Effect of Reaction pH on Characterization of Co-precipitated Cobalt ferrite Nanoparticles

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ABSTRACT

Cobalt ferrite ($CoFe_2O_4$) nanoparticles were prepared by a chemical coprecipitation method at different pH conditions from 10.1 to 13.5. The XRD results reveal that pure cobalt ferrite particles with the inverse spinel structure are only formed at pH values higher than 11. The average particle diameter increases from 11.9 to 15.8 nm as the pH of reaction is increased from 11.1 to 13.5. The obtained results indicate that the ferrite precipitation process proceeds via the formation of cobalt hydroxide and the particle size distribution of this precursor determines the final particle size. It is found that with increasing the pH of reaction, the magnetization increases meanwhile the coercive field decreases. All the samples synthesized at investigated pH values show ferrimagnetic behavior and highest magnetization up to 60 Oe at the highest pH.

Keywords: Cobalt ferrite, nanoparticles, magnetic preparation

I. INTRODUCTION

Cobalt ferrite ($CoFe_2O_4$) is a well-known semihard magnetic material with high coercivity and moderate saturation magnetization. Due to high electromagnetic properties, good chemical stability and mechanical hardness cobalt ferrite have been widely used as applications in magnetic recording media, magnetic resonance imaging, magnetic fluid hyperthermia, biosensors, drug delivery, cell separation, etc. [1, 2].

For preparation of cobalt ferrite nanoparticles, several synthesis methods have been proposed to date such as hydrothermal routes [3], solvothermal [4], thermal decomposition of organic-metal complexes [5] and co-precipitation [2, 6 - 8]. However, properties of cobalt ferrite nanoparticles are different when prepared by different methods as well as when prepared under different reaction conditions. Most of the synthesis routes involved a secondary annealing step that results into larger particles size and broad size distribution of nanoparticles with increases remanance and coercivity, which is not encouraging for most of the industrial applications. Amongst the co-precipitation method has been further developed because of its simplicity, suitable cost and industrial scale yielding. However, in this method, the control of particle size during synthesize process can be known as a main challenge and there are no straightforward procedures available to tailor nanoparticles of desired size and properties.

It is known that the particle size and crystallinity can be controlled by adjusting the supersaturation during the nucleation and crystal growth processes, which in turn, it can strongly be affected by solution chemistry and precipitation conditions such as reaction pH. pH value can cause a variety of physical and chemical properties of ferrite nanoparticles [8].

Hence, in this work the preparation of cobalt ferrite nanoparticles by co-precipitation technique

will be developed. The effect of pH on the structure, size and magnetic properties of cobalt ferrite will be investigate

II. METHODS AND MATERIAL

Materials

Ferric chloride hexahydrate (FeCl₃.6H2O, AR) and Cobalt chloride (CoCl₂.6H2O, AR) are procured from BDH Chemicals Ltd. England; Sodium hydroxide (NaOH) is supplied by Merck.

Cobalt ferrite preparation

In this work, Cobalt ferrite nanoparticles were prepared by the co-precipitation procedures as follows. The solutions of 1M FeCl₃ and 0.5M CoCl₂ both in 1M HCl were prepared as stock ones. The mixture of 20 mL of the stock solutions with the molar ratio of Fe^{3+} to Co^{2+} as 2:1 was added into a reaction vessel containing 100 mL of the 1.2 M NaOH solution which was previously adjusted to the required pH (from 10.2 to 13.5) with concentrated HCl, heated to the desired temperature (65°C). During the reaction of 2 hours, the solution was vigorously stirred with a constant speed and kept the pH by adding 1.2 M NaOH solution. The resulting precipitates were collected by a strong magnet and then washed with distilled water for several times until the pH reached to neutral. Finally the precipitates were annealed in an oven at 600°C for 2 hours.

Structural analysis

The crystalline structure of the magnetic nanoparticles was characterized by X-ray diffraction (XRD) measurements were performed on powder samples obtained after annealing, using a D8-Advance Bruker AXS diffractometer with CuKα radiation (λ = 1.542 Å) operating at 25°C.

