Rev. Fac. Ing. Univ. Antioquia N.° 50 pp. 9-16. Diciembre, 2009

Effects of the synthetic method on the particle size and purity of magnetite

Efecto del método de síntesis en el tamaño de partícula y pureza de la magnetita

Beatriz Jaramillo Tabares, Alejandro Alberto Zuleta Gil, Franklin Jaramillo Isaza[*]

Grupo de Corrosión y Protección (GCP), Universidad de Antioquia, calle 62 N.º 52-59, SIU, Torre 2, Laboratorio 330, Medellín, Colombia.

(Recibido el 10 de febrero de 2009. Aceptado el 24 de agosto de 2009)

Abstract

The characterization of magnetites synthesized by methods reported with some modifications is presented. The influence on purity and particle size of the obtained oxides is discussed. The samples were characterized by Mössbauer Spectroscopy at room temperature, particle size analysis by light scattering and by transmission electron microscopy of naked particles. The results showed that depending on the method of synthesis there are variations on stoichiometry and composition of magnetites, being this difference more important when the rate of addition of the alkaline solution to the combined ferrous and dispersant solution is changed. Moreover, it has been found strong agglomeration evidenced by TEM, however the sizes of the individual crystallites are in the nanometer scale.

----- *Keywords:* Magnetite synthesis, nanometric magnetite, magnetite characterization

Resumen

Se presenta la evaluación de magnetitas sintetizadas bajo diferentes condiciones reportadas en la literatura y con algunas modificaciones, su influencia en la pureza y en el tamaño de partícula de los óxidos obtenidos. Las muestras se caracterizaron mediante espectroscopía Mössbauer a temperatura ambiente, análisis por dispersión de luz y microscopía electrónica de transmisión. Los resultados Mössbauer mostraron variaciones estequiométricas y de composición, que fueron más notables cuando una combinación de solución ferrosa y dispersante se agregó rápidamente a una solución alcalina. Además,

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[*] Autor de correspondencia: teléfono: + 57 +4 +219 66 15, correo electrónico: bejarami@udea.edu.co (F. Jaramillo).

se encontró que el tamaño de partícula también cambia dependiendo del método de síntesis.

----- *Palabras clave:* Síntesis de magnetita, espectroscopía Mössbauer, tamaño de partícula, magnetita nanoparticulada

Introduction

Magnetite (Fe_3O_4) is a ferromagentic oxide widely studied due to its broad range of applications such as ferrofluid, pigment, storage information material, biomedical applications, catalyst, among others [1-5]. It has been found that magnetite nanoparticles show superparamagnetic behavior and their properties are strongly influenced by the method of synthesis. The main reported methods are sonochemical [6], chemical co-precipitation [7-9] forced hydrolysis reaction [10], micro-emulsion [11], hydrothermal [12-14], pyrolysis [15] and electrochemical synthesis [16]. Moreover there are some studies [17,18] related to the effect of pH, temperature and stirring conditions in purity, stoichiometry and particle size variations of synthetic magnetites.

Magnetite has an inverse spinel structure, with a face-centred cubic unit cell based on 32 O^{2-} that contain 8 Fe^{3+} ions on the tetrahedral sites (A sites) and 16 Fe ions on the octahedral sites (B sites); 8 of which are Fe^{2+} end the other 8 are Fe^{3+}. Its formula is written as $Y[XY]O_4$ where $X=Fe^{2+}$, $Y=Fe^{3+}$ and the brackets denote octahedral sites [13]. At room temperature the Mössbauer spectrum of magnetite shows two magnetic components. A sextet corresponding to Fe^{3+} on the tetrahedral sites (A), with higher hyperfine field and a sextet with lower hyperfine field due to $Fe^{2,5+}$ on the octahedral sites (B).

The lines corresponding to B-sites are broader and larger than A-sites because of hopping of electrons between Fe^{2+} and Fe^{3+} ions occurs only on the B-sites, leading to the well known "$Fe^{2,5+}$" ionic state [18]. A simplified formula of magnetite can be written as $Fe_{3-x}O_{4,}$ where the oxidation parameter x can vary continuously from zero, for a stoichiometric magnetite, to $^1/_3$ for maghemite (γ-Fe_2O_3). This parameter can be calculated from the Mössbauer spectra [16] using the expression $x=(2R-1.06)/(5.3+6R)$, where R represents the ratio of the subspectral area of the A sites to the subspectral area of B sites.

