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Dependence of the composition, morphology and magnetic properties with the water and air exposure during the Fe_{1-v}O/Fe₃O₄ core–shell nanoparticles synthesis

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Abstract The thermal decomposition of organometallic precursors in the presence of surfactants and a long-chain alcohol is a valuable method to synthesize magnetic nanoparticles (MNPs) because it provides good control of the final morphology and crystallinity of the magnetic material. These parameters, and consequently the magnetic properties, depend on several details of the experimental procedure of chemical synthesis. We have studied the role of the *predecomposition* step, heating the system to 373–393 K in inert gas flux, on the final composition and morphology of the system. By adding this intermediate step, we were able to produce MNPs with a Fe_{1-v}O/

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Centro de Investigación y Tecnología Química, UTN-CONICET, Ciudad Universitaria, 5016 Córdoba, Argentina Fe_3O_4 core-shell structure and sizes of 20–25 nm. When the same synthesis protocol was used skipping the *pre-decomposition* stage, monophasic MNPs of 11 nm with ferrite structure were obtained. These differences in the composition have a major effect on the resulting magnetic properties of MNPs, and are related to some by-reactions in the synthesis solution during the preparation procedure.

Keywords Core–shell nanoparticles · Magnetic nanoparticles · Iron oxide · Thermal decomposition synthesis · Wustite · Ferrite

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Introduction

In the early 2000s, the groups of Sun (Sun and Zeng 2002; Sun et al. 2004) and Hyeon (Park et al. 2004; Hyeon et al. 2001) reported the synthesis of magnetic ferrite nanoparticles by thermal decomposition of organometallic precursors in the presence of surfactants and a long-chain alcohol (hereafter referred as "the thermal decomposition method" for simplicity). Their method produced narrow size distributions and high crystallinity which in turn improved some magnetic properties of the magnetic nanoparticles (MNPs). Despite the seemingly apparent simplicity of this chemical route, the resulting materials have a final composition, morphology and magnetic properties that depend rather strongly on several subtleties along the chemical synthesis procedure, making difficult to attain good reproducibility. It has been reported that minor differences in the choice of the solvent (Park et al. 2004; Quiao et al. 2017), the precursor/surfactant ratio (Vargas and Zysler 2005), the heating rate (Lavorato et al. 2014) and other experimental parameters have strong impact on the obtained colloids. While aiming to produce magnetite Fe_3O_4 or maghemite γ -Fe₂O₃ nanoparticles, the reducing synthesis atmosphere can yield in the formation of wüstite phase (Fe_{1-v}O) with very different morphology and general properties (Hou et al. 2007). Wüstite is a Fe^{2+} -rich iron oxide phase that is paramagnetic (PM) at room temperature and develops antiferromagnetic (AFM) order below the Néel temperature $T_N = 198$ K (McCammon 1992). During the synthesis of iron oxide nanoparticles by thermal decomposition in octadecene under inert atmosphere, it is not unusual to obtain wüstite nanoparticle cores with ferrite shell due to an immediate oxidation (Khurshid et al. 2013; Lohr et al. 2019); therefore, the complete oxidation to ferrite has to be achieved through post-synthesis thermal treatment (Hufschmid et al. 2015). As it is well known, bimagnetic nanoparticles with a core-shell structure have different magnetic properties from those expected in single-phase ferrimagnetic (FiM) or antiferromagnetic (AFM) singledomain nanoparticles (Kavich et al. 2008; Sun et al. 2012). Several after-synthesis treatments are used to fully oxidize the particles to eliminate wüstite undesired phase. For instance, the addition of 1% oxygen in the reaction environment after the formation of wüstite nanoparticles was studied by Kempt et al. in 2016 (Kemp et al. 2016), showing almost complete oxidation of the system. Also, the addition of molecular oxygen during the synthesis was proposed by Unni et al. (Unni et al. 2017). Chen et al. (Chen et al. 2016) showed that a mixture of octadecene and di-benzyl ether as solvents gives some control on the final composition (regarding the Fe oxidation state) of the resulting material. In addition, the concentration and type of reagent also takes an important role on the reduction of iron (III) to iron (II) in 1-octadecene (Escoda-Torroella et al. 2021; Mourdikoudis and Liz-Marzán 2013). Bronstein et al. (Bronstein et al. 2011) found that the incorporation of a low (i.e. less than 1% wt) amount of water into the solvent resulted in an increased particle size dispersion. In fact, the size and shape of the core-shell wüstite-ferrite system depends on the nucleation/crystallization stages and oxidation process (Hou et al. 2007) and hydration of the organometallic precursors is known to affect this process (Cotin et al. 2018).

The effects of the initial step in which the solution is heated up to 373-393 K under inert gas flux or atmosphere, hereafter called as "pre-decomposition step" because it takes place previously to the complete decomposition of the oleates and nucleation, have not been studied so far in detail. Due to the complex chemistry behind the nanoparticle synthesis method based on the thermal decomposition of acetylacetonates precursors with by-reactions and by-products, its effects on the morphology, composition and consequently the magnetic properties and potential uses in technological applications of the particle are still not clear. The knowledge on the role of the "pre-decomposition step" in the synthesis and in the resulting material may allow the capability of a deeper control on the architecture and composition of synthesized nanoparticles in an atomic level, allowing the design of systems with different properties and multifunctional systems for several potential applications. In this work, we studied the influence of the so-called *pre-decomposition* step and of the in situ post-synthesis oxidation by the air entrance on the resulting phases of the process. Complete morphological, compositional and magnetic characterization on the synthesized magnetic nanoparticles has been performed to provide a deeper understanding of the chemical mechanisms involved.

