



Iron-copper bimetallic nanoparticles embedded within ordered mesoporous carbon as effective and stable heterogeneous Fenton catalyst for the degradation of organic contaminants



Yanbin Wang^a, Hongying Zhao^b, Guohua Zhao^{a,b,*}

^a School of Materials Science and Engineering, Tongji University, 4800 Caoan Road, Shanghai 201804, PR China

^b Department of Chemistry, Key Laboratory of Yangtze River Water Environment, Ministry of Education, Tongji University, 1239 Siping Road, Shanghai 200092, PR China

ARTICLE INFO

Article history:

Received 12 July 2014

Received in revised form

19 September 2014

Accepted 22 September 2014

Available online 28 September 2014

Keywords:

Ordered mesoporous carbon

Heterogeneous Fenton

Iron-copper bimetallic

Organic contaminants

ABSTRACT

Iron-copper bimetallic nanoparticles embedded within ordered mesoporous carbon composite catalyst (CuFe-MC) was synthesized via a “one-pot” block-copolymer self-assembly strategy. The catalyst was characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), etc. The results showed the catalyst was ordered 2D hexagonal mesostructure and iron-copper nanoparticles highly dispersed in the matrix of ordered mesoporous carbon. The composite was used as a heterogeneous Fenton catalyst and showed a promising application in the degradation of non-biodegradable organic contaminants. Eight organic compounds were chosen as model contaminants, such as phenol, bisphenol A (BPA), etc. Efficient total organic carbon (TOC) removal of each organic contaminant was achieved by using CuFe-MC as catalyst, which was higher than that by Fe²⁺ ion at the same reaction condition. BPA was selected to further investigate the high catalytic activity of CuFe-MC. CuFe-MC presented high adsorption capacity for BPA due to its high BET surface area (639 m² g⁻¹) and mesostructure. The results of BPA degradation showed that the catalytic activity of CuFe-MC was much higher than Fe-MC and Cu-MC. Electron spin resonance (ESR) and high performance liquid chromatography (HPLC) results indicated that the concentration of generated hydroxyl radicals ([•]OH) with CuFe-MC was much higher than Fe-MC and Cu-MC. The low iron leaching of CuFe-MC suggested its good stability. Moreover, it could be easily separated by using an external magnet after the reaction and remained good activity after being recycled for several times, demonstrating its promising long-term application in the treatment of wastewater.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Classic homogeneous Fenton oxidation is one of the powerful and widely used Advanced Oxidation Processes (AOPs) for the treatment of wastewater containing recalcitrant organic pollutants, such as pesticides, organic synthetic dyes, pharmaceuticals and personal care products [1]. However, the major defect of homogeneous Fenton reaction is the involvement of a large amount of iron salts that are presented in the effluents and requiring an additional separation step to separate iron-containing sludge. Besides, the narrow pH range (pH 2–3) is another limitation for its application [2,3]. In order to tackle these problems, heterogeneous Fenton

catalysis has been developed and used as a promising alternative for which the principal goal is the development of efficient and stable solid catalysts. Various solid catalysts, e.g., nano zero-valent iron (nZVI) [4], iron oxide minerals (goethite, hematite, magnetite and ferrihydrite), iron-immobilized clays [5], and Fe-containing zeolites [6], are used to activate H₂O₂ and generate highly reactive and non-selective [•]OH. Nevertheless, most of these catalysts show lower catalytic activity than homogeneous Fe²⁺ and need the aid of ultrasound [7,8] and UV/visible light irradiation [9,10], increasing the cost for wastewater treatment.

