

Available online at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/jes

Selective oxidation of benzyl alcohols to benzoic acid catalyzed by eco-friendly cobalt thioporphyrzine catalyst supported on silica-coated magnetic nanospheres

Huan Li, Lan Cao, Changjun Yang*, Zhehui Zhang, Bingguang Zhang, Kejian Deng*

Key Laboratory of Catalysis and Material Sciences of the State Ethnic Affairs Commission & Ministry of Education, College of Chemistry and Material Science, South-Central University For Nationalities, Wuhan 430074, China

ARTICLE INFO

Article history:

Received 30 December 2016

Revised 31 March 2017

Accepted 8 May 2017

Available online 15 June 2017

Keywords:

Cobalt thioporphyrzine

Magnetic nanospheres

Composite catalyst

Photocatalytic oxidation

Substituted benzyl alcohol

Benzoic acid

ABSTRACT

A novel magnetically recoverable thioporphyrzine catalyst ($\text{CoPz}(\text{S-Bu})_8/\text{SiO}_2@\text{Fe}_3\text{O}_4$) was prepared by immobilization of the cobalt octakis(butylthio) porphyrzine complex ($\text{CoPz}(\text{S-Bu})_8$) on silica-coated magnetic nanospheres ($\text{SiO}_2@\text{Fe}_3\text{O}_4$). The composite $\text{CoPz}(\text{S-Bu})_8/\text{SiO}_2@\text{Fe}_3\text{O}_4$ appeared to be an active catalyst in the oxidation of benzyl alcohol in aqueous solution using hydrogen peroxide (H_2O_2) as oxidant under Xe-lamp irradiation, with 36.4% conversion of benzyl alcohol, about 99% selectivity for benzoic acid and turnover number (TON) of 61.7 at ambient temperature. The biomimetic catalyst $\text{CoPz}(\text{S-Bu})_8$ was supported on the magnetic carrier $\text{SiO}_2@\text{Fe}_3\text{O}_4$ so as to suspend it in aqueous solution to react with substrates, utilizing its lipophilicity. Meanwhile the $\text{CoPz}(\text{S-Bu})_8$ can use its unique advantages to control the selectivity of photocatalytic oxidation without the substrate being subjected to deep oxidation. The influence of various reaction parameters on the conversion rate of benzyl alcohol and selectivity of benzoic acid was investigated in detail. Moreover, photocatalytic oxidation of substituted benzyl alcohols was obtained with high conversion and excellent selectivity, specifically conversion close to 70%, selectivity close to 100% and TON of 113.6 for para-position electron-donating groups. The selectivity and eco-friendliness of the biomimetic photocatalyst give it great potential for practical applications.

© 2017 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences.

Published by Elsevier B.V.

Introduction

Selective oxidation of primary and secondary alcohols to the corresponding carboxylic acids (or aldehydes) and ketones, respectively, are pivotal reactions in organic synthesis. Oxidation catalysis plays an essential role in both energy production and energy conservation, as over 90% of all chemical processes are catalytic processes. However, oxidation is among the most problematic processes (Zhang et al., 2013a). Many stoichiometric

oxidants with heavy metals are expensive and toxic, and thus economically and environmentally unsustainable. As the demand for “greener” processing increases, the ideal system for catalytic oxidation is the use of molecular oxygen or hydrogen peroxide as the primary oxygen source together with recyclable catalysts in nontoxic solvents (Noyori et al., 2003; Punniyamurthy et al., 2005). However, because of the potential explosion hazards associated with the use of molecular oxygen or hydrogen peroxide as oxidants, one of the ways to alleviate the hazards is the use of

* Corresponding authors. E-mails: yangchangjun@mail.scuec.edu.cn (Changjun Yang), dengkj@scuec.edu.cn (Kejian Deng).

water as an inert, non-flammable solvent. In this context, water has several advantages: it is abundantly available, inexpensive, odorless, non-toxic and non-flammable (Sheldon, 2015).

Many transition metal catalysts have been used to mimic the predominant oxidation catalysts in nature, namely the cytochrome P450 enzymes (Montellano, 2005). Most biological oxidation processes mediated by P450 enzymes are highly and often completely stereoselective and ecologically sustainable. However, biological oxidation processes involve sophisticated electron and proton transfer steps in the activation of O₂ or H₂O₂ and are currently difficult to implement with a synthetic catalyst (Denisov et al., 2005). Metalloporphyrins, known as the best models for cytochrome P450 monooxygenase, have been widely used as catalysts for organic molecular oxidation (Xu et al., 2015; Santosda et al., 2014). Metalloporphyrazines (MPz) are especially interesting because their chemical properties are similar to metalloporphyrins and their stability and accessibility are similar to metallophthalocyanines (Sorokin, 2013).

