table 1. Under visible light irradiation for 4 h, the homogeneous $CuCl_2$ in acetonitrile and acetone afforded 92.5% and 95% conversion of benzyl alcohol with a selectivity of 95% for benzaldehyde, respectively (entries 1 and 7). In the absence of light irradiation, no conversion of

Received: March 26, 2015
Revised: May 12, 2015
Published: May 14, 2015

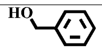
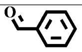
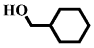
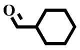
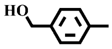
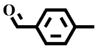
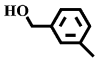
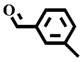
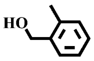
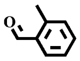
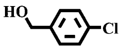
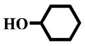
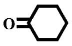
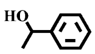
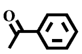
DOI: 10.1021/acscatal.5b00644
ACS Catal. 2015, 5, 3760−3766

Table 1. Photocatalytic Oxidation of Benzyl Alcohol by $CuCl_2$/Solvent[a]

entry	solvent[b]	time [h]	conversion [%]	yield [μmol]	selectivity [%]
1[c]	acetonitrile	4	92.5	**185**	95
2	acetonitrile	2	6.5	**626**	96
3	acetonitrile	4	11.8	**1137**	96
4[d]	acetonitrile	4	trace	**trace**	
5[e]	acetonitrile	2	8.83	**851**	95
6[f]	acetonitrile	2	12.4	**1195**	95
7[c]	acetone	4	95	**190**	95
8	acetone	2	5.6	**539**	92
9	acetone	4	9.1	**877**	92
10[g]	acetone	4	trace	**trace**	
11[e]	acetone	2	7.53	**725**	92
12[f]	acetone	2	9.8	**944**	92
13	other	4	trace	**trace**	

[a] General reaction conditions: benzyl alcohol (9.6 mmol), catalyst (0.1 mmol), solution volume (10 mL), O_2 atmosphere (balloon pressure), light intensity (400 mW·cm^{-2}, 420−780 nm wavelength range), room temperature (air cooling, 25 °C). [b] Other: solvent-free, benzotrifluoride, dimethyl sulfoxide, *N*,*N*-dimethylformamide, ethyl acetate or phenylacetonitrile. [c] Benzyl alcohol (0.2 mmol), solution volume (1 mL). [d] 80 °C, no light. [e] Light intensity of 700 mW·cm^{-2}. [f] Light intensity of 1200 mW·cm^{-2}. [g] 55 °C, no light.

Table 2. Photocatalytic Oxidation of Different Alcohols by $CuCl_2/CH_3COCH_3$[a]

Entry	Substrate	Conversion [%]	Product	Selectivity [%]
1		29		>95
2		18		80
3		30		>95
4		27.5		>95
5		26		>95
6		34		>95
7		25		67
8		42		88

[a] General reaction conditions: substrate (0.2 mmol), catalyst ($CuCl_2$, 0.1 mmol), solvent (acetone, 1 mL), light intensity (300 mW·cm^{-2}, 420−780 nm wavelength range), room temperature (air cooling, 25 °C), irradiation time (1 h), O_2 atmosphere (balloon pressure).

benzyl alcohol was observed even when heating to 80 °C in acetonitrile and 55 °C in acetone (a temperature close to its boiling point) (entries 4 and 10). This further confirms why the addition of other organic ligands was required in the aerobic oxidation of alcohol using copper-based catalysts in thermal catalysis. Similarly, the photocatalytic oxidation reaction cannot also occur in the absence of one of $CuCl_2$ and solvent (acetonitrile or acetone). When acetonitrile or acetone was replaced by other solvents such as dimethyl sulfoxide, *N*,*N*-dimethylformamide, benzotrifluoride, ethyl acetate, or phenylacetonitrile, the oxidation of benzyl alcohol cannot occur (entry 13). Upon irradiation with high-intensity visible light, the increased yields of benzaldehyde were observed (entries 5, 6, 11, 12, and Figure S1), which indicates that the oxidation of benzyl alcohol over $CuCl_2$ in solvent is a typical photocatalytic reaction. The scope of this photocatalytic oxidation of benzyl alcohol was also extended to a variety of other alcohols (Table 2).

