

Steric effects of homogeneous CuCl_2 /solvent system for photocatalytic selective oxidation of benzyl alcohol

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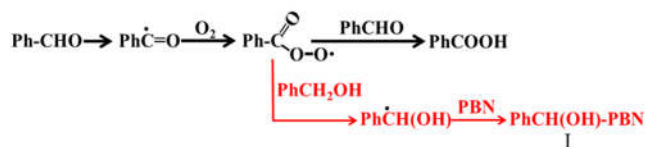
Homogeneous catalytic conversion of benzyl alcohol into benzaldehyde was widely reported, while the selectivity may be limited due to the overoxidation of benzaldehyde in the presence of benzyl alcohol. Importantly, such overoxidation reaction mechanism in homogeneous reaction system is still elusive. In this work, the homogeneous CuCl_2 /solvents system was used as a model system to explore the difference between the ideal system and the homogeneous system for the selectivity oxidation of benzyl alcohol to benzaldehyde and the autoxidation of benzaldehyde to benzoic acid. It was found that sterically hindered solvents (ligands) lead switch of catalytic performance of CuCl_2 /solvents photocatalytic system towards oxidation of benzyl alcohol. Within the environment of the copper complex, sterically hindered solvents as scaffolds provide more probability of collision and interaction between copper complex and benzyl alcohol by blocking the produced benzaldehyde, which makes high yield of benzaldehyde.

Introduction

The selective oxidation of alcohols into carbonyl compounds is one of the fundamental transformations in both laboratory synthesis and industrial production since aldehydes and ketones are ubiquitous intermediates for producing pharmaceuticals, agrochemicals and perfumes *et al.*. A variety of catalytic systems, such as conventional Pd(II) system,¹ semiconductor photocatalyst,² and famous copper(I)/ligand catalytic system,³ are developed for selectively converting benzyl alcohol into benzaldehyde.

How to control the selectivity of benzaldehyde is the key factor since benzaldehyde spontaneously undergoes autoxidation to yield benzoic acid simply upon exposure to air at room temperature. However, there are only few investigations about the overoxidation in the reaction process.⁴ Until 2014, Hutchings and co-workers uncovered the long unsolved mystery why benzaldehyde can be formed in high yield from benzyl alcohol by a thorough mechanistic study using EPR spin trapping experiments.⁵ An interception step has been proposed as scheme 1: the presence of benzyl alcohol (even as little as 2wt%) can quench the oxidation of benzaldehyde to benzoic acid principally by intercepting the acylperoxy radicals, which are responsible for the oxidation of benzaldehyde to benzoic acid. Hutchings's research can be well acknowledged that benzyl alcohol, even at low concentrations in benzaldehyde, inhibits the autoxidation. Despite this work provides an important advance in this highly competitive field of heterogeneous catalytic systems, it is still a challenge to explain why a certain number of benzaldehyde unexpectedly transfer to benzoic acid in the presence of benzyl alcohol in some homogeneous systems which includes more application models in this field. The overoxidation

step is expected to be inhibited for obtaining high yield of benzaldehyde. Additionally, the processes are more complicated and the mechanism is still elusive in homogeneous systems with different metal complexes and different solvents than the conditions without of any catalyst in Hutchings's EPR experiment.



Scheme 1 Interception step for autoxidation of benzaldehyde in the presence of benzyl alcohol. PBN: N-tert-butyl- α -phenylnitron.

Our previous work has shown that common copper ion and cheap organic solvent (acetone or acetonitrile) can be used repeatedly for the selective oxidation of benzyl alcohol into benzaldehyde without the necessity of other organic additives.⁶ Herein, we choose CuCl_2 /solvent complex as model catalyst to explore the origin of the selectivity switch between the benzyl alcohol-to-benzaldehyde selective oxidation. It has been found that the overoxidation not only depends on the autoxidation of benzaldehyde, but is strongly affected by the probability of collision and interaction between copper complex (catalyst) and substrate. By using the sterically more hindered solvents can improve the probability of collision and interaction between copper complex and benzyl alcohol, which could boost up the catalytic activity to yield more benzaldehyde. We show the generality of this effect and the structural requirements of the molecules capable of increasing the limiting yield of benzaldehyde.