The properties of magnetite are strongly influenced by particle size, purity and stoichiometry. Most of the recent applications reported in the literature have taken advantage of the nanometric size. However, many of those papers focus mainly on the size rather than stoichiometry or purity of the oxides, and problems like the formation of other phases as maghemite and goethite in the synthesis of magnetite are poorly discussed. In the present work the influence of modifications on the purity and stoichiometry of the oxides in the conventional synthetic hydrothermal method is studied. Such modifications include addition rate and order of the precursors, and usage of dispersant. An improvement on the hydrothermal method is presented in order to obtain a balance between size and purity.

Experimental

Materials

$FeCl_2.4H_2O$ and $FeCl_3.6H_2O$ (Merck), NaOH (Carlo Erba) and $NaNO_3$ (Merck), polyethylene-glycol 4000 (Merck) were used without any further purification. The water used in all experiments was de-ionized with conductivity 0.054 μScm^{-1}.

Synthesis and characterization

Three different methods of synthesis were evaluated, with some variations in each of them to finally obtain eight different magnetites. For a typical synthesis a degassed solution of ferrous chloride was added at a controlled rate to a degassed aqueous solution containing NaOH/$NaNO_3$. In other cases the addition was done in the other way around. In some cases polyethylene-glycol (PEG) was used as a dispersant to increase the viscosity of the system and evaluate its effect on the final particle size of the oxides. Stoichiometric quantities of the precursors were used and taken from the literature [7, 17]. Thus the precipitate obtained was decanted in a dialysis tubing cellulose membrane, and placed in a bath of distilled water. The anions of the suspension were removed by osmosis through the membrane. The water of the bath was replaced many times until the conductivity of the bath was constant and similar to the deionised water (0.054 µS Scm^{-1}). The resulting was filtered and dried at 40 ºC for 48 hours. The prepared samples were stored in a desiccator under nitrogen atmosphere. All the used methods are described on Table 1. These are classified on three groups, group 1 (M1) corresponding to chemical co-precipitation from Fe^{2+} and Fe^{3+}, group 2 (M2, M2a y M2b), in which the oxidizing solution was added to the ferrous solution, and group 3 (M3, M3a, M3b, M3c) in which the ferrous solution was added to the oxidizing solution.

Table 1 Variables considered in simple preparation of the magnetites

Sample	*Variables considered*
M1	Chemical co-precipitation from Fe^{+2} and Fe^{+3} aqueous salt solutions, molar ratio of Fe^{+3}:Fe^{+2} = 2:1, by addition of NH_4OH to control pH [17].
M2	Hydrothermal. The alkaline solution, $NaNO_3$ and NaOH, is added dropwise and slowly to the ferrous chloride solution [11].
M2a	Hydrothermal. The alkaline solution, $NaNO_3$ and NaOH, with PEG as a dispersant is added dropwise and slowly to the ferrous chloride solution [11, 19].
M2b	Hydrothermal. Adding dropwise and slowly the alkaline solution, $NaNO_3$ and NaOH, with PEG to the ferrous chloride solution also containing PEG.
M3	Hydrothermal. Adding the ferrous chloride solution dropwise and slowly to the alkaline solution, $NaNO_3$ and NaOH [13]
M3a	Hidrothermal. Adding the ferrous chloride solution dropwise and slowly to the alkaline solution, $NaNO_3$ and NaOH, with PEG.
M3b	Hydrothermal. Adding dropwise and slowly (0,8 mL/s) the ferrous chloride solution to the alkaline solution, $NaNO_3$ and NaOH, with PEG [10, 11, 18]
M3c	Hydrothermal. Adding dropwise but more quickly (1,6 mL/s) the ferrous chloride solution with to the alkaline solution, $NaNO_3$ and NaOH, with PEG.

[*] When PEG is used, the ratio is 6 g PEG:1 g Fe total.