The $CuCl_2$-based crystals were synthesized in acetonitrile and acetone through evaporation in a glovebox under N_2 atmosphere and characterized by single crystal X-ray diffraction. As shown in Figure 1 and Table S1, the asymmetric unit of $CuCl_2(CH_3CN)$ (a) contains one Cu^{2+} cation, two Cl^- anions and one acetonitrile molecule.[25] Compound $Cu(H_2O)Cl_2(CH_3COCH_3)$ (b) consists of one-half Cu^{2+} cation, one Cl^- anion, one-half water molecule and a quarter of guest acetone molecule. Both solutions absorb light in the visible regions of the spectrum, and the conversion of benzyl alcohol is proportional to the strength of the absorption peak of the solution (Figure 1c and d). Similar to the cases of acetonitrile and acetone, the system of $CuCl_2$ in butanone also has a new absorption band in the visible light region and exhibited a higher reaction efficiency than that in acetonitrile and acetone (Figure S2 and Table S2). In all cases, only the coexistence of $CuCl_2$ and solvent (acetonitrile, acetone, or butanone) have absorption band in the visible light region, and no obvious changes were observed before and after the addition of benzyl alcohol. This indicates that a visible-light responsive complex between $CuCl_2$ and solvent is responsible for the photocatalytic oxidation of benzyl alcohol.

Isotope-Labeling Studies. When O_2 in the above reaction (Figure 2a) was replaced by $^{18}O_2$, labeled benzaldehyde ($C_6H_5CH^{18}O$) was detected in acetonitrile system after photoirradiation for 5 h, whereas unlabeled one was obtained in acetone system under the similar conditions (Figure 2c and b). This result seems to indicate that whether oxygen atom transfer from molecular oxygen to the product happened or not depends on the solvent used in the photocatalytic oxidation of alcohols. Control experiments carried out with ^{18}O-enriched benzyl alcohol and O_2 gave unlabeled benzaldehyde (Figure 2e) in acetonitrile and acetone, which implies that oxygen atom in molecular oxygen can easily transfer to the product in both solvents. The above two completely contradictory results in acetone make us to explore the role of molecular oxygen in photocatalytic oxidation of benzyl alcohol.

In the absence of irradiation and $CuCl_2$, the system of $H_2{}^{18}O$, benzaldehyde, and solvent was stirred for 10 min. Labeled benzaldehyde ($C_6H_5CH^{18}O$) was detected in CH_3CN whereas labeled acetone ($CH_3C^{18}OCH_3$) was detected in acetone (Figure S3). This indicates that the oxygen atom transfer from H_2O to aldehydes or ketones easily occurred. For comparison, the ^2H NMR spectra of pure $C_6H_5CD_2OH$ and D_2O in CH_3CN were tested (Figure 3a and b). In our experiments, deuterium-containing water was detected by ^2H NMR during the photocatalytic oxidation of benzyl-α,α-d_2 alcohol ($C_6H_5CD_2OH$) in acetonitrile (Figure 3c) since molecular oxygen can combine with the liberated hydrogen from benzyl alcohol to produce water. Thus, whether O_2 participated in the oxidation of benzyl alcohol should exclude the influence of the water produced during the reaction process. In our system, the formed water was excluded by adding molecular sieve 3A with excellent adsorption of water into the reaction solution.[26−29] As