Photochemical reaction is intrinsically advantageous because activation is obtained by absorbing a photon, whereas most chemical methods involve the use of toxic/polluting reagents (Maldotti et al., 2002). To this end, we aim to use visible light (sunlight) to induce reversible redox processes at the metal center, avoiding all the disadvantages derived from the use of chemical reagents. In previous work, we found that metallothioporphyrazines with alkylthio substituents exhibited excellent photocatalytic activity in degradation of organic pollutants (Su et al., 2009; Zhang et al., 2013c; Zhou et al., 2016). Meanwhile, magnetic nanoparticles (MNPs) can be used as a new kind of catalyst support due to their good stability and facile separation by magnetic forces (Wang et al., 2013; Liu et al., 2017). Their unique magnetic separation capability makes MNPs much more effective than conventional filtration or centrifugation because it can prevent the loss of the catalyst. When the biomimetic catalyst is combined with SiO₂-coated Fe₃O₄ (SiO₂@Fe₃O₄) MNPs, the separation and recycling of the catalyst are facilitated, and operating cost and properties can be optimized (Wang et al., 2013). Herein, we report the loading of cobalt octakis(butylthio)porphyrazine (CoPz(S-Bu)₈) onto SiO₂@Fe₃O₄ MNPs to form a composite catalyst and its application in photocatalytic oxidation of benzyl alcohol.

1. Experimental procedures

1.1. Materials and methods

All of the reagents used for catalyst synthesis and characterization were purchased from Aladdin Industrial Corporation. Fourier transform infrared (FT-IR) spectra were recorded on a FT-IR spectrometer (NEXUS-6700, Nicolet, USA). The Xe lamp (XD350W-1, Changzhou Siyu Environmental Sci-Tech Co., Ltd., China) was used as the light source to perform the photocatalytic experiment. The morphologies of magnetic nanoparticles were observed by transmission electron microscopy (TEM, Tecnai G220s-Twin, FEI, USA). Diffuse reflectance spectra (DRS) were measured using an ultraviolet-visible (UV-Vis) spectrophotometer (UV-2600, Shimadzu, Japan). Analysis of the oxidation products of benzyl alcohol

was carried out by a high-performance liquid chromatography system (Ultimate 3000, Dionex, USA). The radical was measured by electron paramagnetic resonance (EPR) spectroscopy, which was carried out on a Bruker EMX spectrometer (EPR-A200, Bruker, Switzerland) with a Quanta-Ray Nd:YAG laser.

1.2. Synthesis of cobalt octakis(butylthio) porphyrazine

Firstly, magnesium chips (0.056 g) and iodine crystals as an initiator were added into *n*-butanol (100 mL). The mixture was stirred under reflux for 24 hr until the magnesium chips disappeared, indicating that magnesium butoxide had successfully formed. Then 2,3-bis(butylthio)maleonitrile (Zhou et al., 2016) (2 g, 0.0078 mol) was added to the above mixture, which was heated under reflux for 24 hr. The mixture was cooled to room temperature and then dried by rotary evaporation. The residue was purified by column chromatography on silica gel using ethyl acetate/petroleum ether as eluent (1:5, V/V), giving MgPz(S-Bu)₈ (1.49 g, yield 73.5%). MgPz(S-Bu)₈ (1.041 g) was added to CF₃COOH (3 mL) in the dark and stirred for 5 hr. The resulting purple solution was added to ice-water to promote precipitation. The precipitate was filtered, then washed with water until the filtrate was colorless, and dried under vacuum. The residue was purified by column chromatography on silica gel using dichloroethane/petroleum ether as eluent (1:1, V/V), giving H₂Pz(S-Bu)₈ (0.666 g, yield 65.4%). CoPz(S-Bu)₈ was synthesized by the reaction of Co(OAc)₂·4H₂O with a certain amount of H₂Pz(S-Bu)₈ in 40 mL dimethylformamide (DMF) for 12 hr at 70°C under nitrogen atmosphere. After reaction, the mixture was added to ice-water (200 mL) and stirred until precipitation was complete. After cooling to room temperature, the precipitate consisting of the crude product and excess metal salts was filtered and then washed with water until the filtrate was colorless. The residue was dried under vacuum and then purified by column chromatography on silica gel using dichloromethane/methanol as eluent (10:1, V/V), giving the final product with a yield of 73.5%. For the characterization of H₂Pz(S-Bu)₈ and CoPz(S-Bu)₈, see (Zhou et al., 2016).

1.3. Preparation of composite catalyst CoPz(S-Bu)₈/SiO₂@Fe₃O₄

Magnetite Fe₃O₄ nano-spheres were prepared by a one-pot hydrothermal method (Zhang et al., 2013b). Typically, 10 g FeCl₃·6H₂O and 3.6 g trisodium citrate dihydrate were first dissolved in 300 mL ethylene glycol under vigorous stirring for 1 hr. Then 15 g sodium acetate was added with stirring for 30 min, and the mixture was sealed in a Teflon-lined stainless-steel autoclave and heated at 200°C for 10 hr. After that, the autoclave was cooled to room temperature. The as-prepared black product was thoroughly washed with deionized water and ethanol several times, and finally dried at 60°C for 6 hr.

The as-synthesized Fe₃O₄ was suspended in 35 mL ethanol and 6 mL deionized water and sonicated for 15 min. 1.5 mL of tetraethyl orthosilicate (TEOS) was added slowly to the mixture, which was then sonicated for 10 min. Aqueous ammonia (10%, 1.4 mL) was then added slowly over 10 min under mechanical stirring. The mixture was heated at 40°C for 12 hr. The iron oxide

nanoparticles with a thin layer of silica ($\text{SiO}_2@\text{Fe}_3\text{O}_4$) were separated by an external magnet, washed three times with ethanol, and then dried under vacuum (Rezaeifard et al., 2012).