The samples of synthesized magnetites were characterized by Mössbauer spectroscopy at room temperature. Mössbauer spectra were obtained in the transmission mode using a constant acceleration with a Co/Rh source and a triangulate signal to control source velocity with constant acceleration. The spectra were fitted using MOSF program which is based on a nonlinear least-square method assuming Lorentzian line shapes. A three or four sextets model has been used. The two first attributed to magnetite, sextet 1 (S1) corresponding to Fe^{3+} ions on the tetrahedral sites (A) and sextet 2 (S2) to $Fe^{2.5+}$ on octahedral sites (B), sextet 3 (S3) and 4 (S4) to goethite. Light scattering experiments to obtain particle size distributions were accomplished in a Malvern Instruments, Mastersizer 2000 Ver. 5.22 equipment by dispersion of the oxides in ethanol with 1% of PEG. TEM images were obtained in a Tecnai 20 TW, D345, FP 5020 / 10 Phillips microscope at 200 kV and 25-30 mA.

Results and discussion

Results showed different features on the final product comparing the synthesis obtained by hydrothermal and co-precipitation route. These variations are mainly attributable to solution mixing order.

The co-precipitation method (M1) normally gives a brownish solution when the reagents are mixed. As caution, the water used in solutions was degassed over 30 min. This color can remain during all the reaction and finally give a brown-like oxide. In contrast, the hydrothermal method with dropwise addition of alkaline/oxidizing solution to the ferrous solution (M2, M2a y M2b), with or without PEG presented the formation of a black suspension localized at the contact of the drop with the solution and homogenized throughout out the flask while the reaction took place. Finally, When the ferrous solution was added to the alkaline/oxidizing solution (M3, M3a, M3b y M3c), a suspended solid was also formed from the localized oxidation of Fe^{2+} to Fe^{3+}, the suspension looked like green rusts that quickly change to black magnetite in the alkaline medium, this is in agreement with the results previously reported for this synthetic strategy [20].

According to the Mössbauer Spectra (Figure 1), all samples presented magnetite as the main component (see Table 2 for sextets 1 and 2). In all the fittings the hyperfine parameters corresponded to magnetite (Bhf_1:49T, Bhf_2:46 T, δ_1:0.15mm/s, δ_2:0.56mm/s) and goethite (Bhf_1:38.2 T, δ_1:0.25mm/s) [19]. Sample M1 presented around 30% of a second phase (sextet 3) assigned to goethite according to the characteristic hyperfine parameters [21]. Sample M2 was fitting using a model with four sextets, S1 and S2 corresponding to magnetite and sextets third and fourth corresponding to goethites of different particle size (see Figure 3b). Samples M2a, M3a, M3b, M2b, M3c were fitted using a three sextets model. S1 and S2 correspond to magnetite and S3 corresponding to goethite. Sample M3 was fitted using two sextets (S1 and S2) which correspond to a highly pure magnetite.

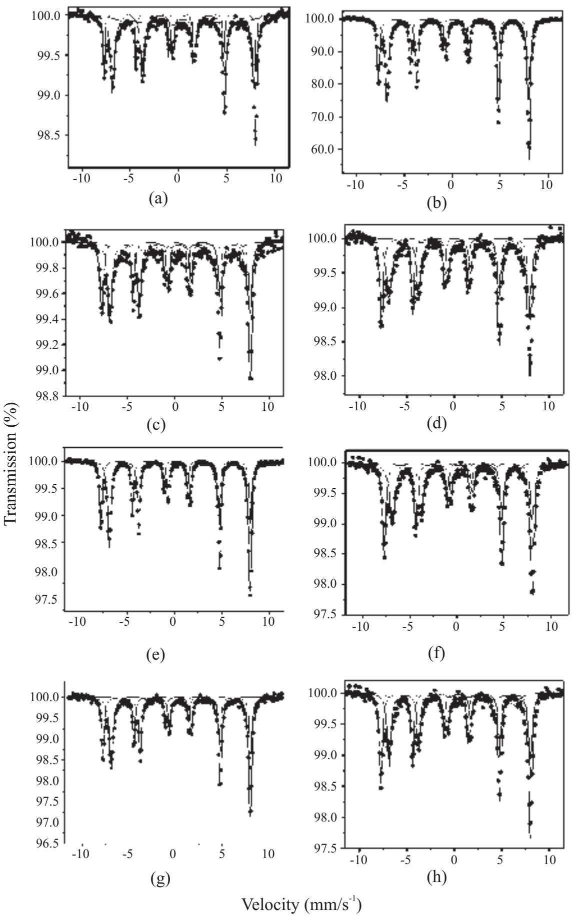

Figure 1 Room temperature Mössbauer spectra of synthetized magnetites. (a) M1, (b) M2, (c) M2a, (d) M2b, (e) M3, (f) M3a, (g) M3b, (h) M3c

