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Preparation of nano-sized magnetic particles from spent pickling liquors by ultrasonic-assisted chemical co-precipitation

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ABSTRACT

The aim of this study is to develop a new method for the preparation of high-value, environmentally friendly products from spent pickling liquors. An ultrasound treatment was introduced into a chemical co-precipitation process to control the size of the particles produced. The particles were characterized by X-ray powder diffraction and transmission electron microscopy. The magnetic parameter was measured with a magnetic property measurement system. The product consisted of ferrous ferrite (Fe_3O_4) nano-sized cubic particles with a high level of crystallinity that exhibited super-paramagnetism.

1. Introduction

Spent pickling liquors containing high concentrations of iron and residual acid are hazardous waste products of the surface treatment of steel. Generally, the liquors are neutralized and the metals precipitated, followed by discharge. However, this procedure generates large amounts of unstable sludge, which need to be disposed of to avoid secondary pollution. Due to the high concentration of iron, spent pickling liquors may represent a cheap source of raw material for the production of many kinds of chemicals. In the past decade, some new approaches have been investigated for the treatment of spent pickling liquors, including anion-exchange/membrane electrowinning [1], microwave-hydrothermal process [2], electrodialysis [3], membrane distillation [4], selective precipitation [5,6], solvent extraction [7], and use in the production of concrete [8]. These investigations have led to the disposal of spent pickling liquor without any toxic effluent in some cases, but most of these processes lead to the production of iron salts, iron oxides or reuse of the acid, which may suffer some market restrictions. Ciminelli et al. [2] has emphasized the importance of producing a more valuable product from spent pickling liquors with regard to both environmental considerations and cost. So, there is a need for a simple treatment method that will yield high-value products from spent pickling liquors.

Ferrous ferrite (Fe_3O_4) is a traditional magnetic material that has found many applications in magnetic storage media, solar energy transformation, electronics, and catalysis. When it is dispersed as nano-scale particles, the physical and chemical properties are quite different from those of the bulk material, and often exhibits desirable properties, such as high-field saturation and extra anisotropy contributions [9], suggesting physical applications and uses in biomedicine. For example, in recent years, there have been many reports of the applications of nano-sized Fe_3O_4 in magnetic resonance imaging (MRI) contrast agents [10], biosensor [11], and embolotherapy [12]. Although Fe_3O_4 has been synthesized through different approaches [13], the chemical co-precipitation process is the most common. However, in most cases, the particles formed are only just within the micrometer scale [14], and it is difficult to control the size distribution and scale in an ordinary chemical co-precipitation process [15]. The rapid progress of microelectronic technology and other fields of industry require continuous reduction of component size, stimulating the demand for synthesis of ultra-fine particles and functional materials.

Much attention has been paid to ultrasound/chemical (sonochemical) methods for the production of nanomaterials [16]. The transmission of ultrasound in a liquid phase provides mixing conditions favorable for chemical reaction, and generates transient extreme temperature or high shear-rate through acoustic cavitations, which has a specific effect on a chemical reaction that is very suitable for the formation of nanoparticles. Several kinds of nanoparticles have been synthesized by this method [17–20]; for example, inorganic nanoparticles of Fe_2O_3, CdS, Mn_3O_4, and

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ZnS have properties ideally suited to catalysis, luminescence, high-density recording media, and non-linear optical devices, demonstrating the advantages of sonochemical methods in yielding smaller particles [21].

There are two main approaches to fabricate Fe_3O_4 nanoparticles: one is chemical co-precipitation [9,22], which always needs a surfactant to control the particle size and distribution and the other is sonochemistry [11,23,24], which always needs an expensive precursor as the source of iron. Generally, Fe_3O_4 nanoparticles produced by the sonochemical method are either amorphous or crystalline. The amorphous particles are always obtained by sonolyzing the volatile precursor inside the collapsing bubble, and the crystalline particles are obtained by the sonochemical reaction that occurs in the interfacial liquid region around the cavitation bubbles with non-volatile salts. In previous works, Kim et al. [10] compared the properties of Fe_3O_4 nanoparticles obtained by sonochemical and chemical co-precipitation methods with the same precursor, and found that the products of both methods had spinel magnetite crystal structure, but the magnetite nanoparticles produced by the sonochemical method had a higher level of crystallinity. Jiang et al. [9] obtained highly crystalline Fe_3O_4 nanoparticles by chemical co-precipitation, and found that the pivotal factor was the homogeneous pH condition in the process of forming the Fe_3O_4 nanoparticles. Ciminelli et al. [2] indicated that single-phase magnetite was obtained at pH 13 (110 °C for 5 min); otherwise, lower pH values and temperatures led to the production of other iron oxides. Kim et al. [25] discussed the importance of pH values in controlling the crystal size of Fe_3O_4.

