Nano-sized magnetic iron oxides as catalysts for heterogeneous Fenton-like reactions—Influence of Fe(II)/Fe(III) ratio on catalytic performance

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HIGHLIGHTS

▶ Nano-sized Fe(II, III) oxides tested as catalysts for heterogeneous Fenton reaction.

▶ All showed relatively low catalytic activity for phenol oxidation at neutral pH.

▶ Fe(II)-containing oxides (e.g. magnetite) not stable in presence of H_2O_2 but oxidized.

▶ Residual Fe(II) content in the catalyst core is of minor benefit for catalytic activity.

▶ Selectivity of oxidation tested with structurally distinct compounds.

GRAPHICAL ABSTRACT
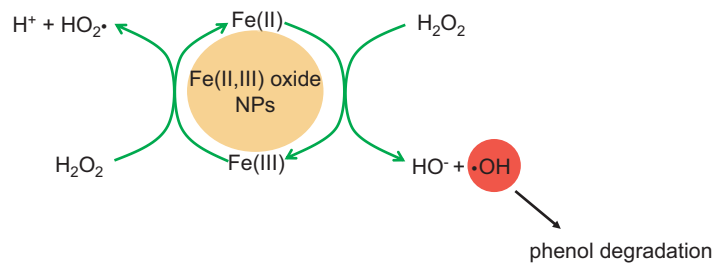
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ABSTRACT

Nano-sized Fe(II, III) oxides with various Fe(II)/Fe(III) ratios were characterized and tested as catalysts for the oxidative degradation of phenol via Fenton-like reactions at neutral pH. Under conditions typically applied for wet peroxide oxidation, Fe(II) in magnetite is oxidized to Fe(III), successively converting the mineral into maghemite. The residual Fe(II) content in the catalyst core is of only minor benefit for the catalytic activity in phenol oxidation, i.e. magnetite is not superior to maghemite. Achievable reaction rates for phenol degradation appeared to be rather low, e.g. phenol half-life of about 12 h when $3\,g\,L^{-1}$ magnetite and $5\,g\,L^{-1}$ H_2O_2 were applied. Preceding surface-reduction of maghemite by $NaBH_4$, leading to an over-stoichiometric Fe(II) content compared to magnetite, only enhanced the non-productive decomposition of H_2O_2 rather than the rate of phenol degradation. Reaction rates were shown to be relatively insensitive to catalyst concentration in the range of $1–10\,g\,L^{-1}$, probably resulting from a scavenging of reactive species by the catalyst surface, whereby particle agglomeration seems to play a key role. Degradation experiments with various structurally distinct compounds were carried out, indicating a similar selectivity of the heterogeneous Fenton-like system to that known for oxidation with $^\bullet$OH.
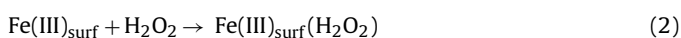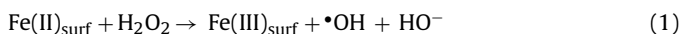
1. Introduction

Advanced oxidation processes (AOPs) involving the production of highly reactive hydroxyl radicals ($^\bullet$OH) have shown great potential for the treatment of organic pollutants in water and soil at large scales. The $^\bullet$OH for AOPs can be produced in a system with dissolved iron and hydrogen peroxide (homogenous Fenton reaction) according to the Haber–Weiss mechanism [1]. They are strong, relatively non-selective oxidants which are able to destroy a wide range of organic substrates [2]. The main shortcomings of the homogeneous Fenton process are the necessity of working at low pH ($\sim$3) and the formation of iron oxide sludge. To overcome these drawbacks, research has focused on the idea of replacing dissolved iron with solid catalysts in so-called heterogeneous Fenton-like reactions. The general requirements for heterogeneous catalysts in wet

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oxidation are: high efficiency related to contaminant removal rates and H_2O_2 utilization, minimum leaching, stability over long periods of application, and effectiveness at extended ranges of pH and temperature.

A large number of studies dealing with heterogeneous catalysts suitable for the Fenton system have been previously reported. Garrido-Ramirez et al. reviewed several solid materials indicating good efficiency for Fenton-like reactions [3]. Promising results were achieved for metal-supported catalysts such as transition-metal-exchanged zeolites [4] or mesoporous materials [5], pillared interlayered clays containing Fe or Cu [3], as well as non-porous solids such as iron oxide minerals (e.g. magnetite, maghemite, hematite, goethite) [6–9]. Novel modified S-doped α-Fe$_2$O$_3$ [10], and mixed iron oxides containing metals such as Co, Cu, Mn, Ni, V, Zn, have also been used with some successes [11–13]. However, the introduction of heavy metals as catalyst constituents must be scrutinized with respect to its environmental compatibility. The mechanism of mineral-catalysed H_2O_2 activation is still poorly understood. In analogy to the Haber–Weiss mechanism, Voelker and Kwan suggested that the activation of H_2O_2 via iron-surface species is achieved via the followings steps (Eqs. (1)–(3)) [14].

$$Fe(II)_{surf} + H_2O_2 \rightarrow Fe(III)_{surf} + {}^\bullet OH + HO^- \tag{1}$$

$$Fe(III)_{surf} + H_2O_2 \rightarrow Fe(III)_{surf}(H_2O_2) \tag{2}$$

$$Fe(III)_{surf}(H_2O_2) \rightarrow Fe(II)_{surf} + HO_2{}^\bullet + H^+ \tag{3}$$

Recently, utilization of nano-range (1–100 nm) catalysts in water purification has become more popular [15]. In terms of catalysts or reagents for water purification, the nanoparticles offer a high specific surface area (SSA), and in some cases (e.g. for nZVI [16]) different properties in comparison to their bulk phase might positively influence the reaction efficiency. For water treatment in reactor systems, high reaction rates are desirable, whereby nanoparticles can be beneficial since few or no mass-transfer limitations are expected. This can be an advantage for the treatment of large contaminant molecules such as dyes and pharmaceuticals, which are considerably limited in diffusion through microporous catalysts. On the other hand, the separation and recycling of nanocatalysts at a technical scale still presents a challenge.

