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Synergy of Miniemulsion and Solvothermal Conditions for the Low Temperature Crystallization of Magnetic Nanostructured Transition Metal Ferrites

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ABSTRACT: Crystalline first row transition metal (Mn, Fe, Co, Ni, Cu and Zn) ferrites were prepared by an unprecedented synergetic combination of miniemulsion synthesis and solvothermal route, pursuing unconventional conditions in terms of space confinement, temperature and pressure. This synergy allowed for obtaining six different crystalline ferrites at much lower temperature (i.e., 80 °C) than usually required and without any post-synthesis thermal treatment. X-ray diffraction (XRD) revealed that analogous ferrites synthesized by miniemulsion at ambient pressure or in bulk (i.e., from an aqueous bulk solution and not in the confined space of the miniemulsion droplets) either at ambient pressure or under solvothermal conditions did not result in comparatively highly crystalline products. To follow the structural evolution at local level as a function of reaction time and depending on the synthesis conditions, X-ray absorption spectroscopy (XAS) was used to determine the cation distribution in these structures. Well-defined nanostructures were observed by transmission electron microscopy (TEM). Concerning their functional behavior, the synthesized ferrites presented superparamagnetism and were found to be active oxidation catalysts, as demonstrated for the oxidation of styrene, taken as a model reaction. Thanks to the magnetic properties, the ferrites can be easily recovered from the reaction medium, after the catalysis, by magnetic separation and reused for several cycles without losing activity.

Introduction

Ferrites are inorganic materials experiencing a great development and interest not only for their thermal, mechanical and chemical stability^{1, 2} and for their magnetic properties,³⁻⁵ but also for their outstanding electric and structural properties,6 making them appealing for a wide array of applications. In particular, ferrites are being exploited for catalysis^{7, 8} and photocatalysis⁹ of several reactions, such as C-C and C-X coupling reactions,⁷ alkylation reactions,¹⁰ and oxidation reactions of alcohol to aldehydes,¹¹ of CO,¹² of styrene,^{13,14} and of toluene.^{15, 16} The ferrite-catalyzed production of hydrogen through the photocatalytic water splitting is as well a promising application of these materials.^{17, 18} Furthermore, ferrites are magnetic materials, being hence easily recoverable from the reaction medium, which is important for achieving sustainable and green methodologies for chemical reactions.¹⁹ Until recently, ferrites have been mainly prepared by solid-state synthesis and high temperature approaches,²⁰⁻²³ but more sustainable and low-temperature methods of synthesis are searched for.^{24, 25} The wet-chemistry preparation of multinary oxides has led to materials that are usually single-phase, more homogeneous and characterized by smaller crystallites than those prepared by conventional solid-state reactions.²⁴ Among wetchemistry routes,²⁴ the most commonly employed techniques for

synthesis of ferrites are sol-gel,²⁶ non-aqueous sol-gel,²⁷⁻²⁹ hydrothermal and solvothermal routes,^{30, 31} coprecipitation,^{32, 33} and microemulsion.^{34, 35} An innovative way to obtain crystalline inorganic materials at low or even room temperature while using a wet-chemical strategy is the miniemulsion technique.^{36,37} Miniemulsions are kinetically stabilized emulsions (i.e., droplets of a liquid dispersed in a second immiscible liquid) with droplet sizes in the range of 50 to 500 nm. The formation of a miniemulsion requires high shear forces and, after this homogenization process, a "steady state" is reached. A miniemulsion is considered kinetically stable (metastable) because it is stable against Ostwald ripening (an osmotic pressure agent is added to counterbalance it) but only critically stabilized against coalescence (a small amount of surfactant is required). In contrast, microemulsions are thermodynamically stable and are formed by simple mechanical stirring. Both micro- and miniemulsion have been employed to produce metal oxides, by exploiting the confined space of droplets for precipitation/crystallization reactions.^{34, 38, 39} However miniemulsions have several advantages compared to microemulsions: generally microemulsions require a high amount of surfactant, and the droplets of a microemulsion cannot be considered as nanoreactors since they experience a dynamic equilibrium that makes the droplets coalesce and exchange their content and, in addition, the yield for syntheses in microemulsion is very low, due to the very low solid content.

A hydrothermal (or solvothermal) synthesis is defined as "a heterogeneous chemical reaction in aqueous media (or organic solvent in the case of solvothermal) above room temperature (normally above 100 °C) and a pressure greater than 1 atm". 40, 41 These nonstandard conditions are usually achieved by employing pressurized reactors or closed vessels where the developed pressure is autogenous. Non-classical crystallization pathways can be investigated with solvothermal conditions:^{30,42} at high pressure and temperature, relevant physical parameters of the solvent (ionic product, density, viscosity, dielectric constant) change; thus the solubilization and the crystallization of compounds that normally would not occur are allowed.^{23, 24} Herein, by exploiting the combination of two different kinds of not conventional conditions, i.e. space confinement provided by miniemulsion with the unconventional solvent properties provided by subcritical solvothermal conditions, we synthesized crystalline ferrites and assessed the effects of the synthesis conditions on the crystallization process and on the targeted functional properties of the final materials (namely, the magnetic and catalytic properties). Our working hypothesis was that the synergy of the unconventional conditions provided by the simultaneous use of the two routes could lead to an improved crystallinity of the products when compared to materials prepared from conventional miniemulsions (i.e., at ambient pressure) and/or simple solvothermal synthesis. Further investigations concerning the role of the synthetic approach and, in the case of the solvothermal synthesis, also of the reaction time, were carried out for zinc ferrite. Zinc ferrite was chosen as a model because, among the spinel ferrites discussed in this work, is the only one displaying a complete direct structure in the bulk phase.

Experimental Section

Chemicals

Iron(III) chloride hexahydrate (ACS reagent 97%, Sigma Aldrich), iron(II) chloride tetrahydrate (puriss., \geq 99.0% (RT), Sigma Aldrich), cobalt(II) chloride hexahydrate (ACS reagent 98%, Sigma Aldrich), copper(II) chloride dihydrate (ACS reagent \geq 99.0%, Sigma Aldrich), manganese(II) chloride tetrahydrate (99+% for analysis, Acros organic), nickel(II) chloride hexahydrate (ReagentPlus, Sigma Aldrich), zinc(II) chloride (98+% anhydrous, Alfa Aesar), and sodium hydroxide (pellets, ACS reagent \geq 98%) were used without further purification. Commercial polyglycerine polyricinoleate (Grinsted PGPR 90 Kosher, Danisco) was used as received. Cyclohexane (HiPerSolv, Chromanorm, VWR chemicals) and Milli-Q water (Millipore, resistance 18.2 M Ω cm) were used to prepare solutions and suspensions.

For the preparation of samples for transmission electron microscopy analyses, D-(+)-trehalose dihydrate (Fisher BioReagents), uranyl acetate dihydrate (Riedel de Haën) and 1-ethyl-3-methylimidazolium tetrafluoroborate (ionic liquid EMI-BF4) (Aldrich) were employed.

For the catalytic tests 1,2-dichlorethane (ACS reagent, \geq 99.0%, Sigma Aldrich), *tert*-butyl hydroperoxide solution in decane (TBHP, 5.5 mol L⁻¹, Sigma Aldrich) and dichloromethane (HPLC

grade, Fisher Scientific) were used as received, styrene (ReagentPlus, containing 4-tertbutylcatechol as stabilizer, \geq 99%, Sigma Aldrich) was purified with liquid chromatography on an aluminum oxide column to remove the stabilizer.

Synthetic Protocol

In a typical synthesis, the inorganic precursors were dissolved in Milli-Q water to prepare a solution with Fe:metal molar ratio of 2:1. This aqueous solution was mixed with the organic phase (1 wt% solution of PGPR in cyclohexane), in a weight ratio of 1:4. Both the aqueous and the organic phase were stirred together to promote a pre-emulsification. The mixture was then ultrasonified by a Branson digital sonifier W-450D (1/2" tip, 2 min sonication time, 70% amplitude, pulse 1 s, pause 0.1 s). Immediately after the ultrasonication, an excess (i.e., 12 times the moles of Fe) of NaOH 16.6 M aqueous solution was added to the just prepared stable miniemulsion and this mixture was ultrasonified again with the same parameters described above to trigger the penetration of NaOH inside the droplets and to promote the precipitation of the inorganic precursors within the confined space of the droplets. The miniemulsion was either (i) placed immediately at 80 °C and ambient pressure without stirring in a glass vial or (ii) poured in a Teflon-lined autoclave reactor (45 mL, mod. 4744 Parr Instrument), sealed and placed at 80 °C without stirring for different heating times (3, 6, 12 and 24 h). After the reaction time, the suspension was centrifuged (13 000 rpm, 5 min) to collect the solid product. This product was washed afterwards by centrifuging once with a 1:1 mixture of acetone and ethanol and three times with distilled water. The solid obtained was dried under vacuum at room temperature for 15 h and subsequently grinded.