Particle size measurement

The average crystal size was estimated by using the Debye-Scherrer equation [9]

$$d = \frac{0.9\lambda}{\beta\cos(\theta)}$$

$$d = 0.9 \, \lambda/\beta \cos\theta$$

Where d, λ, θ and β are the crystallite size, X-ray wavelength, Bragg diffraction angle and full width at the half maximum (FWHM) of the diffraction peak

Besides, the size and shape of Cobalt ferrite nanoparticles was observed directly by transmission electron microscopy (TEM) technique with the instrument JEOL EM 1010. The average particle size can be computed from TEM image as follows

$$d = \frac{\sum_{i=1}^{N} d_i}{N}$$

Where d is average diameter, d_i is diameter of ith particle and N is number of particles taken into account

Magnetic properties

Vibrating sample magnetometer (VSM) MicroSense EZ9 was used for magnetization measurements. These measurements were taken from 0 to 16 kOe field. From this field versus magnetization curve patterns, saturation magnetization values of the samples were measured.

III. RESULTS AND DISCUSSION

A. Effect of pH on the particle structure

The XRD analysis indicates that the pure cobalt ferrite was only formed at the pH greater than 11 (See Figure 1). With the lower pH, the precipitates are mainly hematite α-Fe₂O₃. A possible explanation is that the formation of iron hydroxide precursors is mainly at low pH solution and therefore the Fe/Co molar ratio in the final product increases leading to increase the formation of hematite phase in the calcined products.

At the pH values above 11, the XRD patterns (Figure 1) of the synthesized nanoparticles show the characteristic peaks (111), (220), (311), (400), (422), (511), (440) and (533) which are matched to the cubic spinel structure (JCPDS card no. 22-1086) and the pH variation has no noticeable effect on the morphology.
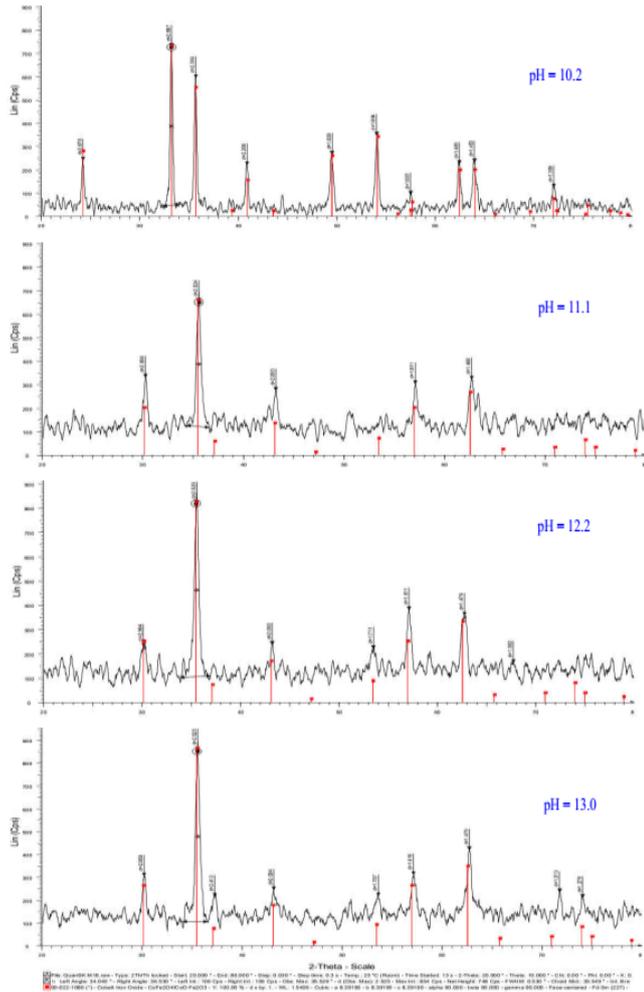
Figure 1: X-ray diffractograms of magnetic samples synthesized at different pH values

B. Effect of pH on the particle size

The sizes of nanoparticles prepared at different pH values are reported in Table I. As mentioned in the previous section, the crystallite size is calculated from the XRD and the average diameter is measured from the TEM image (Figure 2). Since the experimental particle size distributions (PSDs) resemble very much a log-normal distribution (right skewed), non-linear least squares fits of a log-normal profile to the PSDs were carried out to yield the width of the PSDs displayed in Table I. The variation in the particle size as a function of reaction pH is shown in Figure 3.