Experimental

Photocatalytic oxidation procedures

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All the photocatalytic reactions were performed in a 50 mL quartz glass bottle at ambient temperature. In a typical sealed reaction system, 0.1 mmol of anhydrous CuCl_2 was thoroughly dispersed in 10 mL solution (0.96M benzyl alcohol) 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) for copper complexes involved reactions. 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 \times 0.32 mm \times 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. $^{18}\text{O}_2$ -labeling experiments proceeded under similar conditions to the photocatalytic oxidation of benzyl alcohol except that the normal O_2 atmosphere was replaced by $^{18}\text{O}_2$ (97%), and the pressure of $^{18}\text{O}_2$ was about 0.1 MPa. After reaction, the oxygen isotope abundance of the as-obtained products was measured by GC-MS.

EPR experiments

X-band continuous wave EPR spectra were recorded at room temperature in CuCl_2 /solvent systems using a Bruker A300 instrument. The typical instrument parameters were: centre field 3270G, sweep width 1000G, sweep time 41s, time constant 10ms, MW power 20 mW, modulation 100 kHz and modulation amplitude 1G. For PBN involved measurements, different instrument parameters were set: centre field 3515G, sweep width 60G, sweep time 41s, time constant 10ms, MW power 5mW, modulation 100 kHz and modulation amplitude 1G.

UV-vis experiment

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).

Results and discussion

Fig. 1 shows the amount change of benzaldehyde and benzoic acid as a function of illumination time in different catalytic systems. As shown in Fig. 1a, the amount of benzaldehyde was increased approximately linearly with illumination time before 6h in CuCl_2 /acetone system without further oxidation to benzoic acid, and the increasing rate became mild from 6h to 8h with the increasing of benzoic acid. Surprisingly, the benzoic acid was increased while the amount of benzaldehyde was declined slower. This phenomenon is different from the early report that benzyl alcohol can inhibit the overoxidation of benzaldehyde. Addition of another 9.6 mmol of benzyl alcohol to this reaction mixture resulted in a rapid increasing of benzaldehyde until the second ~ 810 μmol s of benzyl alcohol was converted to benzaldehyde (dashed line),

which indicates the system still has ability to run the oxidation with additional substrate. That is to say, a small ratio of benzaldehyde to benzyl alcohol in CuCl_2 /acetone system could cease the oxidation of benzyl alcohol. When acetone was replaced by butanone as the solvent under similar conditions (Fig. 1b), a significantly improved yield of benzaldehyde was observed. The yield of benzaldehyde reached 55.4% after 8h irradiation and no longer increased with benzoic acid increasing. Meanwhile, the photocatalytic oxidations of benzyl alcohol were also investigated in other ketones solvents, since these solvents pose greater steric hindrance than butanone. Like butanone, the catalyst system consisting CuCl_2 /2-pentanone, CuCl_2 /3-pentanone or CuCl_2 /cyclohexanone (Fig. 1c, 1d and 1e) were also shown improved performance with respect to that of CuCl_2 /acetone for the oxidation of benzyl alcohol in different reaction rate. Although the reaction rate in CuCl_2 /cyclohexanone was lowest in these systems, the yield of benzaldehyde was also higher than that in CuCl_2 /acetone.