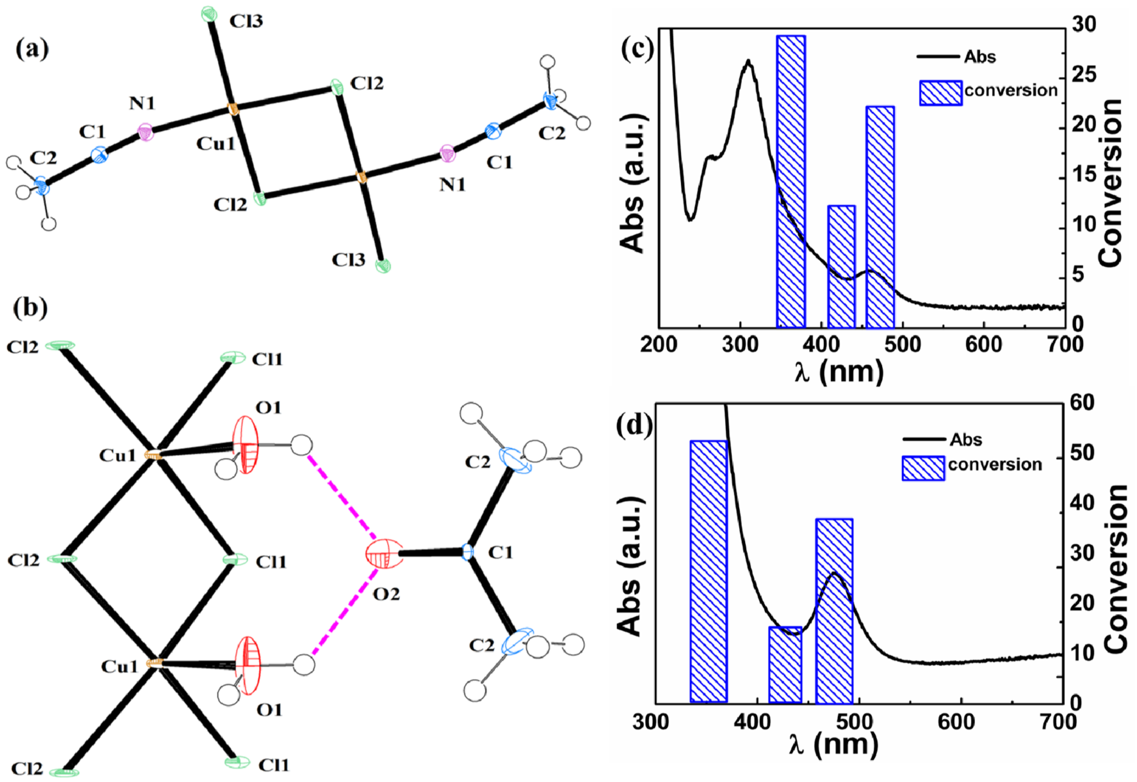


Figure 1. Representation of the X-ray crystal structure of (a) $CuCl_2(CH_3CN)$ and (b) $Cu(H_2O)Cl_2(CH_3COCH_3)$. Influence of incident light wavelength on benzyl alcohol conversion in the $CuCl_2/CH_3CN$ (c) and $CuCl_2/CH_3COCH_3$ systems (d). Reaction conditions: benzyl alcohol (0.2 mmol), catalyst ($CuCl_2$, 0.1 mmol), solvent (acetonitrile or acetone, 1 mL), O_2 atmosphere (balloon pressure), light intensity (100 $mW \cdot cm^{-2}$), wavelength (460−490, 410−440, and 340−360 nm), room temperature (air cooling, 25 °C), irradiation time (2 h).

shown in Figure 3d, the introduction of molecular sieve 3A removed the produced water in the reaction and hardly affected the reaction behavior. The system of benzyl alcohol, $^{18}O_2$, and molecular sieve 3A in CH_3CN gave unlabeled benzaldehyde (Figure 2d), obviously different from the system without molecular sieve. That is to say, molecular oxygen was not really incorporated into the final product during the photocatalytic oxidation of benzyl alcohol in CH_3CN. This is consistent with the result of using acetone as solvent because a large amount of acetone could easily exchange its oxygen atom with that of the formed water and greatly decreased the oxygen exchange between H_2O and benzaldehyde (Figure S3). In other words, the use of acetone as solvent eliminated the influence of the formed water on the isotopic tracer results. When benzyl alcohol was replaced by cyclohexanol, a same oxygen transfer process was further demonstrated (Figure 2g and f).

The photocatalytic oxidation of benzyl alcohol over typical heterogeneous phototocatalyst TiO_2 was also tested to further identify the chemical pathway of molecular oxygen. Under UV light irradiation, the system of benzyl alcohol and $^{18}O_2$ in CH_3CN, benzotrifluoride (Btf), or CS_2 gave labeled benzaldehyde ($C_6H_5CH^{18}O$) (Figure 2i, k, and m). When using ^{18}O-enriched benzyl alcohol and O_2, unlabeled benzaldehyde was obtained (Figure 2o). These phenomena are apparently consistent with Zhang's results that molecular oxygen was incorporated into the product.[7,8] However, the control reactions using dimethyl sulfoxide (DMSO) or acetone as solvent (Figure 2h) and the cases of adding molecular sieve 3A into the system (Figure 2j, l, and n) indicated that molecular oxygen was not involved into the product during the oxidation processes, which is good agree with that using homogeneous $CuCl_2$ catalyst because the solvents containing double bond oxygen and molecular sieve 3A eliminated the influence of the formed H_2O in TiO_2 system (Figure 3e and f). When the formed water was eliminated by adding stoichiometric reagent of CaH_2 into the reaction system, similar isotopic result was also observed (Figure 2p). Therefore, both in homogeneous and heterogeneous photocatalytic systems, molecular oxygen was not incorporated into the final product.

Proposed Catalytic Mechanism and Implications in Synthesis. In the homogeneous $CuCl_2$/solvent system, a simplified mechanism for the oxidation of alcohols is depicted in Scheme 1, similar to that using Pd catalysts.[10] When $CuCl_2$ was dissolved into acetonitrile or acetone, a complex **A** with visible-light absorption was formed. Benzyl alcohol binds to **A** through an unshared pair of electrons on hydroxyl oxygen, forming Cu-bound alcohol **B**. Under visible light irradiation, intramolecular deprotonation of **B** forms **C** followed by subsequent *α*-hydride elimination with another **A** to give benzaldehyde, HCl, and CuCl species **E**. **E** is oxidized to Cu(II) complex (A) by molecular oxygen,[30,31] further initiating a second catalytic cycle. In the absence of oxygen, the oxidation of benzyl alcohol using $CuCl_2$/solvent occurred only in a stoichiometric ratio, and ceased when Cu(II) was completely reduced to Cu(I) (Figure 4 and Table S3). This suggests that Cu(II) complex is responsible for the occurrence of the oxidation of benzyl alcohol. When O_2 was introduced into this system, Cu(I) complex (E) changed into Cu(II) complex which can further transform of benzyl alcohol to benzaldehyde. The involvement of radical species was ruled out since the introduction of typical radical scavengers such as TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl) and PBN (*N*-*tert*-butyl-

