



# Carboxylic acid effects on the size and catalytic activity of magnetite nanoparticles



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## ARTICLE INFO

### Article history:

Received 9 December 2013

Accepted 26 August 2014

Available online 16 September 2014

### Keywords:

Magnetite nanoparticles

Carboxylic acid

Epoxidation

Hydrogen peroxide

## ABSTRACT

Magnetite nanoparticles ( $\text{Fe}_3\text{O}_4$ -NPs) were successfully synthesized in diethylene glycol in the presence of carboxylic acids. They were characterized using XRD, SEM and FTIR. Carboxylic acid plays a critical role in determining the morphology, particle size and size distribution of the resulting particles. The results show that as-prepared magnetite nanoparticles are monodisperse and highly crystalline. The nanoparticles can be easily dispersed in aqueous media and other polar solvents due to coated by a layer of hydrophilic polyol and carboxylic acid ligands in situ. Easily prepared  $\text{Fe}_3\text{O}_4$ -NPs have been shown to be an active, recyclable, and highly selective catalyst for the epoxidation of cyclic olefins with aqueous 30%  $\text{H}_2\text{O}_2$ .

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## 1. Introduction

Stable and nontoxic magnetic iron oxide nanoparticles (NPs) have been applied for detection and separation of proteins [1], to improve the sensitivity of magnetic resonance imaging [2], immunoassay [3], drug [4] and gene delivery [5,6]. Moreover, the use of nanoparticles attracted a lot of attention in the field of catalysis due to their high surface area [7]. In addition, the magnetic nature of, for example, magnetite particles offers the opportunity for the effective and fast recycling of such materials [8,9]. Nanoparticle catalysis in liquid phase has been used since 19th century by applying Pt-NPs to decompose hydrogen peroxide [10,11]. The catalytic properties of the NPs can be modified by particles size. The most obvious size-dependence relationship results from the change in the percentage of surface atoms which are responsible for the catalytic properties when changing the diameter. Growth mechanisms of various  $\text{Fe}_3\text{O}_4$  nanostructures have been reported [12] and it is possible to prepare magnetic nanocrystals with controlled size, shape, and uniformity [13].

Although there is a general interest to transform a successful homogeneous catalyst into a heterogeneous one [14], this strategy is not necessary for nanoparticle catalysts. Unsupported nanoparticles are free in solution, thereby such as homogeneous catalysts they show high activity and selectivity because of their high surface area [15]. A homogenous catalyst usually shows more activity and

selectivity than a heterogeneous one because of access substrate [16]. In principle, the same condition is provided for the NP catalyst in a solvent and therefore nanocatalysis is a bridge between homogeneous and heterogeneous catalysis [17]. The size of the particle and the structure of the surface play the dominant role in determining the high efficiency of an NP system. Nanostructured compounds may encompass the advantages of both homogeneous and heterogeneous catalysis and offer unique activity with high selectivity in catalysis. Interaction of unprotected small particles will, however lead to agglomeration or aggregation from the cohesive surface energy [17]. As a result of their colloidal instability, many nanoparticles need to be stabilized via additional (capping) agents which provide a steric, electrostatic or electrosteric particle stabilization [15]. Till now, the investigation of “free” nanoparticles as catalysts has been rare [18,19]. Clearly, the development of “free” nanoparticles with tunable catalytic activity is of great significance for the synthesis of hydrocarbons.

Among the variety of methods for synthesizing magnetic nanoparticles [20–23], the polyol method has been paid more attention [24]. The polyols in this method often serve as reducing agent and stabilizer to prevent interparticle aggregating. In order to stabilize and prevent further the aggregation phenomenon, one can also use different carboxylic acids in conjunction with polyol as stabilizer. The carboxyl group in carboxylic acid can provide coordination to the nanoparticles and thereby the NPs are stabilized. It is well-known that sodium citrate can attach to Au and provides a negatively charged surface for Au nanoparticle stabilization [25,26]. Furthermore, sodium citrate and cetyltrimethylammonium