Experimental

Synthesis

Four samples were prepared in a similar way by the thermal decomposition of the Fe³⁺ acetylacetonate $(Fe(C_5H_7O_2)_3-Fe(acac)_3,$ Aldrich 97%), all of them with using the same concentration of 11.3 mM dispersed in 40 mL of octadecene $(CH_3(CH_2)_{15}CH = CH_2,$ Aldrich 90%) containing 24.6 mM of oleic acid $(CH_3(CH_2)_7CH = CH(CH_2)_7COOH,$ Pan-Reac, PharmaGrade), 25.1 mM of oleylamine $(CH_3(CH_2)_7CH = CH(CH_2)_7CH_2NH_2, Aldrich 70\%)$ and 1.3 mM of 1,2-octanediol (CH₃(CH₂)₅CH(OH) CH₂OH, Aldrich 98%). A 3-neck flask was used with a sided neck for the N_2 (White Martins, 5.0) flux together with a sealed tube for the thermocouple, other vertical sided neck for a condenser and the central neck for mechanical stirring (~100 rpm) of the synthesis solution during all process for all samples. Supplemental Material S1 gives a representative schema of the apparatus used in the syntheses of the samples characterized. In order to study the byproducts formed during the pre-decomposition step, a modified apparatus was used in a new synthesis (with a representative schema also given in Supplemental Material S1), recovering the evaporated material at 393 K and 473 K to be analysed. Three samples labelled DH200, DH150 and DH030 were synthetized with a similar process: first, the solution was heated to 373–393 K during 30 min with a N_2 flux of 0.5 mL/ min and without the condenser in the pre-decomposition step. Then the system was closed with the condenser keeping the N2 flux, and the solution was heated up to 473 K with a temperature rate of about 3 K/min and kept at this temperature for~5 min. After that, the solution was heated up to the reflux condition (610–615 K) with a heating ramp of ~ 20 K/ min and it was kept in this temperature for 60 min. After this period, the heating source was removed to get a fast cooling of the solution. The condenser and the N_2 flux were removed at different temperatures for each sample: 473 K for DH200, 423 K for DH150 and 303 K for DH030. A fourth sample, called H030, was synthesized without the pre-decomposition step and without N₂ flux. For this sample, similar amounts of all reactants were used, but the condenser was kept during the whole synthesis, starting from room temperature, and the heating process was continued up to 473 K with a controlled increment of temperature (about 3 K/min) and without N₂ flux. After that, the procedure was similar to that used for sample DH030, with the reaction system kept isolated, and the N₂ flux was used during the whole cooling until 303 K. In order to obtain the recovered material from the evaporation, a synthesis with the same amounts of chemicals in a modified apparatus described in Supplemental Material S1 was performed, following the temperature ramp and N₂ flux condition of sample DH030. This last synthesis was used only to study the material evaporated between 393 and 473 K and the nanoparticles obtained were not characterized.

After synthesis, samples DH200 and DH150 were washed by adding 400 mL of ethanol (96%, Porta) to the synthesis solution in order to precipitate the particles by centrifugation (30 min with 14,000 rpm). After that, the precipitate was washed with a solution containing ethanol and acetone (99.9%, Sigma-Aldrich) in a ratio of 10:1, which was followed by centrifugation (30 min at 14,000 rpm) in 2-mL Eppendorf's tubes containing also 0.5 mL of chloroform and 1 mL of deionized water (0.5 mL of solution containing nanoparticles in each Eppendorf). After this procedure, the nanoparticles were kept in chloroform. Sample DH030 was stored in the synthesis solution at low temperature (246 K) to avoid subsequent oxidation process. Finally, sample H030 was magnetically extracted from the synthesis solution, which was made after adding 400 mL of ethanol, and stored in chloroform.

Characterization

Thermogravimetric (TGA) and differential thermal analysis (DTA) were performed simultaneously in a Shimadzu DTG-60H analyser to determine the organic mass percentage in the as-made nanoparticles. To establish this mass composition accurately is relevant for a precise measure of the mass magnetization of the nanoparticles. Therefore, each as-made powder sample was heated up to 1173 K with a heating rate of 3 K/min in Ar flux (100 mL/min), while the weight loss was measured, which corresponds to the amount of the organic compound in nanoparticles. TGA and DTA measurements were also used in order to determine the amount of water and volatiles in the initial solution. For this, a drop of the solution was measured with a temperature ramp of 2 K/min from room temperature to 383 K and held for 45 min in Ar flux.

Fourier transformed infrared (FTIR) spectra of the systems were measured in a uATR PerkinElmer Spectrum Two equipment in the range of 450–4000 cm⁻¹ with resolution of 4 cm⁻¹. To perform these measurements, a drop of solution was placed over the crystal of the uATR and dried with N₂ flow, resulting in a film of nanoparticles covering the entire crystal. For the measurements of the synthesis solution, a liquid recipient over the crystal was used. Baseline and uATR corrections were performed with software Spectrum from PerkinElmer.

Structural characterization was carried out using a PANalytical Empyrean powder X-ray diffractometer (Cu K α , λ =0.15418 nm). Samples were cleaned with hot acetone (313 K) during 24 h to remove the organic material and a zero diffraction sample holder was used in the measurement.