$\text{CoPz}(\text{S-Bu})_8$ (40 mg) was firstly dissolved in 20 mL dichloromethane under ultrasonic action. Then the solution was added dropwise into a suspension containing 1 g $\text{SiO}_2@\text{Fe}_3\text{O}_4$ and 20 mL dichloromethane under stirring. The stirring was continued for 24 hr until adsorption equilibrium to obtain magnetic nanoparticles loaded with cobalt porphyrazine. After reaction, the solvent was removed under reduced pressure to give a solid residue. The residue was dried at 40°C for 24 hr. Thus the magnetic nanoparticle-supported $\text{CoPz}(\text{S-Bu})_8$ was formed. The loading of $\text{CoPz}(\text{S-Bu})_8$ on the magnetic nanoparticles was verified by FT-IR and DRS before and after $\text{CoPz}(\text{S-Bu})_8$ loading on the magnetic nanoparticles, and the loading content of $\text{CoPz}(\text{S-Bu})_8$ was equal to 4.0%.

1.4. Photocatalytic oxidation of benzyl alcohols

The catalytic oxidation of benzyl alcohol was carried out in a 50-mL quartz reaction flask equipped with a reflux condenser. In a typical photocatalytic reaction, benzyl alcohol (0.10 mmol) and the as-prepared composite catalyst (0.02 g) were placed into the flask containing 25 mL H_2O , then the reaction mixture was continuously stirred at room temperature. H_2O_2 (0.3 mmol, 30%) was then added dropwise slowly into the reaction flask within 5 min and the reaction was continued for 12 hr. During the reaction, 0.5 mL of the sample was withdrawn periodically from the mixture and filtered to remove the catalyst, then the percentage conversion was determined by analysis with a high-performance liquid chromatography system equipped with a reversed-phase C18 column (00G-4252-E0, Phenomenex, USA) and detection at 250 nm. The column temperature was maintained at 30°C. The optimized mobile phase consisted of acetonitrile and water with the volume ratio at 70:30. The flow rate was set at 1.0 mL/min. The oxidation products benzaldehyde and benzoic acid were identified by comparison with known standard samples, which were purchased from Aladdin. When the photocatalytic oxidation of benzyl alcohols was carried out under alkaline conditions such as with addition of KOH or K_2CO_3 , benzoic acid was in the form of the corresponding benzoic acid potassium salt. Potassium benzoate is soluble in water and could also be analyzed by high-performance liquid chromatography, the quantity of potassium benzoate was consistent with the yield of benzoic acid, therefore the benzoic acid product of benzyl alcohol oxidation under alkaline conditions could be accurately quantified. All experimental data was repeated three times and the average was taken to eliminate any discrepancies.

2. Results and discussion

2.1. Preparation of composite catalyst $\text{CoPz}(\text{S-Bu})_8/\text{SiO}_2@\text{Fe}_3\text{O}_4$

The starting point for the synthesis of $\text{CoPz}(\text{S-Bu})_8$ was the precursor 2,3-bis(butylthio)maleonitrile, which was obtained from the reaction of disodium dithiomaleonitrile salt with

n-bromobutane. Thereafter the metal-free octakis(butylthio)porphyrazine ($\text{H}_2\text{Pz}(\text{S-Bu})_8$) was obtained in a yield of 72.3% via the template reaction of the precursor with magnesium butoxide. Coordination of Co^{2+} into the center of the porphyrazine ring was carried out by the reaction of $\text{Co}(\text{OAc})_2$ with $\text{H}_2\text{Pz}(\text{S-Bu})_8$ at the reflux temperature of DMF, giving rise to $\text{CoPz}(\text{S-Bu})_8$ with a yield of 86.7%.

The solubility of all metallothioporphyrazines is poor. To enhance the solubility and facilitate purification, the peripheries of the porphyrazine macrocycle were grafted with long chain butylthio groups. However, the as-synthesized $\text{CoPz}(\text{S-Bu})_8$ was still insoluble in aqueous solution. It is necessary to support the $\text{CoPz}(\text{S-Bu})_8$ on the carrier $\text{SiO}_2@\text{Fe}_3\text{O}_4$ so as to form a suspension in aqueous solution to react with substrates, using its lipophilicity. Moreover, because Fe_3O_4 particles encounter problems with surface acid etching and self-aggregation, the outside of Fe_3O_4 was coated with SiO_2 . At the same time, the SiO_2 coating was able to stabilize the porphyrazine macrocycle, thus Fe_3O_4 with a SiO_2 shell was chosen as the carrier for the as-synthesized $\text{CoPz}(\text{S-Bu})_8$.

Magnetite Fe_3O_4 nano-spheres prepared by a one-pot hydrothermal method (Zhang et al., 2013b) obviously differ from those prepared by a coprecipitation method (Wang et al., 2013; Liu et al., 2017), in which the Fe_3O_4 nano-particles have an amorphous and non-uniform morphology. The TEM image of the $\text{SiO}_2@\text{Fe}_3\text{O}_4$ with a typical core-shell structure is presented in Fig. 1. The black sphere is the core Fe_3O_4 particle and the SiO_2 coating is about 10–20 nm thick with a gray appearance. The $\text{SiO}_2@\text{Fe}_3\text{O}_4$ core-shell structure has a diameter range of about 200–400 nm.