Bulk syntheses (i.e., direct precipitation from an aqueous solution) were performed for the sake of comparison with the materials prepared with our miniemulsion method. A typical bulk procedure started from the aqueous solution of the inorganic salts, keeping the same amount of precursors and NaOH solution of the miniemulsion protocol, but the NaOH was added directly to the salts solution and the precipitation occurred immediately. The mixture was placed at $80 \,^{\circ}$ C without stirring either in the Teflon-lined autoclave reactor for the solvothermal reaction or at ambient pressure in a glass vial, as the miniemulsion synthesis. It should be pointed out that the same volume of cyclohexane was added to the bulk synthesis to have the same pressure in the reaction vessel. The centrifugation and the washing procedure was the same performed for the samples produced in miniemulsion.

Sample Characterization

X-ray diffraction of the washed and vacuum dried powders was performed with a Philips PW 1820 diffractometer with monochromatic Cu K_a radiation ($\lambda = 1.5418$ Å, 40 kV, 30 mA, $\Delta\theta$ (scan step) = 0.02°, 5 s per step). Inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7900) was conducted to estimate the molar ratio between the iron and the other metal present in the ferrite. The solid samples were digested in aqua regia at 80 °C for 5 h before the analysis. The interfacial tension between the continuous and the disperse phase of a typical miniemulsion was determined using the pendant drop method with an optical goniometer (OCA35, Dataphysics, Germany). The liquid media (liquid of lower density, in our case, cyclohexane–PGPR 0.77 g/cm2)) was deposited in a polystyrene cuvette. A drop of the higher density liquid (in our case, water–salts

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1.1543 g/cm2) was immersed in the cuvette, evaluating the interfacial tension through a drop shape analysis software. Averaged values from data were recorded. The interfacial tension value was also cross checked with the spinning drop tensiometer Dataphysics SVT 20N. A FEI Tecnai F20 transmission electron microscope (TEM) operated at an acceleration voltage of 200 kV was used for the measurements. The micrographs were recorded on a 2k CCD camera (Gatan Ultrascan 1000). The dispersion was dropped on a carbon coated grid and the liquid phase was evaporated. To avoid artifacts, the samples were prepared by embedding the material in a matrix of trehalose. To increase the contrast, negative staining with uranyl acetate was applied. Alternatively, by using another preparation method, the samples were embedded in a matrix of the ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate, which remains liquid due to the very low vapor pressure under the high vacuum of the electron microscope chamber. Further details of the preparation method are reported elsewhere.⁴³ Specific surface area and porosity were determined by measuring the nitrogen physisorption at the critical temperature with an Autosorb MP1 instrument (Quantachrome). The specific surface area was calculated according to the Brunauer-Emmett-Teller (BET) theory in the range of P_s/P_0 0–1.0. Before the measurements, the products were degassed at 200 °C for 24 h under vacuum to ensure the complete removal of any previously adsorbed material. Magnetic measurements were performed by a superconductive quantum interference device (SQUID) magnetometer (Quantum Design MPMS II). Gelatin capsules were filled with the weighed samples and mounted in a low magnetic moment sample holder. Fe (7112 eV) and Zn (9659 eV) K-edge spectra were collected at the bending magnet of the XAFS beamline at the Elettra synchrotron facility (Trieste, Italy), under standard ring conditions (2.0 GeV, 300 mA). For energy selection, a Si (111) double-crystal monochromator was used. Spectra were collected in a detuned configuration of the monochromator. Data collection was carried in

transmission mode using an ionization chamber placed downstream with respect to the sample. Internal energy calibration was accomplished by simultaneous measurement of the absorption of a Mn foil placed between two ionization chambers located after the sample. Each sample was prepared as a pellet, using cellulose as a dispersant medium. Data reduction and analysis was performed using the Demeter package;⁴⁴ in particular, background removal was performed by the Autobk routine of the Athena software, which was also used for data alignment and calibration. The extracted EXAFS functions were fitted exploiting the software Artemis. Passive electron reduction factors (S02) were obtained from the fit to bulk metallic reference (0.8 for Fe and 0.75 for Zn) and then kept constant in the fits for all the solid solutions.

Catalysis Experiments

The catalytic activity of the ferrites was tested for the oxidation of styrene. The reaction was performed at 70 °C: the catalyst (20 mg, 0.09 mmol), 1,2-dichloroethane (25.4 mmol) and purified styrene (4.3 mmol) were placed in a vial and the addition of the TBHP (13.0 mmol) started the reactions. The closed vial was deposited in a thermoshaker (HLC, MKR 23) at 600 rpm and 70 °C. Sampling volumes of 100 μ L were collected at different times and diluted with 2.4 mL of dichloromethane to quench the reaction. To assure the separation of the catalyst from the reaction solution a neodymium magnet was used. 80 µL of the dichloromethane solution were withdrawn and poured in a vial with 920 µL of dichloromethane to achieve the concentration range suitable for the following analysis. Decane, present in the TBHP solution, was employed as an internal standard. The samples were analyzed by a gas chromatograph coupled with mass spectrometer (Shimadzu, GCMS-QP2010 Ultra) to follow the oxidation and to identify the products. The magnetic catalyst was recovered with a neodymium magnet after the reaction and the powder was washed three times with dichloromethane.



Figure 1. Combination of inverse miniemulsion process and solvothermal conditions for the synthesis of spinel ferrites.

The oxidation of the styrene was carried out for three additional cycles using the recovered powder to test the reusability of the catalyst. A blank reaction in the absence of the catalyst was carried out to demonstrate the catalytic activity of ferrite

Results and Discussion

Physicochemical and Structural Characterization of the Samples

The preparation of a generic spinel ferrite involves typically the precipitation of the iron and the divalent metal hydroxides immediately after the addition of a NaOH solution to an aqueous solutions of salts, as reported in literature.⁴⁵ In such a case, the mixture of hydroxides is heated at a certain temperature (e.g., 390 °C) to produce the ternary metal oxides. In our work, we adopted the combination of miniemulsion synthesis and subcritical solvothermal conditions to synthesize crystalline spinels at much lower temperature (i.e., 80 °C) than generally reported in literature, exploiting the precipitation of the hydroxides in the confined space of the miniemulsion droplets under non-standard conditions. Generally, the inverse miniemulsion procedure (Figure 1) involves two phases: a dispersed (aqueous) phase and a continuous (organic) phase in which the lipophilic surfactant is dissolved. In our synthesis, the surfactant employed was commercial polyglycerol polyricinoleate (PGPR), dissolved in cyclohexane. PGPR was selected as a surfactant because it is a lipophilic surfactant with a low hydrophilic-lipophilic balance (HLB) (around 1.5),⁴⁶ suitable to stabilize inverse miniemulsions. On the other hand, in our work the disperse phase is an aqueous solution of the inorganic precursors. After the formation of the miniemulsion by high sheer forces produced by the ultrasounds and the addition of the NaOH solution to start the precipitation inside the water droplets, the system was placed in a Teflon-lined autoclave reactor under subcritical solvothermal conditions, generated upon heating of the closed vessel. The autogenous pressure is 2.105 Pa, 2 bar, at 80 °C and 3.10⁵ Pa, 3 bar, at 100°C as calculated with Antoine's equation.⁴⁷ In the case of the zinc ferrite a comparison among different approaches was conducted (the labeling of the samples used in the following is indicated in brackets): i.) miniemulsion under solvothermal conditions (ME-HP), ii.) miniemulsion at ambient pressure (ME) and iii.) bulk procedure, which involves the mixing of the inorganic precursors and the precipitating agent and directly the precipitation of the products, either at ambient pressure (bulk) or combined with solvothermal conditions (bulk-HP).

