Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Applied Catalysis B: Environmental 65 (2006) 217–226
APPLIED CATALYSIS B: ENVIRONMENTAL
www.elsevier.com/locate/apcatb

Photocatalytic degradation of organic pollutants catalyzed by layered iron(II) bipyridine complex–clay hybrid under visible irradiation

Mingming Cheng, Wanhong Ma, Chuncheng Chen, Jiannian Yao, Jincai Zhao *

Laboratory of Photochemistry, Center for Molecular Science, Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080, China

Received 4 October 2005; received in revised form 23 January 2006; accepted 30 January 2006
Available online 15 March 2006

Abstract

An organic–inorganic layered hybrid was prepared by intercalation of $Fe(bpy)_3^{2+}$ into laponite clay. UV–vis diffuse reflectance, X-Ray diffraction, and SEM confirmed the intercalation and the strong host–guest interaction of $Fe(bpy)_3^{2+}$ molecules with the clay matrix. Compared with laponite, the hybrid formed a solid layered structure due to the linking of laponite platelets by $Fe(bpy)_3^{2+}$ molecules. Upon visible light irradiation ($\lambda > 420$ nm), the hybrid was found to be highly effective for the degradation of nonbiodegradable cationic organic pollutants such as Rhodamine B (RhB) and *N*,*N*-dimethylaniline by activating H_2O_2 at neutral pH values, but inactive toward anionic organic compounds such as Orange II and Sulforhodamine-B. The adsorption and degradation of organics on the hybrid could be controlled by changing the pH value of the suspension. The total organic carbon (TOC) removal yield of RhB was 41%. pH effect trials and the final degraded products further indicate that unless the target is adsorbed onto the clay layers the reaction could not occur. Neither $^\bullet OH$ nor $^\bullet OOH/O_2^{\bullet -}$ EPR signals were detected during the reaction. The solid support of laponite not only alters the photochemical properties of $Fe(bpy)_3^{2+}$ but also provides a rigid microenvironment for the enrichment of local substrate molecules and thus enhances the interaction of the active center with the substrate.

Keywords: Iron complex; Laponite; Photocatalytic; Pollutant

1. Introduction

Removal of recalcitrant and nonbiodegradable toxic pollutants in water by green chemical technology has been extensively studied in recent years [1–3]. Green chemical technology suggests the use of hydrogen peroxide or molecular oxygen as the oxidant and water as the solvent. Activation of H_2O_2 by metal complex such as metalloporphyrin, metallphathcyline, and tetraamidomacrocyclic ligands [4,5] is active research topic in dealing with organic pollutants. Immobilization of metal complex onto solid support could exhibit unique advantage over homogeneous systems for their long life time, facile recovery, and easy separation of the catalyst [6] due to the stabilization and isolation of the metal complex. Resin has been used for the preparation of catalysts in organic pollutants treatment [7–9]. However organic solids such as polymer and resin are highly vulnerable to be destroyed at high temperature, in strong acidic or basic media, and in organic solvents, which would bring about secondary contamination. What is more, the nonequivalence of the active sites in the crosslinked networks of polymer is a great drawback that affects its activity and stability.

Inorganic materials, such as silica, clay, and zeolite have been proved to be good solid support for metal complex [10–13]. The superiority of inorganic solid supports in thermostabilization, resistance to organic solvents, and rigidity of mechanical strength over organic supports makes them more promising and more widely used in all kinds of reactions [6]. Recently, clay based inorganic materials, mainly pillared clays (PILCs), were used as supports for the encapsulation of transition metal complex, which provides an alternative method for the preparation of heterogeneous catalysts of metal complex–clay hybrid [14–16]. Some scientists have encapsulated metal complex into the large pores of Al-PILC [17]. Other methods for the deposition of metal complex on clay are ion exchange, dry impregnation, and incipient wetness. Most of the metal complex–clay hybrids were used in a variety of catalytic oxidation processes in the dark [12,15,18]. Light irradiation that could accelerate the oxidation reaction is rarely involved in the catalytic systems, especially in the degradation of pollutants

---

* Corresponding author. Tel.: +86 10 8261 6495; fax: +86 10 8261 6495.
E-mail address: jczhao@iccas.ac.cn (J. Zhao).

0926-3373/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcatb.2006.01.010

[19]. The photocatalytic mechanisms are still in disputations in the heterogeneous systems.