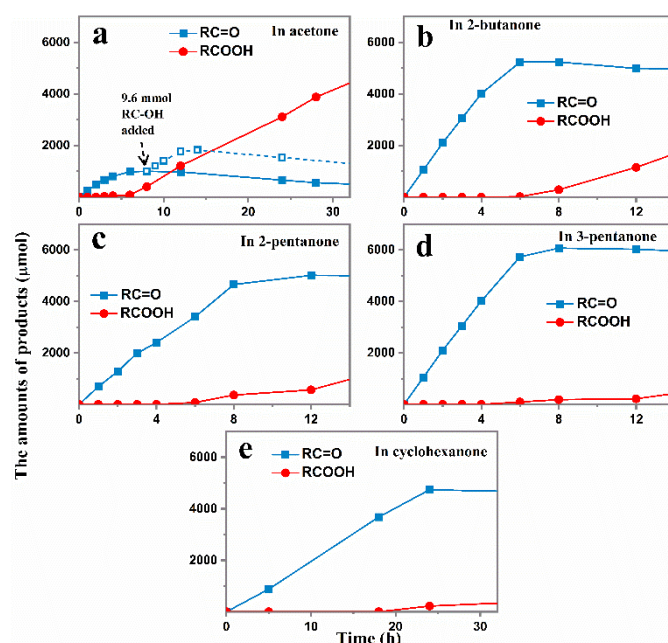


Fig. 1 a: Effect of reaction concentration on the aerobic oxidation of benzyl alcohol in different systems: Benzyl alcohol (BA), O_2 atmosphere (balloon pressure). b-f: CuCl_2 (solvent) catalyzed oxidation of benzyl alcohol under O_2 atmosphere. Reaction conditions: catalyst (CuCl_2 , 0.01 M), benzyl alcohol (0.96 M), solution volume (10 mL), O_2 atmosphere (balloon pressure), light intensity (400 $\text{mW}\cdot\text{cm}^{-2}$, 420–780 nm wavelength range).

In the above mentioned experiments, xenon lamp was used as extra light energy source, which is high energy consumption device and not a good candidate for applications. Thus, we choose daylight lamp that is most widely used and cheapest in the world as light source for the experiments. The performance of CuCl_2 /butanone, CuCl_2 /2-pentanone and CuCl_2 /3-pentanone in the oxidation of benzyl alcohol using daylight lamp as light source were compared in Table 1. The high yield of benzaldehyde was obtained after 24h reactions in the three systems. These results showed good application perspective of the copper/solvents system in the oxidation of benzyl alcohol.

Table 1 Photocatalytic oxidation of benzyl alcohol by CuCl₂/solvents.^a

Entry	Solvent	Yield [μmol]	Conversion[%]
1	butanone	2122	22.1
2	2-pentanone	1882	19.6
3	3-pentanone	2611	27.2

^aGeneral reaction conditions: catalyst (CuCl₂, 0.01 M), benzyl alcohol (0.96 M), solution volume (10 mL), O₂ atmosphere (balloon pressure).

Based on the results that the presence of benzaldehyde affects the oxidation of benzyl alcohol in copper complex systems, we further explored the oxidation of benzaldehyde in copper complex systems (Fig. 2). Without CuCl₂, all benzaldehyde was converted to benzoic acid after 5h, which indicates benzaldehyde proceeds spontaneously autoxidation to yield benzoic acid. However, CuCl₂ in acetone only afforded 2.5% conversion of benzaldehyde after 5h photoreaction, which demonstrates that the overoxidation of benzaldehyde to benzoic acid was inhibited in this system. The inhibition of CuCl₂/acetone for autoxidation of benzaldehyde was similar as using benzyl alcohol (~6% conversion of benzaldehyde). Considerable benzoic acid was obtained when acetone was changed by butanone, 2-pentanone or cyclohexanone. And there was no big difference for the conversion of benzaldehyde in the three solvents, which afforded 37%, 47% or 41.2%, respectively. However, the inhibition effect of CuCl₂/3-pentanone was so weak that the conversion of benzaldehyde was nearly 95% and analogous to the system without CuCl₂. These results showed that the autoxidation of benzaldehyde was markedly reduced in CuCl₂/acetone compared with in sterically more hindered solvents.

