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Wet milling *versus* co-precipitation in magnetite ferrofluid preparation

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Abstract: Various uses of ferrofluids for technical applications continuously raise interest in the improvement and optimization of the preparation methods. This paper deals with the preparation of finely granulated magnetite particles coated with oleic acid in hydrocarbon suspensions following either chemical co-precipitation from iron salt precursors or wet milling of micron size magnetite powder with the goal to compare the benefits and disadvantages of each method. Microstructural measurements showed that both methods gave similar-sized magnetite particles of 10–15 nm. The wet-milled magnetite suspension had a higher saturation magnetization than that obtained in the relatively rapid co-precipitation synthesis. The different efficacies of ferrophase incorporation into kerosene could be related to the different mechanisms of oleic acid bonding to the surface of the nanoparticles. Comparative data showed that wet milling represents a viable alternative to the traditional co-precipitation method since despite of longer processing time, the impact of chemicals on the environment and remnant water in the final product could be avoided.

Keywords: magnetite nanoparticles; kerosene suspensions; X-ray diffraction; TEM; magnetometry; IR spectra.

INTRODUCTION

Magnetic iron oxide nanoparticles and their fluid dispersions have been of scientific and technological interest since the 1960s. One of the most widely used and explored technique for the synthesis of submicron magnetic particles is the co-precipitation method.^{1–8} Based on this simple and efficient procedure, condensing divalent and trivalent iron salts in reactions with hydroxide bases, magnetite crystalline nanoparticles form with a relatively broad size distribution. Due to their magnetic moments, these particles tend to aggregate. Agglomeration

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could be prevented by using electrostatic or steric stabilization. Oleic acid was proven to be the best surfactant that forms a stabilizing shell around the magnetite particles due to its highest affinity to the surface of superfine magnetite compared to other surfactants.^{5–8} The particle size and morphology can be changed by varying the parameters of synthesis, such as temperature, pH, concentration of components^{2–3} or by using different surfactants for the stabilization in organic solvents.⁴ A hydrophilic surface coating is used when aqueous dispersions are required for biomedical applications.^{4,9,10}

Although small particles can be easily achieved by chemical precipitation, it has been shown that, in practice, the mechano–chemical method of wet milling is also a simple, efficient and environment-protective method for obtaining finely granulated magnetic ferrite particles.^{11–14} In spite of the possible drawback of long grinding times, the mechano–chemical technique offers certain advantages which may place it as a useful method for obtaining nanometric particles in colloid suspensions, in particular, ferrofluids.

In this study, soft magnetic colloids were prepared by the two methods, and their microstructural and magnetic properties are comparatively discussed herein.

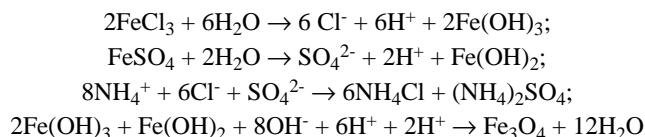
EXPERIMENTAL

Synthesis by co-precipitation

Ferrous sulphate heptahydrate (99 %), ferric chloride hexahydrate (99 %), 25 % ammonium hydroxide, oleic acid (90 %), hexane (95 %) and kerosene reagent grade were purchased from Sigma–Aldrich and used without further purification. Distilled water was deionised prior to use.

The first colloidal sample, S1, was obtained by chemical precipitation of magnetite in a multistep process (Fig. S-1 of the Supplementary material to this paper), starting from stoichiometric amounts of aqueous solutions of ferric and ferrous salts that were condensed by reaction with excess base (*i.e.*, ammonium hydroxide NH₄OH) to form magnetite nanoparticles.

