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Journal of Magnetism and Magnetic Materials 149 (1995) 6–9

Journal of magnetism and magnetic materials

Synthesis of very fine maghemite particles

A. Bee *, R. Massart, S. Neveu

Laboratoire de Physicochimie Inorganique, URA 1662 Structure et Réactivité des Systèmes Interfaciaux, Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris, France

Abstract

The effect of citrate ions on the growth of magnetite particles is investigated. 'Ultrafine' particles have been obtained (diameter of the order of 20 Å) that were converted to maghemite. The characterisation of the maghemite particles by various techniques (X-ray diffraction, transmission electron microscopy, magnetic measurements) is described.

1. Introduction

The effects of several organic anions such as carboxylate and hydroxyl carboxylate ions on the formation of ferric oxides or oxihydroxides have been studied extensively [1–3]. In particular, citrate ions are known to interfere with the formation and growth of these oxides [4–6].

In the present work, the changes introduced by the addition of various amounts of citrate ions on the size of γ-Fe_2O_3 particles are investigated. In absence of citrate, the typical size of the maghemite particles is about 8 nm. With citrate ions present, the size can be as small as 2 nm. Ferrofluid made with the small magnetic particles thus obtained could be suitable for biomedical applications. In particular, in vivo, the small size of these particles enables them to cross the endothelial barrier and so to reach more various target cells [7].

This paper describes the synthesis of maghemite particles with a controlled average size and the characterisation of the material obtained. The synthesis is based on a coprecipitation of Fe(II) and Fe(III) salts in an alkaline medium [8] in the presence of citrate ions.

2. Experimental procedure

2.1. Synthesis of γ-Fe_2O_3 particles

The maghemite particles are synthesized according to a method described elsewhere [8]. Concentrated ammonium hydroxide (250 mL, 11 mol L^{-1}) is added to an acidic aqueous solution of iron(II) chloride and iron(III) chloride ($[Fe_{total}] = 0.13$ mol L^{-1} with $V_{total} = 3.8$ L and $[Fe(II)]/[Fe(III)] = 0.5$) containing various amounts of citric acid trisodium salt. The molar ratio of citrate to metallic species (FeII + FeIII), denoted R, varies from 0 to 10%. The precipitate, consisting of anionic magnetite particles (Fe_3O_4), is isolated by centrifugation and washed twice by stirring for 10 min in distilled water. The precipitate is then stirred in a solution of nitric acid (400 mL, 2 mol L^{-1}). The magnetite particles obtained after another centrifugation are then oxidized to maghemite at 90°C for 30 min by ferric nitrate (600 mL, 0.34 mol L^{-1}), isolated again and peptised in water. The pH of the resulting suspension is about 2. The oxidation step is superfluous for the smallest particles.

2.2. Characterisation of the particles obtained

Powder X-ray diffractograms are obtained with an X-ray diffractometer (Philips PW1130) using Co Kα radiation ($\lambda = 1.7905$ Å). The average crystallite size (d_{RX}) of the particles prepared with different amounts of citrate ions is determined from the linewidth of the (3 1 1) plane reflection, using the Scherrer equation.

The morphology and size of the particles are observed by transmission electron microscopy (Jeol 100CX2).

The volume fraction ϕ of magnetic material was calculated from the iron content (determined by chemical analysis) assuming all iron to be present as γ-Fe_2O_3.

The magnetisation measurements are directly performed on a predetermined volume of ferrofluid using a vibrating sample magnetometer. The set-up of the apparatus is described elsewhere [9]. Curves of magnetization M versus H allow the determination of the magnetic characteristics of the particles (average magnetic size d_M and the saturation magnetisation M_s). For fluids with a given volume fraction in magnetic material ϕ, the saturation magnetisation of the magnetic material of the particles $m_s = M_s/\phi$ is obtained and compared with $\overline{m}_s$, the saturation magnetisation of the bulk γ-Fe_2O_3 material ($\overline{m}_s = 360$ kA m^{-1}). Determination of m_s and d_M, using the whole magnetisation curve, cannot be achieved for the smallest

* Corresponding author. Fax: +33-44 27 36 75.