Recently, iron-copper bimetallic catalyst system has attracted increasing attention [11–13]. For instance, Frank et al. [13] reported iron-copper bimetallic catalyst supported on MCM-41 showed higher catalytic activity than Cu or Fe single supported on MCM-41. In addition, it maintained high catalytic activity even after 10 consecutive runs. Interestingly, similar results were reported on CuFeZSM-5 zeolite [14], Fe-Cu bimetallic oxides supported

* Corresponding author at: Department of Chemistry, Tongji University, 1239 Siping Road, Shanghai 200092, PR China, Tel.: +86 21 65981180; fax: +86 2165982287.
E-mail address: g.zhao@tongji.edu.cn (G. Zhao).

aluminum-containing MCM-41 [12] and mixed Fe, Cu, Al-clays [15]. Our group previously reported magnetic ordered mesoporous copper ferrite (meso-CuFe₂O₄) as a heterogeneous Fenton catalyst for the degradation of imidacloprid [16]. The efficient removal of imidacloprid was achieved and the catalytic activity of meso-CuFe₂O₄ was much higher than nano-Fe₃O₄.

For obtaining a highly catalytic activity of heterogeneous Fenton catalyst, it is necessary for enhancing the dispersity of catalysts and preventing severe aggregation [17]. To achieve these goals, the utilization of porous materials, such as zeolite [5], mesoporous silica [18], active carbon [19], mesoporous carbon and multi-walled carbon nanotubes [20], as supporting materials has been developed. Among them, ordered mesoporous carbon is an interesting material due to its excellent mechanical strength, chemical stability and extraordinary textural characteristics, such as large specific surface area, uniform pore size and accessible mesopores. Generally speaking, for the sake of incorporating heterogeneous catalysts into ordered mesoporous carbon, there are two approaches as follows: (I) impregnating mesoporous carbon into precursor solution, then translating it into required composite catalyst, (II) introducing precursor during the synthesis process of mesoporous carbon, namely “one-pot” synthesis strategy [21,22]. However, the composite catalysts prepared by the impregnation method show poor stability due to the weak interaction force between the catalyst and supporting materials in acid media. In contrast, the composite catalysts fabricated by “one-pot” strategy show excellent stability because of the spatial effect of ordered mesoporous carbon. Moreover, efficient catalytic activity is achieved owing to heterogeneous catalyst highly dispersed in ordered mesoporous carbon. For example, Kong et al. [23] reported a coordinatively unsaturated manganese monoxide-containing mesoporous carbon catalyst which was used in wet peroxide oxidation of phenol. It showed excellent stability, without obvious activity losing or metal leaching after reusing 20 times. Furthermore, the high specific surface area of mesoporous carbon is contributed to the adsorption for organic contaminants in wastewater. Such as, Zhang et al. [24] synthesized mesoporous carbon capsules encapsulated with magnetite nanoparticles, exhibiting higher adsorption capacities and faster adsorption rates of pollutants molecules compared with commercial activated carbon.

In this work, we demonstrated an ordered mesoporous carbon composite catalyst. Iron-copper bimetallic nanoparticles highly dispersed in the matrix of ordered mesoporous carbon. Here, “one-pot” block-copolymer self-assembly strategy and in situ reduction were used to synthesize this composite catalyst. For evaluating its catalytic activity in the heterogeneous Fenton reaction, eight persistent organic compounds were chosen as model contaminants. For comparisons, the monometallic composite catalysts (Fe-MC and Cu-MC) were prepared by the similar method. The main purpose of this study is to elucidate the role of ordered mesoporous carbon and the synergistic effect of iron and copper in the degradation of organic contaminants.

2. Experimental

2.1. Chemicals

Poly(propylene oxide)-block-poly(ethylene oxide)-block-poly(propylene oxide) triblock copolymer Pluronic F127 (PEO₁₀₆PPO₇₀PEO₁₀₆, $M_w = 12,600$) was purchased from Sigma-Aldrich. 5,5-dimethylpyrrolidine-1-oxide (DMPO) was obtained from Aladdin Industrial Corporation. Phenol (C₆H₅OH, 99.98 wt%), formalin solution (HCHO, 37.0–40.0 wt%), sodium hydroxide (NaOH, minimum 96.0%), hydrochloric acid (HCl, 36.0–38.0 wt%), ethanol (C₂H₅OH, minimum 99.7 wt%), iron (III)

nitrate nonahydrate (Fe(NO₃)₃·9H₂O, 98.0 wt%) and copper (II) nitrate trihydrate (Cu(NO₃)₂·3H₂O, 98.0 wt%) were purchased from Shanghai Chemical Corporation. All chemicals were used as received without any further purification. Water used in all synthesis was distilled and deionized.