TABLE I
EFFECT OF pH ON THE PARTICLE SIZE

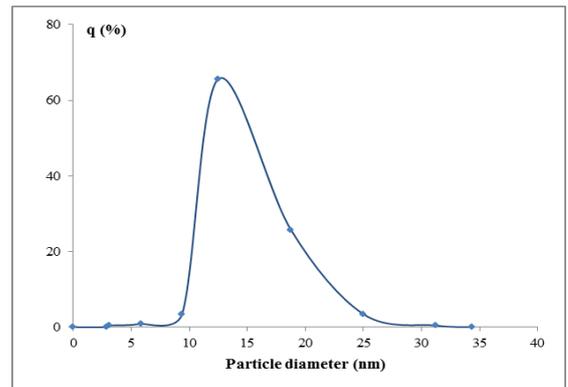| No	pH	Crystallite size (nm)	Particle size (nm)	Width of PSD (nm)
1	10.8	-	-	-
2	11.1	11.1	11.9	0.26
3	12.2	14.7	14.3	0.28
4	13.0	15.5	15.1	0.33
5	13.5	15.8	15.8	0.45
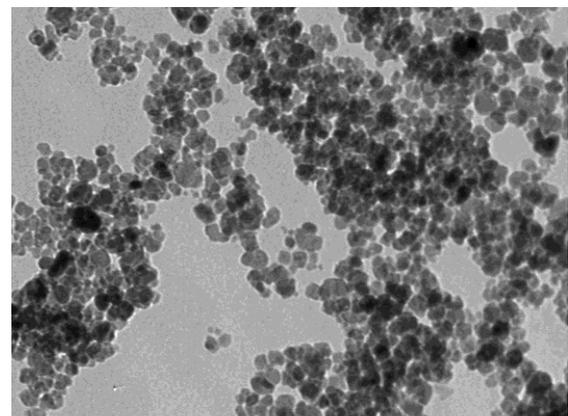
Figure 2: A typical TEM image and PSD of prepared nanoparticles (Sample 3)

It is learnt that the higher pH results in the larger sized particles. The mean particle size increases from 11.9 nm to 15.8 nm when the pH is increased from 11.1 to 13.5. A good agreement is also found in the calculated results of crystallite size of the nanoparticles using the Debye-Scherrer's formula.

This confirms that the particles had a single-crystal structure. The pH dependence of particle size may be attributed to that the elevated pH probably has slowed the formation of ferrite nuclei and thereby allows them to grow larger by the attachment of ions from the solution. An alternative explanation is a possible contribution of the particle growth following the agglomeration mechanism. At high pH values, the condensation reaction of $Co(OH)_2$ precursors is able to happen, and agglomeration of the nanoparticles occurs. This trend is in good agreement with those reported in literature [7, 10]. The PSD narrowed with decreasing pH confirms the precipitation process in which the size of $Co(OH)_2$ precursor determines the final particle size.
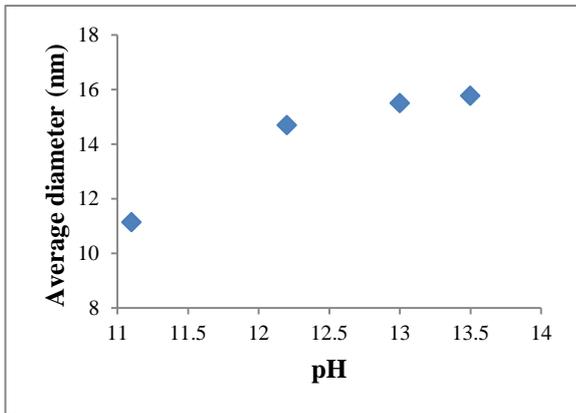