Among the reports of the fabrication of Fe_3O_4 nanoparticles, the sonochemical and chemical co-precipitation methods both have relative advantages and disadvantages. Chemical co-precipitation is simple and cheap. The sonochemical method requires expensive organometallic compounds as precursors, but offers better control of the size and size distribution of particles. There have been few reports of the production of ferrite nanoparticles from spent pickling liquors, but Konishi et al. [26] and López et al. [27] have investigated the synthesis of complex ferrite (nickel ferrite and zinc ferrite) by microbial oxidization of Fe(II) to Fe(III) in dilute conditions.

An ultrasound-assisted chemical co-precipitation procedure may offer a promising method for the synthesis of nano-sized ferrite particles with spent pickling liquor as a precursor. In the present investigation, it was focused on the development of a new method to prepare high-value products from spent pickling liquors with advantages for the environment. Two related aspects were considered: (1) to investigate the possibility of producing magnetic nanoparticles from spent pickling liquors instead of expensive organometallic compounds in an ultrasonic process and (2) to characterize the products. We proposed a procedure of ultrasonic-assisted chemical co-precipitation, and characterized the products with X-ray powder diffraction (XRD) and transmission electron microscopy (TEM); the magnetic property was measured with a magnetic property measurement system (MPMS).

2. Basic mechanism

2.1. Formation of Fe_3O_4

In alkaline solutions, Fe(III) and Fe(II) precipitate spontaneously with a small solubility product constant. If there is only Fe(III) or Fe(II) in the solution, the precipitates are only the hydroxides of Fe(III) or Fe(II), which can be expressed as:

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3\downarrow \tag{1}$$

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2\downarrow \tag{2}$$

If these two kinds of ion are mixed in alkaline conditions, the hydroxides formed may be adsorbed mutually, produce a new kind of mixture that is highly unstable in normal conditions, and can be stripped of water in its molecular structure. That is the reaction of producing Fe_3O_4, which can be expressed as:

$$Fe^{2+} + 2Fe^{3+} + 8OH^- \rightarrow Fe(OH)_2 + 2Fe(OH)_3 \tag{3}$$

$$nFe(OH)_2 + 2nFe(OH)_3 \rightarrow \left[Fe^{3+}\langle\substack{OH\\OH}\rangle Fe^{2+}\langle\substack{OH\\OH}\rangle Fe^{3+}\right]_n \tag{4}$$

$$\left[Fe^{3+}\langle\substack{OH\\OH}\rangle Fe^{2+}\langle\substack{OH\\OH}\rangle Fe^{3+}\right]_n \rightarrow nFe_3O_4 + nH_2O \tag{5}$$

2.2. Particle growth and ultrasound function

Once a core of Fe_3O_4 crystal is formed, the liquid phase becomes a two-phase system and, because of the tremendous surface energy, small crystals tend to aggregate to form larger particles. The mechanism expressed by Eq. (5) indicates the formation process of the Fe_3O_4 core, which involves adsorption and dehydration of the hydroxides of Fe(II) and Fe(III). By this mechanism, the growth pattern is simply the aggregation of particles and, in most cases, the stability of particles can be expressed as:

$$W = (a+b)\int_{a+b}^{\infty} \exp\left[\frac{V(R)}{k_B T}\right]\frac{dR}{R^2} \tag{6}$$

where W is the stability factor of particles, a and b are the radius of the two particles, respectively, R is the distance between the two particles, and $V(R)$ is the function of potential energy of interaction, and k_B is Boltzmann's constant. When the distance between particles is decreased to a certain extent, short-range reactions (such as van der Waals forces) may lead to strong attraction between particles. Generally, in the process of reaction without any external disturbance around a crystal, the particles of Fe_3O_4 can approach each other and aggregate easily, growing gradually into larger particles that reach the micrometer scale or larger. So, it is important to maintain sufficient distance between particles for the stability of the multi-phase system.

The novel effects of ultrasound spreading through a liquid phase are regarded to arise from acoustic cavitations, which consist of the creation, growth and implosive collapse of gas vacuoles in solution. As a result of these effects, an alternating pressure field occurs within the bubbles during cavitational collapse [28], which leads to a transient high-temperature, high-pressure environment or high shear-rate in solution, and provides conditions suitable for forming crystal nuclei with a high-reaction rate. Abundant crystal cores formed instantaneously decrease the degree of oversaturation of solution, which restricts growth of the crystal core. At the same time, transient high temperature during sonication that arisen from ultrasonic cavitation and the large amounts of tiny bubbles produced on the surface of solid particles decrease the dangling bonds and defects on the surface of the nuclei, and the surface state of the nuclei becomes stable [29]. So, with the action of ultrasonic cavitation, a high shear-rate is maintained throughout the solution, and the distance between particles can be sustained by the bubbles until the end of the reaction. In addition, the shock-wave that arisen by acoustic cavitation leads to strong shearing and fragmentation into particles, disrupting the aggregation between particles and control the size and size distribution, the surface activity of particles may also be restrained [30].

The influence of shearing on the aggregation of particles can be expressed by the dimensionless Peclet number (Pe) as [31]:

$$Pe = 3\pi\,\eta_c\sigma^3\frac{u}{4k_B T} \tag{7}$$