Another suitable wet-chemistry route for the synthesis of ferrites is the coprecipitation of oxalates: the metal precursors, in the presence of oxalic acid, form the oxalates after the addition of the precipitating agent (generally a concentrated base). This synthesis can be followed by either thermal treatment at high temperature or by lowtemperature subcritical hydrothermal processing to afford the final crystalline oxides. 48, 49 In an initial stage of the work, we employed the combination of the aforementioned coprecipitation of the oxalates with the miniemulsion technique to achieve the formation of spinel ferrites. The inorganic precursors and the oxalic acid were dissolved in the aqueous disperse phase and the precipitating agent (NaOH) was added to the miniemulsion. However, this procedure did not lead to single-phase crystalline materials, and the oxalic acid was still present despite several washings. This finding can be traced back to the environment of the confined space of a miniemulsion droplet, which is completely different from the environment of a standard bulk synthesis.⁵⁰ The precipitation of the hydroxides was found to be a more successful and reliable route.

X-ray diffraction (XRD) provides information not only about phase purity and crystallite size of the crystalline materials but, more

importantly, also about their structural evolution towards the crystalline phase as a function of sample composition, pressure higher or equal to ambient one, reaction time, and temperature. Crystallization of the zinc ferrite was therefore followed by analyzing *ex-situ* samples after different reaction times (Table 2). Information on the structural evolution in the long range was integrated and complemented by the one on the local range delivered by XAS measurements (see below).

The diffractograms of all ferrites produced from miniemulsion under solvothermal conditions are reported in Figure 2. The diffractograms of iron, cobalt and copper ferrites match with the reference patterns of the corresponding MFe₂O₄ present in the ICDD PDF-2 database. Although the diffractograms of manganese, nickel and zinc ferrites are matching with the corresponding references patterns of MnFe₂O₄ (ICDD card No. 01-074-2403), NiFe₂O₄ (ICDD card No. 00-054-0964) and ZnFe₂O₄ (ICDD card No. 00-022-1012) (see Supporting Information for the complete comparison) the stoichiometry obtained from Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is not compatible with the ratio M:Fe=1:2 (Table 1).

Table 1. Results of the ICP-MS analysis measured on ferrites synthesized in miniemulsion-solvothermal conditions.

Metal (M) present	Reaction	[M] / [Fe]	
in the ferrite	temperature / °C	Molar	
		0.99 ± 0.03	
Со	80	0.510 ± 0.005	
Ni	100	1.00 ± 0.03	
Cu	80	0.50 ± 0.01	
Zn	80	0.305 ± 0.003	

The autogenous pressure present in the autoclave during the experiments was 200 kPa for the reactions at 80 $^{\circ}\rm C$ and 300 kPa for the reaction at 100 $^{\circ}\rm C$

The synthesis of manganese and nickel ferrites required, to obtain a crystalline material, a molar ratio between the precursors of metal: Fe 1:1, differently from the other ferrites synthesized with molar ratio metal:Fe 1:2; hence the molar ratio 1:1 adopted for the synthesis is probably the reason of the values measured by the ICP-MS. In addition to the pattern of MnFe₂O₄, the diffraction pattern of the manganese compound is matching as well with the reference pattern of Fe₃Mn₃O₈ (ICDD card No. 01-075-0034), as reported in Figure 2. Fe₃Mn₃O₈ is another kind of spinel ferrite, less common, facedcentered cubic and with the same point group ($Fd\overline{3}m$) as the Jacobsite MnFe₂O₄, but with a slightly contracted lattice. The explanation of the molar ratio Zn/Fe 0.3 obtained by ICP-MS cannot be ascribed to a different ratio between the precursors adopted, since the amounts of zinc and iron chlorides used were in the common ratio 1:2, but probably to the formation of a more favored crystalline phase, similar to the iron-rich ferrite (Zn_{0.664}Fe_{0.336}) (Fe_{1.934}Zn_{0.066})O₄ corresponding to the ICDD card No. 01-086-0508 (Franklinite ferroan, see Figure 2). The crystal structure of this phase is also in this

case spinel and face-centered cubic (space group $Fd\,\overline{3}m$) like the Franklinite ZnFe₂O₄.

In the case of the nickel ferrite, the molar ratio Ni:Fe 1:1 corresponds actually to the molar ratio adopted for the synthesis between Fe and Ni chlorides, as aforementioned. However, the diffractogram of this sample presents the typical reflections of NiFe2O4 and faint reflections ascribed to Ni(OH)₂, as reported in Figure 2; therefore, the sample obtained is a mixture of them. The syntheses were performed in an alkaline aqueous solution of the metal salts at a measured value of pH of 13.8. According to the pH-concentrations diagram of aqueous solution of nickel ions, a description of the behavior (i.e., concentrations and chemical forms) of the ions as a function of the pH, nickel hydroxide, and further oxo-hydroxo species, characterized by very low K_{sp}, already precipitate at pH 7. In our reaction conditions at pH 13.8, Ni should be present as insoluble hydroxide. Since the formation of the ferrites, under the chosen experimental conditions, occurs upon coprecipitation and dehydration of the corresponding hydroxides, it can be inferred that part of the hydroxide has not been decomposed to give the targeted material.

The diffractogram of CuFe₂O₄ displays, as well, the presence of the reflections ascribable to CuO, but the stoichiometry assessed by ICP-MS is as expected 1:2, consistent with nominal molar ratio between Cu and Fe chlorides of 1:2 used in the synthesis.

To define better the six ferrites produced in miniemulsion–solvothermal conditions in terms of sites occupation and quantify the relative amount of the spurious phases, Rietveld refinement was performed on the collected diffractograms. These procedures evidenced, for most ferrites, the presence of two different populations with different sizes. The crystallite sizes and relative weights are reported in Table S1.

In conclusion, though slight variation in the metal/Fe ratio, all the obtained ferrites are classified as spinels, with a face-centered cubic crystal system and $Fd\overline{3}m$ space group: the achievement of such crystalline spinel ternary oxides from the combination of miniemulsion and solvothermal conditions is, to the best of our knowledge, an unprecedented result. Our synergetic route allowed to obtain (except in the case of Ni and Cu, where, though much less intense reflections ascribed to Ni(OH)₂, and CuO, respectively, were also detected) phase pure crystalline materials and at lower temperature, 80 °C with respect to temperatures above 150 °C employed in other routes.51 The low temperature synthesis and the absence of post-synthesis thermal treatment are appealing from the perspective of sustainability and to avoid coalescence and coarsening, resulting in uncontrolled growth, of the nanoparticles. The achievement of crystallinity and of spinel formation for all samples is the result of a long process of optimization that involved the accurate selection of reagent molar ratios and reaction temperature: Mn and Ni ferrites were, as already mentioned, not obtained as expected from the molar ratio M:Fe 1:2, but rather with a 1:1 M:Fe molar ratio. Furthermore, a clearly crystalline NiFe2O4 was obtained only working at 100 °C (at 80 °C the product was not crystalline). Interestingly, as visually assessed, the miniemulsions were stable for few hours and no phase separation occurred. Despite of the boiling point of the cyclohexane (82 °C), they remained stable even after heating at 80 or at 100 °C for 24 h.



Figure 2 X-ray diffractograms of the ferrites produced using the solvothermal–miniemulsion route at 80-100 °C: (a) Fe₃Mn₃O₈ with its reference pattern ICDD card No. 01-075-0034 reported as vertical lines (b) Fe₃O₄ with ICDD card No. 00-019-0629 (c) CoFe₂O₄ with ICDD card No. 00-019-0629 (c) CoFe₂O₄ with ICDD card No. 00-054-0964 and the reference pattern (continuous line) ICDD card No. 01-073-1520 (e) CuFe₂O₄ with its reference pattern (continuous line) ICDD card No. 01-073-1520 (e) CuFe₂O₄ with its reference pattern (continuous line) ICDD card No. 01-077-0010 and the reference pattern of CuO (dashed line) ICDD card No. 01-086-0508, related to (Zn_{0.664}Fe_{0.336})(Fe_{1.934}Zn_{0.066})O₄.