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bromide (CTAB) have been applied to dissolve core–shell Fe<sub>3</sub>O<sub>4</sub>/Au nanoparticles into water by making the surface hydrophilic [27]. Oleic acid and oleylamine are two common surfactants used for NP stabilization and for the control of NP size and morphology. FePt alloy NPs can be prepared by reducing FeCl<sub>2</sub> and Pt(acac)<sub>2</sub> by LiBEt<sub>3</sub>H in the presence of oleic acid and oleylamine [28]. Oleic acid and oleylamine are appropriate surfactants to synthesize monodisperse spherical Fe<sub>3</sub>O<sub>4</sub> nanoparticles [20]. Water-soluble Fe<sub>3</sub>O<sub>4</sub>-NPs were synthesized by bifunctional 2,3-dimercaptosuccinic acid [29]. Yang and co-workers used Fe(acac)<sub>3</sub>/benzyl ether/1,2-hexadecanediol and oleic acid/oleylamine as surfactants to synthesize monodisperse Fe<sub>3</sub>O<sub>4</sub> nanocubes with controllable sizes of 6 to 30 nm [30]. Superparamagnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles were functionalized with 11-sulfoundecanoic acid and 10-phosphono-1-decanesulfonic acid ligands to create separable solid acid catalysts for carbohydrate hydrolysis [31]. The activity of the acid-functionalized nanoparticles was higher than the traditional solid acid catalyst Amberlyst-15 for the hydrolysis of starch in aqueous solution. In addition, the acid functionalization of nanoparticles may have the potential to surpass polymerization and silica functionalization by producing more active, stable, and tunable acid catalysts for application in green chemical processes. In previous works, Sun et al. [32] have reported the preparation of monodisperse magnetite nanoparticles by the high-temperature solution reduction of Fe(acac)<sub>3</sub> (acac = acetylacetonate) by 1,2-hexadecanediol in the presence of oleic acid and oleylamine. Hou et al. [33] have synthesized magnetite nanoparticles through solvothermal reduction of Fe(acac)<sub>3</sub> by hydrazine in the presence of ethylene glycol, oleic acid and trioctylphosphine or hexadecylamine. Caruntu and co-workers [34] have prepared magnetite nanocrystals by hydrolysis of a stoichiometric ratio of FeCl<sub>3</sub>·6H<sub>2</sub>O, FeCl<sub>2</sub>·4H<sub>2</sub>O and NaOH in diethylene glycol.

Selective oxidation of hydrocarbons is of great interest in synthetic organic chemistry and chemical industry for the preparation of oxygen containing compounds [35–39]. Finding new active and selective epoxidation catalysts for those processes that require an elimination of by-products is of great interest [40]. Magnetite nanoparticles (Fe<sub>3</sub>O<sub>4</sub>-NPs) can be completely recovered by means of an external magnetic field owing to its magnetic property; therefore, it is often used as a magnetically separable catalyst [41]. Beller et al. prepared Fe<sub>2</sub>O<sub>3</sub>-NPs which were highly stable, active, and highly selective for various oxidation reactions using hydrogen peroxide [18]. The high recyclability of these Fe<sub>2</sub>O<sub>3</sub>-NPs has also been demonstrated, indicating they are well suited for continuous processes [18].

One way to attach acidic ligands is to choose ligands that have two acids groups: one that can bind to magnetite and one that will eventually serve as the catalytic site. Portet et al. [42] attached disulfonic acids to magnetite leaving one sulfonic acid group exposed to solution. However, using a sulfonic acid to bind to magnetite is not optimal due to the sulfonic acid group's weak binding affinity toward the magnetite surface [42–44]. In this work we report a facile polyol approach (reduction of FeCl<sub>3</sub> with diethylene glycol) to the synthesis of Fe<sub>3</sub>O<sub>4</sub>-NPs in the presence of different bifunctional and unfunctional carboxylic acids (including succinic acid, oxalic acid, benzoic acid and formic acid) as an electrostatic stabilizer and urea as an alkali source to investigate the effects of stabilizers (acids) on aggregation of NPs in diethylene glycol at 200 °C. The resultant samples were characterized in detail by different techniques. Furthermore, the catalytic performance of Fe<sub>3</sub>O<sub>4</sub>-NPs was evaluated on the selective oxidation of cyclohexene and cis-cyclooctene. The second benefit of using carboxylic acid is its cocatalyst effect. In 1998, it was discovered [45] that the oxidizing power of dinuclear manganese complex as catalyst in the H<sub>2</sub>O<sub>2</sub> oxidation can be dramatically increased if a small amount of a carboxylic acid is added to the reaction solution.