The FT-IR spectra of $\text{SiO}_2@\text{Fe}_3\text{O}_4$, $\text{CoPz}(\text{S-Bu})_8$ and $\text{CoPz}(\text{S-Bu})_8/\text{SiO}_2@\text{Fe}_3\text{O}_4$ are shown in Fig. 2. Typically, the vibration peak near 1084 cm^{-1} can be assigned to the asymmetric stretching vibration of the siloxane bond Si-O-Si associated with the condensed silica network. The C-H stretching vibration can be observed in both $\text{CoPz}(\text{S-Bu})_8$ and $\text{CoPz}(\text{S-Bu})_8/\text{SiO}_2@\text{Fe}_3\text{O}_4$ at 2928 cm^{-1} .

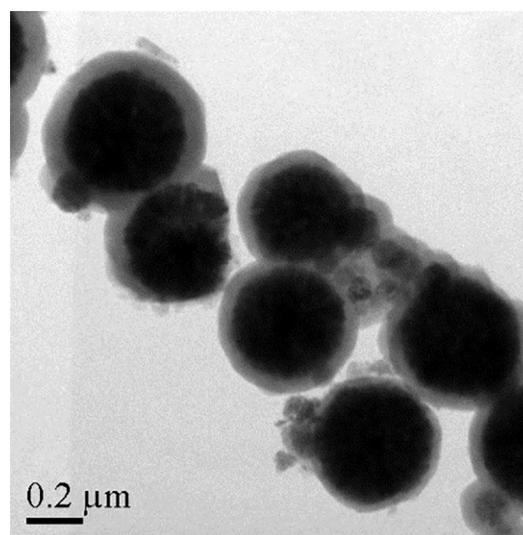


Fig. 1 – Transmission electron microscopy (TEM) image of $\text{SiO}_2@\text{Fe}_3\text{O}_4$.

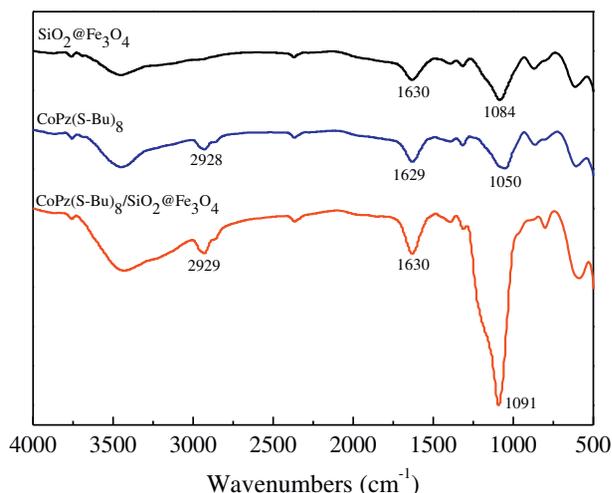


Fig. 2 – Fourier transform infrared (FT-IR) spectra of $\text{SiO}_2@\text{Fe}_3\text{O}_4$, cobalt octakis(butylthio) porphyrazine ($\text{CoPz}(\text{S-Bu})_8$) and composite catalyst ($\text{CoPz}(\text{S-Bu})_8/\text{SiO}_2@\text{Fe}_3\text{O}_4$).

The DRS of $\text{SiO}_2@\text{Fe}_3\text{O}_4$ and $\text{CoPz}(\text{S-Bu})_8/\text{SiO}_2@\text{Fe}_3\text{O}_4$ are shown in Fig. 3. The composite $\text{CoPz}(\text{S-Bu})_8/\text{SiO}_2@\text{Fe}_3\text{O}_4$ showed the characteristic Q-band absorption of $\text{CoPz}(\text{S-Bu})_8$ near 670 nm and B-band absorption near 355 nm respectively. There was no discernable characteristic absorption peak for the carrier $\text{SiO}_2@\text{Fe}_3\text{O}_4$. The results of FT-IR and DRS characterization demonstrated that the $\text{CoPz}(\text{S-Bu})_8$ was loaded on $\text{SiO}_2@\text{Fe}_3\text{O}_4$ successfully.

2.2. Oxidation of benzyl alcohol catalyzed by $\text{CoPz}(\text{S-Bu})_8/\text{SiO}_2@\text{Fe}_3\text{O}_4$

To assess the activity of the as-prepared composite catalyst $\text{CoPz}(\text{S-Bu})_8/\text{SiO}_2@\text{Fe}_3\text{O}_4$, the oxidation of benzyl alcohol was carried out using the green oxidant H_2O_2 and the $\text{CoPz}(\text{S-Bu})_8/\text{SiO}_2@\text{Fe}_3\text{O}_4$ catalyst suspended in aqueous solution under irradiation by a Xe lamp simulating sunlight. As we all know,