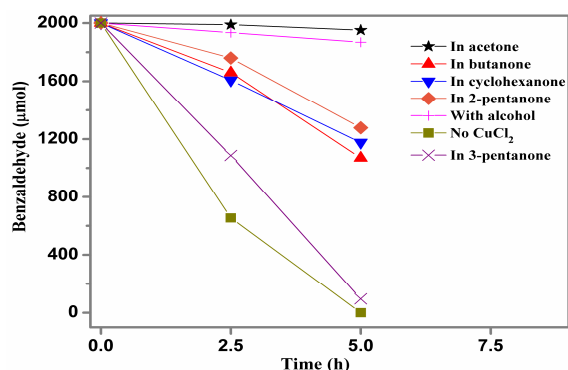


Fig. 2 Aerobic oxidation of benzaldehyde. Reaction conditions: catalyst (CuCl₂, 0.05 M), benzaldehyde (1 M), solution volume (2mL).

Fig. 3 shows the energy level diagram of d orbitals in Cu(II) ion (based on the crystal field theory) with HOMO-LUMO orbitals of the benzyl alcohol (molecular orbital theory). Under visible light irradiation, the electron in t_{2g} orbital goes into e_g of copper complex (Fig. 3b). This step has been proved by UV-vis experiment (Fig. 4, a-e) and makes copper complexes yellow brown. The electron in the highest occupied molecular orbital of benzyl alcohol would transfer into t_{2g} orbital of copper ion, due to the suitable energy match between the two counterparts. The breaking of O-H bond of alcohol in the reaction can be illustrated by the following two steps: 1, the incident photon

induced d-d transfer, in which the efficiency depends on the number of photons; 2, the spontaneous electron transfer from benzyl alcohol to copper ion, in which the efficiency depends on the temperature. In our experiment, to increase light intensity and reaction temperature all can accelerate the reaction rate (not show).

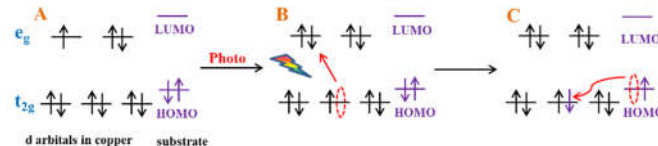


Fig. 3 The mechanism of light absorption of copper complex.

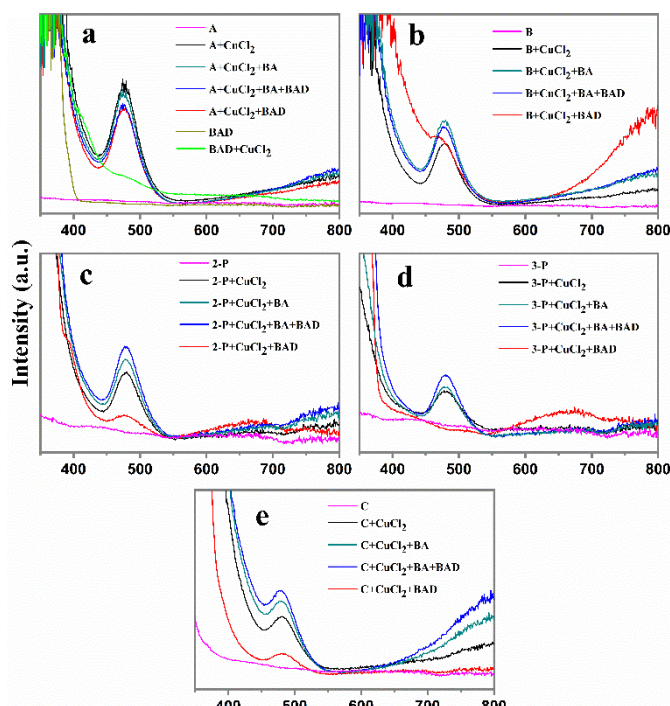


Fig. 4 a-e: UV-vis absorption spectroscopies of CuCl₂/solvents systems. CuCl₂ (18 μmol), A: acetone (3 mL). B: butanone (3 mL). 2-P: 2-pentanone (3 mL). 3-P: 3-pentanone (3 mL). C: cyclohexanone (3 mL). BA: benzyl alcohol (50 μL). BAD: benzaldehyde (50 μL).