Figure 3: Particle size as a function of reaction pH

C. Effect of pH on the magnetic properties

The magnetization curves of the coprecipitated $CoFe_2O_4$ nanoparticles are shown in Figure 4. Magnetic properties are also listed in Table II. The prepared nanoparticles show ferrimagnetic behavior, but the saturation magnetization values (Ms) are lower than the bulk $CoFe_2O_4$ (~80 emu/g). This decline in the saturation magnetization may be attributed to the surface order/disorder interaction of the magnetic spin moment and the disturbance in the spinel structure inversion as a result of Laplace pressure.

TABLE III

MAGNETIC PROPERTIES OF THE PREPARED PARTICLES

pH	Average diameter (nm)	Ms (emu/g)	Hc (Oe)
11.1	11.9	55.4	841
12.2	14.3	56.4	706
13.0	15.1	57.4	628
13.5	15.8	60.1	605

It can be seen that the saturation magnetization values decreases from 60 emu/g to about 55 emu/g as the magnetite size is decreased from 15.8 nm to 11.9 nm. The smaller the particle the greater curvature the surface is to increase the level of crystal disorientation and resulting in the reduction of saturation magnetization. It is important to note that the magnetization values found at particles with different sizes are quite higher in comparison with others [2, 7] and a reasonable explanation is the absence of possible impurities such as hematite and maghemite. In addition the absence of surfactants is also an important reason to get the higher saturation magnetization.

The coercivity (Hc) increases from 605 to 841Oe with the decrease of particle size. This result can be attributed to the increase of domain walls as pinning factors for movement of magnetic domains [2, 5].
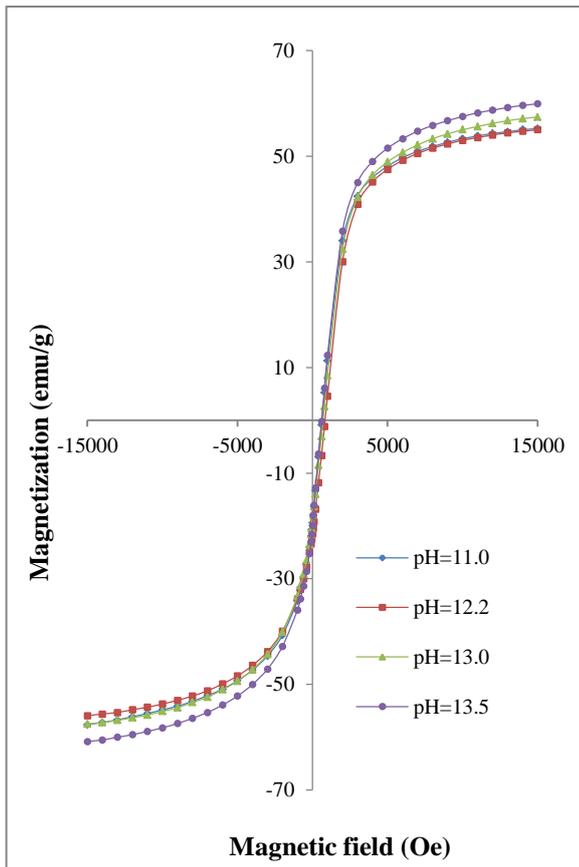
Figure 4: Magnetization curves for the cobalt ferrite particles synthesized at different pH values

IV. CONCLUSION

In this paper, $CoFe_2O_4$ nanoparticles were synthesized at different pH conditions. The formation of single phase spinel structure was observed at the pH values above 11. The crystallite and average particle size decreased with increasing reaction pH. The conditions allow controlling magnetite particle size in the range from 11 nm to 16 nm with narrow size distribution. The magnetic properties of nanoparticles strongly depend on its size and crystallinity. The prepared nanoparticles show the ferrimagnetic behavior.

V. ACKNOWLEDGEMENT

VI. REFERENCES

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