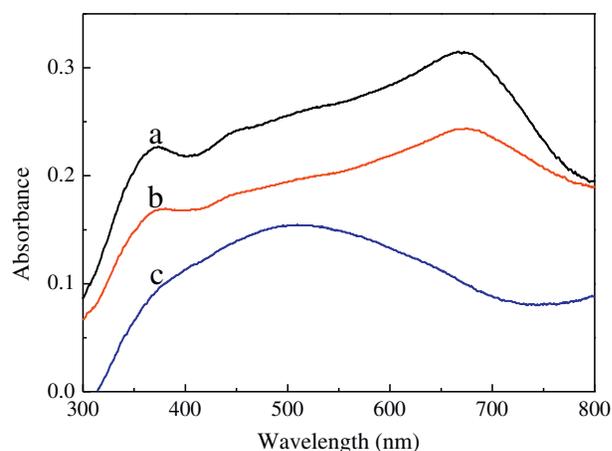


Fig. 3 – Diffuse reflectance spectra (DRS) of $\text{CoPz}(\text{S-Bu})_8/\text{SiO}_2@\text{Fe}_3\text{O}_4$ before reaction (a) and after reuse five times (b) as well as that of $\text{SiO}_2@\text{Fe}_3\text{O}_4$ (c).

activating H_2O_2 can produce $\text{HO}\cdot$ and $\text{O}_2^{\cdot-}$, therefore the photocatalytic oxidation is a radical reaction, which may non-selectively oxidize benzyl alcohol into different products, even CO_2 (Su et al., 2009; Liu et al., 2017). In this respect, the biomimetic catalyst displayed a unique advantage: the products of photocatalytic oxidation of benzyl alcohol only included benzaldehyde and benzoic acid. The influence of various reaction parameters on the conversion rate of benzyl alcohol (BAL) and selectivity of benzoic acid (BZA) was investigated in detail.

Table 1 lists the effect of reaction time on the conversion and selectivity from entry 1 to entry 4. The conversion increased with prolonged reaction time, but the conversion increments became smaller and smaller. Thus 12 hr was chosen as the optimal reaction time.

Comparing entry 4 with entry 5, the conversion increased to 21.2% as the concentration of H_2O_2 increased (with mole ratio of H_2O_2 to benzyl alcohol ranging from 2:1 to 3:1). Meanwhile, from entry 5 to entry 8, the conversion presented a maximum of 36.4% as the illumination intensity (I (W/cm^2)) increased from 0.40 to 0.45. This indicated that $0.42 \text{ W}/\text{cm}^2$ is the optimal illumination intensity and a three-fold molar ratio of H_2O_2 relative to benzyl alcohol is the optimal quantity taking into account cost considerations, while also not reducing the selectivity for benzoic acid.

From entry 7 and entries 11 to 16, it could be seen that the reaction temperature had an obvious influence on the conversion and selectivity, although the reaction was a light-induced radical reaction. This indicated that room temperature was the optimal temperature.

From entry 9, the conversion of benzyl alcohol in the presence of bare $\text{SiO}_2@\text{Fe}_3\text{O}_4$ was 20.0%, and when the composite $\text{CoPz}(\text{S-Bu})_8/\text{SiO}_2@\text{Fe}_3\text{O}_4$ replaced the bare $\text{SiO}_2@\text{Fe}_3\text{O}_4$ (entry 7), the conversion increased to 36.4% from 20.0%. This implies that $\text{CoPz}(\text{S-Bu})_8$ plays an important role in the photocatalytic process. Meanwhile, the active surface sites on the composite catalyst are covered with $\text{CoPz}(\text{S-Bu})_8$, so the catalytic efficiency of composite $\text{CoPz}(\text{S-Bu})_8/\text{SiO}_2@\text{Fe}_3\text{O}_4$ mainly derives from the $\text{CoPz}(\text{S-Bu})_8$, rather than any significant effect from bare $\text{SiO}_2@\text{Fe}_3\text{O}_4$. At the same time, the conversion was not raised when the catalyst loading of $\text{CoPz}(\text{S-Bu})_8$ was increased by a factor of 20 in entry 10. This demonstrated that the $\text{CoPz}(\text{S-Bu})_8$ showed obvious photocatalytic activity for the oxidation of benzyl alcohol into benzoic acid, with a biomimetic structure beneficial to high selectivity to avoid over-oxidation of the substrate, and the carrier $\text{Al}_2\text{O}_3@\text{Fe}_3\text{O}_4$ had also a positive effect on oxidation reaction. In view of the chemical inertness and stability of the silica coating (Peng et al., 2001) as well as the semiconducting properties of Fe_3O_4 , some positive influence on the photocatalytic activity of $\text{CoPz}(\text{S-Bu})_8$ may be derived from Fe_3O_4 because of possible defects in the compact SiO_2 coating.

Different additives were added into the reaction system respectively, at a one-to-one molar ratio with the substrate. IBAL (entry 1) could not promote the reaction because it is insoluble in water and is a reducing compound that tends to consume oxidants. From Table 2 it can be seen that alkaline additives, such as KOH (entry 2), K_2CO_3 (entry 3) and DBU (entry 4), were beneficial to both the conversion of benzyl

Table 1 – Effect of reaction time on the conversion of BAL.