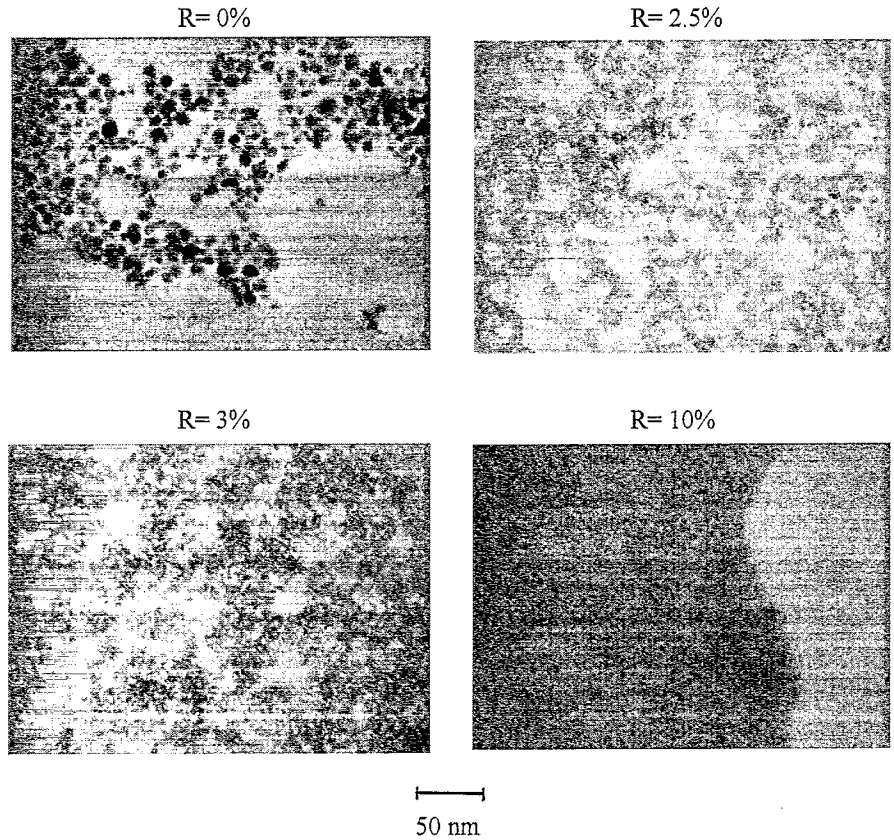

Fig. 1. Electron micrographs of maghemite particles prepared in the presence of citrate ions.

particles ($d_M \leq 3$ nm) as for these samples saturation is not reached at the maximum field of 1 T.

3. Results

Typical electron micrographs obtained for γ-Fe_2O_3 particles prepared with various concentrations of added citrate are presented in Fig. 1.

The particles are roughly spherical and polydisperse. Their size decreases with increasing concentration of citrate. Without citrate, the mean diameter is about 8 nm. For low proportions of citrate ($R \leq 2\%$) the size decreases only gradually with R, but for $R > 2\%$, the decrease is rather strong. For $R = 3\%$, the size is about 2 nm. Above 4%, agglomerates of very fine particles are formed.

Fig. 2 shows how the powder X-ray diffractograms change with the addition of citrate. The peaks are broadening with increasing R. Assuming that this broadening of the diffraction peaks reflects only the decrease of crystallite size, d_{RX} can be evaluated from the peak due to the (3 1 1) plane reflection; d_{RX} is plotted versus R in Fig. 3. For the smallest particles ($d_{RX} \leq 2$ nm), d_{RX} cannot be obtained.

Magnetic measurements allow the determination of m_s

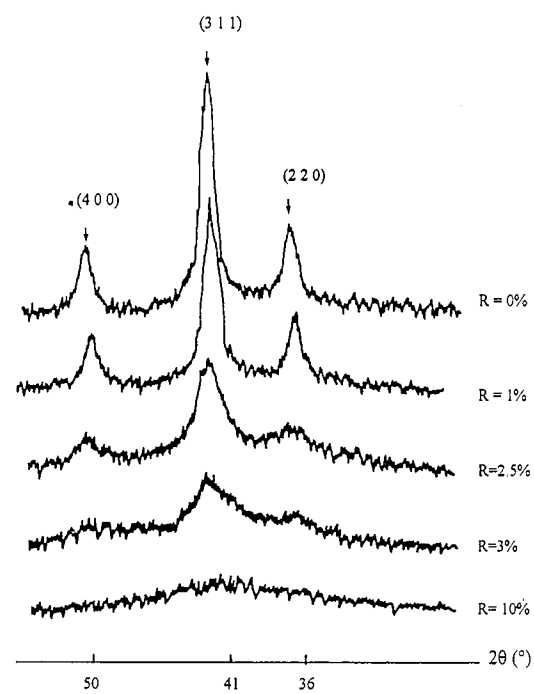

Fig. 2. Powder X-ray diffractograms of maghemite particles prepared in the presence of citrate ions.

Table 1
Values of sizes and m_s for maghemite particles prepared with citrate ions

	d_{RX} [nm]	d_M [nm]	$\phi \times 10^2$ [mol L^{-1}]	M_s/ϕ [kA m^{-1}] (G)	$m_s/\overline{m}_s$ [%]
0	8.2	6.9	1.97	231 (2909)	64
1	7.9	5.9	0.52	249 (3130)	69
2	6.6	4.4	1.52	224 (2817)	62
2.5	4.7	3.5	1.76	**143 (1796)**	–
3	2.2	–	2.78	**78 (978)**	–
4	2.3	–	0.46	**42 (529)**	–

(Table 1). In the range where m_s can be determined, it is found to be independent of the particle size except for the smallest particles ($d_M < 5$ nm). In order to confirm the latter result, magnetic measurements using a stronger field will be done in the future. The experimental value of m_s is about 65% of the saturation magnetisation of bulk γ-Fe_2O_3 material. This means that the magnetic order is not perfect in the whole particle. For $R > 2\%$ the saturation magnetisation is not reached and the boldface values of Table 1 are those obtained at 1 T.