As anticipated before, to investigate the effect of the different routes (miniemulsion and bulk, either at ambient pressure or under solvothermal conditions) on the crystallinity of the samples, a comparison of the XRD patterns of the iron-rich zinc ferrites is reported in Figure 3. Only the sample prepared by the synergetic approach (miniemulsion under solvothermal conditions) is highly crystalline, whereas the application of miniemulsion at ambient pressure and bulk in both of the conditions yield a poorly crystalline material. Rietveld refinement conducted on the pattern of the sample prepared by the synergetic approach (Table S1) evidences also in this case the presence of two size populations (4 nm: 57%; 13 nm: 43%). However, because of the low signal-to-noise ratio, a precise determination of the cation-site occupancy was not possible.



Figure 3 Iron-rich zinc ferrite produced with different routes compared with the reference pattern ICDD card No. 01-086-0508: (a) miniemul-

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sion at ambient pressure (ME) (b) miniemulsion under pressure (solvothermal route) (ME–HP) (c) bulk at ambient pressure (bulk) (d) bulk under pressure (solvothermal route) (bulk–HP).

The enhanced crystallinity of the sample synthesized by the synergy of miniemulsion and solvothermal route may be explained by the Laplace pressure acting on droplets.^{36, 38} The Laplace pressure is the pressure difference between the inside and the outside of a curved surface and it is caused by the surface tension at the liquid/liquid interface; this pressure is higher for small droplets and causes the disappearance of smaller ones in favor of the bigger ones (Ostwald Ripening). The Ostwald ripening is counteracted in miniemulsion, to guarantee the stability of the system, by the presence of an osmotic pressure agent (a substance soluble in the disperse phase-in our case the inorganic salts-but not in the continuous). The Laplace pressure is high in the small droplets of the miniemulsion and may promote the crystallization of inorganic systems at lower temperature than required (or even at room temperature), without any thermal treatment afterwards.^{52, 53} The additional external pressure due to the solvothermal route is likely to enhance this effect. The interfacial tension between the two phases (water with the salts and cyclohexane with PGPR) was experimentally determined with the pendant drop method and a value of $\gamma = (2.9 \pm$ 0.7) mN m⁻¹ was obtained (see Figure S4; value measured at room temperature, the possible effect of temperature is neglected). This surprisingly low valued was confirmed by measurements of the interfacial tension with the spinning drop method. The Laplace pressure exerted by droplets is given by the Young-Laplace equation:

$$\Delta P_{\text{Laplace}} = P_{\text{inside}} - P_{\text{outside}} = \frac{2\gamma_{\text{water/cylclohexane}}}{r_{\text{droplet}}}$$

For ideal spherical droplets of 100 nm of diameter, the resulting value of $\Delta P_{\text{Laplace}}$ is about 1.2·10⁵ Pa (1.2 bar). Accordingly, the pressure inside the droplets would be of about 3.4 bar (4.2 bar in the case of nickel, prepared at 100 °C), more than three times higher than atmospheric pressure, which evidences the advantages derived by the synergy miniemulsion–solvothermal conditions. The positive effect of pressure had been already pointed out in the case of simple hydrothermal synthesis of ferrites,⁴⁹ by comparing results obtained by using hydrothermal synthesis and by using reflux synthesis conditions at ambient pressure. In that case, the beneficial effect of applied pressure in terms of enhanced purity and yield was pointed out.

A typical cell volume for a ferrite would be of the order of 590 Å³, which multiplied by Avogadro's number would lead to a molar volume of 3.55×10^{-4} m³ mol⁻¹. Multiplying the pressure inside the droplets (3.4×10^5 Pa) by the molar volume, a value of 120.7 J mol⁻¹ (ca. 29 cal mol⁻¹) is obtained. We are not aware of reliable data on nucleation and growth activation energies for the studied ferrites, but we would expect values of the order of tenths up to hundreds of kilocalories per mol for the nucleation, and of a few kilocalories per mol up to tenths of kilocalories per mol. The estimated energy of ca. 29 cal/mol exerted by the curved interface of the bubbled is less relevant for the nucleation process (which occurs anyway also in the bulk solution), but would not be negligible growth processes.

As anticipated, the effect of the different routes was also determined on a short-range scale by performing X-ray absorption spectroscopy (XAS) experiments at Elettra synchrotron facility. XAS has been shown a very powerful tool to investigate nanosized ferrites, in particular to determine the cation distribution and thus the inversion degree of these structures. ⁵⁴ Analyses were performed at both Zn and Fe K-edges to enhance the local chemical sensitivity through a combined picture of both species and corresponding chemical environments. All the Zn K-edge X-ray absorption near-edge structure (XANES) spectra (Figure 4) present a white line composed of three peaks, at 9665 (A), 9668 (B) and 9672 eV (C), with a shoulder (D) at about 9679 eV. Features B and D were shown to be indicative of the degree of inversion, with peak B increasing for higher inversion, while shoulder D decreases.54 In addition, the position of these features slightly decreases in ferrites with higher inversion degrees. The experimental outputs evidence how the cationic distribution is relatively highly inverted for samples prepared by the synergetic approach or the miniemulsion at ambient pressure, while it decreases for the bulk preparation. The sample prepared by simple solvothermal method is likely a fully direct ferrite.

The position of the edge in the Fe K-edge XANES spectra (Figure 5) is typical for an oxidation state +3. The pre-edge peak provides valuable information. First of all, the position of the pre-edge peak is often a preferred way to determine the oxidation state with respect to the edge position, since it is less affected by multiple-scattering phenomena.⁵⁵⁻⁵⁷ In addition, this peak is symptomatic of the symmetry around the absorber. It arises from a $1s \rightarrow 3d$ transition, which is forbidden by dipole selection rules and hence weak, but the intensity of which increases for noncentrosymmetric environments, i.e. tetrahedral ones.⁵⁸



Figure 4 Zn K-edge XANES spectra of samples prepared with different synthetic approaches.

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Figure 5 Fe K-edge XANES spectra of iron-rich zinc ferrites prepared with different synthetic approaches.

The pre-edge position and relative intensities were analyzed after background removal with an arctangent function 55, 56 and deconvolution with pseudo-Voigt components. Divalent iron ions usually show a pre-edge peak centered around 7112.5–7113 eV, while for trivalent iron ions this is located around 7114–7114.5 eV.⁵⁵ The centroid positions determined for the experimental samples confirm an oxidation of +3 for all samples, being centered at 7114.2–7114.3 eV (Table S3). A small contribution of Fe2+, limited to less than 4%, is also present, compatible with the ferrite being rich in iron, and thus requiring the presence of divalent iron to keep electroneutrality.

In addition, the pre-edge peak area decreases in going from tetrahedral to octahedral site symmetry^{54,56}. The experimental data at Fe K-edge disagree with what had been evidenced by measurements at Zn K-edge, showing an opposite trend. The samples prepared by miniemulsion at ambient pressure or coupled with the solvothermal step show similar pre-edge areas (Table S3). Interestingly, the bulk sample show the greatest area, contrary on the indications given by the Zn K-edge. This likely indicates the presence of Fe₃O₄ moieties, not discernible in the XRD diffractograms due to similar patterns.

The Fourier transforms (FTs) of the EXAFS functions recorded at the two different edges are reported in Figure 6. The second shell that is the region between 2 and 4 Å is particularly meaningful, since it is mainly composed by the cation-cation contributions and can thus provide a qualitative indication of the inversion degree. In particular, the distance between two cations in octahedral sites is about 3.0 Å, whereas for two cations in tetrahedral sites this distance is about 3.65 Å; two cations occupying neighboring octahedral and tetrahedral sites are about 3.5 Å apart. (from crystal structure: $M_{O_h} - M_{T_d} = 3.00$ Å, $M_{O_h} - M_{T_d} = 3.51$ Å, $M_{T_d} - M_{T_d} = 3.66$ Å).



Figure 6 FTs of spectra recorded at a) Zn and b) Fe K-edges.

As seen in Figure 6a, the second shells in the Zn K-edge FTs are clearly formed by two components. Following the previous reasoning, the presence of a noticeable component at about 3 Å indicates a partially inverted spinel. In agreement with the XANES findings, this component is much less intense in the sample prepared by the simple solvothermal method, indicating that for this sample the inversion degree is lower. This, as outlined, is a very relevant result.