Table 2 shows the calculated oxidation parameter *x* of stoichiometry for magnetite, being samples M3 and M3b those with smaller *x*. It can be noticed that samples M2b, M3a and M3c showed a decrease in intensity on sextet corresponding to B-sites, resulting in a decrease of the stoichiometry. This result can be attributed to the addition rate of the ferrous solution, which has to be controlled (0.8 mL/s) in order to obtain a more stoichiometric oxide, like sample M3b.

Table 2 Hyperfine Parameters of synthetized magnetites

Sample	*Component*	B_{hf} *(T)*	*δ (mm/s)*	ΔE_Q *(mm/s)*	*Area (%)*	x^*
M1	*Sextet 1*	48.9	0.15	0.0	16.9	±0.06
	Sextet 2	45.9	0.54	0.0	53.2	
	Sextet 3	38.0	0.26	-0.27	29.9	
M2	*Sextet 1*	48.7	0.26	0.0	47.0	0.073
	Sextet 2	45.7	0.66	0.0	50.6	
	Sextet 3	38.6	0.26	-0.27	1.0	
	Sextet 4	28.1	0.27	-0.26	1.4	
M2a	Sextet 1	48.6	0.16	0.0	31.8	0.029
	Sextet 2	45.8	0.56	0.0	47.8	
	Sextet 3	37.9	0.25	-0.21	20.3	
M2b	Sextet 1	48.5	0.28	0.0	41.4	0.050
	Sextet 2	45.7	0.64	0.0	53.1	
	Sextet 3	37.4	0.25	-0.18	5.4	
M3	*Sextet 1*	48.9	0.28	0.0	38.3	0.020
	Sextet 2	45.7	0.67	0.0	61.7	
M3a	*Sextet 1*	49.0	0.16	0.0	39.8	0.103
	Sextet 2	45.9	0.56	0.0	34.1	
	Sextet 3	38.5	0.25	0.0	29.1	
M3b	*Sextet 1*	49.0	0.16	0.0	35.7	0.012
	Sextet 2	45.9	0.55	0.0	61.4	
	Sextet 3	37.7	0.26	-0.29	2.8	
M3c	*Sextet 1*	48.9	0.15	0.0	43.8	0.087
	Sextet 2	46.0	0.55	0.0	42.4	
	Sextet 3	39.6	0.30	-0.18	13.8	

$^*x$: oxidation parameter. $x = (2R-1.06)/(5.3+6R)$

For clarity, figure 2 shows the amount of goethite found in all the obtained samples calculated from the Mössbauer spectra (Figure 1 and Table 2). Remarkable differences in the amount of goethite were observed depending on the method of synthesis and the rate of addition of the reactive solutions. Method M1 gives the highest amount of goethite (~30%), probably due to differences on co-precipitation kinetics of Fe^{2+} and Fe^{3+} ions, giving as result a stoichiometric changes in balance, which are favorable for the oxi-hydroxide α-FeOOH formation. When the ferrous solution is added to the oxidizing/alkaline solution (M3), pure and stoichiometric magnetite was obtained in comparison to that when oxidizing/alkaline solution was added to the ferrous solution (M2). Moreover, when a solution of PEG and oxidizing/alkaline (M2a and M3a) was used at 0.2 mL/s, independently of the order of addition, an increase on the amount of goethite was observed.