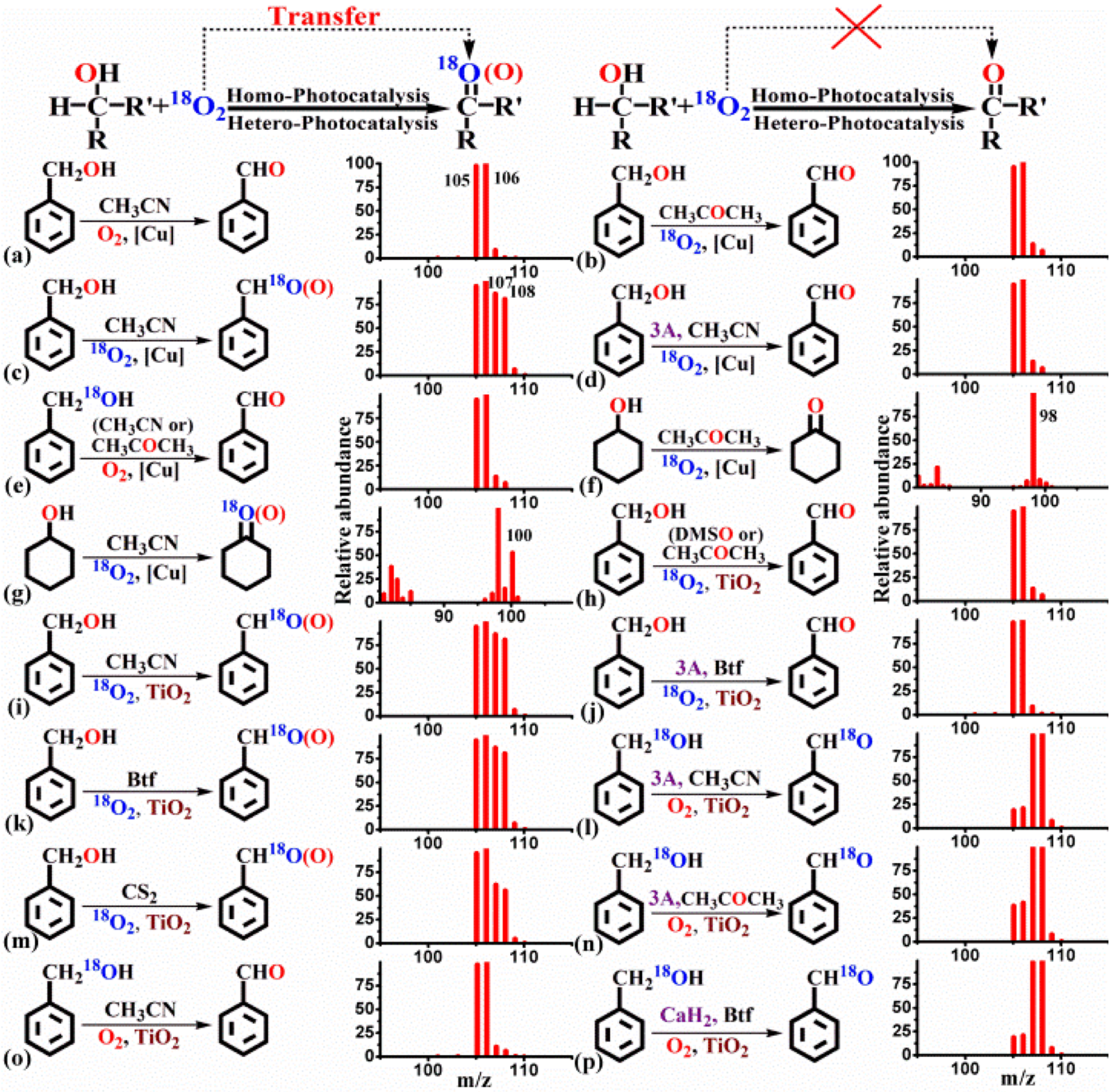


Figure 2. GC-MS analysis of the products during the photocatalytic oxidation of benzyl alcohol (a−e and h−p) and cyclohexanol (f and g) by $CuCl_2$ (a−g) and TiO_2 (h−p) using an isotopic tracer technique. (a) In acetonitrile. (b and c) Using $^{18}O_2$ in acetone (b) and acetonitrile (c). (d) Using 3A molecular sieve and $^{18}O_2$ in acetonitrile. (e) Using ^{18}O-enriched benzyl alcohol in acetonitrile or acetone. (f and g) Using $^{18}O_2$ in acetone (f) and acetonitrile (g). (h and i) Using $^{18}O_2$ in DMSO or acetone (h) and acetonitrile (i). (j) Using 3A molecular sieve and $^{18}O_2$ in benzotrifluoride (Btf). (k) Using $^{18}O_2$ in Btf. (l) Using ^{18}O-enriched benzyl alcohol and 3A molecular sieve in acetonitrile. (m) Using $^{18}O_2$ in CS_2. (n) Using 3A molecular sieve and $^{18}O_2$ in acetone. (o) Using ^{18}O-enriched benzyl alcohol in acetonitrile. (p) Using CaH_2 and ^{18}O-enriched benzyl alcohol in Btf.

α-phenylnitrone) can hardly inhibit the oxidative reaction (Table S4).[32,33] In addition, the oxidation of alcohols is accompanied by the formation of water which can exchange its oxygen with the oxygen in benzaldehyde. This led to a false impression that molecular oxygen was incorporated into the product during the photocatalytic oxidation of benzyl alcohol.

The nature of the oxidation of benzyl alcohol by homogeneous Cu-based complex also conveys important information for the photocatalytic oxidation of benzyl alcohol by TiO_2 photocatalyst. As portrayed in Figure 5, benzyl alcohol was first adsorbed on the surface of TiO_2 to form alcoholate species[34,35] and then be oxidized by a two-electron transfer (TET) process[36] in which O_2 acted as the scavengers of two electrons and protons to produce water (or hydrogen peroxide) and did not participate in the oxidation of benzyl alcohol after excluding the oxygen exchange between water and benzaldehyde.