The size values obtained from the magnetisation curves are in good agreement with the above results. The curve of d_M versus R is shown in Fig. 3. The standard deviation is about 0.3 for all the systems studied.

4. Discussion

Organic ions are known to affect the formation of metal oxides or oxihydroxides through the two following processes [1]:

(1) the chelation of these ions with metal ions preventing nucleation;

(2) the adsorption of these ions on the nuclei produced by hydrolysis inhibiting the growth of the nuclei.

Kandori and co-workers [1] have observed a maximum value for the size of β-FeOOH particles in the presence of EDTA at a low concentration. This phenomenon was interpreted as an inhibition of nucleation: the first process dominates. This leads to the formation of larger particles because the number of nuclei formed decreases, and after nucleation only particle growth takes place. In our experiments the second process appears to dominate, citrate ions adsorbed on the nuclei inhibiting the growth of particles. For a value of $R > 2\%$, the size of maghemite particles decreases drastically. This value of R is in good agreement with the number of citrate ions adsorbed on the surface, which was obtained in a previous study on the adsorption of citrate ions on the surface of maghemite particles. For example, for a particle size of 8 nm, the maximal amount of adsorbed citrate per mole of iron is about 2% [10]. This adsorption at the oxide surface is based on a ligand exchange where the surface hydroxyl groups are replaced by the adsorbed anion. The formation of surface complexes requires both deprotonated carboxy and α-hydroxy groups [11].

The presence of citrate ions in solution during the crystal growth of γ-Fe_2O_3 affects the size of the resulting particles as well as their chemical properties. Notably, the pH dependence of the stability of the magnetic fluids obtained is changed. The peptisation of such particles by changing the pH is followed, the experimental set-up is described elsewhere [10]. A usual ferrofluid ($R = 0\%$) is stable for pH < 5 (acidic ferrofluid) and for pH > 8 (alkaline ferrofluid). For a value of $R \geq 3\%$, the ferrofluid obtained by peptisation of the small particles is stable from pH 3.5 to 11. In an acidic medium, the two free carboxylate functions of the adsorbed ligand are protonated (pK = 4.30, 5.65); the particles therefore bear no charge and flocculate. Nevertheless, the ferrofluid is stable in a physiological medium (pH 7) in the anionic state, and so can be used for biomedical applications.

5. Conclusion

Magnetic fluids with particles smaller than 3 nm, which, thus far, were difficult to make, can be produced in the presence of citrate. These fluids are used for studies of

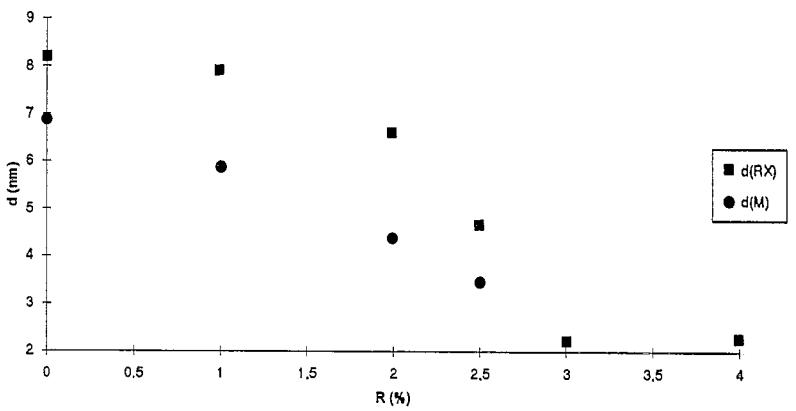

Fig. 3. Crystallite size d_{RX} (■) and magnetic size d_M (●) versus R.

phase transition phenomena, and also allow ionic magnetic fluid stable in presence of great amounts of salt to be obtained [12]. They will also be used for incorporation in complex colloidal systems for which the interlamellae distance is small and which may accept only very small grains [13].

Anyway, for any medical applications, a very strict control of size is necessary as this latter may be at the origin of the dispersion biodistribution of the particles, and small magnetic particles are at the present time extensively studied by specialists in medical imaging.

Acknowledgements: We are greatly indebted to Mrs M. Carpentier for technical assistance and to Mr M. Lavergne for the transmission electron microscopy (Groupement Regional de Mesures Physiques de l'Université Pierre et Marie Curie).

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