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Effect of divalent metal hydroxide solubility product on the size of ferrite nanoparticles

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Abstract

We study the effect of divalent metal hydroxide solubility product on the size and magnetic properties of nanoparticles formed during co-precipitation. We synthesized ferrite nanoparticles by varying the solubility product from 10^{-13} to 10^{-17} by using different divalent cations of Mn, Co, Fe and Zn, where the average particle size decreased from 29.1 to 8.9 nm. The Mn, Co and Fe ferrites were magnetic in nature with saturation magnetization of 44.6, 47.38 and 56.19 emu/g respectively, whereas the Zn ferrite was paramagnetic. The increase in particle size observed with increasing solubility product of divalent metal hydroxide is in agreement with the nucleation theory.

Keywords: Co-precipitation; Solubility product; Ferrite nanoparticles; Particle growth

1. Introduction

Due to several technological applications of magnetic nanoparticles, researchers have been working on new and cost effective synthesis methods [1–7]. The cubic spinel structured $MO{\cdot}Fe_2O_3$ (M=Fe, Mn, Co, Ni, Zn, etc.) has been among the most frequently used systems to understand fundamental aspects of nanomagnetism [8]. It also has several applications in various fields such as ferrofluids [9], recording media [10], biomedical [8], electronic devices [8] and fundamental studies [11].

The synthesis techniques used, in recent years, to produce nanoparticles are mechano-chemical [5], laser pyrolysis [7], co-precipitation [6], sol–gel [2], solvo-thermal [3], hydrothermal [4] and very recently bacterial aerobic synthesis techniques [1]. Each synthesis procedure has its own merits and de-merits and is useful to prepare certain nanoparticles with specific properties. Among the above preparation techniques, one of the most convenient and versatile techniques is co-precipitation of M^{2+} and Fe^{3+} by an alkali in an aqueous solution [6] or in reverse micelle [12] or using liquid foam as template [13]. Co-precipitation reaction occurs at low temperatures, has biocompatible yield with low impurity levels and is cost effective. Size of particles can be tuned by optimizing the reaction parameters such as temperature, pH and ionic strength imposed by non-complexing salt [6,14].

Precipitation reactions consist of a nucleation step followed by particle growth stages and these two simultaneous processes govern the product morphology. Due to the difficulties in isolating nucleation and growth processes, the fundamental mechanism of precipitation reactions is still not fully understood. When the product contains more than two elements, the process becomes more complex, as multiple elements must be precipitated simultaneously. In co-precipitation reactions, it is necessary to understand the fundamental aspects of the process and the effects of physical and chemical properties of the individual elements used in the system to manipulate the growth of nanoparticles to the desired size and shape. In the ferrite system, the critical radius (r^*) of the nucleated particle size and the structure depends on the individual properties of both the metal ions. Moreover, the pathways from soluble Fe^{3+} and M^{2+} to thermodynamically stable metal ferrite involve intermediate products which have a vital role in the growth process. Here, we investigate the effect of divalent metal hydroxide solubility product on the size and magnetic properties of nanoparticles formed during co-precipitation.

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2. Experimental

2.1. Preparation of magnetic nanoparticles

The synthesis of ferrite nanoparticles was carried out by precipitating freshly prepared (GR grade) M(II) and Fe(III) salt solutions of stoichiometric proportions in alkaline medium at constant stirring, where M=Fe, Mn, Co, Zn. On vigorous stirring, the solution pH was rapidly increased to 12, by the addition of 6 N NaOH at 90 °C. At a constant rate, the addition of alkali was finished in 10 s for all the samples and they were left for 60 min for digestion. Then, the pH of the dispersion was adjusted to ~6–7, with diluted HCl. As protonation was done, the particles were separated from the dispersion. The top water layer with salts was discarded. The obtained particles have been washed with triply distilled water at 60 °C on vigorous stirring, until the washed water was free of ionic impurities (checked for chloride ions in top water layer with $AgNO_3$ solution). Later, the water-washed particles were treated with acetone and particles were dried at 35 °C for 48 h in inert atmosphere. Acetone washes were carried out to avoid the particle drying process at higher temperatures and to eliminate water content. Especially, in the case of magnetite ($FeO{\cdot}Fe_2O_3$), Fe^{2+} is more sensitive to aerial oxidation and hence higher temperature enhances the oxidation process. The details of the preparation procedure are discussed elsewhere [15].