In view of the fact that O_2 is only involved in the regeneration of the catalyst, the photocatalytic oxidation of benzyl alcohol by $CuCl_2$/solvent is a successive dehydrogenation reaction in essence. Thus, we propose that if the oxidation potential of the excited catalyst is large enough to complete the dehydrogenation of various substrates and there is also a reasonable route for the chemical transformation of the liberated hydrogen, various synthesis reactions can be occurred. As expected, the photocatalytic oxidative homocoupling of phenylacetylene was successfully performed by $CuCl_2$/acetonitrile in the presence of molecular oxygen and visible light (Figure 6). Under visible light irradiation (300 mW·cm^{-2}) for 12 h, phenylacetylene was converted into biphenylacetylene in a high yield, about 1209 μmol. When prolonging irradiation time or changing the light intensity to enhance the number of incident photons, a linear increase in the yield of 1,4-diphenylbutadiyne was observed, which confirmed that the reaction proceeded in a photocatalytic manner (Figure S4).

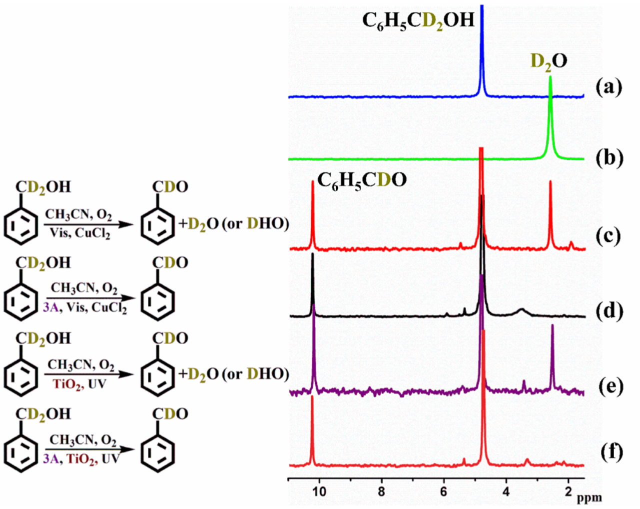
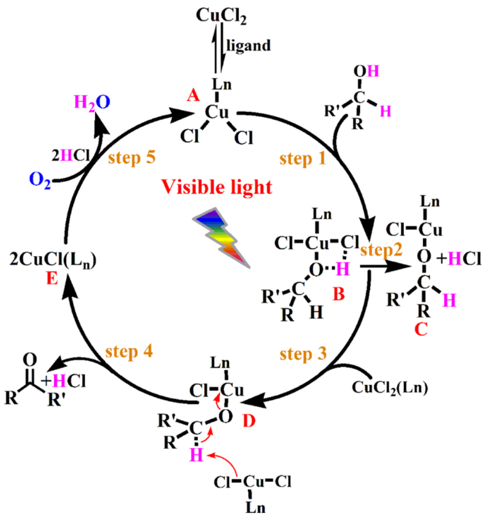


Figure 3. ^2H NMR spectra of C_6H_5CDO and deuterium-containing water in CH_3CN. (a) Pure $C_6H_5CD_2OH$ in CH_3CN. (b) Pure D_2O in CH_3CN. Products in the oxidation of $C_6H_5CD_2OH$ using $CuCl_2$/CH_3CN in the presence (d) and absence (c) of molecular sieve 3A. Products in the oxidation of $C_6H_5CD_2OH$ using TiO_2 in the presence (f) and absence (e) of molecular sieve 3A.