Transmission electron microscopy (TEM) and (HRTEM) images were high-resolution TEM obtained with a Tecnai F20 G2 (Thermo Fisher Scientific) microscope operating at 200 kV at room temperature. TEM grids with DH200, DH150 and H030 MNPs were prepared by dispersing dried powder samples in isopropanol and dropping the solution onto a carbon-covered grid. DH030 was prepared for TEM measurements by dropping the synthesis solution onto a grid and washing it by the immersion in ethanol at 323 K. For this, the oxygen diluted in ethanol was removed by heating to evaporation point (343 K) and cooling to 323 K with N_2 bubbling in the solution. The mean particle size $(\langle D \rangle)$ was determined after measuring the diameter of \sim 300 particles with using the software Digital Micrograph Analysis Tool® from Gatan and fitting the corresponding histogram with a lognormal distribution. This software was also used for processing HRTEM images, including fast Fourier transform (FFT) and interplanar distance determination.

Magnetization measurements as a function of temperature (M(T)) and isothermal curves at T=5 K as a function of the applied field (M_{5K}(H)) were measured in a commercial Quantum Design MPMS-5S SQUID magnetometer. M(T) curves were measured with an applied field of 50 Oe in zero-field cooling

and field cooling (FC) protocols. $M_{5K}(H)$ curves were measured in both conditions: after ZFC protocol and after a FC protocol. For the FC protocol, the sample was cooled from T = 300 K to 5 K (starting above the $T_N \sim 200$ K of the Fe_{1-v}O AFM phase) with an applied field of H_{FC} = 50 kOe. Isothermal curves at $T = 300 \text{ K} (M_{300\text{K}}(\text{H}))$ were measured in a LakeShore 7300 vibrating sample magnetometer. In order to avoid agglomeration and to immobilize the MNPs for the magnetic measurements, the samples were conditioned by dispersing the nanoparticles in toluene and this solution was mixed with an epoxy resin, followed by the toluene evaporation. Saturation magnetization (M_s) at 300 K of all samples were determined by the M_{300K}(H) measurement of a known mass of the powder samples, which was corrected by discounting the mass of the organic component as determined by the DTA-TGA measurements. The measured normalization is corrected by comparing the $M_{300K}(H)$ curves of both samples: powder and dispersed ones.

Results

Figure 1 presents the X-ray diffraction patterns of the four samples, where the symbols + and * correspond to the diffraction peaks of Fe_{1-v}O wüstite structure (JCPDS card number 00–006-0615) and Fe_3O_4 cubic spinel (JCPDS card number 00-019-0629), respectively. According to the XRD patterns, samples DH200, DH150 and DH030 (which included the predecomposition step in the synthesis procedure) are mainly composed of the Fe_{1-v}O phase, with a minor presence of Fe_3O_4 (magnetite) phase, as indicated by the peak corresponding to the plane (311). Two peaks between $32^{\circ} < 2\theta < 39^{\circ}$ were fitted with two pseudo-Voigt functions (with using 0.8 as the profile shape factor for both) corresponding to the two phases in the samples: peak (111) at ~ 36° for $Fe_{1-v}O$ phase and the (311) at ~ 35° for Fe_3O_4 phase. The area obtained by the fitting for each peak $(A_{W(111)} \text{ and } A_{M(311)})$ was normalized by its intensity given in the respective JCPDS cards. The ratio $A_{M(311)}/A_{W(111)}$ were 2.0, 2.6 and 0.9 for samples DH200, DH150 and DH030, respectively.

Figure 2 shows representative TEM images for all the nanoparticles systems (left panel), with the corresponding diameter histogram (right panel). The histograms were fitted with a lognormal distribution, and



Fig. 1 XRD patterns of samples DH200, DH150, DH030 and H030. Symbols + and * in the lowest panel correspond to the indexed peaks of $Fe_{1,y}O$ phase (JCPDS card number 00–006-0615, red bars) and Fe_3O_4 phase (JCPDS card number 00–019-0629, blue bars), respectively

the obtained mean diameters are 27.5 nm, 26.7 nm, 23.8 nm and 11.2 nm for samples DH200, DH150, DH030 and H030, respectively. The size dispersion obtained from the lognormal fitting is $w \approx 0.2$ for all samples, indicating that the nanoparticles size dispersion is not affected by water presence at the initial solution. This result is different to that observed by Bronstein et al. in synthesis from iron oleate (Bronstein et al. 2011).

Figure 3 shows representative HRTEM images of all samples. According to the images presented in the left panel of Fig. 3a, b and c, the core-shell structure is clearly observed in the nanoparticles of samples synthesized with using the pre-decomposition step: DH200 (a), DH150 (b) and DH030 (c). HRTEM image of sample H030 (left panel of Fig. 3d), prepared without the pre-decomposition step, shows a monophasic nanoparticle. The central panel of all samples gives the fast Fourier transform (FFT) of the nanoparticles. For samples DH200, DH150 and DH030, the reflections observed in the FFT can be addressed to ferrite structure and also to wüstite structure. For sample H030, the monophasic sample, the same interplanar distance associated to the plane (220) of ferrite structure is observed in both core and shell regions. In order to determine the spatial distribution of each phase present in images a–c, we obtained the inverse FFT by selecting reflections (311) or (222) of magnetite and reflection (111) of wüstite, corresponding to the spacing distances of 0.253 nm, 0.242 nm and 0.249 nm, respectively. The right panel of all figures presents a colour overlay of these inverse FFT (IFFT) obtained from selected spots indicated in the corresponding FFT. Red colour corresponds to the wüstite phase and green to magnetite one.