In the Fe K-edge FTs, the inversion degree is mainly evident in the contribution at 3.5 Å, corresponding to the interactions involving tetrahedral sites. For this edge, samples prepared by simple miniemulsion or by the combined approach present a higher occupation of Fe cations in T_d sites, symptomatic of higher inversion. The in-depth analysis of the EXAFS curves, detailing the features hinted by XANES and the Fourier Transforms, is reported in the Supporting information. Briefly, the Zn-O and Fe-O distances expected from the direct zinc ferrite structure (Zn in T_d A sites, Fe in O_h B ones) are 1.98 and 2.03 Å respectively. For Zn in A sites and Fe in B sites, the metal-to-oxygen bond distances determined by EXAFS are, for all samples, in agreement with these values (average values: 1.96 and 2.04 Å respectively). For Zn occupying B sites, an average bond distance of 2.04 Å was determined, slightly shorter than the expected value for divalent zinc in octahedral symmetry (2.10 Å). Finally, the insertion of trivalent Fe ions in the A sites leads to a shortening of M-O distances to about 1.88 Å, in accordance with Fe³⁺ in T_d sites (1.86 Å, Fe²⁺ in T_d: 2.00 Å). The distances determined for metal-metal interactions were $M_{O_h} - M_{O_h}$ =3.00 Å, $M_{O_h} - M_{T_d}$ =3.50 Å, $M_{T_d} - M_{T_d}$ =3.63 Å

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Analogously, to understand the effect of the heating time on the structural evolution, the synthesis of the samples in miniemulsion under solvothermal conditions at different treatment times (time 0, 3 h, 6 h, 12 h and 24 h) was carried out. In Figure 7 the diffractograms collected at different reaction times of the iron-rich zinc ferrite are reported whereas, for sake of comparison, the diffractograms of the other ferrites are shown in the Supporting Information. As expected, the crystallinity of the samples increases with time, the reflections becoming sharper and more intense. The sample collected at time 0 was centrifuged and washed immediately after the second miniemulsification without placing it at 80 °C and, as demonstrated by its diffractogram, it is poorly crystalline. As reported in Figure 7, Zn ferrite synthesized after only 3 h of reaction shows instead a crystalline pattern: this result is interesting in the pursuing of greener synthetic routes, because a crystalline product was achieved after a reaction of just 3 h at 80 °C, without further thermal treatment, only exploiting the non-standard conditions made available by the combination of miniemulsion and the solvothermal routes. Increasing the time of the reaction, other conditions being equal, the reflections become sharper, hence crystallinity increases.



Figure 7 Crystallization of iron-rich zinc ferrite synthesized in miniemulsion–solvothermal condition at different reaction times: (a) time zero (b) after 3 h (c) after 6 h (d) after 12 h and (e) after 24 h. The vertical lines are the reference pattern of $(Zn_{0.664}Fe_{0.336})(Fe_{1.934}Zn_{0.066})O_4$ ICDD card No. 01-086-0508.

Similar experiments with different reaction times were performed for all the six ferrites and the results are summarized in Table 2 (the diffractograms are reported in the Supporting Information). The values of crystallite size determined by the Scherrer formula⁵⁹ are, within the experimental error, constant, for each series of material, through all the experiments and the size of the crystallites depends strongly on the composition of the ferrite. Mn spinel has the biggest crystallites, followed by $CoFe_2O_4$; Zn ferrite and Fe_3O_4 show a similar size and $CuFe_2O_4$ has the smallest crystallites. NiFe₂O₄ starts to show distinguishable reflections after 12 hours, so that the Scherrer formula cannot be applied before. The constancy of the values of the crystallite size through all the experiment at different times points out that, even with very short processing time, except nickel ferrite, crystalline and stable materials are produced.

Table 2 Crystallite size (L), calculated with the Scherrer formula, for all the six ferrites produced in miniemulsion–solvothermal conditions.

	<i>L</i> Mn	LFe	<i>L</i> Co	LNi	<i>L</i> Cu	<i>L</i> Zn
	ferrite	ferrite	ferrite	ferrite	ferrite	ferrite
	/ nm	/ nm	/ nm	/ nm	/ nm	/ nm
3 h	37	9	13	-	6	8
6 h	37	12	14	-	6	10
12 h	34	11	15	24	7	13
24 h	36	13	14	29	7	10

The time zero is not reported because all these samples were poorly crystalline and the Scherrer formula could not be applied.

The time-resolved evolution of zinc ferrite nanostructures was also followed by means of Zn and Fe K-edges XAS. The Zn K-edge XANES evidences once more the relevance of the combined miniemulsion and solvothermal approach. The sample at t = 0 h, thus not subjected to any solvothermal treatment, indeed shows less defined features with respect to the other samples, indicating that the local structure around the Zn absorber sites is different, in agreement with a poorly crystalline sample. This might also be related to a size effect. With increasing treatment time, on the other hand, no significant difference could be detected, in agreement with the similar crystallite size.



Figure 8 Zn K-edge XANES spectra of samples prepared with different reaction times.

In a similar way, the Fe K-edge spectra registered after different reaction times are very similar, except for the starting sample (Figure 9). In this case, the pre-edge peak is slightly more intense than the following samples, indicating a less centrosymmetric local structure. This is confirmed by the fitting of the EXAFS function, since the Debye-Waller factors determined at both edges for the starting samples are higher than samples synthesized with longer times, due to a more disordered structure, in agreement with a smaller crystallite size (Table S6). Page 9 of 16

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Figure 9 Fe K-edge XANES spectra of iron-rich zinc ferrite samples prepared with different solvothermal treatment time.

X-ray diffraction (XRD) results on crystallinity were complemented with morphological investigations by transmission electron microscopy (TEM) (Figure 10). The images reported were obtained by embedding the nanoparticles in an ionic-liquid matrix, as reported in the Experimental Section (alternative measurements prepared by embedding the nanoparticles in a trehalose matrix with negative staining of uranyl acetate are reported in the Supporting Information, Figure S10). Despite the natural tendency to aggregate upon solvent evaporation, single primary particles are distinguishable. Noticeably, the miniemulsion route has the advantage of yielding samples that are less aggregated than the ones produced in bulk, since the particles are synthesized independently inside the droplets, acting as nanoreactors, and not in a single-event precipitation. Particle sizes were estimated by statistical treatment of TEM images. Two size populations were observed and a mean value was calculated from them (Table 3). The average sizes of the two populations are matching the sizes calculated by the Scherrer formula and by Rietveld refinement.

Since these materials are potentially applicable as heterogeneous catalysts, the specific surface area and the porosity, factors affecting the interaction with the substrates, are important features to be investigated. The physisorption of nitrogen at the critical temperature and the following calculation with the BET method allow assessing that the produced ferrites are mesoporous materials: their pores have sizes between 2 and 50 nm (Table 3). The hysteresis loop (Figure S11) is typical of slit-shaped pores, resembling the hysteresis loop H4 reported in the official definition of IUPAC.⁶⁰ The theoretical surface area calculated from the sizes obtained by statistical treatment of TEM micrographs was compared with the specific surface experimentally obtained from nitrogen physisorption experiments (BET isotherms, Table S7).



Figure 10 TEM images of the ferrites samples: the images are reported in the order of the periodic table.

The theoretical values, calculated for the ideal case of spherical and non-porous particles from the average size, are—except for the case of the manganese ferrite—generally smaller than the experimentally measured ones, which is a hint of the porosity of the materials that leads to a higher specific surface area. We also compared the experimental surface areas for the iron-rich zinc ferrites produced with the different routes. In this case, the sample synthesized by the miniemulsion–solvothermal route has the highest specific surface area, followed by the one produced in miniemulsion at ambient pressure and the two samples prepared in bulk solution (Figure S13). The hysteresis loops of the bulk samples seem different from the ones of the miniemulsion samples and they resemble more the H2 hysteresis loop officially defined by IUPAC,⁶⁰ typical of "inkbottle" pores (Figure S13). Both miniemulsion and bulk materials can be considered as mesoporous.

Table 3 Crystallite size calculated with the Scherrer formula (L), average particle size measured by TEM of the two size populations, specific surface area and average pore diameter of the ferrites synthesized in miniemulsion–solvothermal conditions for 24 h.

