Shape-controlled nanostructured magnetite-type materials as highly efficient Fenton catalysts

Liwei Hou [a], Qinghua Zhang [b], François Jérôme [b], Daniel Duprez [b], Hui Zhang [a,**], Sébastien Royer [b,*]

[a] Department of Environmental Engineering, Wuhan University, P.O. Box C319, Luoyu Road, 129#, Wuhan 430079, PR China
[b] Université de Poitiers, CNRS UMR 7285, IC2MP, 4 rue Michel Brunet, 86022 Poitiers Cedex, France

ARTICLE INFO

ABSTRACT

Nanostructured Fe$_3$O$_4$ particles were obtained through hydrogen thermal reduction of α-Fe$_2$O$_3$ particles synthesized via an ionic liquid assisted hydrothermal process. The morphology and microstructure of the nano-sized Fe$_3$O$_4$ particles were characterized by using X-ray diffraction, N$_2$ physisorption, transmission electron microscopy, and temperature-programmed reduction. As-prepared magnetite samples show microcube, nanosphere, and porous nanorod morphologies. Activity of the nanostructures was evaluated for the Fenton reaction, using phenol as model molecule. While commercial Fe$_3$O$_4$ presents very limited activity, rod-type nanostructure exhibited exceptional activity toward phenol removal under mild conditions; 98% phenol was converted, and the total organic carbon (TOC) abatement was 74%. The reusability of porous nanorods of Fe$_3$O$_4$ was also investigated after three successive runs, which demonstrated the promising application of the catalyst in the oxidative degradation of organic pollutants. In addition, the material activity is strongly affected by the reduction degree, highlighting the beneficial effect of Fe^0/Fe$_3$O$_4$ mixed phase formation to achieve higher activity.

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1. Introduction

Iron oxides are transition metal oxides, natural minerals and geocatalysts, existing in the natural aqueous environment, and also suspending in aerosol, clouds, and fogs as fine particles [1,2]. Because iron oxides are inexpensive and relatively non-toxic in comparison to other transition metals (including nickel, chromium, copper), they are preferred for the extensive application in many fields, such as corrosion processes [3,4], electromagnetic devices [5], and catalytic reactions [6–9]. The versatility of the surface composition among Fe^0, Fe^{II} and Fe^{III} over different types of iron oxides (Fe^0, FeO, α-Fe$_2$O$_3$, γ-Fe$_2$O$_3$, Fe$_3$O$_4$, α-FeOOH, β-FeOOH, γ-FeOOH and δ-FeOOH) ensure tunable properties, conferring to some composition high activity for heterogeneous Fenton reactions at the catalyst/solution interface [10]. Significantly different catalytic activities are then observed to be dependant on the material crystallographic and surface properties, due to variable valences of iron that can be stabilized [10].

More recently, several environmental applications of iron compounds (*e.g.*, as reducing agents and as promoters in the Fenton

reaction) have been intensively investigated [11]. For example, Fe^0 has been proposed as a low-cost and nontoxic material in environmental remediation processes [12,13]. Different iron compounds, such as Fe^0, Fe$_3$O$_4$ [14] and Fe^0/Fe$_3$O$_4$ [15] have been reported to promote the Fenton reaction. Although the kinetic of these processes is highly complex and dependent on numerous different parameters, an important rate-limiting step is the production of radicals. In this respect, the exposed site valence on the iron surface and the presence of oxide/hydroxide layers that cover the iron particles should strongly influence the rate of the process [16]. The development of new processes to increase iron oxide efficiencies and to widen the application of these systems in environmental remediation processes is of great interest.