This structural analysis indicates that the core of the samples prepared with the pre-decomposition step corresponds to the reduced phase Fe_{1-v}O while the shell is the oxidized ferrite phase. The relation between the volumetric fractions of the core with the whole nanoparticles volume of these samples calculated from the mean diameter obtained by HRTEM is consistent with the fraction phases estimated from XRD. Sample DH030 presents a core volume fraction (as estimated from TEM measurements) of $\sim 42\%$, which implies a thinner shell compared to the other two samples exposed to air entrance to the flask at higher temperature during the synthesis. Although smaller than that one for samples DH200 and DH150, this value is larger than the expected from the XRD profile, which is probably related with some oxidation during the preparation of the TEM specimen. The grid with the DH030 NPs was kept exposed to air at room temperature for 6 months and, after that, new HRTEM images were acquired; a representative image is presented in Supplemental Material S2. It is visible that the thickness of the shell is larger than the observed in the as-prepared sample. In fact, the volumetric fraction of the core is reduced to 29% in the aged sample, indicating that a progressive oxidation process of the wüstite core takes place at room temperature, continuously increasing the fraction of Fe_3O_4 phase in the nanoparticles.

Comparing the images of the DH200 and DH150 samples, a clear difference in their morphology is noticed, where DH200 nanoparticles present larger surface roughness and a less sharp interface between the core and shell than the DH150 nanoparticles. These characteristics probably result from

Fig. 2 Left panel: transmission electron microscopy (TEM) images of all samples. Right panel: diameter histogram of the respective sample constructed by measuring the diameter of more than 300 nanoparticles from different regions of TEM specimen. The histograms were fitted with a lognormal distribution and the obtained mean diameter < D > and size dispersion w are given in the images



Fig. 3 Left panels show representative HRTEM images of nanoparticles in all samples: DH200 (a), DH150 (b), DH030 (c) and H030 (d). The central panel gives the FFT obtained from the corresponding nanoparticles. The right panel gives a colour overlay of the inverse FFT (IFFT) obtained from the selected points indicated in the corresponding FFT: red corresponds to the wüstite phase and green to magnetite one



a more drastic oxidation process in the DH200 sample, as consequence of the air exposure at higher temperature. However, sample DH200 was opened at a higher temperature and it presents a lower amount of oxidized phase than sample DH150. A possible reason for this is that the fast oxidation surface process lead to a crystalline ferrite phase which passivates and reduces the oxygen diffusion to the core of nanoparticles. On the contrary, the sample exposed to air at lower temperature 303 K presents lower oxidation degree, as expected. In opposition to the samples synthesized with the *pre-decomposition* step, the HRTEM image of sample H030 shows mostly monophasic nanoparticles whose structure can be associated to the oxygenrich ferrite phase, despite some nanoparticles with core–shell morphology could be also observed in this sample. Moreover, the size of the H030 sample is 11 nm, much smaller than the size of the nanoparticles fabricated removing the water in the synthesis, i.e. 24–27 nm. The synthesis without the *pre-decomposition* water removing step is turbulent,

probably due to the abruptly vaporization of water condensed that drops into the hot solution (593 K) which produces pressure changes and air entrance from the condenser column. On the contrary, the synthesis removing water and in N_2 flux is quiet and without turbulence or *explosions*.

It is known for bulk materials that the wüstite $(Fe_{1-v}O)$ decomposes into metallic iron and magnetite (Fe_3O_4) (Cornell and Schwertmann 2003). The metastable magnetite contains Fe²⁺, which further oxidizes even under ambient conditions to Fe³⁺, resulting in maghemite (γ -Fe₂O₃). Maghemite transforms ultimately at temperatures higher than 673 K to the hematite phase (Cornell and Schwertmann 2003; Medilli et al. 2012). Similar stability is found for nanomaterials with nanocrystalline maghemite being stable even for temperatures up to 670 K (Krispin et al. 2012). In this way, it is expected that the iron oxide phases present in the sample prepared by thermal decomposition are the wüstite and the ferrites, magnetite or maghemite. In the H030 XRD pattern, only the peaks corresponding to the ferrite (magnetite or maghemite) phase are observed. Therefore, the synthesis performed without the predecomposition step results in the oxidation of the whole nanoparticle with respect to the wüstite.

Magnetic properties of nanoparticles strongly depend on the morphology, crystallinity and composition of the system. In this way, they are strongly related to the synthesis procedure and thermal history of the sample. In particular, we found that the morphology and composition of our samples depend on the pre-decomposition step, and the air exposure at different temperatures, of the initial and the final cooling step of the synthesis, respectively. M(H) curves at 300 K of as-made DH200, DH150 and H030 powders were measured to obtain the magnetic saturation M_S. The mass fraction of organic was determinate by TGA of the nanoparticles to normalize magnetic results, and there is 7%, 13% and 25% for samples DH200, DH150 and H030, respectively. In this way, the M_S values obtained are 20.4, 27.2 and 80.5 emu/g for DH200, DH150 and H030, respectively. The low magnetization value of DH200 and DH150, compared with the H30 sample, is compatible with a larger fraction of wüstite phase with respect to maghemite, in agreement with the results of XRD. The estimation of M_S for sample DH030 was not presented, since this sample was preserved in the synthesis solution to minimize the oxidation.