Scheme 1. Proposed Mechanism for the Photocatalytic Oxidation of Benzyl Alcohol by Homogeneous $CuCl_2$/Solvent



Similarly, in heterogeneous Pt/TiO_2 photocatalytic systems, the homocoupling or other oxidative reactions of diverse substrates proceeded smoothly under N_2 atmosphere, accompanying the continuous evolution of H_2 (Figure 7 and Figure S5). In the absence of O_2, benzyl alcohol can also be converted into benzaldehyde, and the yields of benzaldehyde and H_2 increased in a similar trend (B). When using benzylamine as the substrate, both the oxidation reaction to afford imine and the hydrogen-producing reaction were proceeded simultaneously (C), and a satisfying yield of 890 μmol for 36 h reaction was obtained. Also, the direct coupling of toluene containing saturated C−H bond occurred to form bibenzyl and hydrogen (Figure 7c). All these reactions indirectly implied that O_2 just served as a terminal hydrogen acceptor and was not incorporated into the final product. Therefore, by discerning the role of oxygen in the photocatalytic oxidation, it is possible to design the reactions to obtain required products.

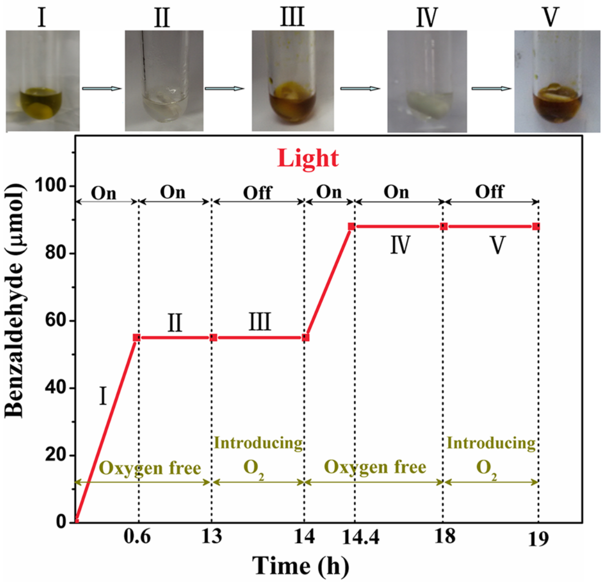


Figure 4. Periodic oxidation of benzyl alcohol by $CuCl_2(CH_3CN)$ with visible light. Reaction conditions: catalyst ($CuCl_2$, 0.1 mmol), solvent (CH_3CN, 3 mL), benzyl alcohol (0.96 mmol), light intensity (500 mW·cm^{-2}, 420−780 nm wavelength range).

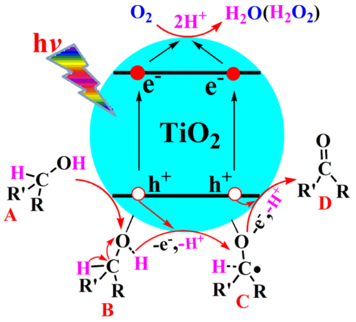


Figure 5. Possible processes for TiO_2 catalyzed oxidation of alcohol.

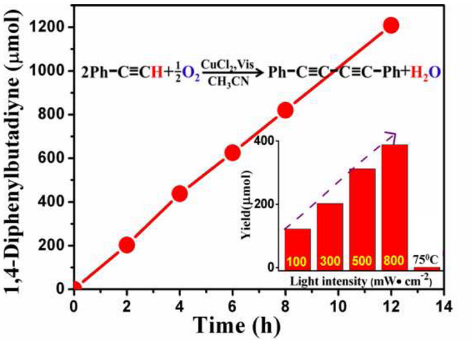


Figure 6. $CuCl_2(CH_3CN)$ catalyzed oxidation of phenylacetylene under O_2 atmosphere. Reaction conditions: catalyst ($CuCl_2$, 0.1 mmol), phenylacetylene (200 μL), solvent (CH_3CN, 1.8 mL), light intensity (300 mW·cm^{-2}, 420−780 nm wavelength range). (inset) Influence of light intensity on the product yield (2 h irradiation).