Metal pre- sent in the ferrite	Reaction temperature / °C	Pressure / kPa	L/nm	Average sizes / nm		Average size / nm	Specific Sur- face Area / m ² g ⁻¹	Average pore diameter / nm
Mn	80	200	36	5±1	11±2	8±2	80	9

Only Fe	80	200	13	6±1	21±9	14±6	93	12
Со	80	200	14	7.1±0.9	11±2	9±2	149	3
Ni	100	300	29	6±1	21±7	13±5	101	5
Cu	80	200	7	6±1	14±2	10±2	173	2
Zn	80	200	10	6±1	12±3	9±3	203	3

As outlined in the introduction, these nanomaterials feature also appealing magnetic properties. The room temperature (RT) magnetic behavior of the nanoparticles was characterized by measurements of the magnetic hysteresis in a SQUID magnetometer and is shown in Figure 11. Saturation magnetization values for each sample are reported in the corresponding plots.



Figure 11 Magnetization of the ferrites synthesized in miniemulsionsolvothermal conditions: (a) $Fe_3Mn_3O_8$ (b) Fe_3O_4 (c) $CoFe_2O_4$ (d) $NiFe_2O_4$ (e) $CuFe_2O_4$ (f) iron-rich Zn ferrite. The saturation magnetization values are reported as inset in the corresponding plots.

All samples show a superparamagnetic behavior except the $CoFe_2O_4$, which exhibits a ferromagnetic hysteresis loop at RT. The data displayed have been generated by subtraction of the small diamagnetic contribution of an empty capsule that was measured separately. For the Fe₃O₄ nanoparticles, a maximum value of 64 emu g⁻¹ is observed at 4 T (i.e. 40000 Oe) that can be compared to a theoretical saturation magnetization for magnetite of 96.5 emu g⁻¹ (assuming 4 Bohr magnetons per formula unit (μ B/f.u.) in the inverse spinel structure). As nanoparticles possess a high surface to volume ratio and the number of interacting neighbors at a surface is reduced, a reduction of the saturation moment must be expected and is frequently observed.⁶¹ The measured behavior can be reproduced within the measurement error using a superposition of Brillouin

functions calculated for superparamagnetic particles. The superparamagnetic clusters sizes (between 4-7 nm) calculated from the magnetic data are smaller than the crystallite sizes from X-rays outputs. However, in an X-ray experiment larger particles of a distribution will dominate as the scattered intensity scales with the scattering amplitude of a particle squared, while the magnetization increases linearly with the particle volume. In addition, a perfect magnetic spin alignment is not guaranteed in the nanoparticles such that the magnetic data rather give lower bounds on the particle sizes. For the other MFe₂O₄ compounds, an essential magnetic defect is the degree of inversion. E.g. for $CuFe_2O_4$ with $Cu(3d^9)$ and $Fe(3d^5)$ in a high spin state, one calculates 9 μ B/f.u. (5+5–1) for the normal spinel structure, while the inverse spinel structure has only 1 μ B/f.u. (5+1-5).⁶² This sets the bandwidth from 24 emu g⁻¹ up to 217 emu g⁻¹. We observe 30 emu g⁻¹ at B = 4 T which points more to an inverse spinel structure and is in agreement with the measurements on ball milled nanoparticles of this compound.⁶³ For the Zn based sample the observed saturation value of 41 emu g-1 at 4 T is in agreement with reported results on ZnFe₂O₄ nanoparticles of similar size by Guo et al.⁶⁴ A visual inspection of Figure 11 shows a most square like hysteresis curve for the Mn (Ni) compounds. The fitted values indicate superparamagnetic moments considerably larger than for the magnetite particles as determined from the magnetization curve. Indeed, the evaluation of the X-ray diffraction data (see Table 2) yielded the largest particle size for the Mn compound, followed closely by NiFe₂O₄, with both values being a factor 2–3 larger than that of the Fe₃O₄ nanoparticles. A pronounced hysteresis with a coercive field of 80 mT is only observed for CoFe₂O₄. For bulk samples a saturation magnetization of 74 emu g⁻¹ is observed⁶⁵ while high temperature treated nanoparticles of 25 nm size resulted in a saturation magnetization of 61.7 emu g⁻¹ and a coercive field of about 50 mT.66 Our low temperature processed nanoparticles of smaller size show a maximum magnetization at 4 T external field of 49 emu g⁻¹. In summary, the magnetic properties of the nanoparticles prepared by the low temperature solvothermal method are comparable to that of conventionally processed nanoparticles, which renders them suitable for a multitude of applications.

Catalytic Tests

The ferrite nanoparticles produced in miniemulsion are solventborn and, even after several washings, a part of the surfactant used (PGPR) adsorbed on their surface is still present; the particles are thus dispersible in organic solvents. For this important property, a reaction in organic medium, the oxidation of styrene, was selected to demonstrate the catalytic performances of the synthesized ferrites. This reaction has a strategic application as well: olefin epoxidation is one of the most important processes in the chemical industry and styrene oxide, one of the products (Figure 12), is an intermediate for fine chemicals and pharmaceuticals.⁶⁷ New efficient and recyclable heterogeneous catalysts for this reaction are therefore sought for.



Figure 12 Oxidation of styrene with t-butyl hydroperoxide.

Additionally, the ferrites are magnetic particles, therefore are easily separable from the reaction medium and recoverable to catalyze further other reactions. The oxidation reactions were carried out using 1,2-dichloroethane as a solvent because it increases the styrene conversion when compared to the other halogenated solvents.⁶⁸ The oxidant employed was t-butyl hydroperoxide in decane, chosen for its dispersibility in the organic solvent. In Table 4 the results of the oxidation with different catalysts are reported. With 100% conversion, manganese, cobalt, and copper ferrites display the highest styrene conversion after 24 h. The catalysts are selective mostly for styrene oxide and benzaldehyde (with comparable percentages) and only a small amount of phenylacetaldehyde is produced. The other three ferrites do not show any particular catalytic activity since the styrene conversion is only slightly higher than the one of the blank reaction, performed without any catalyst. Possible reasons proposed to explain the different catalytic activity among the tested ferrites are the different amount of oxygen vacancies in the spinel materials that facilitate the adsorption of the peroxide to form the molecular oxygen for the oxidation¹³ and that the Fe³⁺ cation from the octahedral sites of the ferrite reacts with the peroxide molecule to form metaloxyradical (Fe⁴⁺-O) and hydroxyl radicals as an initiation step. These species, which are formed on the surface of the catalyst, will then oxidize the alkene substrates.^{69,70} In certain cases also the other metal of the ferrites can form metal-oxyradical species with a transitional oxidation of the metal.71

Table 4 Styrene oxidation catalyzed by ferrites produced by the combination of miniemulsion and solvothermal route: conversion and selectivity after 24 h of reaction.

Metal present in the ferrite	Styrene con- version %	Benz-alde- hyde se- lectivity %	Phenyl- acet-alde- hyde se- lectivity %	Styrene oxide se- lectivity %
Mn	100	48	16	36
Fe	16	27	17	56
Со	100	39	15	46
Ni	15	28	18	54
Cu	100	56	16	28
Zn	8	0	40	60
Blank no cat- alyst	6	23	9	68

The same oxidation of styrene was performed several times with the same amounts of chemicals and with the same conditions using the same catalysts (Co, Cu and Mn ferrites) from the same batch to test the reproducibility of the results and those evaluations confirmed, in the range of the experimental error, the results reported in Table 4.

The cobalt, copper and manganese ferrites that showed relevant catalytic activities after a first cycle of reaction were separated from the reaction medium and collected with the help of a neodymium magnet. The recovered catalysts were then washed several times, dried and employed for other cycles of reaction. Interestingly, the catalyst showed in all the cases (except a little loss of activity and, especially in the case of copper ferrite, a slower kinetics), that the overall conversion is excellent reaching, in the case of copper and manganese ferrites, 100% of conversion also at 4th cycle of repetition.





Figure 13. Recyclability of the catalysts, ferrites produced by miniemulsion–solvothermal route. Conversion after different reactions with the same catalyst are reported (the solid line is guiding the eye): (a) $Fe_3Mn_3O_8$ (b) $CoFe_2O_4$ (c) $CuFe_2O_4$. In the insets, the pictures of the catalysts recovered with a magnet are reported.