As shown in Fig. 4a-e, the new generation of an absorbing region ranging from 450 nm to 500 nm may indicate that the coordinating structure (complex) between copper chloride and different ketones were formed. The introducing of benzyl alcohol with and without benzaldehyde have no big differences on absorption peak. But the peak intensity in the region of 450-500nm of copper complexes was obviously decreased in the presence of benzaldehyde without benzyl alcohol except the CuCl₂/acetone system, which indicates that benzyl alcohol could protect the structure of CuCl₂/solvent from benzaldehyde in steric more hindered solvents, while the peak formed by CuCl₂/acetone would not be affected by benzaldehyde in the absence of benzyl alcohol. It is noteworthy that, The absorbing region ranging from 450 nm to 500 nm in CuCl₂/3-pentanone was disappeared, which means the structure of CuCl₂/3-pentanone was destroyed by benzaldehyde. These results illustrate that, although the structure of copper complexes in steric more hindered solvents were changed with benzaldehyde,

the benzyl alcohol could bond with CuCl_2 /solvent structure prior to benzaldehyde.

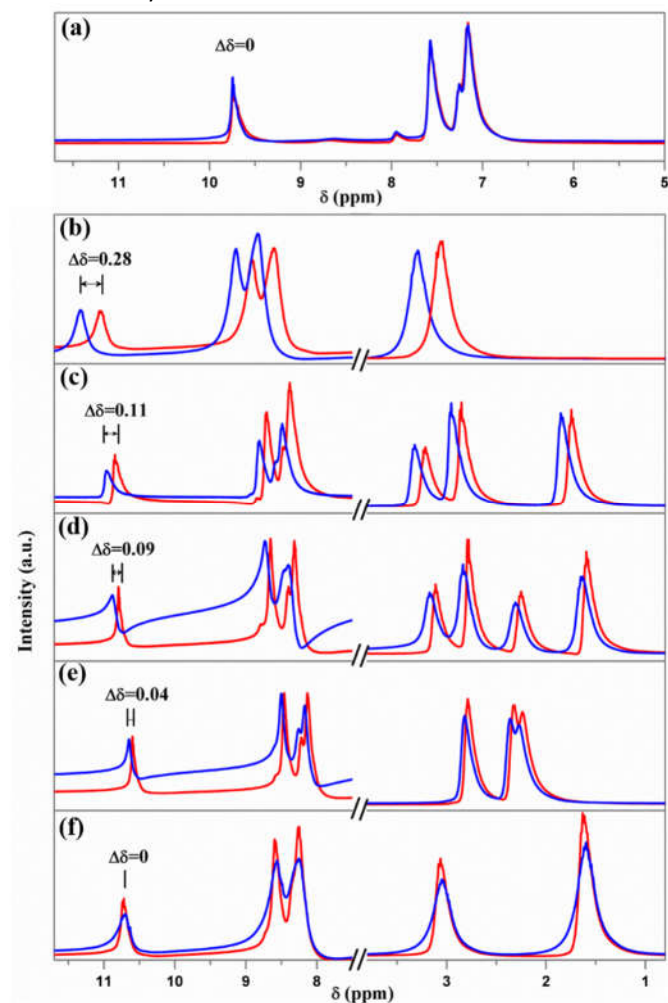


Fig. 5 a-f: ^1H NMR spectra of benzaldehyde in different solvents with (blue line) and without CuCl_2 (red line). a, pure benzaldehyde without solvent; b, in acetone; c, in butanone; d, in 2-pentanone; e, in cyclohexanone; f, in 3-pentanone.

The NMR experiments were used to determine the chemical environment of benzaldehyde. CuCl_2 in pure benzaldehyde afforded no shift of benzaldehyde (Fig. 5a). The introducing of different solvents behaving distinct spatial structure afforded a significant NMR shift of benzaldehyde with the presence of CuCl_2 (Fig. 5b-e). This phenomenon suggests that benzaldehyde is affected by copper complex. The only exception is the case of CuCl_2 /3-pentanone with an indistinguishable H shift (Fig. 5f), which indicates that there is no interaction between benzaldehyde and copper/3-pentanone.