## 2. Experimental

### 2.1. Materials

Ferric chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O, 98% Fluka), urea (99.5% Merck), diethylene glycol (DEG) (99% Merck, a polyhydric alcohol with a boiling point of 244–245 °C), oxalic acid (99% Merck), benzoic acid (98% Fluka), formic acid (85% Fluka), succinic acid (99% Merck), citric acid (99.9% Fluka), n-octane (Merck), acetonitrile (99.9% Merck), cyclooctene (95% Merck), cyclohexene (95% Merck), H<sub>2</sub>O<sub>2</sub> (35% Fluka) and NH<sub>3</sub> (25% Merck) from were used as received. The exact concentration of aqueous hydrogen peroxide (concentration 8.95 mol dm<sup>-3</sup>) was determined before use by titration with standard KMnO<sub>4</sub>.

### 2.2. Characterization

The phase of the products was examined by XRD on a powder XRD diffractometer (D8ADVANCE, Bruker, Germany) using Cu Ka ( $\lambda = 0.154056$  nm) radiation. The morphology and microstructure of the as-prepared samples were detected on a scanning electron microscopy (SEM). Fourier transform infrared (FT-IR) spectra for magnetite nanoparticles were recorded on a Perkin–Elmer Spectrum One spectrometer after making pellets with KBr powder. The reaction products of the oxidation were determined and analyzed by an HP Agilent 6890 gas chromatograph equipped with a HP-5 capillary column (phenyl methyl siloxane 30 m × 320  $\mu$ m × 0.25  $\mu$ m) with flame ionization detector.

### 2.3. Preparation of magnetite nanoparticles

A reported method with slight modification has been used for the synthesis of magnetite [24]. FeCl<sub>3</sub>·6H<sub>2</sub>O (0.81 g, 3 mmol), carboxylic acid 1 mmol (namely succinic acid 0.118 g, oxalic acid 0.090 g, benzoic acid 0.122 g, formic acid 0.037 ml (1.22 g/mL)) and urea (1.80 g, 30 mmol) were completely dissolved in diethylene glycol (30 mL) by vigorous mechanical stirring. The solution was sealed in a Teflon lined stainless steel autoclave (50 mL capacity) and then heated at 200 °C for 4 h. After cooling down to room temperature, the black magnetite were separated magnetically and washed with ethanol and deionized water for several times to eliminate organic and inorganic impurities, and then dried at 60 °C for 6 h.

### 2.4. General procedure for oxidation

The oxidation of cyclohexene with hydrogen peroxide was performed in a 25-mL round-bottom flask placed in a thermostatic oil bath. In a typical experiment the flask was charged with the suspension of Fe<sub>3</sub>O<sub>4</sub>-NPs (1.0 mg) in 3 mL acetonitrile, n-octane as internal standard and cyclohexene (2 mmol). The oxidation reaction was started with addition of 6 mmol aqueous 30% hydrogen peroxide and the mixture was stirred vigorously with magnetic stirrer bar at 80 °C for 6 h. At appropriate intervals, aliquots were removed and analyzed by gas chromatograph. Alkene conversion and yields are based on the starting cyclohexene. The oxidation products were identified by comparison of their retention times with those of authentic samples. The conversion was determined by the following equation

%Conversion

$$= \frac{[(A(\text{substrate})/A(\text{standard}))]_{t=0\text{ h}} - [(A(\text{substrate})/A(\text{standard}))]_{t=x\text{ h}}}{[(A(\text{substrate})/A(\text{standard}))]_{t=0\text{ h}}} \quad (1)$$

A = peak area in GC chromatogram.

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