In the present study, we report a novel kind of solid photocatalyst, FeBL, synthesized by intercalation of the complex iron(II) 2,2′-bipyridine, $Fe(bpy)_3^{2+}$ into an inorganic solid, laponite clay. $Fe(bpy)_3^{2+}$ molecules could be intercalated into the lamellar interlayers by cation exchange. Laponite is a kind of artificial clay consisting of colloidal disks which is a high purified lithium magnesium silicate with the general formula $(Na_{0.7}^{+}[Si_8(Mg_{5.5}Li_{0.3})O_{20}(OH)_4]^{0.7-})$ and does not contain iron impurities [20]. Particles of laponite have a thickness of 1 nm and a diameter of around 30 nm. Laponite clay bears the largest swelling ability among clays and is known to swell completely and dissociate into unit layer fragments in water [21,22]. The lamellar solids can accommodate a great diversity of guest molecules (ionic and even nonionic organic molecules) and exhibit a very rich intercalation chemistry because of their exchange capacity and the expandability of their interlayer spaces [23]. The face of laponite clay possesses a constant negative charge due to isomorphic octahedral substitution of Mg^{2+} by lower valence cation of Li^{+}. The inorganic matrix of laponite provides a rigid microenvironment for $Fe(bpy)_3^{2+}$ molecules to be assembled in the interlayers which alter the photochemistry of $Fe(bpy)_3^{2+}$ molecules and enhances the stability of the catalyst. FeBL catalyst exhibited a high activity for the degradation of Rhodamine B in the presence of H_2O_2 upon visible light irradiation at neutral pH values, with TOC removal yield of 41% and very high efficiency of H_2O_2 usage. The catalyst showed high stability in that it could be repeatedly used without ruining of structure and loss of photocatalytic activity. The photodegradation of other organic pollutants of cationic dyes Malachite green, Acridine orange, anionic dyes Orange II, Sulforhodamine-B, and *N*,*N*-dimethylaniline were also examined. Intermediates formed during the degradation of RhB were detected by incorporating GC–MS and EPR to study the degradation process. This approach provides an efficient organic–inorganic hybrid photocatalyst for the treatment or pretreatment of organic pollutants under visible irradiation.

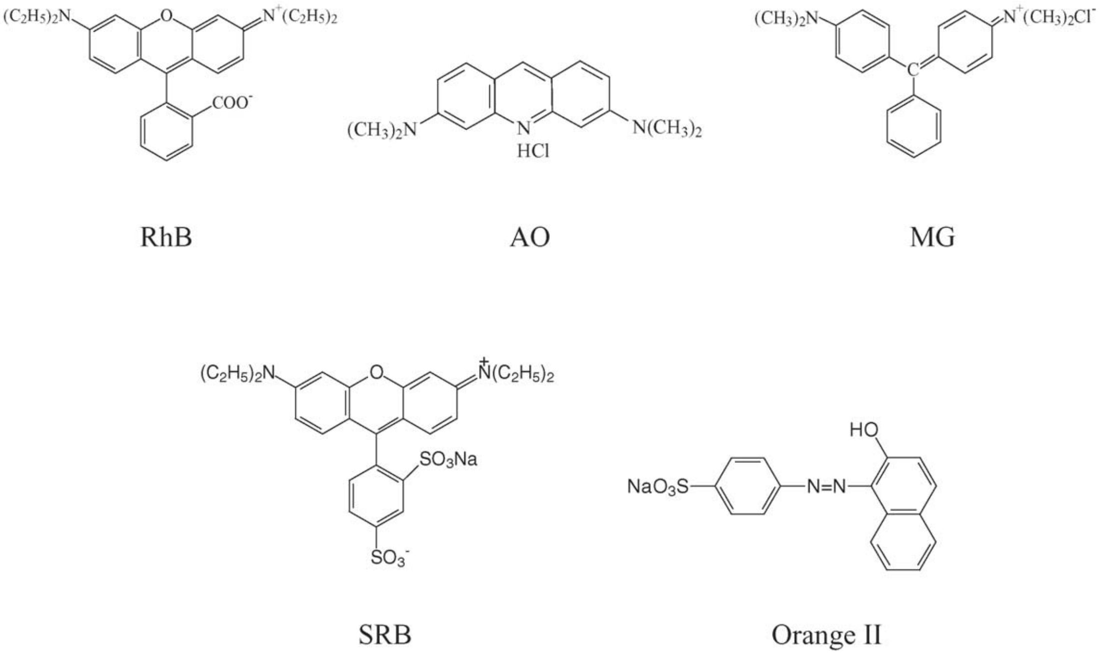
2. Experimental

2.1. Materials and reagents

The laponite clay was supplied by Fernz Specially Chemicals, Australia, and used as received. The clay powder has a cation exchange capacity (CEC) of 55 mequiv/100 g of clay. Rhodamine B (RhB), Malachite green (MG), Acridine orange (AO), *N*,*N*-dimethylaniline (DMA), Orange II, Sulforhodamine-B (SRB), hydrogen peroxide (30% aqueous solution), 2,2′-bipyridine, and ferrous perchlorate were of laboratory reagent grade and used without further purification. Horseradish peroxidase (POD) for measurement of H_2O_2, was purchased from the Huamei Biologic Engineering Co. (Luoyang, Henan, China). The *N*,*N*-diethyl-*p*-phenylenediamine (DPD) reagent was from Merck (p. a) (Whitehouse Station, NJ). The reagent 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO), used as the spin-trapping reagent in EPR studies, was purchased from the Sigma Chemical Co. (St. Louis, MO). Ultrapure water was used throughout this study. The solution pH was adjusted by diluted aqueous solutions of NaOH or $HClO_4$. For reference, the structure of RhB, AO, MG, SRB, and Orange II is shown further (Scheme 1).

2.2. Catalyst preparation

$Fe(bpy)_3(ClO_4)_2$ was prepared and purified as previously reported [24]. A stoichiometric amount of the ligand (2,2′-



RhB AO MG

SRB Orange II

Scheme 1. Structures of RhB, AO, MG, SRB, and Orange II.