

Available online at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/jes

JES
 JOURNAL OF
 ENVIRONMENTAL
 SCIENCES
www.jesc.ac.cn

1 Selective oxidation of benzyl alcohols to benzoic acid catalyzed 2 by eco-friendly cobalt thiophorphyrazine catalyst supported on 3 silica-coated magnetic nanospheres

Q3 Q2 Huan Li, Lan Cao, Changjun Yang*, Zhehui Zhang, Bingguang Zhang, Kejian Deng*

5 Key Laboratory of Catalysis and Material Sciences of the State Ethnic Affairs Commission & Ministry of Education,
 6 College of Chemistry and Material Science, South-Central University For Nationalities, Wuhan 430074, China
 7

90 A R T I C L E I N F O

11 Article history:
 12 Received 30 December 2016
 13 Revised 31 March 2017
 14 Accepted 8 May 2017
 15 Available online xxxx

35 Keywords:
 36 Cobalt thiophorphyrazine
 37 Magnetic nanospheres
 38 Composite catalyst
 39 Photocatalytic oxidation
 40 Substituted benzyl alcohol
 41 Benzoic acid
 42

A B S T R A C T

A novel magnetically recoverable thiophorphyrazine catalyst (CoPz(S-Bu)₈/SiO₂@Fe₃O₄) 16 was prepared by immobilization of the cobalt octakis(butylthio) porphyrine complex 17 (CoPz(S-Bu)₈) on silica-coated magnetic nanospheres (SiO₂@Fe₃O₄). The composite 18 CoPz(S-Bu)₈/SiO₂@Fe₃O₄ appeared to be an active catalyst in the oxidation of benzyl alcohol 19 in aqueous solution using hydrogen peroxide (H₂O₂) as oxidant under Xe-lamp irradiation, 20 with 36.4% conversion of benzyl alcohol, about 99% selectivity for benzoic acid and turnover 21 number (TON) of 61.7 at ambient temperature. The biomimetic catalyst CoPz(S-Bu)₈ was 22 supported on the magnetic carrier SiO₂@Fe₃O₄ so as to suspend it in aqueous solution to 23 react with substrates, utilizing its lipophilicity. Meanwhile the CoPz(S-Bu)₈ can use its 24 unique advantages to control the selectivity of photocatalytic oxidation without the 25 substrate being subjected to deep oxidation. The influence of various reaction parameters 26 on the conversion rate of benzyl alcohol and selectivity of benzoic acid was investigated in 27 detail. Moreover, photocatalytic oxidation of substituted benzyl alcohols was obtained with 28 high conversion and excellent selectivity, specifically conversion close to 70%, selectivity 29 close to 100% and TON of 113.6 for para-position electron-donating groups. The selectivity 30 and eco-friendliness of the biomimetic photocatalyst give it great potential for practical 31 applications. 32

© 2017 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. 33

Published by Elsevier B.V. 34

48 Introduction

49 Selective oxidation of primary and secondary alcohols to the
 50 corresponding carboxylic acids (or aldehydes) and ketones,
 51 respectively, are pivotal reactions in organic synthesis.
 52 Oxidation catalysis plays an essential role in both energy
 53 production and energy conservation, as over 90% of all
 54 chemical processes are catalytic processes. However, oxida-
 Q4 tion is among the most problematic processes (R. Zhang et al.,

2013; X.-B. Zhang et al., 2013; Z. Zhang et al., 2013). Many 56 stoichiometric oxidants with heavy metals are expensive and 57 toxic, and thus economically and environmentally unsustain- 58 able. As the demand for “greener” processing increases, the 59 ideal system for catalytic oxidation is the use of molecular 60 oxygen or hydrogen peroxide as the primary oxygen source 61 together with recyclable catalysts in nontoxic solvents (Noyori 62 et al., 2003; Punniyamurthy et al., 2005). However, because of 63 the potential explosion hazards associated with the use of 64

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

molecular oxygen or hydrogen peroxide as oxidants, one of the ways to alleviate the hazards is the use of water as an inert, non-inflammable 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 O_2 or H_2O_2 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; R. Zhang et al., 2013; X.-B. Zhang et al., 2013; Z. Zhang et al., 2013; 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 SiO_2 -coated Fe_3O_4 ($SiO_2@Fe_3O_4$) 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 $SiO_2@Fe_3O_4$ 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 CF_3COOH (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 $H_2Pz(S-Bu)_8$ (0.666 g, yield 65.4%). $CoPz(S-Bu)_8$ was synthesized by the reaction of $Co(OAc)_2 \cdot 4H_2O$ with a certain amount of $H_2Pz(S-Bu)_8$ 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 $H_2Pz(S-Bu)_8$ and $CoPz(S-Bu)_8$, see Zhou et al. (2016).

1.3. Preparation of composite catalyst $CoPz(S-Bu)_8/SiO_2@Fe_3O_4$

Magnetite Fe_3O_4 nano-spheres were prepared by a one-pot hydrothermal method (R. Zhang et al., 2013; X.-B. Zhang et al., 2013; Z. Zhang et al., 2013). Typically, 10 g $FeCl_3 \cdot 6H_2O$ 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 Fe_3O_4 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

Download English Version:

<https://daneshyari.com/en/article/5754022>

Download Persian Version:

<https://daneshyari.com/article/5754022>

[Daneshyari.com](https://daneshyari.com)