3. CONCLUSIONS

In conclusion, we have developed a homogeneous visible-light photocatalytic system consisting common copper ions and

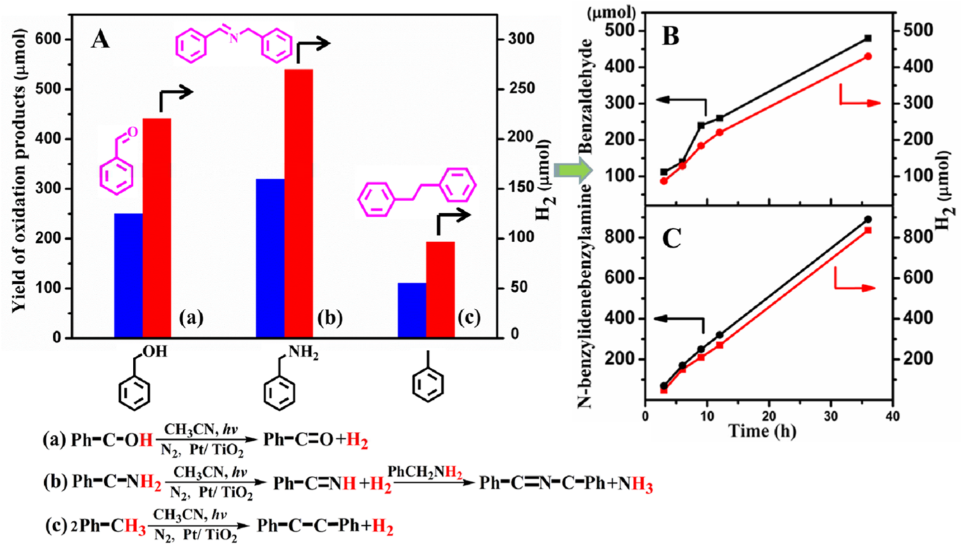


Figure 7. (A) oxidation profile for dehydrogenation reaction. Reaction conditions: 0.1 mmol of catalyst, 1.5 mL of solvent (CH_3CN), 0.5 mL of substrate, irradiation for 12 h. Time-yield curves for the oxidation of benzyl alcohol (B) and benzylamine (C) by Pt/TiO_2.

cheap organic solvent for the selective oxidation of benzyl alcohol into benzaldehyde using molecular oxygen as the oxidant. The results of the isotopic tracer experiments showed that molecular oxygen did not transfer to benzaldehyde and only involved in the catalyst regeneration both in homogeneous and heterogeneous photocatalytic systems. The understanding of the role of molecular oxygen helps us to further design new classes of synthetic organic reactions by photocatalytic processes.

4. EXPERIMENTAL DETAILS

Selective Oxidation of Typical Alcohols by Copper Complexes and TiO_2-Based Photocatalysts. All the photocatalytic reactions were performed in a 10 mL quartz glass bottle at ambient temperature. In a typical sealed reaction system, 0.1 mmol of anhydrous $CuCl_2$ or TiO_2 was thoroughly dispersed in 1 mL solution (0.1 mL benzyl alcohol and 0.9 mL solvent) with a magnetic stirrer under O_2 (balloon pressure). A 300 W xenon lamp (PLS-SXE300C, Beijing Perfect Light Co) equipped with an IR-cutoff filter ($\lambda < 780$ nm) was set on one side of the reactor, providing the visible light ($\lambda > 420$ nm) and UV light ($\lambda > 320$ nm) through the combination of different filters for copper complexes involved reactions. UV source was also provided by 4-W UV lamps with certain wavelengths centered at 365 nm (Philips, TUV 4W/G4 T5) for the cases of using TiO_2 or Pt/TiO_2 as typical photocatalysts. After reaction, the reaction mixture was filtered through a porous membrane (20 μm in diameter) and then injected into the GC equipped with FID detector (Agilent Technologies, GC7890A) for analysis. A HP-5 5% phenyl methyl siloxane column (30 m × 0.32 mm × 0.5 μm) was used. The chemical structures of the products were confirmed by comparison with standard chemicals and GC-MS (Agilent Technologies, GC6890N, MS 5973). The conversion for the substrate was described as the ratio of the moles of the reactant consumed in the reaction to the initial moles of the reactant. The selectivity was defined as the ratio of the moles of the product to that of the reactant consumed in the reaction. $^{18}O_2$-labeling experiments proceeded under similar conditions to the photocatalytic oxidation of benzyl alcohol except that the normal O_2 atmosphere was replaced by $^{18}O_2$ (97%), and the pressure of $^{18}O_2$ was about 0.1 MPa. After reaction, the oxygen isotope abundance of the as-obtained products was measured by GC-MS. Anaerobic oxidation of benzyl alcohols: All manipulations of air-sensitive (or moisture-sensitive) materials were carried out with techniques of using standard Schlenk vessels or in glovebox under N_2 atmosphere. Part of the experiments introduced molecular sieve 3A (or CaH_2) as the dehydration reagent to remove the moisture in reaction media. All the other oxidative reactions or dehydrogenative reactions employed the same procedures as mentioned above. The gaseous product such as H_2 was analyzed by a TCD detector on Agilent 7890A equipped with a TDX-01 packed column (3 m × 1.25 mm). Some of the deuterated products were detected by ^{2}H NMR on Bruker AVANCE III 500 operating at 76.8 MHz. D_2O (20 μL D_2O dissolved in 1 mL CH_3CN) and benzyl alcohol (C_6H_5−CD_2OH) (20 μL C_6H_5−CD_2OH dissolved in 1 mL CH_3CN) were selected as reference substances.