Following the Massart procedure,¹⁵ 300 mL of 1 mol L⁻¹ FeSO₄·7H₂O solution and 300 mL of 2.8 mol L⁻¹ FeCl₃·6H₂O solution were heated at a temperature of 80–85 °C (under atmospheric conditions) and then 200 mL of 25 % NH₄OH solution – as a precipitation agent – was added drop-wise under continuous stirring. A 20 % excess amount of NH₄OH was used to ensure the formation of magnetite nanoparticles and no other iron oxides. About 30 min after the co-precipitation reaction, phase separation was observed. Following magnetic decantation and repeated washing with deionised water, to remove salt residues, the ferrophase was further washed with ethanol to remove water traces, and subsequently filtered on a paper filter. The main chemical reactions could be given as:



Thus, the mixed iron oxide Fe_3O_4 resulted from intermediate iron hydroxides in the aqueous reaction medium. Next, the magnetite particles were coated with oleic acid 1:6 (V/V) dispersed in hexane, the mixture being heated up to 80 °C under continuous stirring. After hexane evaporation, kerosene was added as the dispersion fluid, with continuous stirring for 60 min.

Wet milling preparation procedure

The second sample, S2, was obtained by mechano-chemical processing of micrometric magnetite particles (Fig. S-2 of the Supplementary material) in a vibrating ball mill.

The raw material was industrial magnetite powder (residual product from charcoal processing), with an average particle diameter of 1 μm , prepared by hydrothermal method, that was milled within a laboratory device with four sealed hardened steel cups, of about 700 mL each containing 4.5 and 13.5 mm diameter steel balls; mixing was realized by using a 380V/50Hz engine with a power supply of 1.1 kW at rotation speed about 900 rev min^{-1} . About 400 mL kerosene/oleic acid in the ratio of 6:1 (V/V) were put in every cup over an excessive amount of magnetite and wet milled for about three thousand hours (daily cycles of 12 h milling / 12 h resting). The oleate-coated ferrophase suspended in kerosene was collected from the top of the steel cups after 24 h decantation, while excess ferrophase remained as sludge at the bottom. Further centrifugation was realized at 3500 rev min^{-1} for 10 min.

Physical characterization

Microstructure and magnetic properties of the magnetic colloid samples were characterized by transmission electron microscopy (TEM), powder X-ray diffraction (XRD), magnetometry, and infrared spectrophotometry (FT-IR).

The TEM measurements were performed on a Philips CM100 Biotwin instrument, with 80 kV voltage and 180,000 magnification. The original colloid samples were diluted with toluene, a few droplets were deposited on a carbon-coated copper grid and left to dry over night protected from environmental particle contamination.

The X-Ray powder diffraction patterns were recorded on a Bruker D8 Advance instrument using CuK_α radiation in Bragg-Brentano geometry, with a scanning interval of 0.02°. The fluid samples were deposited on glass plates and dried. After drying, the remaining surfactant gave rise to strong background scattering, thus long measuring times of 14 h were required.

Magnetization investigation was carried out by a Gouy magnetometer¹⁶ at room temperature using an air-tight nonmagnetic cylindrical sample holder of 3 mm in diameter and 25 mm in height, placed perpendicularly to the magnetic field.

The volume fraction of the ferrophase was calculated from the density values of the ferrofluid, kerosene and magnetite. Densities were measured at room temperature by pycnometric method.

The infrared absorption spectra were recorded in KBr discs using Bruker Vertex 70 FT-IR spectrometer.

RESULTS AND DISCUSSION

Electron microscopy

TEM images are shown in Fig. 1a and b. Mainly, quasi-spherical particles were seen in all recorded TEM images for both samples. The surfactant coating gave negligible contrast compared to iron oxide, hence the size of the observed

particles corresponded to the size of the magnetite cores. Better uniformity of the nanoparticles spreading on the support grid was obtained for the wet-milled sample, while groups of closely disposed particles were observed for the co-precipitated sample.

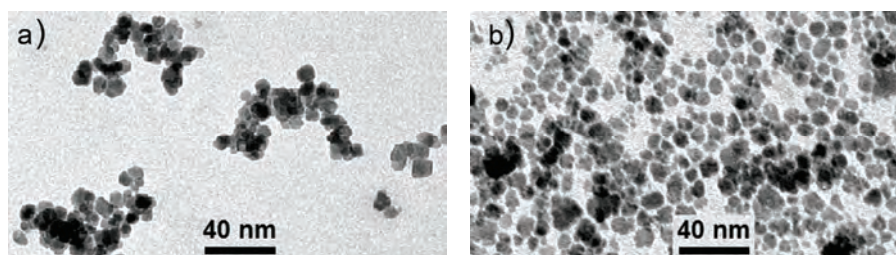


Fig. 1. TEM images of samples: a) S1 and b) S2.

