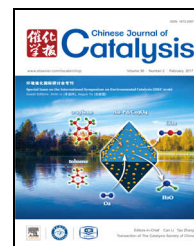


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Effect of carrier and axial ligand on the photocatalytic activity of cobalt thioporphyrazine



Yi Liu, Xuanmu Zhou, 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 Sciences, South-Central Universities for Nationalities, Wuhan 430074, Hubei, China

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ABSTRACT

The photocatalytic activity of cobalt octakis(butylthio) porphyrzine (CoPz(BuS)₈) was assessed through photodegradation of the dye rhodamine B (RhB) in water under irradiation with a Xe lamp and aerated conditions. The photocatalytic activity of CoPz(BuS)₈ loaded on Al₂O₃ or SiO₂@Fe₃O₄ nanoparticles or coordinated with an axial azide ligand was also investigated. The results demonstrated that the photocatalytic activity of CoPz(BuS)₈ loaded on Al₂O₃ was higher than that loaded on SiO₂@Fe₃O₄. The kinetic curves of RhB degradation in aqueous solutions at different pH indicated the pseudo first-order kinetics of the reaction. The highest degradation rate for CoPz(BuS)₈ loaded Al₂O₃ at pH = 4 after 160 min was 84.6%. However, the advantages of easier separation and recycling as well as the ability to terminate the reaction at any time for the CoPz(BuS)₈ loaded SiO₂@Fe₃O₄ cannot be ignored. When electron-rich NaN₃ was coordinated with CoPz(BuS)₈ as an axial ligand and loaded on Al₂O₃, the resulting catalyst produced more active oxygen species such as O₂⁻ and HO• to promote the quicker degradation of RhB than that by the other catalysts. For the N₃-coordinated CoPz(BuS)₈ loaded on Al₂O₃, the reactions at pH = 4 and 7 distinctly deviated from first-order kinetics, and the degradation rate reached 77.6% after 80 min at pH = 4.

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1. Introduction

Porphyrzines (Pzs) and porphyrins (Prs) have similar structures to phthalocyanines (Pcs) but tend to have better solubility, especially those bearing long-chain substituents. In recent years, porphyrzinooids bearing heteroatomic substituents, especially alkylthio groups at peripheral positions, have gained increasing attention [1–6]. Although alkylthioporphyrazine complexes share the structural, redox, and magnetic properties of unsubstituted metalloporphyrazines, they show unique electronic spectra and chemical reactivity [1]. Alkylthi-

oporphyrazines have been used for chemical sensing, nonlinear optics, medical applications, and cancer photodynamic therapy [2–6]. Unlike Prs, Pzs bearing a variety of substituents can be easily accessed, making them easier for electronic property adjustment and further application [7,8]. These advantages make Pzs promising alternatives to Pcs in a wide range of roles [9].

Low-pollution water is generally purified by advanced oxidation processes (AOPs), and treatment of industrial waste water is also often combined with AOPs. AOPs can degrade and even mineralize the toxic pollutants in waste water using reac-

* Corresponding author. Tel: +86-27-67843930; Fax: +86-27-67842752; E-mail: zehuizh@mail.ustc.edu.cn

Corresponding author. E-mail: dengkj@scuec.edu.cn

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tive oxygen species (ROS) like hydroxyl radicals ($\text{HO}\cdot$). Such process is increasingly seen under the viewpoint of environmentally friendly or “green” chemistry, taking into account three points of unlimited natural resource: (a) oxygen (from air) as an oxidant, (b) often water as the solvent, and (c) visible light (solar radiation) for photooxidation [10]. Photochemical homogeneous and heterogeneous catalytic oxidation processes with metalloporphyrins (MPs) and metallophthalocyanines (MPcs) have been carried out in oxygen-saturated aqueous solutions of thiols, sulfides, and phenols [10]. After MPs or MPcs are excited, their metal center binds to an oxygen, which after a subsequent binding/interaction with a substrate, leads to the oxidized substrate in one of two ways. Singlet oxygen ($^1\text{O}_2$) may be formed by type-II energy transfer reactions, or a superoxide anion radical (O_2^-) may be produced by type-I electron transfer reactions [10,11]. Compared with Pc, Pr is a better electron donor, thus tending to generate type-I reactions. In turn, Pc is a better light harvester than Pr, tending to generate type-II reactions. Thioporphyrazine is both a better electron donor and better light harvester than Pc and Pr, tending to generate both type-I and type-II reactions during photocatalytic degradation of pollutants [12,13].

Apart from Pz, the axial ligand is also an important factor influencing the catalytic properties of metallothioporphyrazines. For example, in the early 1990s, Sorokin et al. [14] used a sulfonated iron Pc as a biomimetic catalyst to successfully degrade 2,4,6-trichlorophenol from the pulp/paper industry when acetonitrile was added to the reaction system. Acetonitrile behaved as an axial ligand to promote the catalysis. Liu et al. [15] found that low-activity μ -oxodiironporphyrin converted to an active monomer with an axial chloride ligand in chlorinated solvent.