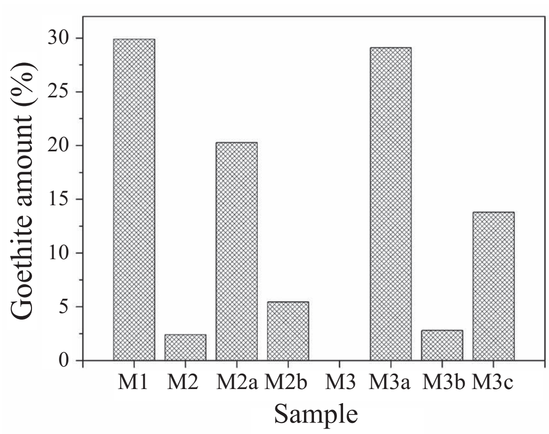

Figure 2 Amount of goethite in samples

An increase of the viscosity seems to promote the oxidation process of Fe^{2+} to Fe^{3+} favoring the formation of additional phases like goethite. Further decrease in the amount of goethite (3%) was observed for an addition rate of 0.8 mL/s (M3b) and an increase up to about 14% was observed for M3c (1.6 mL/s).

It is worth noting that the methods M2 and M3, despite being very similar in terms of procedure, it appears that just changing the order in the addition of the solutions resulted in substantial changes in the stoichiometry and purity of the obtained magnetites. This may be due to the fact that on method M3 each drop of Fe^{2+} solution is oxidized immediately in the right ratio 1:2 upon making contact with the solution of NaOH and $NaNO_3$. In method M2, by adding the oxidizing/alkaline solution to the Fe^{2+}, the transformation process is much localized at the top of the solution and the concentration of Fe^{2+} decreases in the surroundings of the drop. In this case more Fe^{2+} needs to contact the oxidizing agent in order to the reaction to take place gradually.

Figure 3 shows the particle size distribution obtained by light scattering from the dispersions. As the particles in ethanol/PEG were not completely stable, this technique gave information mainly about aggregation and sizes of the bulky particles (see TEM below). Excepting samples M2a and M3a (alkaline/oxidative solution containing PEG and addition rate at 0.2 mL/s) the size distribution of the magnetites was bi- and tri-modal. In general, it was found particle sizes between 1 and 10 mm, being 1 mm the most common size. Samples M3b and M2b (Figure 3d and Figure 3g) showed particle size distributions between 0,1 and 1 mm, with greater percentage at 0,1 mm for the oxide obtained using method M3b. It may be noted that the way and rate of addition of solutions, as well as its composition (with or without PEG), had influence both in purity of magnetite and in the size and aggregation of the particles. Samples without PEG (M1, M2, M3) showed particle size between 1 and 10 mm; however samples with PEG in the oxidizing/alkaline solution (M2a, M3a) exhibited particle sizes closer to 1 mm. On the other hand, samples with PEG in the ferrous solution gave particles sizes of 0,1 and 10 mm, being the smallest for those in which the solution was added slowly (M3b).

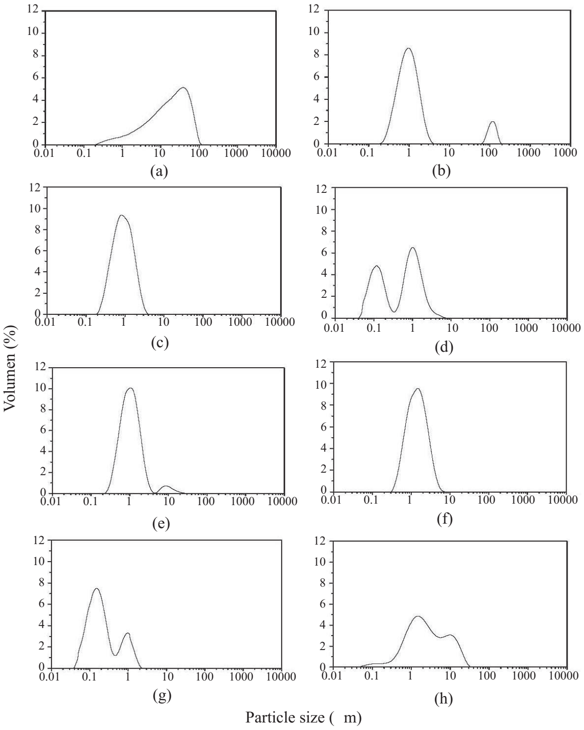

Figure 3 Particle size distribution. (a) M1, (b) M2, (c) M2a, (d) M2b, (e) M3, (f) M3a, (g) M3b, (h) M3c.