The possible interaction between benzaldehyde and copper complex is depicted in Fig. 6 (in the absence of benzyl alcohol). When the solvent (ligand) is acetone (Fig. 6a), the copper center is anchored with acetone. Benzaldehyde can easily pass through acetone to bond with copper center due to the small steric hindrance of the ligand acetone. The structure of CuCl_2 /acetone is rarely affected by the exotic benzaldehyde as shown in Fig. 4a that the UV-vis absorption peak of CuCl_2 /acetone systems was hardly changed with the additional benzaldehyde. The bonding between benzaldehyde and

CuCl_2 /acetone greatly weaken the overoxidation of benzaldehyde in bulk solution. So the overoxidation of benzaldehyde to benzoic acid was inhibited in CuCl_2 /acetone (Fig. 2). When the solvent is butanone (Fig. 6b) (or 2-pentanone, cyclohexanone), the introducing benzaldehyde had destroyed a part of ligands butanone (or 2-pentanone, cyclohexanone) of the CuCl_2 /butanone structure, which makes the UV-vis intensity of CuCl_2 /butanone decrease (Fig. 4b, 4c and 4e) and NMR shift of H nucleus in CHO group. The ligand butanone with benzaldehyde occupying more space around copper center block other guest benzaldehyde and make them stay in bulk solution. Benzaldehyde in bulk solution is oxidized to benzoic acid in the presence of molecular oxygen via radical pathway as Hutchings's report⁵ (scheme 1), which is consistent with the evidence that autoxidation of benzaldehyde was partially allowed in these copper complexes (Fig. 2). When the solvent is replaced by 3-pentanone (Fig. 6c), the introducing benzaldehyde is bound together with ligand 3-pentanone due to the appropriate space effect around copper center, meanwhile make copper center separate with the ligand 3-pentanone. Therefore, the structure of copper/3-pentanone was completely destroyed so that the UV-vis absorption peak of CuCl_2 /3-pentanone in the presence of benzaldehyde was disappeared (Fig. 4d). It is because the introducing benzaldehyde is not bond to copper center in CuCl_2 /3-pentanone system, the chemical shift of benzaldehyde of NMR spectra was not changed after adding CuCl_2 into 3-pentanone (Fig. 5f). Besides, the benzaldehyde was much easier to be oxidized to benzoic acid in bulk solution (Fig. 2).

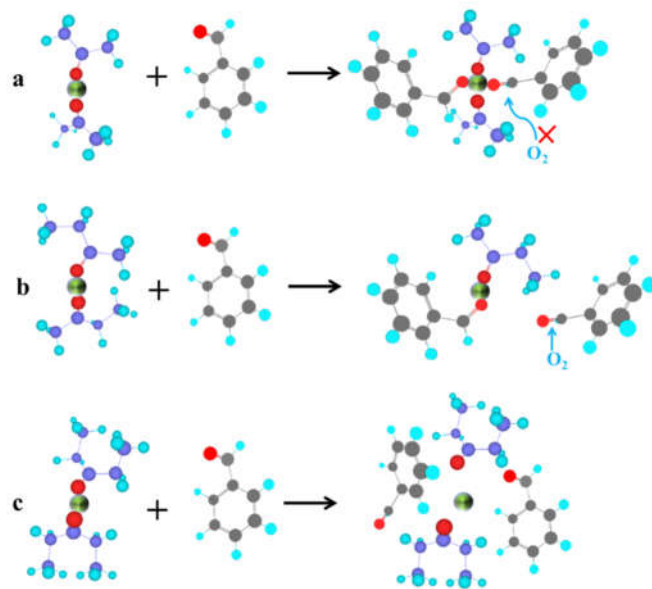


Fig. 6 The interaction between solvents and copper center: a, acetone and copper center; b, butanone and CuCl_2 . c, 3-pentanone and copper center.