Synthesis and Characterization of $CuCl_2$ Based Crystal. Typically, anhydrous copper(II) chloride (1g, 7.3 mmol) was dissolved into acetonitrile (100 mL) in a glovebox under N_2 atmosphere to give a yellow-green solution. The as-obtained solution was filtered to remove the residual solids after stirring for 1 h. The filtrate stayed in glass beaker for an ultralong period (more than 5 days) to ensure a moderate evaporation rate in anhydrous environment. Finally, the yellow-green crystals of $CuCl_2(CH_3CN)$ were obtained and removed from the filtrate for further characterization. This procedure was also applied to the synthesis of $Cu(H_2O)Cl_2(CH_3COCH_3)$ except that acetonitrile was changed to acetone. Variable-temperature X-ray single-crystal diffraction data of $Cu(H_2O)Cl_2(CH_3COCH_3)$ and $CuCl_2(CH_3CN)$ were collected on Super Nova CCD diffractometer with the graphite monochromated Cu−Kα radiation (λ = 1.54184 Å). The CrystalClear software package (Rigaku) was used for data collection, cell refinement and data reduction. Crystal structures were solved by the direct methods and refined by the full-matrix method based on F2 using the SHELXLTL software package.[37] All non-hydrogen atoms were refined anisotropically and the positions of hydrogen atoms were generated geometrically. Crystallographic data and details of data collection and refinement for $Cu(H_2O)Cl_2(CH_3COCH_3)$ and $CuCl_2(CH_3CN)$ are given in Table S1. The liquid UV−vis spectra of the solution samples were recorded from 200 to 800 nm by using a Cary 5000 UV−vis-NIR spectrophotometer (Varian, America).

Preparation and Characterization of Pt/TiO_2 Photocatalyst. Pt/TiO_2 photocatalyst was prepared by a precipitation deposition method using chloroplatinic acid as the platinum source. A 1 g portion of P-25-TiO_2 was dispersed into 100 mL H_2O with stirring for 1 h, and 2.8 mL H_2PtCl_6 (0.1 g/mL) solution (1g $H_2PtCl_6 \cdot 7H_2O$ dissolved in 100 mL H_2O) was further added into the as-obtained P25-water system. Then, the pH of this solution was adjusted by slowly dropwise adding of NaOH (0.1 mol/L) to reach about 9. The as-obtained H_2PtCl_6−P25 mixed system was reduced with aqueous solution of 0.1 mol/L $NaBH_4$ containing 0.1 mol NaOH, then it was centrifugated and washed thoroughly with distilled water (remove the remaining Na^+ and Cl^- ions). Finally, the solid product was dried at 80 °C for 10 h.

Preparation of ^{18}O Enriched Alcohol. The method to synthesize ^{18}O enriched alcohol is similar to the previous report by Zhang.[7] The detailed procedure was described as follows. A 0.1 g portion of Na was added into 1.5 mL ^{18}O enriched water (90% $H_2{}^{18}O$, J&K Chemical Technology) in a flask, 1.0 mL 1-chloromethylbenzene was added into the flask. The mixture was heated to 368 K and refluxed for 48 h with continuous stirring. The product was purified by distillation. The ^{18}O enriched benzyl alcohol was examined by GC-MS, and the abundance of $C_6H_5CH_2{}^{18}OH$ was about 90%. A 20 μL portion of the mixture product was stirred in 1 mL CH_3CN to be examined by GC and GC/MS. The data show that 20 μL of the mixture product contains 118 μmol of 1-chloromethylbenzene and 70 μmol of ^{18}O benzyl alcohol.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b00644.

> All extra reaction data, additional crystallographic information, and the copies of mass spectra for all the resulted products in different reactions (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Dr. Yuanyuan Tang, Dr. Zeping Wang, M.S. Kun Huang, and Dr. Liuyi Li for single crystal X-ray diffraction analysis and constructive discussion. This work was financially supported by the National Nature Science Foundation of China 21077023, the National Basic Research Program of China 2014CB239303, the Natural Science Foundation of Fujian Province of China 2015J01046, and the Independent Research Project of State Key Laboratory of Photocatalysis on Energy and Environment 2014B01.

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