Although the observed particle distribution by light scattering was found to be in the micrometer size due to aggregates, TEM images contribute to validate the individual size of the particles. Figure 4 shows the transmission electron micrographs of samples M1, M2a y M3b.

TEM images showed particle sizes much less than 100 nm for sample M1 (about 10 nm). This is in agreement with the literature for magnetites obtained from Fe^{2+} and Fe^{3+}[17,24]. Particles at around 100 nm were obtained for sample M3b, similar to the result obtained by particle size distribution for the same sample. On light scattering analysis, the second peak is, in general, associated to aggregation, as was also confirmed by TEM. The individual particles of nano-magnetites tend to aggregate by formation of strong magnetic dipole-dipole interactions in order to reduce the surface energy of its high surface area/volume ratio [22]. It has been suggested in the literature that the presence of PEG prevents the aggregation of nanoparticles into larger particles and could kinetically control the growth rates of various crystalline faces affecting the diffusion rate of Fe^{+3} on the surfaces of Fe_3O_4 nanocrystallites and their epitaxial growth [25]. As showed in Figure 4, for M2a and M3b, PEG helped to dispersed the magnetite particles in both cases, however in terms of particle size and distribution the order of addition of the reagents had a more important effect for each sample, as observed by TEM and light scattering.

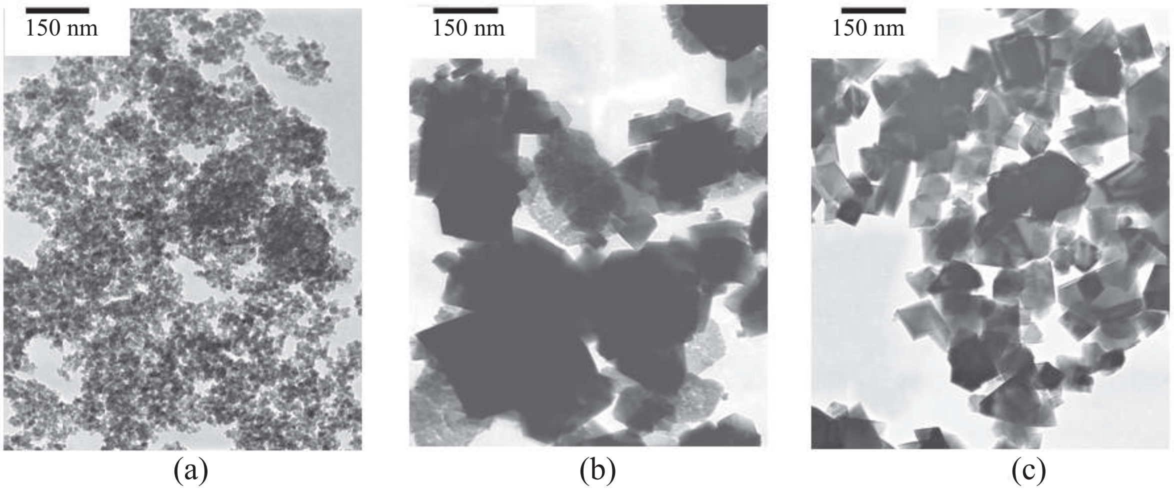

Figure 4 TEM images. (a) M1, (b) M2a, (c) M3b

Conclusions

It was verified, that the order and rate of addition of the reactive solutions and the presence of PEG as dispersant has a major effect on the purity, stoichiometry and particle size of the obtained oxides. In general, as expected, the size of the particles decreased when used PEG as dispersant; however its presence affected the purity of the oxides and favored the formation of goethite. Highly pure magnetite was obtained by adding the iron solution on the alkaline/oxidizing (M3), however for this sample the average particle size is expected to be higher than 200nm according to the light scattering measurements. On the other hand the magnetite M3b obtained by adding the ferrous solution to the alkaline/oxidizing solution with PEG presented both interesting particle size (higher than 40 nm) and relative good purity (about 2.8% of goethite). Even though co-precipitation method (M1, Fe^{2+}/Fe^{3+}), exhibited smallest particle size (~ 10 nm), from Mössbauer analysis can be deduced that is not a highly pure magnetite.

Acknowledgements

The authors wish to acknowledge financial support by Excellence Centre of Novel Materials –CENM- and COLCIENCIAS.

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