Among the various iron oxide minerals, magnetite (Fe_3O_4), containing both Fe(II) and Fe(III) in molar ratio 1:2, is a promising catalyst for oxidative processes using H_2O_2 [6,12,17]. Furthermore, the magnetic properties of magnetite allow easy and complete separation from the treated medium by means of magnetic separation [18]. Its catalytic properties are often assigned to its Fe(II) content, which is considered to be the key parameter in Fenton-like reactions [6,8,19]. Moreover, the octahedral site in the magnetite structure, containing both Fe(II) and Fe(III) ions, allows the Fe species to be reversibly oxidized and reduced while keeping the same structure [12]. However, magnetite is known to be instable under oxidizing conditions (H_2O_2, O_2) where it is slowly oxidized to maghemite (γ-Fe$_2$O$_3$) [20–23], which has the same spinel-type structure but contains only Fe(III). Although several models have been proposed to describe the magnetite oxidation kinetics, the most common model suggests that the diffusion of Fe(II) to the particle surface is the rate-determining step [24,25]. Other models are based on changes in magnetite redox potential upon oxidation, which induce changes in the reactivity of the material [21].

While for larger particles the formation of a passivating shell can prevent complete oxidation of magnetite, nanomagnetite could be more sensitive towards this process. However, in most previous studies dealing with magnetite as Fenton-like catalyst, the potential change in Fe(II)/Fe(III) ratio during the oxidation reaction was not explicitly considered. Xue et al. [19] used two commercial Fe(II, III) oxides with different particle size and determined their Fe(II)/Fe(III) ratio before application as catalyst for Rhodamine

B degradation by H_2O_2. They concluded that the Fe(II, III) oxide with larger particle size (<5 μm) and higher Fe(II)/Fe(III) ratio (0.43) exhibited better oxidation efficiency for dye removal than the nano-sized material (<50 nm, original Fe(II)/Fe(III) ratio of 0.24) on the basis of both, mass and surface area normalization. Differences in mineral structural properties (crystallography, Fe(II) content) were considered to be potential reasons for the different oxidation efficiencies of the two samples [19]. The difference in particle size and agglomeration tendency of the studied Fe(II, III) oxides leading to different conditions for consumption of reactive species by the catalyst surface, might have played an additional role.

Thus, the aim of this study was to elucidate the effects of Fe(II)/Fe(III) ratio in magnetic nano-sized iron oxides on phenol removal and H_2O_2 decomposition at neutral pH. For this purpose: (i) commercial Fe(II, III) oxide, (ii) freshly synthesized 'stoichiometric' magnetite, and (iii) iron oxides with over-stoichiometric Fe(II) content derived from magnetite were examined. Moreover, the stability and reusability of the catalyst, which are key parameters for practical applications, were investigated.

2. Experimental

2.1. Chemicals

Nano-sized Fe(II, III) oxide (≥98% trace metal basis, particle size <50 nm) was obtained from Sigma–Aldrich, Germany. Iron(III) chloride hexahydrate (99%), iron(II) chloride tetrahydrate (99%), hydrogen peroxide (30 wt%), phenol (>98.8%), *p*-cresol (>98%), MTBE, *cis*-1,2-dichloroethene (*cis*-DCE), 1,2-dichloroethane (1,2-DCA), chlorobenzene (MCB), ammonia solution (25 wt%) and n-hexane were obtained from Merck, Germany and used as received. Titanium(IV) oxysulphate solution (1.9–2.1%) for determination of H_2O_2 was obtained from Fluka, Germany.

2.2. Synthesis and reductive pre-treatment of Fe(II, III) oxide

2.2.1. Magnetite synthesis

Magnetite was prepared in the laboratory by the well known procedure of co-precipitation of Fe^{2+} and Fe^{3+} (molar ratio 1:2) in basic solution (NH_4OH). 0.043 mol $FeCl_3·6H_2O$ and 0.0216 mol $FeCl_2·4H_2O$ were dissolved in 400 mL deionized water (deaerated with Ar) under vigorous stirring in inert atmosphere. 15 mL of NH_4OH was quickly added to the solution and black precipitates of magnetite were obtained. Afterwards, the magnetite was washed several times with deionized water (using magnetoseparation), dried in vacuum, and stored in a dark glass bottle.

2.2.2. Reductive pre-treatment of commercial Fe(II, III) oxide

Activation of Fe(II, III) oxide was based on reduction of the surface in order to obtain a higher Fe(II)/Fe(III) ratio. The treatment was carried out *in situ* by adding 1.5 M $NaBH_4$ to the batch reactor containing 3 g L^{-1} of the catalyst in deionized water. After 24 h of shaking, the catalyst was removed by magnetoseparation, washed three times with deionized water and used directly in oxidation experiments.

2.3. Catalyst characterization

X-ray powder diffraction data of all three samples were collected at room temperature on a D8 diffractometer (Bruker) with Cu–K$_\alpha$ radiation and a step size of $2\theta = 0.01°$ (LynX Eye detector). In the cases of freshly prepared samples, a drying step under inert atmosphere was performed and the samples were subjected directly to analysis. Primary particle size distribution was determined via transmission electron spectroscopy (TEM). For TEM imaging (Philips-CM), the dry particles were embedded into glue