Entry	Temperature (°C)	Time (hr)	I (W/cm ²)	n _{Catalyst} /n _{Substrate}	n _{Oxidant} /n _{Substrate}	BAL conversion	BZA selectivity
1	25	3	0.40	1:170	2:1	5.22%	97.1%
2	25	6	0.40	1:170	2:1	9.50%	98.0%
3	25	9	0.40	1:170	2:1	13.4%	98.3%
4	25	12	0.40	1:170	2:1	15.6%	98.5%
5	25	12	0.40	1:170	3:1	21.2%	98.4%
6	25	12	0.41	1:170	3:1	24.3%	98.5%
7	25	12	0.42	1:170	3:1	36.4%	98.8%
8	25	12	0.45	1:170	3:1	29.0%	98.6%
9	25	12	0.42	0:170	3:1	20.0%	98.6%
10	25	12	0.42	1:10	3:1	31.9%	99.8%
11	50	12	0.42	1:170	3:1	28.2%	95.6%
12	40	12	0.42	1:170	3:1	31.1%	83.6%
13	30	12	0.42	1:170	3:1	34.9%	99.3%
14	20	12	0.42	1:170	3:1	30.5%	96.7%
15	10	12	0.42	1:170	3:1	17.9%	94.5%
16	0	12	0.42	1:170	3:1	10.8%	92.9%

Reaction conditions: The additive is K₂CO₃ with the same molar quantity as BAL, and the solvent and oxidant in this catalytic system are H₂O and H₂O₂ respectively. I: illumination intensity; n_{Catalyst}: molar quantity of catalyst; n_{Substrate}: molar quantity of substrate; n_{Oxidant}: molar quantity of oxidant; BAL: benzyl alcohol.

alcohol and the selectivity for benzoic acid. Meanwhile, acidic additives, such as H₂SO₄ (entry 5), HCl (entry 6), AcOH (entry 7) and NH₄Cl (entry 8), dramatically promoted the conversion of benzyl alcohol, but the selectivity for benzoic acid was slightly decreased. Therefore, K₂CO₃ was the optimal additive taking all factors into consideration.

The photochemical oxidation of benzyl alcohol has been studied (Hansen and Sydnes, 1989) and several mechanisms have been proposed to account for the diversity of products obtained under various conditions. The present study demonstrated higher selectivity for the oxidation product benzoic acid, and the active species were further examined in the presence of the composite catalyst CoPz(S-Bu)₈/SiO₂@Fe₃O₄ by EPR spectroscopy. No obvious signals of superoxide anion radical (O₂^{·-}) were detected in EPR experiments using free radical trapping; however, strong signals of hydroxyl radical (HO[·]) were detected, as shown in Fig. 4. This implied that the HO[·] radical is the main reactive oxygen species in the presence of the catalyst. The different additives markedly affected the signal strength of HO[·], such that the signal strength of HO[·] was higher for acidic additives than for alkaline additives; this result was consistent with the corresponding effects of additives on catalytic activity. However,

the selectivity for benzoic acid was slightly decreased in the presence of acidic additives compared with alkaline additives.

2.3. Stability and repeatability of composite CoPz(S-Bu)₈/SiO₂@Fe₃O₄

Because the CoPz(S-Bu)₈/SiO₂@Fe₃O₄ catalyst possessed the advantages of easy separation and recycling, the repeatability and stability of CoPz(S-Bu)₈/SiO₂@Fe₃O₄ were also investigated, and the results for five repeated catalytic cycles are shown in Fig. 5. The results indicated that CoPz(S-Bu)₈ was stable based on the DRS results shown as curve b in Fig. 3, although the catalytic activity did decrease slightly because of the limited physical absorption between CoPz(S-Bu)₈ and SiO₂.

The catalytic efficiency of CoPz(S-Bu)₈/SiO₂@Fe₃O₄ is not very satisfactory in terms of the conversion rate in comparison to other catalysts in previous works (Beydoun et al., 2002). Possibly, the SiO₂ coating hindered the transfer of electrons or active oxygen from Fe₃O₄ to CoPz(S-Bu)₈ on the SiO₂@Fe₃O₄ carrier, (Liu et al., 2017; Benferrah et al., 2016) suppressing the photocatalytic reaction.

2.4. Oxidation of substituted benzyl alcohol catalyzed by CoPz(S-Bu)₈/SiO₂@Fe₃O₄

The oxidation of substituted benzyl alcohols photocatalyzed by CoPz(S-Bu)₈/SiO₂@Fe₃O₄ under optimal reaction conditions was conducted, as shown in Table 3. The experimental results showed that the conversion rate of substituted benzyl alcohols was higher than that of benzyl alcohol. This demonstrated that substituents on the benzene ring have some influence on the conversion. With an electron-withdrawing substituent on the benzene ring, such as shown in entry 1, the conversion is relatively lower; meanwhile with an electron-donating substituent on the benzene ring, such as in entry 2, 3, 4 and 5, the conversion is relatively high, especially for substitution on the para-position of the benzene ring. Whether a substituent is electron-withdrawing or electron-

Table 2 – Influence of additives on the conversion of BAL.

Entry	Additive	Dosage (mmol)	BAL conversion	BAD selectivity	BZA selectivity
1	IBAL	0.1	10.3%	1.55%	98.3%
2	KOH	0.1	18.0%	3.29%	96.7%
3	K ₂ CO ₃	0.1	36.4%	1.22%	98.8%
4	DBU	0.1	14.7%	4.15%	95.8%
5	H ₂ SO ₄	0.1	57.6%	7.43%	86.5%
6	HCl	0.1	50.3%	6.3%	85.4%
7	AcOH	0.1	40.6%	5.48%	91.5%
8	NH ₄ Cl	0.1	36.8%	27.6%	72.4%

IBAL: isobutylaldehyde; DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene; AcOH: acetic acid; BAD: benzaldehyde; BAL: benzyl alcohol.