Magnetite (Fe$_3$O$_4$)-based heterogeneous systems have attracted attention due to their unique properties and their potential applications in numerous fields, including ferrofluids, targeted drug delivery, and water treatment [17–20]. Especially, magnetite has also been reported to be an efficient catalyst for Fenton-like processes [21–31]. Magnetite exhibits several features that are important for a Fenton reaction: (i) it contains Fe^{2+} that might play an important role as an electron donor to initiate the Fenton reaction; (ii) the octahedral site in the magnetite structure can easily accommodate both Fe^{2+} and Fe^{3+}, which means that Fe^{2+} can be reversibly oxidized and reduced in the same structure; and (iii) Fe$_3$O$_4$ has peroxidase-like activity and can activate H$_2$O$_2$ [14]. In addition, recent works demonstrated that bringing Fe^0 particles

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* Corresponding author. Tel.: +33 0 549453479; fax: +33 0 549453499.
** Corresponding author. Tel.: +86 0 27 68775837; fax: +86 0 27 68778893.
E-mail addresses: eeng@whu.edu.cn (H. Zhang), sebastien.royer@univ-poitiers.fr (S. Royer).

into contact with Fe_3O_4 particles through grinding increases the activity of magnetite for H_2O_2 decomposition [15,32]. Thus, activity in the Fenton reaction was improved over these mixed phase materials.

As far, a wide variety of method has been reported to synthesize Fe_3O_4 nanoparticles, including sol–gel methods [33], wet-chemical methods [34], hydrothermal methods [35], and co-precipitation [36]. However, these methods tend to form Fe_3O_4 particles with isotropic shapes. Nevertheless, various Fe_3O_4 nanostructures with different morphologies have been successfully synthesized, including nanotubes, nanowires, nanofilms, spheres, nanorods, and other novel structures using routes such as coprecipitation, microemulsion, and so on [37–39].

Recently, reduction of premade isotropic β-FeOOH or α-Fe_2O_3 particles into Fe_3O_4 was proposed [40–42]. Compared with other methods, reduction of premade α-Fe_2O_3 is a simple and effective method. Generally, the reduction of α-Fe_2O_3 involves an annealing process under reductive atmosphere at moderate temperature (about 300–500 °C). However, the annealing treatment of the premade materials may result in undesirable aggregation and sintering. Since the shape of formed Fe_3O_4 particles is dependent on that of premade α-Fe_2O_3, it is important to achieve α-Fe_2O_3 synthesis with various shapes prior to the reduction process. As reported in our previous work [43], ionic liquids (ILs) assisted hydrothermal route is found to be an effective method to synthesize α-Fe_2O_3 nanoparticles of various shapes, such as cubes, nanorods as well as nanoplates. Compared with the traditional hydrothermal methods, high surface area can be achieved due to reduction in crystal size by employing the ILs as the soft template. Because the properties of nanomaterials are influenced by their structure, size, and shape [37], the preparation of Fe_3O_4 nanoparticles with different sizes and morphologies is an important issue.

Herein, we report an environmentally benign "green" route to the synthesis of Fe_3O_4 nanoparticles with various morphologies, achieved by reduction of pre-made α-Fe_2O_3 materials. The physical and chemical characterization of Fe_3O_4 was performed, and the effect of the morphology and crystal structure of Fe_3O_4 on the catalytic wet peroxide oxidation process was investigated. Because of their unique porous structure, the potential applicability of nanorods of Fe_3O_4 in heterogeneous Fenton reactions was evaluated with respect to changes in the catalyst and the H_2O_2 concentrations, as well as with respect to the material's stability. Further activity improvement was achieved optimizing the Fe^0/Fe_3O_4 balance through reduction temperature.

2. Experimental

2.1. Materials

All chemicals employed in the preparation of the α-Fe_2O_3 in ionic liquid media and derived Fe_3O_4 catalysts were used as purchased: 1-methylimidazole ($C_4H_6N_2$, ≥99%, Sigma-Aldrich), 1-Chlorodecane [($CH_3(CH_2)_9Cl$, 98%, Sigma-Aldrich], ethyl acetate ($CH_3COOC_2H_5$, 99.8%, Sigma-Aldrich), $FeCl_3·6H_2O$ (≥98%, Sigma-Aldrich), potassium acetate (CH_3COOK, ≥99%, Sigma-Aldrich), and sodium hydroxide (NaOH, ≥98%, Sigma-Aldrich). For the heterogeneous Fenton reaction, phenol (C_6H_5OH, ≥99%, Sigma-Aldrich) and hydrogen peroxide solution (H_2O_2, 32 wt.% in H_2O, Sigma-Aldrich) were used as received. The ionic liquid (C_{10}mimCl) used here was synthesized and used to prepare three kinds of α-Fe_2O_3 with different morphologies via the hydrothermal method (see details in SI, Materials). Fe_3O_4-M catalysts, where M represents the morphology of the catalyst, were obtained through the reduction of the α-Fe_2O_3 under H_2 at a flow rate of 60 mL min^{-1} at 300 °C for 1 h. The samples were denoted Fe_3O_4-C ('C' for microcube), Fe_3O_4-S ('S' for microsphere), and Fe_3O_4-R ('R' for nano-rods).