The EPR spectrum was employed to study the inhibition of autoxidation of benzaldehyde in the presence of benzyl alcohol in CuCl_2 /butanone in contrast with that in CuCl_2 /acetone. The N-tert-butyl-a-phenylnitron (PBN) spin-trapping EPR spectrum of the irradiated CuCl_2 /butanone with benzyl alcohol showed sextet characteristic peaks of the $\text{PhCH}(\text{OH})$ -PBN adduct (Fig. 7,

and corresponding to the adduct I in Scheme 1), which is defined as an intermediate product in the reaction between benzyl alcohol and acylperoxy radical (scheme 1). This confirmed the formation of inhibiting effect for the autoxidation of benzaldehyde by benzyl alcohol in bulk solution during the selective oxidation of benzyl alcohol in CuCl₂/butanone system, which is good agree with Hutchings's view that benzyl alcohol could intercept intermediate radicals that is from the autoxidation of benzaldehyde. In contrast, no EPR signal corresponding to the PhCH(OH)•PBN adduct was observed in CuCl₂/acetone system under similar condition, which means that the benzaldehyde is more likely to connect with CuCl₂/acetone than stay in bulk solution.

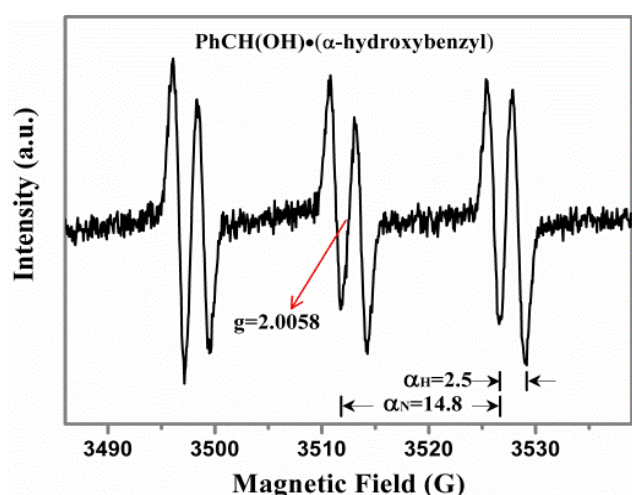


Fig. 7 Evidence for the formation of α -hydroxybenzyl radical ($g=2.0058$) in the system of CuCl₂/butanone under visible light irradiation.

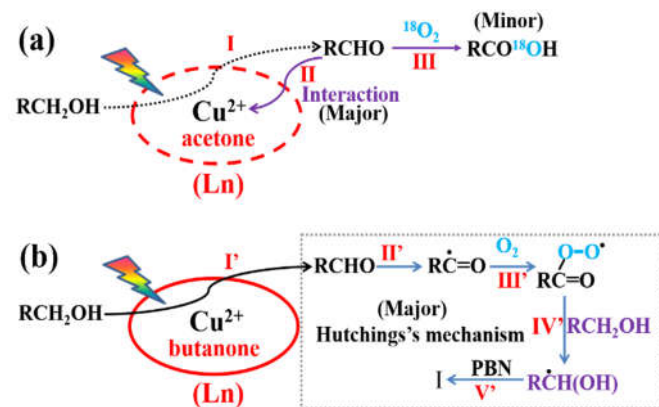


Fig. 8 Proposed reaction scheme for solvent effect in the oxidation of benzyl alcohol.

On the basis of the above experimental evidences and discussions, the following mechanism is proposed for the selective oxidation of benzyl alcohol by CuCl₂/solvents complexes (Fig. 8): The first step is the alcohol oxidation (step I or I'). How can visible light induce the oxidation of benzyl alcohol by copper complex is depicted on Fig. 3. The yield of benzaldehyde in the oxidation of benzyl alcohol depends on the probability of collision and interaction between copper complex and benzyl alcohol.