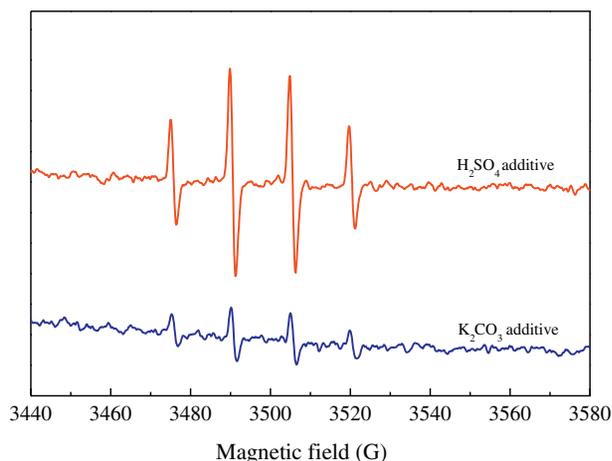


Fig. 4 – Electron paramagnetic resonance (EPR) spectroscopy of dimethyl pyridine N-oxide (DMPO) adduct with HO· generated in the photocatalytic process in the presence of CoPz(S-Bu)₈/SiO₂@Fe₃O₄ with different additives. Reaction conditions: 4 mg CoPz(S-Bu)₈/SiO₂@Fe₃O₄ was added into 5 mL water containing 6 μL hydrogen peroxide, then 60 μL DMPO was added into in the suspension.

donating, as long as it can be beneficial to activation of the α-hydrogen of benzyl alcohol, the corresponding alcohol will have a good conversion rate.

3. Conclusions

To enhance the catalytic activity and recoverability of the catalyst, the cobalt octakis(butylthio) porphyrzines complex (CoPz(S-Bu)₈) was immobilized on silica-coated magnetic nanospheres (SiO₂@Fe₃O₄). The photocatalytic activity of CoPz(S-Bu)₈/SiO₂@Fe₃O₄ was assessed through oxidation of benzyl alcohol in water under Xe-lamp irradiation using H₂O₂. It was demonstrated that the CoPz(S-Bu)₈ catalyst possesses

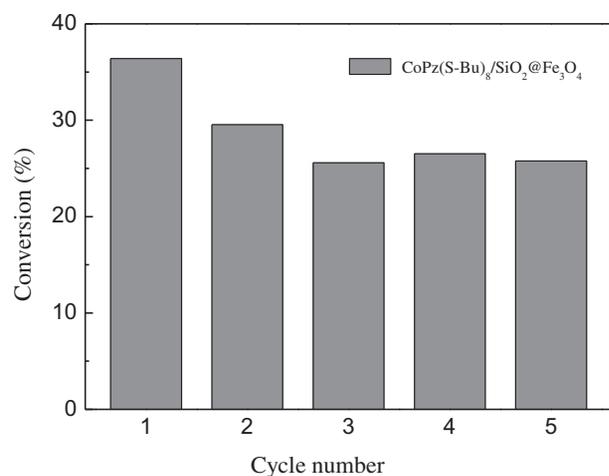


Fig. 5 – Recycling experiments for oxidation of benzyl alcohol catalyzed by CoPz(S-Bu)₈/SiO₂@Fe₃O₄ under optimal reaction conditions.

Table 3 – Photocatalytic oxidation of substituted alcohols.

Entry	Substrate	Conversion	BZA selectivity	TON
1		38.5%	>99%	65.5
2		39.8%	>99%	67.7
3		42.2%	>99%	71.7
4		48.3%	>99%	82.1
5		66.8%	>99%	113.6

Oxidation reaction were conducted under the optimal condition: 20 mg composite CoPz(S-Bu)₈/SiO₂@Fe₃O₄, 0.1 mmol substrate, 0.3 mmol H₂O₂, 0.1 mmol K₂CO₃. TON: turnover number.

high capability for the activation of H₂O₂. Both acidic and alkaline additives promoted the conversion of benzyl alcohol, while the alkaline additive was more beneficial to high selectivity for benzoic acid. With the aid of EPR free-radical trapping experiments, it was demonstrated that HO· is the main reactive oxygen species in this photocatalytic process. Meanwhile, the substituents of benzyl alcohol have an influence on its conversion, with electron-donating substituents on the benzene ring of benzyl alcohol leading to enhanced conversion to the corresponding acid. The catalytic efficiency of CoPz(S-Bu)₈/SiO₂@Fe₃O₄ is not very satisfactory from the viewpoint of conversion rate, but its selectivity and eco-friendliness are advantageous. This work provides valuable information for the organic chemical industry.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Nos. 21272281 and 20977115), Natural Science Foundation of Hubei Province (2014CFB919), “the Fundamental Research Funds for the Central Universities”, South-Central University for Nationalities (CZY14003) and the Science and Technology Plan Innovation Team of Wuhan City (2015070504020220).