Figure 4 presents the M(H) curves measured at 300 K for DH200, DH150 and H030 nanoparticles dispersed in epoxy resin to avoid the mechanical rotation of the nanoparticles and to reduce the effects of magnetic interparticle interactions. These curves exhibit a reversible behaviour and they were fitted with a Langevin function expected for superparamagnetic ferrite nanoparticles together with a linear component ascribed to the paramagnetic response of wüstite phase or disordered surface magnetic moments:

$$M(H,T) = A\left[coth(KH) - \frac{1}{KH}\right] + BH$$
(1)

where A, B and K are constants related to the magnetization saturation, the paramagnetic susceptibility and the Langevin argument, respectively, being directly related with the Langevin function for a superparamagnetic domain added to a paramagnetic contribution:

$$M(H, T) = M_{S} \left[\coth\left(\frac{\mu H}{k_{B}T}\right) - \left(\frac{k_{B}T}{\mu H}\right) \right] + BH \quad (2)$$



Fig. 4 Magnetization curves M(H) at T=300 K for samples DH200, DH150 and H030 dispersed in epoxy resin to avoid the mechanical rotation of the nanoparticles and to reduce the effects of magnetic interparticle interactions. The solid red lines correspond to the fits with a Langevin function together with a linear component (Eq. 1) and the parameters obtained are given in Table 1

where k_BT is the thermal energy and μ is the magnetic moment of the domain. The coefficients obtained from the fits with Eq. 1 are presented in Table 1 and the uncertainty obtained from the fits is the last digit. The linear component (B) of samples DH200 and DH150 is considerably larger than the corresponding one of H030, supporting the presence of larger paramagnetic phase fraction in DH samples, as expected.

M(T) curves of all samples measured in ZFC and FC protocols with a cooling field H=50 Oe are presented in Fig. 5. A notable decrease in the 187 K < T < 235 K temperature range is observed in the DH200, DH150 and DH030 samples, which is associated to the AFM transition of wüstite phase. This signal overlaps with an irreversible behaviour associated to the blocked temperature of the ferrite phase at the shell, at larger temperature than the Néel transition. From this figure, a sharper AFM transition can be noticed for the DH030 system in agreement with the majority of wüstite. At $T \sim 115$ K, the M(T) curves of these three samples with the pre-decomposition step present a decrease of the magnetization, probably related to the Verwey transition of the Fe_3O_4 . This is more evident in the insest of Fig. 5, where the $dM_{\ensuremath{ZFC}}/dT$ plots of the ZFC curves are shown. In the M(T) curves of sample H030, the AFM transition could not be resolved (Fig. 5), in agreement with the ferrite single phase found for this system.

M(H) curves measured at 5 K after a field cooling procedure from 300 K with an applied field of H_{FC} = 50 kOe (M_{FC} (H)) and after cooling without magnetic field (M_{ZFC} (H)) are presented in Fig. 6. M_{FC} (H) curves of samples DH200, DH150 and DH030 show asymmetric loops characterized by high exchange bias field (H_{bias}) of 2580 Oe, 4090 Oe and 2700 Oe, respectively. This high bias indicates a strong magnetic coupling between the AFM and

Table 1 Parameters obtained from the fitting of the M(H) curves at 300 K of samples DH200, DH150 and H030 dispersed in epoxy resin (Fig. 4) with a Langevin function together with a linear component (Eq. 1 and Eq. 2)

Sample	A (emu/g)	B (×10 ⁻⁴ emu ² / erg.g)	K (Oe ⁻¹)
DH200	12.9	8.6	0.0019
DH150	18.1	11.0	0.002
H030	80.5	1.9	0.011



Fig. 5 M(T) curves of samples DH200, DH150, DH030 and H030 dispersed in epoxy resin measured in ZFC and FC protocols with H = 50 Oe. The insets present the respective dM_{ZFC}/dT curves in the temperature range of 0 and 175 K, with a maximum (black solid line) in the indicated temperature



Fig. 6 Magnetization M(H) curves measured at 5 K after field cooling from 300 K with a H=50 kOe (M_{FC}(H)) and after cooling without magnetic field (M_{ZFC}(H)). H_{bias} indicates the bias field observed in the M_{FC}(H) curve, while H_c^{ZFC} indicates the coercive field for the M_{ZFC}(H) curve

FiM phase at the core/shell interface (Salazar-Alvarez et al. 2007). In addition, these samples present a larger coercive field (H_c^{ZFC} =3720 Oe, 3513 Oe and 3200 Oe, respectively) than the expected for the ferrite, also indicating the magnetic coupling between the core and shell phases (Lavorato et al. 2017). $M_{FC}(H)$ curve of the sample H030 does not present exchange bias and the coercive field is H_c =235 Oe, confirming its monophasic ferrite composition.

In order to explore the effects of *pre-decomposition* step on the final composition and morphology of the nanoparticles, Fig. 7a and b presents TGA and DTA measurements, respectively, for an aliquot (about 15 mg) of the as-prepared synthesis solution. The measurement was performed by heating the sample with an Ar flux of 100 mL/min to 383 K, with a heating rate of 3 K/min. After that, the sample was kept about 45 min at this temperature. This temperature variation emulates the ramp used in the *predecomposition* step for samples DH200, DH150 and



Fig. 7 a TGA and **b** DTA measurements for an aliquot (about 15 mg) of the as-prepared synthesis solution performed by heating the sample to 383 K with a heating rate of 3 K/min and kept about 45 min at this temperature maintaining an Ar flux of 100 mL/min. Arrows indicate the direction of temperature variation

DH030. A strong reduction of the mass of about 15.5 *wt%* is observed in an endothermic process measured in the TGA/DTA curves.