Using several images for every sample, histograms of the particle size distribution were constructed by the manual counting of over a thousand particles (Fig. 2a and b). Both graphs have asymmetric shapes, the distribution tails extending up to 25 nm, while most of the particles were between 5 and 15 nm in diameter. The largest frequency corresponds to 10 nm diameter in sample S1 and to 7 nm in sample S2.

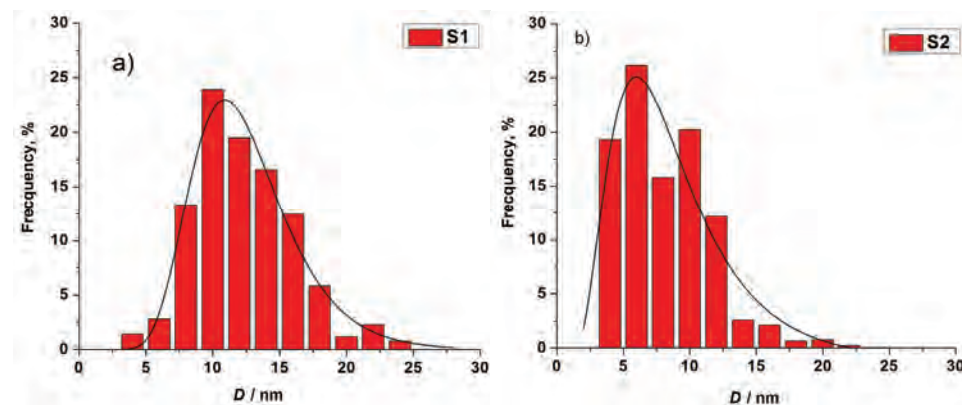


Fig. 2. Size distributions of magnetic nanoparticles obtained by a) the co-precipitation route S1 and b) the mechano-chemical route S2. The solid lines are the fits to the log-normal size distribution.

Log-normal size distribution curves were found to fit fairly well each data set. The mean values of the physical diameter D_{TEM} as well as the standard deviation σ_{TEM} of the fitted log-normal distributions are given in Table I.

TABLE I. Physical and magnetic parameters of the ferrophase in the two prepared ferrofluids

Sample	ϕ / %	D_{XRD} / nm	σ_{XRD} / nm	D_{TEM} / nm
S1	2.3	9.1	0.30	11.7
S2	5.6	8.7	0.30	7.6
	σ_{TEM} / nm	M_{S} / kA m ⁻¹	D_{M} / nm	σ_{M} / nm
S1	0.28	3.6	7.7	0.39
S2	0.38	13.9	5.4	0.44

X-ray diffraction

The X-ray diffraction data (Fig. 3) for both samples revealed the typical spinel structure of magnetite with a lattice parameter 0.835 nm, as obtained by Rietveld refinement. No traces of impurities were registered. The line shape was modelled as originating from isotropic particle size broadening using the Fullprof program suite. The effective crystallite sizes of 9.1 and 8.7 nm were estimated for S1 and S2 and they were in agreement with the average size of the particle populations measured by TEM.

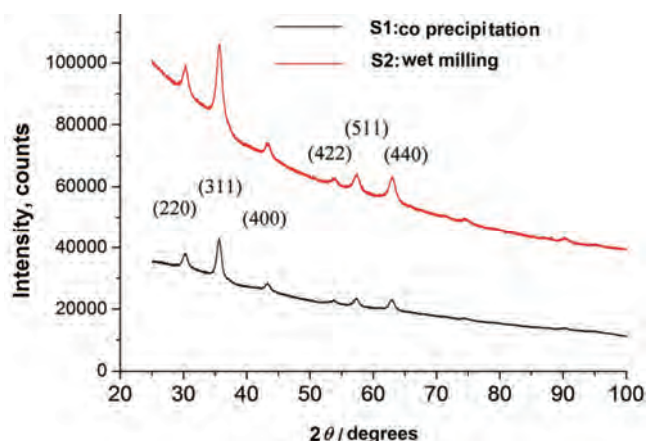


Fig. 3. X-ray diffraction patterns of the dried samples S1 and S2.