2.2. Characterization of magnetic nanoparticles

2.2.1. XRD studies

A MAC Science MXP18 X-ray diffractometer was used for crystal structure and average particle size analysis. 2θ values were taken from 11 to 80° using Cu Kα radiation with step size of 0.04°. The XRD patterns were verified by comparison with the JCPDS data. The broadening of the peak at half height was related to the average diameter (d) of the particle according to Scherrer's formula, i.e. $d=0.9\lambda/\Delta\cos\theta$ where λ is the X-ray wavelength, Δ is the line broadening measured at half-height and θ is the Bragg angle of the particles. The average particle size is obtained from the most intense peak, corresponding to (311) reflection by using the Debye–Scherrer formula.

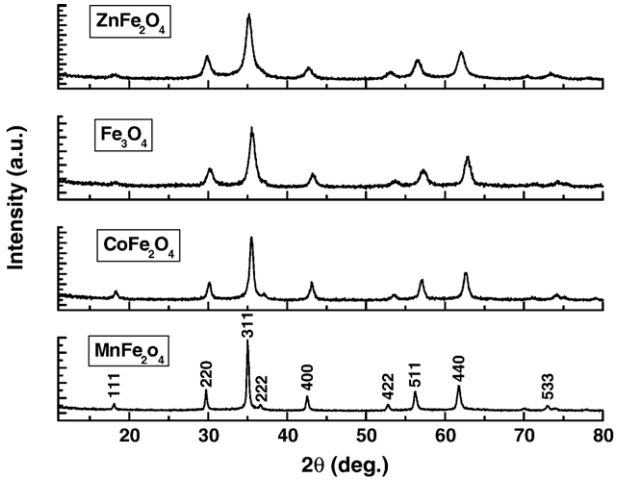

Fig. 1. The XRD patterns of the samples prepared with varying divalent metal ions of Mn, Fe, Co and Zn.

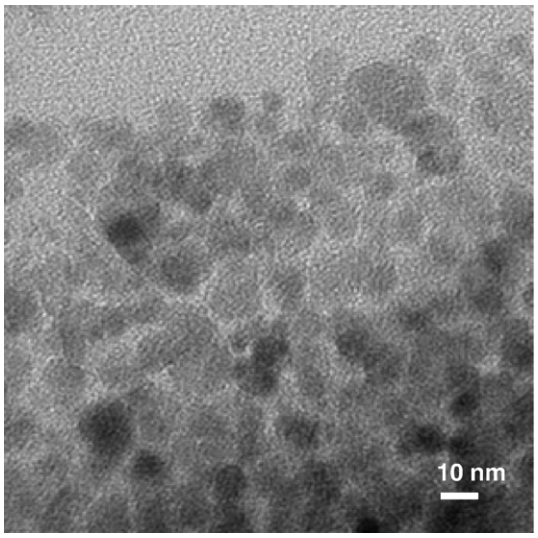

Fig. 2. The TEM image of the Fe_3O_4 sample. The average size of the particles is about 9 nm.

2.2.2. Morphological evaluations

The TEM instrument used was a JEOL 2011 with an acceleration voltage of 200 kV. The average particle size obtained from the Debye–Scherrer formula was in good agreement with the TEM results.

2.3. Magnetic properties

A vibrating sample magnetometer (EG and G Princeton, Model: 4500) was used for the magnetization measurements. These measurements were taken from 0 to ±7 kOe field at room temperatures.

3. Results and discussion

3.1. Crystal structure and particle morphology

On increasing pH, Fe^{3+} ions precipitate as ferrihydrite at pH of 3, whereas divalent metal ions precipitate at higher pH values. The minimum pH values required to precipitate divalent metal hydroxides, when a single cation is used, are 7, ~8, 8 and 9 for Fe^{2+}, Zn^{2+}, Co^{2+} and Mn^{2+}, respectively [16]. In the ferrite precipitation process, while increasing the pH of the salt solution, ferrite nanoparticles are nucleated by the simultaneous reaction of hydrolysis and dehydration. The overall chemical reaction can be written as,

$$M^{2+} + 2Fe^{3+} + 8OH^- \rightarrow MO.Fe_2O_3 + 4H_2O$$

Fig. 1 shows the XRD patterns of the samples prepared with varying divalent metal ions of Mn, Fe, Co and Zn. $MnFe_2O_4$, Fe_3O_4 and $CoFe_2O_4$ have an inverse spinel structure, where $ZnFe_2O_4$ has a normal spinel structure. Size, covalent bonding effects and crystal field stabilization energies of M^{2+} seem to influence the site preference of ions. In inverse spinel structure, divalent metal ions occupy octahedral