Figure 8a gives the FTIR spectra of the preparation synthesis solution common for all samples, previous to the synthesis, together with the FTIR spectra of the solution obtained after the synthesis of samples DH030 and H30, i.e. with and without the *pre-decomposition* step, respectively. Differences in the spectra due to the presence of by-products are expected to be more evident comparing these solutions before and after the synthesis. In fact, the $3400-3100 \text{ cm}^{-1}$ range



Fig. 8 FTIR spectra: **a** as-made H030-like and DH030-like synthesis solutions, where symbols +, l, X, * and # indicate the peaks observed only in the spectrum of DH030-like solution, the peaks with higher and lower intensities in the spectrum of the as-made solution and the peaks with different intensity ratios among the samples, respectively (inset: detail of the wavenumber range around 3300 cm⁻¹); **b** nanoparticles precipitated by centrifugation or with magnetic assistance of samples DH200, H030 and DH030

for the three solutions exhibits a broad peak centred around 3300 cm^{-1} in the spectra of the thermally treated solutions, which is not observed in the spectrum of the preparation synthesis solution, presenting only a narrow peak at 3335 cm⁻¹ related to the oleylamine and the low-energy part of a very broad one related to the oleic acid (see the inset of Fig. 8a). This peak at 3300 cm⁻¹ observed in the solutions after the synthesis could not be addressed to the OH groups of the 1,2-octanediol, since it is not observed for the preparation solution due to the small amounts of this chemical used. Thus, it is probably related to O-H groups present mainly in water, originated in part from by-reactions during the synthesis and to some humidity inserted in the synthesis environment, and also to O-H groups formed in the oxidation of organic compounds. The intensity of this peak at 3300 cm⁻¹ (I_{3300}), defined as its height with respect to the baseline (dotted line in Fig. 8a) normalized by the height of the alkene peak at 2960 cm⁻¹, was relatively small: $I_{3300} = 0.05$ and 0.03 for the solutions of samples H030 and DH030, respectively. The C=Opeak is observed for all solutions around 1720 cm⁻¹ and it is associated to free oleic acid. The intensity of this peak presents a reduced intensity in the thermally treated solutions, which indicates that part of the oleic acid is attached to the surface of the iron oxide particles with COO group, as expected, with a monodentate or bidentate coordination. Consequently, a broad peak around 1650–1450 cm⁻¹ related to the $\nu_{\text{symmetric}}$ and $\nu_{asymmetric}$ modes of the COO bonded to the iron oxide surface (indicated by the symbol X) is observed only in the thermally treated solutions. Thermally treated solutions also presented peaks at ~ 600 cm^{-1} associated to the vibration mode of the Fe-O bond in the nanoparticles. Finally, the FTIR spectrum of the solution obtained after the synthesis of sample DH030 presented four peaks localized at 1500 cm⁻¹, 1087 cm^{-1} , 1037 cm^{-1} and 700 cm^{-1} (indicated by the symbol+) that are not observed in the spectra of as-made solution and the one obtained after the synthesis of sample H030.

Figure 8b gives the FTIR spectra of the nanoparticles of samples H030 (magnetically precipitated), DH200 and DH030, where the first one was magnetically precipitated and the last two by centrifugation. These spectra present small differences in comparison to those of the synthesis solution. However, some of the following differences among them are observed:

- (i) The relative intensity of the peak around 600 cm⁻¹ associated to Fe–O bond (indicated by the dashed square in Fig. 8b) with respect to the alkene peaks around 2900 cm⁻¹ (also indicated in Fig. 8b) is higher for sample H030, magnetically separated, than to the other ones, indicating a bigger nanoparticle/organic compounds ratio in this sample.
- (ii) The peak at around 1720 cm⁻¹ (indicated by empty square in Fig. 8b) observed for samples DH030 and DH200 indicates the presence of free oleic acid in them, with a small increment of 30 cm⁻¹ in this peak position for sample DH030.
- (iii) The spectrum of sample DH030 presents other peaks associated to different organic compounds also observed in the spectrum of the solutions after the synthesis.
- (iv) The distance in the peaks associated to the COO groups bounded to the nanoparticles' surface (indicated by the grey square in Fig. 8b) is bigger for sample DH030, indicating different coordination of oleic acid to the Fe ions at the surface of the nanoparticles in this case, more related to a monodentate coordination in this sample in comparison to the others.

Figure 9a and b presents the FTIR of the recovered material from evaporation and a fraction of the solution, both collected during a replication of the synthesis of sample DH030 in the modified apparatus described in Supplementary Material S1 at different temperatures and times below the reflux condition. The main contribution to all spectra was from octadecene, the solvent used for the synthesis. However, in the FTIR spectrum of the material recovered after 30 min at 393 K, a relatively intense peak corresponding to the O-H stretching is observed. This peak is also observed in a lower relative intensity in the solution collected at the same temperature and time, while is not present in the as-prepared solution (Fig. 8a) previous to the heating. The relative intensity of this peak presents a strong reduction in the recovered material held at 473 K for 2 min, and it reduces even more in the recovered material at 473 K/30 min. In addition to the octadecene and O-H Fig. 9 FTIR spectra of a recovered material obtained from the synthesis solution similar to sample DH030 in the modified apparatus (Supplementary Material S1) at different temperatures and times previous to the reflux condition (inset: detail of Fe-O/O-O/O-H absorption region around 550 cm^{-1}) and **b** synthesis solution collected from the three-neck flask during the synthesis at different temperatures and times (inset: detail of Fe-O/O-O/O-H absorption region around 550 cm^{-1}). **c** FTIR absorbance spectra of the recovered material at 393 K/30 min, the solvent of octadecene used in the synthesis and of the acetylacetone obtained from reference (Wallace and (direc.) 2020)