Pycnometry

The ferrophase volume fraction, ϕ , was calculated from the densities of the constituent materials according to formula:

$$\phi = \frac{(\rho_{\text{F}} - \rho_{\text{L}})}{(\rho_{\text{S}} - \rho_{\text{L}})}$$

where ρ_{F} , ρ_{L} and ρ_{S} are the densities of the ferrofluid, the carrier liquid (kerosene) and of the solid phase (magnetite), respectively. The results revealed that the wet milling procedure resulted in a higher efficiency of magnetite incorporation in kerosene; the volume percentage of magnetite in the wet milling ferro-

fluid S2 being higher than in the co-precipitation fluid S1, *i.e.*, 5.6 compared to 2.3 %.

Magnetometry

Superparamagnetic behaviour without hysteresis loop in the magnetization curves was observed by recording the sample magnetization, M , as a function of the applied magnetic field H up to 500 kA m^{-1} , as shown in Fig. 4. A higher saturation magnetization was obtained for the ferrofluid prepared by wet milling, in accordance with the higher ferrophase volume fraction determined by the pycnometric method. Analyzing the magnetization data, the magnetic moments of the individual particles could be obtained.

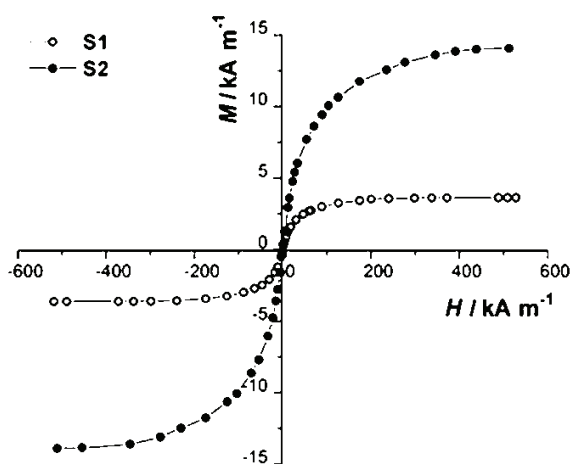


Fig. 4. Magnetization data for the fluid samples S1 and S2 at room temperature.

The magnetization data were modelled using the Langevin function:

$$M / M_s = L(x) = \coth x - \frac{1}{x}$$

where $x = \mu H / k_B T$, in which H is the applied field, k_B is the Boltzmann constant and μ is the magnetic moment of an individual particle, given by $\mu = m_S \pi D_M^3 / 6$, where D_M is the particle magnetic size and m_S is the saturation magnetization of bulk magnetite ($0.48 \times 10^6 \text{ A m}^{-1}$). The magnetic response of the population of particles obeying a log-normal size distribution was fitted to the measured data; integration was performed over the whole range of particle sizes.^{3,4,11} This approach allowed the size distribution to be described by two parameters: the mean value of the particle magnetic size D_M and the width σ_M of the distribution curve. It can be seen (Table I) that the D_M values were smaller than the D_{TEM} ones. The non-magnetic surface layer of the nanoparticles usually results in a smaller magnetic size than the physical size by 1–2 nm.^{4,6} The dimensional parameters of the nanoparticles, the saturation magnetizations of the fluids and

the ferrophase volume fractions are presented in Table I. The three characterization techniques show that the two samples contained magnetic nanoparticles with rather similar shape and size distributions, the width of the latter being about 0.4, which is typical for magnetite particles prepared by co-precipitation.^{3,4}