In this paper, cobalt octakis(butylthio)porphyrazine ($\text{CoPz}(\text{BuS})_8$) was used as a biomimetic catalyst in photodegradation of rhodamine B (RhB) in water under an air atmosphere. The effects of an electron-rich cocatalyst and different inorganic carriers on the performance of the catalyst are also explored.

2. Experimental

2.1. Materials and instruments

All of the reagents used for catalyst synthesis and characterization were purchased from Aladdin Industrial Corporation. All water not specially mentioned was distilled twice before use.

Fourier transform infrared (FT-IR) spectra were recorded on a NEXUS-6700 FT-IR spectrometer (Nicolet). The Xe lamp was purchased from Applied Photophysics Limited. Analysis of the degradation products of RhB was done on a VARIAN ProStar 210HPLC system. The samples were separated using a reversed-phase C18 column (200 mm \times 4.6 mm). The X-ray diffraction (XRD) patterns were obtained on a D8-advance X-ray diffractometer (German Bruker) using $\text{Cu } K_\alpha$ radiation. The morphologies of magnetic nanoparticles were observed on transmission electron microscopy (TEM, Tecnai G20, USA).

2.2. Synthesis of cobaltoctakis(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 h until the magnesium chips disappeared, indicating that magnesium butoxide had successfully formed. Then, 2,3-bis(butylthio)maleonitrile [13] (2 g, 0.0078 mol) was added to the mixture, which was heated under reflux for 24 h. The mixture was cooled to room temperature and then dried by rotary evaporation. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether 1/5) to give $\text{MgPz}(\text{BuS})_8$ (1.49 g, 73.5%).

$\text{MgPz}(\text{BuS})_8$ (1.041 g) was added to CF_3COOH (3 mL) in the dark and stirred for 5 h. The resulting purple solution was added to ice-water to promote precipitation. The precipitate was filtered, washed with water until the filtrate was colorless, and dried under vacuum. The residue was purified by column chromatography on silica gel (1,2-dichloroethane/petroleum ether 1:1) to give $\text{H}_2\text{Pz}(\text{BuS})_8$ (0.666 g, 65.4%).

$\text{CoPz}(\text{BuS})_8$ was synthesized by the reacting $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ with a quantitative amount of $\text{H}_2\text{Pz}(\text{BuS})_8$ in DMF (40 mL) for 12 h 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 ($\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ 10/1) to give the final product with a yield of 73.5%. For the characterization of $\text{H}_2\text{Pz}(\text{BuS})_8$ and $\text{CoPz}(\text{BuS})_8$, see Ref. [13].

2.3. Preparation of catalysts

$\text{CoPz}(\text{BuS})_8$ (4.0 mg) was dissolved in CH_2Cl_2 (50 mL) under ultrasonic action. The solution was added dropwise into a suspension of activated Al_2O_3 (1.0 g) in CH_2Cl_2 (50 mL) under stirring. The stirring was continued for 24 h to reach adsorption equilibrium, providing Al_2O_3 -loaded $\text{CoPz}(\text{BuS})_8$. After removing the solvent by reduced pressure distillation, Al_2O_3 -loaded $\text{CoPz}(\text{BuS})_8$ ($\text{CoPz}(\text{BuS})_8/\text{Al}_2\text{O}_3$) was obtained. The content of $\text{CoPz}(\text{BuS})_8$ was 4.0%.

$\text{SiO}_2@\text{Fe}_3\text{O}_4$ was prepared as described in our previous work [16]. $\text{CoPz}(\text{BuS})_8$ -loaded $\text{SiO}_2@\text{Fe}_3\text{O}_4$ ($\text{CoPz}(\text{BuS})_8/\text{SiO}_2@\text{Fe}_3\text{O}_4$) was synthesized using a similar process to that described above, and the content of $\text{CoPz}(\text{BuS})_8$ was 4.0%.

2.4. Photocatalytic degradation of RhB catalyzed by biomimetic catalysts

$\text{CoPz}(\text{BuS})_8/\text{Al}_2\text{O}_3$, $\text{CoPz}(\text{BuS})_8/\text{SiO}_2@\text{Fe}_3\text{O}_4$, or $\text{CoPz}(\text{BuS})_8/\text{N}_3/\text{Al}_2\text{O}_3$ (20 mg) was added as a catalyst to RhB solution (1.0×10^{-5} mol/L, 50 mL) at different pH. The suspension was stirred for 12 h in the dark to establish an adsorption equilibrium before light irradiation. In a typical photocatalytic reaction, the suspension containing the catalyst and RhB was irradiated by a Xe lamp (light intensity 7.0×10^4 Lumina) in an aerated sus-

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