stretching band, other differences are observed in the low-energy range of the spectra of collected materials. Specifically, the samples collected at 473 K present two peaks at 1040 cm⁻¹ and 1085 cm⁻¹ that are not observed in the material recovered at 393 K. These peaks can be associated to a small amount of acetylacetone or some organic derived in it. In addition, some peaks related to a small amount of acetylacetone (boiling point around 403 K) in the octadecene are also observed in the spectra of all samples. The presence of this compound in recovered material is observed in the absorbance spectra of the recovered material at 373 K/30 min, octadecene and acetylacetone (obtained from reference (Wallace and (direc.), 2020)) are also presented in Fig. 9c.

Discussion

As pointed above, the *pre-decomposition* step at 383 K changes the size, composition and morphology of the iron oxide nanoparticles, and specifically, a core–shell structure is formed where oxidized ferrite phase at the shell can be modulated by the air exposure of the solution at different temperatures; on the contrary, without this step, fully oxidized Fe_3O_4

nanoparticles are formed. Consequently, the magnetic response of the nanoparticles is strongly sensitive to this step in the synthesis procedure, presenting samples with distinct magnetic ordering (AFM and FiM), anisotropies and magnetic moments, as well as different magnetic internal interactions within the particle.

According to the results presented above, the *predecomposition* allows to eliminate some solvents with lower boiling point formed in the temperature range below 473 K, mainly compounds containing O–H groups. There are two possible sources of compounds with O–H groups in the amounts detected: (i) from water formed in by-reactions in this temperature interval and from some humidity present in the synthesis environment, since it is not observed in the FTIR spectrum of as-prepared synthesis solution; (ii) from the oxidation of some organic compound in the synthesis solution.

In a recent work, Scopel et al. (Scopel et al. 2019) synthesized Fe_3O_4 nanoparticles from Fe^{3+} acetylacetonate in the presence of only oleic acid, which acts as solvent and surfactant in the synthesis. These authors proposed that similar dynamics in the nanoparticles formation is expected in this synthesis with the previous formation of the Fe oleate from the acetylacetonate by ligand exchange at low temperatures in a reversible process and the equilibrium is shifted to the acetylacetonate with increasing the pressure in the synthesis environment.

The reduction of Fe^{3+} of the acetylacetonate to Fe^{2+} , to form either wüstite or ferrite phases, is a consequence of the reductive environment of the synthesis: the long-chain alcohol, 1,2-octanediol in our syntheses, the excess oleylamine added to the reaction and the acetylacetonate decomposition (Song et al. 2016). In addition, the reduction of Fe^{3+} to Fe^{2+} is also observed in synthesis performed only in the presence of 1-octadecene and oleic acid, which can be addressed to the 1-octadecene oxidation (Kemp et al. 2016) and the oxidative decarboxylation of iron oleate (Kemp et al. 2016; Kwon et al. 2007). According to Soon Gu Kwon et al. (Kwon et al. 2007), the decomposition of the Fe oleate, used to synthesize the iron oxide nanoparticle in the presence of 1-octadecene, starts around 473 K (with the formation of Fe and Fe-O free radicals with other by-products such as CO, CO₂, H₂, water, ketones, esters and hydrocarbons) and evolves towards its complete decomposition at temperatures around 573 K. These authors

also show that the Fe oleate decomposition is followed by the nucleation and the growing of small iron oxide clusters, which starts around 523 K and consolidates above 583 K. Additionally, it was shown by Kemp et al. (Kemp et al. 2016) that 1-octadecene and its degradation products participated in the formation of the nanoparticles, resulting in larger particles (24.7 nm) in comparison to the synthesis using octadecane (14.4 nm). However, the authors indicate that the main mechanism for the Fe^{2+} formation is due to oxidative decarboxylation of oleic acid and Fe oleate. In fact, the oleate decomposition can be directly associated to the formation of CO₂ during the synthesis (Kwon et al. 2007) due to the ketonic decarboxylation reaction where the oleic acid forms a ketone liberating CO_2 (Hufschmid et al. 2015; Palchoudhury et al. 2011). Nevertheless, the reduction process is associated to the presence of reducing gases such as CO (Hai et al. 2010) (forming CO_2 as by-product), and the presence of oxygen in the synthesis environment may limit the reduction process by the transformation of CO to CO₂. Also, CO and CO₂ could be produced by the partial combustion of organic compounds (Hufschmid et al. 2015).