2.2. Preparation of iron-copper bimetallic composite catalysts

The carbon precursors, soluble Resol Resins, were synthesized from phenol and formaldehyde in a base-catalyzed process [25]. In a typical preparation of composite catalysts, 1.0 g Pluronic F127 was dissolved in 20 g ethanol to form a transparent solution at 35 °C. Then, 0.1010 g Fe(NO₃)₃·9H₂O and 0.0302 g Cu(NO₃)₂·3H₂O (molar ratio 1:2) were added to obtain a dark solution. 5.0 g Resol precursors solution (20 wt%) was added and constantly stirred for 10 min. Subsequently, the mixed solution was poured into multiple dishes to evaporate the ethanol at room temperature for 8 h. Later, the dishes were placed in an oven (100 °C) for 24 h to induce polymerization. Finally, the composites were scraped from the dishes and pyrolyzed at 800 °C for 4 h with a ramping rate of 2 °C/min under nitrogen atmosphere. The obtained composite products were denoted as CuFe-MC-X-T. The X represents the mass of iron precursor (Fe(NO₃)₃·9H₂O) and T represents the calcined temperature. For example, CuFe-MC-1-800 represents that the mass of iron precursor is 0.1010 g and the composite is calcined at 800 °C. While the mass of iron precursor for CuFe-MC-2-800 and CuFe-MC-3-800 are 0.2020 and 0.4040 g, respectively. For the purpose of comparisons, two monometallic composite catalysts, denoted as Cu-MC-1-800 and Fe-MC-1-800, were prepared by the similar method.

2.3. Characterization

TEM images were conducted on a JEM 2100 operated at 200 kV. High resolution scanning electron microscopy (HRSEM) images were obtained on a Hitachi S-4800. XRD patterns were measured on a Bruker D8 Advance X-ray diffractometer using Cu K α ($\lambda = 1.540$ 562 Å, 40 kV, 40 mA) as radiation. N₂ adsorption-desorption isotherms were measured at 77 K with a Micromeritics Tristar3000 analyzer. Before measurement, the samples were degassed in a vacuum at 200 °C for at least 4 h. The metal loadings on ordered mesoporous carbon were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, PE OPTIMA 2100DV). ESR spectra were obtained on a Bruker EMX X^{plus}-10/12 with Microwave Bridge (microwave frequency, 9.853 GHz; microwave power, 20 mW; modulation amplitude, 1 G; modulation frequency, 100 kHz). For ESR measurement, 25 μ L of the sample was collected from the suspension system and immediately mixed with 25 μ L of 0.22 M DMPO to form DMPO·OH adduct.

2.4. Degradation experiments of BPA and sample analysis

Batch degradation experiments of BPA were carried out in a cylindrical reactor with a double jacket for circulation of external thermostatic water to regulate the solution temperature. Before the reaction, all the catalysts were dried in the vacuum drying oven at 120 °C for 2 h. In a standard experiment, 30 mg catalyst was mixed with 100 mL of BPA (100 mg L⁻¹). The suspension was vigorously stirring for 60 min to achieve the adsorption/desorption equilibrium between BPA molecular and catalyst. Then, 300 μ L H₂O₂ (30 wt%) was added into the suspension. The initial pH was adjusted to the required pH by using 0.1 M H₂SO₄. Samples were taken at 10 min intervals using a 5 mL syringe, filtered immediately through a 0.22 μ m filter film and analyzed by HPLC with a Varian Prostar 310 system equipped with Varian AQ-C18 column (4.6 mm \times 150 mm \times 5 μ m). The mobile phase was a mixture of methanol and water (70:30, v/v) with a flow rate of 1.0 mL min⁻¹,

Download English Version:

<https://daneshyari.com/en/article/6500736>

Download Persian Version:

<https://daneshyari.com/article/6500736>

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