Vibrational spectroscopy

The infrared spectra of S1 and S2 together with the spectra of magnetite powder and oleate are shown in Fig. 5a and b. The magnetite skeleton vibrations are seen at the lowest wave numbers, *i.e.*, toward 500 cm^{-1} but also at around 3500 cm^{-1} (Fig. 5a). In the spectrum of the S1 sample prepared by the co-precipitation method, the vibration band at about 3500 cm^{-1} could also arise from OH stretching mode of water molecules (Fig. 5b), this being a consequence of possible traces of water from the technological step of ferrophase synthesis in aqueous medium. The relative diminution of the magnetite band at 3500 cm^{-1} when passing from magnetite powder (Fig. 5a) to S1 and S2 magnetite suspensions (Fig. 5b) could be due to oleate ion bonding to the iron ions of the ferrophase. Moreover, if the intensity of the 3500 cm^{-1} vibrational mode remained relatively higher in the S1 co-precipitation sample compared to the S2 wet milling sample (Fig. 5b), this could be the consequence of the possible lower efficiency of oleate ion bonding in co-precipitation method as well as of the higher content of traces of water arising from the technological step of ferrophase preparation in aqueous medium (missing in the case of the mechano-chemical procedure).

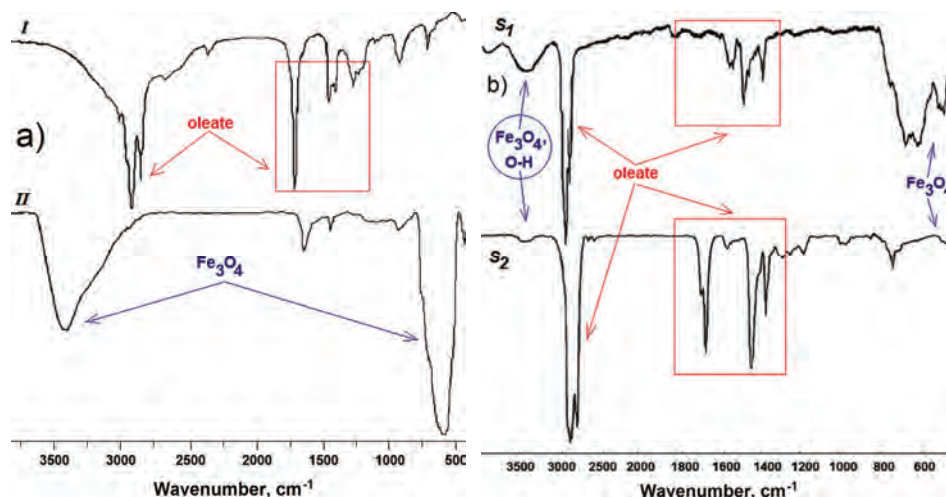


Fig. 5. Vibration spectra of a) the ferrofluid components: magnetite and oleate and b) the samples S1 and S2.

It could be assumed that the stretching vibrations of the C–H bonds of the oleate ion, both symmetric and asymmetric ones, at about 2950 cm^{-1} (Fig. 5a) as well as those from $1500\text{--}1700\text{ cm}^{-1}$ range (carboxyl stretching and bending vibrations) were slightly shifted toward smaller wavenumbers for the colloidal suspensions (Fig. 5b) as a consequence of the magnetite core – organic shell interactions. In addition, the relatively higher intensity of these vibration bands in S2 compared to S1 suggests the higher efficiency of ferrophase coating in the mechano–chemical procedure when water traces are theoretically missing.

The band with the highest wavenumber from this group could be assigned to the deformation vibration of hydroxyl from the carboxyl group, the corresponding interaction being formed during oleate attachment. The remarkably higher relative intensity of this band in the spectrum of the S2 sample compared to that in the spectrum of S1 suggests that possibly non-bound oleic acid remained in the final sample. The amount of the excess surfactant could be decreased by improving the preparation protocol of the wet milling procedure to include an additional dialysis step – which will be included in future investigations.