2.2. Catalysts characterization

The α-Fe_2O_3 and Fe_3O_4 catalysts were systematically characterized using X-ray diffraction (XRD), N_2 physisorption, transmission electron microscopy (TEM), ICP-OES, and temperature-programmed reduction (TPR).

The catalyst structures were verified by X-ray diffraction using a D5005 diffractometer from Bruker equipped with a Cu Kα radiation (λ = 1.5406 Å) source. The signal was recorded for 2θ between 20° and 80° with a recording step of 0.05° every 3 s. Phase identification was made through comparison with the JCPDS database. The crystallite sizes were determined using the Scherrer equation after Warren's correction for instrumental broadening was applied. (1 1 3) reflection was used for calculation of Fe_2O_3 crystal size, while (3 1 1) reflection was used in the case of Fe_3O_4 phase.

The N_2 adsorption measurements were performed on a Micromeritics TRISTAR 3000 instrument. The specific surface area of the catalysts was measured at liquid N_2 temperature (−196 °C), using the Brunauer–Emmett–Teller (BET) method. Prior to analysis, sample was heated under vacuum at 250 °C for 3 h.

The material morphologies were evaluated by transmission electron microscopy (TEM) coupled with energy-dispersive X-ray spectroscopy (EDXS). Micrographs were obtained on a JEOL 2100 instrument (operated at 200 kV with a LaB$_6$ source and equipped with a Gatan Ultrascan camera).

TPR experiments were performed on an AUTOCHEM instrument from Micromeritics. Approximately 50 mg of sample was introduced into the microreactor. The material was initially activated under simulated air (total flow rate = 30 mL min^{-1}) at 300 °C for 1 h. After the sample was cooled to room temperature, a reducing flow (1 vol.% of H_2 in Ar) was stabilized at a flow rate of 30 mL min^{-1}, and the temperature of the reactor was subsequently increased from 50 °C to 1000 °C with a ramp of 5 °C min^{-1}. The change in the H_2 concentration as a function of temperature was recorded using an online TCD.

The total Fe^{2+} content in the bulk of Fe_3O_4 was determined by chemical analysis after the samples were dissolved in acidic media at 60 °C for 48 h under a nitrogen atmosphere. According to Xue et al. [9], 6 mol L^{-1} HCl was used to ensure the dissolution of the catalysts. 1.0 mL of 1,10-phenanthroline (1.0 g L^{-1}) was then added to the dissolved sample to form a colored complex. Finally, complex concentration was measured by UV spectrophotometer at λ fixed at 510 nm [44].

Furthermore, the surface ratio of Fe^{II}/Fe^{III} on the Fe_3O_4 surface was also analyzed by X-ray Photoelectron Spectroscopy (XPS). Analyses were conducted on a Thermo-Fisher ESCALAB 250 system with Al Kα radiation under ultrahigh vacuum (UHV). Binding energies were calibrated with the C1s binding energy fixed at 285 eV as internal reference. Curve fittings were achieved with the XPS Peak software using the Fe2p binding energies region for the analysis.

2.3. Catalytic activity measurement

Catalytic tests were performed under mild conditions (atmospheric pressure and 25 °C) in a 150 mL glass reactor continuously stirred using phenol as reactant and hydrogen peroxide as oxidant. We initially verified that no external or internal diffusional resistances occurred and that the reaction was performed in a kinetic regime. The reaction pH value was adjusted to 4.0 before the oxidation began. In a typical experiment, 100 mL of phenol aqueous solution was prepared with an initial concentration of 600 mg L^{-1}. The catalyst was subsequently added to the solution, which was then stirred in the dark until the adsorption–desorption equilibrium was obtained prior to initiation of oxidation. At the end of this step, we obtain the C_0 concentration. Then, the H_2O_2 solution was added dropwise at a constant rate to the solution