Conclusions

In this work, we successfully explored, as a "proof of concept", the synergy between miniemulsion and solvothermal routes, pursuing unconventional synthesis conditions for the preparation of crystalline first row transition metal ferrites. In particular, the confinement of "nanoreactors" provided by miniemulsion droplets and the nonstandard temperature and pressure conditions provided by the solvothermal route were proven to be very effective to achieve crystalline metal ferrites at lower temperature (i.e. 80 °C) than usually required and without any post-synthesis thermal treatment. X-ray diffraction (XRD) demonstrated the crystallinity of the six spinel ferrites synthesized and that the zinc ones obtained with miniemulsion at ambient pressure and under bulk solution conditions either at ambient pressure or under solvothermal conditions did not result in comparatively highly crystalline ferrites, thus outlining the relevance of the combined synthetic approach. X-ray absorption spectroscopy (XAS) evidenced as Zn ferrites produced in miniemulsion are inverse spinels, whereas the samples produced in bulk, especially in the autoclave, are direct spinels. This is a relevant result since, being the composition equal, a switch from direct to partially inverse spinel could be accomplished. The reason for this occurrence could be clarified in future with in situ and time-resolved studies. The evolution of the crystallization of the ferrites was followed performing ex situ XRD on samples produced with different reaction times. A very noticeable outcome was the crystallization of the targeted compound already after 3 h of reaction when the combination of miniemulsion and solvothermal route, was applied, showing the high potential of this approach in pursuing more sustainable synthetic routes. Elemental measurements by ICP-MS assessed that the stoichiometries were not the expected one, MFe2O4, in the case of the Mn, Ni and Zn ferrite. In particular, Fe₃Mn₃O₈, (Zn_{0.664}Fe_{0.336}) (Fe_{1.934}Zn_{0.066})O₄ and a mixture between NiFe2O4 and Ni(OH)2 were selected as compatible compounds, which are in any case all spinel ferrites. Measurements of nitrogen physisorption at critical temperature and the corresponding calculations with the BET method displayed that the materials are mesoporous with a quite high surface area, making

them suitable for catalytic applications. The ferrites synthesized showed promising functional properties such as superparamagnetism, pointed out with the SQUID (superconductive quantum interference device), and catalytic properties for oxidation of styrene in organic medium, determined following the reactions with the GC-MS (gas chromatography coupled with mass spectrometry). Three of the six ferrites synthesized (Mn, Co and Cu ferrites), well dispersible in organic media, were proven to be catalytically active and reached 100% of conversion of styrene after 24 h. The ferrites can be furthermore, due to the mentioned magnetic properties, easily recovered from the reaction medium with a magnet and reused for several cycles without losing activity, pointing out a promising recyclability of the material.

ASSOCIATED CONTENT

The supporting information is available free of charge via the Internet at http://pubs.acs.org.

Comparisons among the diffractograms of manganese, nickel and zinc ferrites synthesized in miniemulsion-solvothermal route and the reference patterns; Rietveld refinement of the diffraction data of the ferrites produced in miniemulsion-solvothermal conditions; interfacial tension measurement; ICP-MS measurements on the iron-rich zinc ferrites; structural parameters tables determined by fitting of the EXAFS curves registered at Zn and Fe K-edges for the Zn ferrites samples; diffractograms of the ferrites produced with different reaction times; TEM images of the ferrites produced in miniemulsion-solvothermal conditions with sample preparation by embedding the material in a matrix of trehalose and negatively staining with uranyl acetate; adsorption-desorption isotherms and pore size distribution of the ferrites produced by miniemulsion-solvothermal combination; adsorption-desorption isotherms and pore size distribution of the iron-rich zinc ferrites produced with all the four routes; comparison between the surface areas measured and the ones calculated from TEM average particle size; fitting of the magnetization curves and related results.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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REFERENCES

1. Greenwood, N. N.; Earnshaw, A., *Chemistry of the Elements*. 2nd ed.; Butterworth-Heinemann: 1998.

2. Kung, H. H., *Transition Metal Oxides: Surface Chemistry and Catalysis*. Elsevier: Amsterdam, 1989.

3. Dionne, G. F., *Magnetic oxides, 1st Ed.* Springer: London, 2009.

4. Coey, J. M. D., *Magnetism and Magnetic Materials, 1st Ed.* Cambridge University Press: New York, 2010.

5. Muscas, G.; Yaacoub, N.; Concas, G.; Sayed, F.; Hassan, R. S.; Greneche, J. M.; Cannas, C.; Musinu, A.; Foglietti, V.; Casciardi, S.; Sangregorio, C.; Peddis, D., Evolution of the magnetic structure with chemical composition in spinel iron oxide nanoparticles. *Nanoscale* **2015**, *7*, 13576-13585.

6. Fernández-García, M.; Martínez-Arias, A.; Hanson, J. C.; Rodriguez, J. A., Nanostructured Oxides in Chemistry: Characterization and Properties. *Chem. Rev. (Washington, DC, U. S.)* **2004,** 104, 4063-4104.

7. Karimi, B.; Mansouri, F.; Mirzaei, H. M., Recent Applications of Magnetically Recoverable Nanocatalysts in C-C and C-X Coupling Reactions. *ChemCatChem* **2015**, *7*, 1736-1789.

8. Hudson, R.; Feng, Y.; Varma, R. S.; Moores, A., Bare magnetic nanoparticles: sustainable synthesis and applications in catalytic organic transformations. *Green Chem.* **2014**, *16*, 4493-4505.

9. Casbeer, E.; Sharma, V. K.; Li, X.-Z., Synthesis and photocatalytic activity of ferrites under visible light: A review. *Sep. Purif. Technol.* **2012**, 87, 1-14.

10. Sreekumar, K.; Sugunan, S., Ferrospinels based on Co and Ni prepared via a low temperature route as efficient catalysts for the selective synthesis of o-cresol and 2,6-xylenol from phenol and methanol. *J. Mol. Catal. A: Chem.* **2002**, 185, 259-268.

11. Shi, F.; Tse, M. K.; Pohl, M.-M.; Radnik, J.; Brückner, A.; Zhang, S.; Beller, M., Nano-iron oxide-catalyzed selective oxidations of alcohols and olefins with hydrogen peroxide. *J. Mol. Catal. A: Chem.* **2008**, 292, 28-35.

12. PalDey, S.; Gedevanishvili, S.; Zhang, W.; Rasouli, F., Evaluation of a spinel based pigment system as a CO oxidation catalyst. *Appl. Catal., B* **2005**, 56, 241-250.

13. Guin, D.; Baruwati, B.; Manorama, S. V., A simple chemical synthesis of nanocrystalline AFe₂O₄ (A = Fe, Ni, Zn): An efficient catalyst for selective oxidation of styrene. *J. Mol. Catal. A: Chem.* **2005**, 242, 26-31.

14. Zhang, D.-H.; Li, H.-B.; Li, G.-D.; Chen, J.-S., Magnetically recyclable Ag-ferrite catalysts: general synthesis and support effects in the epoxidation of styrene. *Dalton Trans.* **2009**, 10527-10533.

15. Florea, M.; Alifanti, M.; Parvulescu, V. I.; Mihaila-Tarabasanu, D.; Diamandescu, L.; Feder, M.; Negrila, C.; Frunza, L., Total oxidation of toluene on ferrite-type catalysts. *Catal. Today* **2009**, 141, 361-366.

16. Tsoncheva, T.; Manova, E.; Velinov, N.; Paneva, D.; Popova, M.; Kunev, B.; Tenchev, K.; Mitov, I., Thermally synthesized nanosized copper ferrites as catalysts for environment protection. *Catal. Commun.* **2010**, 12, 105-109.

17. Dillert, R.; Taffa, D. H.; Wark, M.; Bredow, T.; Bahnemann, D. W., Research Update: Photoelectrochemical water splitting and photocatalytic hydrogen production using ferrites (MFe₂O₄) under visible light irradiation. *APL Mater.* **2015**, 3, 104001.

 Kim, J. H.; Kim, J. H.; Jang, J.-W.; Kim, J. Y.; Choi, S. H.; Magesh, G.; Lee, J.; Lee, J. S., Awakening Solar Water-Splitting Activity of ZnFe₂O₄ Nanorods by Hybrid Microwave Annealing. *Adv. Energy Mater.* 2015, *5*, 1401933.