Mechanisms of co-precipitation and the mechano–chemical synthesis

In the case of conventional chemical route, the intimate contact of surfactant molecules with nanoparticles depends in principal on two factors: heat supply and stirring efficacy in the sample volume. However, neither of these is easy to control: during intensive heating, the hydrocarbon dispersion liquid evaporates and needs to be carefully added in new small aliquots, while the stirrer makes inhomogeneous contacts with the parts of the suspension volume during stirring. An inert gas atmosphere is required to avoid oxygen reaction with iron during the long stirring times.

Regarding the mechanochemical method, it should be mentioned first that the high kinetic energy of the milling balls favours the occurrence of reactions at temperatures lower than those required for conventional syntheses.^{17,18} During the milling procedure, the innumerable ball–particle collisions favour chemical adsorption of surfactant each time at a different small site (close to 10^{-9} m^3)¹⁹ of a given particle. Inelastic collisions between the particles and the balls fractures the particles leading to the formation of fresh interfaces between the reaction phases by means of dynamic deformation, fracturing, and cold welding, while energies of almost 1 J could develop during intervals of $10^{-4}\text{--}10^{-5}\text{ s}$.^{18,19}

According to Guler and Evin,²⁰ the milling intensity is an important parameter in the occurring reactions. Maurice and Courtney²¹ developed a computational modelling stating that the deformation size in a powder particle that is trapped between balls could be expressed as a function of the distance from the particle centre to the contact area, the relative impact speed, the ball density and the hardness of the particle. The frictional heat dissipated over collision areas is

transferred from balls to particles that empowered the exposed iron ions to react with local surfactant molecules. The ball surface could also be affected but the steel balls release only iron ions; in this respect, it could be hypothesized that such iron ions would also attach to oleate ions so that free oleate vibrational modes are overlapped with those of oleate–iron and oleate–magnetite particles, affecting the intensities in the infrared absorption spectrum.

CONCLUSIONS

Taking into account all above results, it may be concluded that the two preparation methods yield magnetic colloid particles having rather similar quasi-spherical shape and sizes of around 10 nm. The volume fraction of the ferrophase and the saturation magnetization of the colloidal fluids were different: the two times higher volume fraction and the slightly different size distribution of the particles resulted in more than three times higher saturation magnetization in the sample prepared by wet milling. These results show that the mechano–chemical method may be preferred in certain practical situations. With this method, no synthesis of magnetite is required, unlike in synthesis methods involving milling, in which mechanical milling is used for the formation of the ferrite phase from precursors. From this point of view, the process is simpler, as no chemical transformations occur except the bonding of the surfactant molecules to the magnetite surface. In certain cases, the long milling times could be an acceptable disadvantage, outbalanced by the higher efficiency of ferrophase incorporation by coating with oleate ions, and easy control of the particle size by varying the milling time.

SUPPLEMENTARY MATERIAL

Schematic presentations of the synthesis of magnetite are available electronically from <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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ИЗВОД

МОКРО МЛЕВЕЊЕ НАСПРАМ КОПРЕЦИПИТАЦИЈЕ – СИНТЕЗА МАГНЕТИТ-ФЕРОФЛУИДА

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Различите техничке примене ферофлуида доводе до пораста интересовања за унапређење и оптимизацију метода синтезе. У овом раду испитивана је припрема фино гранулисаних честица магнетита превучених олеинском киселином у суспензијама угљово-

дника након хемијске копреципитације из соли гвожђа као прекурсора и након мокрог млевења праха магнетита микронских димензија са циљем да се упореде предности и ограничења ове две методе. Микроструктурна мерења су показала да обе методе дају магентит сличне величине честица, 10–15 nm. Вишу вредност магнетизације при сатурацији показује суспензија магнетита добијена мокрим млевењем у поређењу са релативно брзом синтезом копреципитацијом. Различита ефикасност инкорпорације ферофазе у керозин може потицати од различитог механизма везивања олеинске киселине на површини наночестица. Упоредна анализа показује да мокро млевење представља практичну алтернативну традиционалној копреципитацији јер се, и поред дужег времена процесирања, може се избећи хемијски утицај на животну средину као и трагови воде у финалном производу.

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