In CuCl₂/acetone system, the interaction between CuCl₂/acetone and produced benzaldehyde is prominent (Fig. 8A step II) (Fig. 6a), which makes steric obstacle between new benzyl alcohol and copper complex, thus decreases the probability of collision between benzyl alcohol and copper complex. It is why the yield of benzaldehyde no longer increased before additional alcohol was added. Then step III (overoxidation step) occurs in competition with step II. In a control experiment, when O₂ in the above reaction was replaced by ¹⁸O₂, labeled benzoic acid (C₆H₅CO¹⁸OH) was detected (Fig. 9), which illustrates that molecular oxygen is the only oxygen resource for the overoxidation of benzaldehyde. In the reaction, the variational dynamic equilibrium between copper complex and benzyl alcohol in the presence of benzaldehyde results in the amount change of each component.

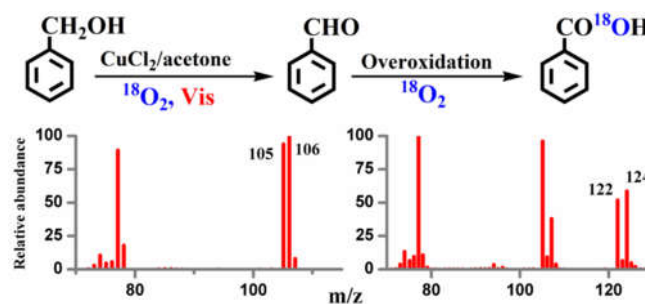


Fig. 9 GC-MS spectra corresponding to the products of ¹⁸O₂ reaction. a: benzaldehyde. b: benzoic acid.

As the solvent is butanone (or more sterically hindered solvents): although there is a significant raise for the highest yield of benzaldehyde in going from acetone to butanone, there is little change in going from butanone to cyclohexanone. We point out the steric hindrance of butanone (or more sterically hindered solvents) with benzyl alcohol constrain step II (the interaction between CuCl₂/solvent and benzaldehyde), thus induces the diffusion of benzaldehyde from copper complex to the bulk solution, resulting in the generation of carbon-centered benzoyl radicals (step II') followed by the formation of α -hydroxybenzyl radical from step III' to V' in bulk solution (Fig. 8B) as Hutchings reported. Therefore, the autoxidation of benzaldehyde in bulk solution is limited in the first stage by benzyl alcohol. While the yield of benzaldehyde reached the summit, a competition for the copper complex arises between benzyl alcohol and benzaldehyde. As a result, the CuCl₂/solvent structure is destroyed by the increasing benzaldehyde.

Due to the different tolerance for benzaldehyde of ligands and benzyl alcohol in the CuCl₂/solvents system, copper complexes exhibit different performance in the selective oxidation of benzyl alcohol. The ketone solvent possessing larger steric space than acetone can provide much more probability of collision and interaction between copper complex and benzyl alcohol, thus higher yield of benzaldehyde was obtained. The ligand effect in the oxidation of benzyl alcohol also conveys important information that produced benzaldehyde must diffuse to the bulk solution rather than be adsorbed on the surface of heterogeneous catalyst or stay in the cage of homogeneous catalyst for the alcohol oxidation by other

catalytic systems.

Conclusions

In summary, the homogenous photocatalytic CuCl₂/solvents system was used as a model system to explore the relationship between the oxidation of benzyl alcohol and the overoxidation of benzaldehyde. It was found that the catalytic activity and the selectivity of benzaldehyde strongly depend on the probability of collision and interaction between copper complex and benzyl alcohol, which can be adjusted by using a sterically hindered solvent. The situation of a real catalytic system for oxidation of benzyl alcohol is far more complicated than the ideal condition that only radicals control. We explored sterically hindered ketone architectures as scaffolds that provide steric space of copper complex in the presence of benzyl alcohol. The ideal scenario for homogeneous catalysis requires a catalyst with a strong activation to the reactants, but a relatively weak bonding (mediated by ligands) of the product. Furthermore, we consider that the CuCl₂/solvents photocatalytic system is a good candidate for large scale synthesis of benzaldehyde under day light lamp irradiation.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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