REFERENCES

- Benferrah, N., Hammadi, M., Philouze, C., Berthiol, F., Thomas, F., 2016. Copper(II) complex of a Schiff base of dehydroacetic acid: characterization and aerobic oxidation of benzyl alcohol. *Inorg. Chem. Commun.* 72, 17–22.
- Beydoun, D., Amal, R., Low, G., McEvoy, S., 2002. Occurrence and prevention of photodissolution at the phase junction of magnetite and titanium dioxide. *J. Mol. Catal. A* 180, 193–200.
- Denisov, I.G., Makris, T.M., Sligar, S.G., Schlichting, I., 2005. Structure and chemistry of cytochrome P450. *Chem. Rev.* 105, 2253–2277.
- Hansen, S.H., Sydnnes, L.K., 1989. Photochemical oxidation of benzyl alcohol. *Acta Chem. Scand.* 43, 395–398.
- Liu, Y., Zhou, X., Zhang, Z., Zhang, B., Deng, K., 2017. Effect of carrier and axial ligand on the photocatalytic activity of cobalt thioporphyrzine. *Chin. J. Catal.* 38, 330–336.

- Maldotti, A., Molinari, A., Amadelli, R., 2002. Photocatalysis with organized systems for the oxofunctionalization of hydrocarbons by O₂. *Chem. Rev.* 102, 3811–3836.
- Montellano, P.R. Ortiz de (Ed.), 2005. *Cytochrome P450 Structure, Mechanism, and Biochemistry*, 3rd ed. Kluwer Academic/Plenum, New York.
- Noyori, R., Aoki, M., Sato, K., 2003. Green oxidation with aqueous hydrogen peroxide. *Chem. Commun.* 1977–1986.
- Peng, G., Wang, Y., Hu, C., Wang, E., Feng, S., Zhou, Y., Ding, H., Liu, Y., 2001. Heteropolyoxo-metalates which are included in microporous silica, Cs_xH_{3-x}PMo₁₂O₄₀/SiO₂ and Cs_yH_{5-y}PMo₁₀V₂O₄₀/SiO₂, as insoluble solid bifunctional catalysts: synthesis and selective oxidation of benzyl alcohol in liquid–solid systems. *Appl. Catal. A Gen.* 218, 91–99.
- Punniyamurthy, T., Velusamy, S., Iqbal, J., 2005. Recent advances in transition metal catalyzed oxidation of organic substrates with molecular oxygen. *Chem. Rev.* 105, 2329–2363.
- Rezaeifard, A., Jafarpour, M., Naeimi, A., 2012. Aqueous heterogeneous oxygenation of hydrocarbons and sulfides catalyzed by recoverable magnetite nanoparticles coated with copper(II) phthalocyanine. *Green Chem.* 14, 3386–3394.
- Santosda, S.V., Infante, T.L., Elianedo, N., Marina, I.Y., Gilson, D.-S., 2014. New manganese porphyrin as biomimetic catalyst of cyclohexane oxidation: effect of water or imidazole as additives. *Appl. Catal. A Gen.* 469, 124–131.
- Sheldon, Roger A., 2015. Recent advances in green catalytic oxidations of alcohols in aqueous media. *Catal. Today* 247, 4–13.
- Sorokin, A.B., 2013. Phthalocyanine metal complexes in catalysis. *Chem. Rev.* 113, 8152–8191.
- Su, R., Sun, J., Sun, Y., Deng, K., Cha, D., Wang, D., 2009. Oxidative degradation of dye pollutants over a broad pH range using hydrogen peroxide catalyzed by FePz(dtnCl₂)₄. *Chemosphere* 77, 1146–1151.
- Wang, S.G., Zhang, Z.H., Liu, B., Li, J.L., 2013. Silica coated magnetic Fe₃O₄ nanoparticles supported phosphotungstic acid: a novel environmentally friendly catalyst for the synthesis of 5-ethoxymethylfurfural from 5-hydroxymethylfurfural and fructose. *Catal. Sci. Technol.* 3, 2104–2112.
- Xu, S., Zhao, Z., Bi, L., Chen, Y., Li, D., Wang, J., Gu, Y., Lu, Y., 2015. Selective aerobic hydroxylation of p-menthane to dihydroterpineols catalyzed by metalloporphyrins in solvent and additive free system. *Catal. Commun.* 59, 26–29.
- Zhang, R., Vanover, E., Chen, T.-H., Thompson, H., 2013a. Visible light-driven aerobic oxidation catalyzed by a diiron(IV) μ-oxo biscorrole complex. *Appl. Catal. A Gen.* 464–465, 95–100.
- Zhang, X.-B., Tong, H.-W., Liu, S.-M., Yong, G.-P., Guan, Y.-F., 2013b. An improved Stöber method towards uniform and monodisperse Fe₃O₄@C nanospheres. *J. Mater. Chem. A* 1, 7488–7493.
- Zhang, Z., Wen, X., Deng, K., Zhang, B., Lv, K., Sun, J., 2013c. Photodegradation of rhodamine B with molecular oxygen catalyzed by a novel unsymmetrical iron porphyrine under simulated sunlight. *Catal. Sci. Technol.* 3, 1415–1422.
- Zhou, Q., Xu, S., Yang, C., Zhang, B., Li, Z., Deng, K., 2016. Modulation of peripheral substituents of cobalt thioporphyrines and their photocatalytic activity. *Appl. Catal. B Environ.* 192, 108–115.