The effect of the *pre-decomposition* step may be addressed to the removal of water present in the solution, adsorbed in the glass wall and/or the humidity in the air contained in the flask, which could be addressed to the mass loss observed in the TGA (Fig. 7a). However, the FTIR analysis of the asprepared solution does not indicate the presence of water, which is observed for the thermally treated solutions. In fact, the FTIR analysis of the water content in the reagents used in the synthesis solution, presented in the Supplemental Material S3 (very similar to the FTIR of the standard compounds (Wallace and (direc.) 2020)), indicates that the amount of water is really small, excepting for the 1,2-octanediol. However, the amount of 1,2-octanediol used in our synthesis solution was very small; thus, the significant amounts of water are likely to be the result of by-reactions during heating at the early stages of the synthesis. These amounts of water could be removed during the *pre-decomposition* step, which is consistent with the higher intensity of the water peak observed in the FTIR spectrum of the thermally treated solution without using this step. Therefore, the weight loss observed in TGA could not be addressed entirely to the removal of water in the reagents, being probably

related to the possible processes occurring in the *predecomposition* step mentioned above: decomposition of the organic reagents (Kemp et al. 2016), esterification of oleic acid with the long-chain alcohol (Lucena et al. 2011) and the formation of the oleylamine and oleic acid complex (Harris et al. 2015).

According to Kemp et al. (Kemp et al. 2016), water is released from the ligand exchange of iron oleate in the presence of excess oleic acid during the heating up procedure, and this released water affects the nanoparticle formation and the final morphology. As pointed out by these authors, the inert gas flux plays an important role to reduce the amount of water formed. The presence of this released water or the humidity remaining is easily observed during the synthesis, by the production of white vapour in the first stages of the condenser and by explosions in the synthesis solution during the reflux step. Also according to Kemp et al. (Kemp et al. 2016), the presence of water in the synthesis plays a major role in the nucleation of the nanoparticles, and its control in the first stage of the synthesis influences the nanoparticle size and the reproducibility of the results. In fact, the water can produce the thermal cracking of oleic acid (Harris et al. 2015). Another possible by-reaction that can release water and affect the free acid in the solution is the esterification of oleic acid with the long-chain alcohol (Lucena et al. 2011). This process depends on the oxidant media and could happen at lower temperatures, around 373-393 K. The presence of ester increases with removing the water, conditions observed in the pre-decomposition step. In addition, during this *pre-decomposition* step, the oleylamine and oleic acid can form base: acid complex in the concentrations range used in our synthesis (Omidghane et al. 2017; Gao et al. 2015), affecting the nucleation and the stability of the final nanoparticles. The FTIR spectrum of the DH030-like solution presents the following peaks: C-C-O and O-C-C groups in an ester present peaks in the 1090 cm⁻¹ and 1030 cm⁻¹ range (Smith 2018), while C-N and N-H groups of amides present peaks at $1550-1500 \text{ cm}^{-1}$ (Parker 1971) and a peak related to N-H group is expected around 710 cm^{-1} .

Finally, Fig. 9 clearly indicates the formation of compounds containing O–H groups, suggesting the formation of water from the possible by-reactions discussed previously. The presence of water and other organic compounds with low boiling point during

synthesis without the *pre-decomposition* step (e.g. acetylacetone with b.p. ~403 K) produces *explosions* in the solution at high temperatures, especially during the nucleation and reflux stages. This unsteadiness in the liquid medium promoted by *explosions* also includes pressure instabilities that allow external moisture to enter the flask, yielding a less reducing synthesis' atmosphere that could affect the Fe oxidation state during the nucleation process. As a result, the formation of wüstite is favoured with the *pre-decomposition* step, while oxidized ferrite phase is the result without this step.

Conclusions

The thermal decomposition method is largely used to synthesize magnetic nanoparticles; however, the impact of several aspects of the synthesis procedure in the composition and morphology is not completely clear, impacting directly on the magnetic properties of the synthesized nanoparticles. In this way, the predecomposition step in the synthesis of iron oxide nanoparticles by the thermal decomposition method of $Fe(acac)_3$ in the presence of oleic acid and oleylamine presents a strong effect on the final composition and morphology of the nanoparticles systems. The main effect of this step, which consists in heating the synthesis solution to 373-393 K with an inert gas flux in open flask, is the removing of water. Using this step results in 20- to 25-nm core-shell nanoparticles, with a $Fe_{1-v}O$ core phase and a ferrite oxidized shell. The thickness of the ferrite can also be modulated by the temperature of the air exposure in the final cooling step. The air exposure at lower temperature results is lower proportion of the oxidized phase. In opposition, monophasic ferrite nanoparticles with 11 nm were produced when the synthesis is performed without this pre-decomposition step. These differences in the size, morphology and composition of the nanoparticles are probably related to the competition between the reducing agents formed during the synthesis and residual or/and released water, as well as to possible reactions involving oleic acid in the pre-decomposition step.

The magnetic properties are strongly influenced by the differences in the composition and morphology of the synthesized systems. We have shown that a *pre-decomposition* step prevents sample oxidation and produces the Fe1-vO wüstite phase, yielding nanoparticles of smaller size and, more important, lowering the magnetization since this phase orders antiferromagnetically at ~200 K. Air exposition during the synthesis and further aging of the samples at room temperature produced increasing oxidation of the nanoparticles yielding wüstite/ferrite core-shell structure with increasing amounts of ferrite phase for longer oxidation times. The AFM phase in the core was found to be strongly coupled with the FiM shell through an exchange bias mechanism, resulting in a larger coercivity field than the expected for the FiM single-phase nanoparticles. Alternatively, when the synthesis is performed without the pre-decomposition step, monophasic ferrite nanoparticles that behave superparamagnetically at room temperature are produced.

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Data availability All data and materials used can be accessed by contacting the authors, excepting sample DH030 due to the natural oxidation process described in the article.

Code availability All software used in this work are commercial.

Declaration

Conflict of interest The authors declare no competing interests.

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