19. Zhu, Y.; Stubbs, L. P.; Ho, F.; Liu, R.; Ship, C. P.; Maguire, J. A.; Hosmane, N. S., Magnetic Nanocomposites: A New Perspective in Catalysis. *ChemCatChem* **2010**, *2*, 365-374. 20. Braga, D.; Grepioni, F., Reactions Between or Within Molecular Crystals. *Angew. Chem., Int. Ed.* **2004**, 43, 4002-4011.

21. Chinnasamy, C. N.; Narayanasamy, A.; Ponpandian, N.; Chattopadhyay, K.; Shinoda, K.; Jeyadevan, B.; Tohji, K.; Nakatsuka, K.; Furubayashi, T.; Nakatani, I., Mixed spinel structure in nanocrystalline NiFe₂O₄. *Phys. Rev. B: Condens. Matter* **2001**, 63, 184108.

22. Harris, V. G.; Fatemi, D. J.; Cross, J. O.; Carpenter, E. E.; Browning, V. M.; Kirkland, J. P.; Mohan, A.; Long, G. J., One-step processing of spinel ferrites via the high-energy ball milling of binary oxides. *J. Appl. Phys.* **2003**, 94, 496-501.

23. Schubert, U.; Hüsing, N., *Synthesis of inorganic materials, 2nd Ed*. Wiley-VCH: Weinheim, 2005.

24. Diodati, S.; Dolcet, P.; Casarin, M.; Gross, S., Pursuing the Crystallization of Mono- and Polymetallic Nanosized Crystalline Inorganic Compounds by Low-Temperature Wet-Chemistry and Colloidal Routes. *Chem. Rev. (Washington, DC, U. S.)* **2015,** 115, 11449-11502.

25. Mao, Y.; Park, T.-J.; Zhang, F.; Zhou, H.; Wong, S. S., Environmentally Friendly Methodologies of Nanostructure Synthesis. *Small* **2007**, 3, 1122-1139.

26. Javadi, S.; Masoudpanah, S. M.; Zakeri, A., Conventional versus microwave combustion synthesis of CoFe₂O₄ nanoparticles. *J. Sol-Gel Sci. Technol.* **2016**, 79, 176-183.

27. Niederberger, M.; Antonietti, M., Nonaqueous Sol–Gel Routes to Nanocrystalline Metal Oxides. In *Nanomaterials Chemistry*, Rao, C. N. R.; Müller, A.; Cheetham, A. K., Eds. Wiley-VCH Verlag GmbH & Co. KGaA: 2007; pp 119-137.

28. Bilecka, I.; Kubli, M.; Amstad, E.; Niederberger, M., Simultaneous formation of ferrite nanocrystals and deposition of thin films via a microwave-assisted nonaqueous sol-gel process. *J. Sol-Gel Sci. Technol.* **2011**, *57*, 313-322.

29. Pinna, N.; Niederberger, M., Surfactant-free nonaqueous synthesis of metal oxide nanostructures. *Angew. Chem., Int. Ed.* **2008,** 47, 5292-5304.

30. Byrappa, K.; Yoshimura, M., *Handbook of Hydrothermal Technology*. Noyes Publications, Park Ridge, New Jersey, U.S.A: 2001.

31. Modeshia, D. R.; Walton, R. I., Solvothermal synthesis of perovskites and pyrochlores: crystallisation of functional oxides under mild conditions. *Chem. Soc. Rev.* **2010**, 39, 4303-4325.

32. Cushing, B. L.; Kolesnichenko, V. L.; O'Connor, C. J., Recent Advances in the Liquid-Phase Syntheses of Inorganic Nanoparticles. *Chem. Rev. (Washington, DC, U. S.)* **2004,** 104, 3893-3946.

33. Lu, A.-H.; Salabas, E. L.; Schüth, F., Magnetic Nanoparticles: Synthesis, Protection, Functionalization, and Application. *Angew. Chem., Int. Ed.* **2007**, 46, 1222-1244.

34. Sanchez-Dominguez, M.; Pemartin, K.; Boutonnet, M., Preparation of inorganic nanoparticles in oil-in-water microemulsions: A soft and versatile approach. *Curr. Opin. Colloid Interface Sci.* **2012**, 17, 297-305.

35. Zarur, A. J.; Ying, J. Y., Reverse microemulsion synthesis of nanostructured complex oxides for catalytic combustion. *Nature* **2000**, 403, 65-67.

36. Landfester, K., The Generation of Nanoparticles in Miniemulsions. *Adv. Mater. (Weinheim, Ger.)* **2001,** 13, 765-768.

37. Landfester, K., Miniemulsions for Nanoparticle Synthesis. *Top. Curr. Chem.* **2003**, 227, 75-123.

38. Muñoz-Espí, R.; Weiss, C. K.; Landfester, K., Inorganic nanoparticles prepared in miniemulsion. *Curr. Opin. Colloid Interface Sci.* **2012**, 17, 212-224.

39. Muñoz-Espí, R.; Mastai, Y.; Gross, S.; Landfester, K., Colloidal systems for crystallization processes from liquid phase. *CrystEngComm* **2013**, 15, 2175-2192.

40. Einarsrud, M.-A.; Grande, T., 1D oxide nanostructures from chemical solutions. *Chem. Soc. Rev.* **2014**, 43, 2187-2199.

41. Rabenau, A., The Role of Hydrothermal Synthesis in Preparative Chemistry. *Angew. Chem., Int. Ed. Engl.* **1985**, 24, 1026-1040.

42. Lobachev, A. N., *Crystallization Processes under Hydrothermal Conditions*, 1st *Ed*. Consultants Bureau: New York, 1973.

43. Renz, P.; Kokkinopoulou, M.; Landfester, K.; Lieberwirth, I., Imaging of Polymeric Nanoparticles: Hard Challenge for Soft Objects. *Macromol. Chem. Phys.* **2016**, 217, 1879-1885.

44. Ravel, B.; Newville, M., ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Rad.* **2005**, 12, 537-541.

45. Zhao, D.; Wu, X.; Guan, H.; Han, E., Study on supercritical hydrothermal synthesis of $CoFe_2O_4$ nanoparticles. *J. Supercrit. Fluids* **2007**, 42, 226-233.

46. McClements, D. J., *Food Emulsions: Principles, Practices, and Techniques, Third Edition.* CRC Press: 2015.

47. Antoine, C., Tensions des vapeurs; vouvelle relation entre les tensions et les températures. *C. R. Acad. Sci.* **1888**, 107, 681-684.

48. Diodati, S.; Nodari, L.; Natile, M. M.; Caneschi, A.; de Julián Fernández, C.; Hoffmann, C.; Kaskel, S.; Lieb, A.; Di Noto, V.; Mascotto, S.; Saini, R.; Gross, S., Coprecipitation of Oxalates: An Easy and Reproducible Wet-Chemistry Synthesis Route for Transition-Metal Ferrites. *Eur. J. Inorg. Chem.* **2014**, 2014, 875-887.

49. Diodati, S.; Pandolfo, L.; Caneschi, A.; Gialanella, S.; Gross, S., Green and low temperature synthesis of nanocrystalline transition metal ferrites by simple wet chemistry routes. *Nano Res.* **2014**, *7*, 1027-1042.

50. Rossmanith, R.; Weiss, C. K.; Geserick, J.; Hüsing, N.; Hörmann, U.; Kaiser, U.; Landfester, K., Porous Anatase Nanoparticles with High Specific Surface Area Prepared by Miniemulsion Technique. *Chem. Mater.* **2008**, 20, 5768-5780.

51. Niederberger, M.; Pinna, N., *Metal Oxide Nanoparticles in Organic Solvents - Synthesis, Formation, Assembly and Applications.* Springer: New York, 2009.

52. Singh, I.; Landfester, K.; Chandra, A.; Munoz-Espi, R., A new approach for crystallization of copper(ii) oxide hollow nanostructures with superior catalytic and magnetic response. *Nanoscale* **2015**, *7*, 19250-19258.

53. Varol, H. S.; Álvarez-Bermúdez, O.; Dolcet, P.; Kuerbanjiang, B.; Gross, S.; Landfester, K.; Muñoz-Espí, R., Crystallization at Nanodroplet Interfaces in Emulsion Systems: A Soft-Template Strategy for Preparing Porous and Hollow Nanoparticles. *Langmuir* **2016**.

54. Carta, D.; Marras, C.; Loche, D.; Mountjoy, G.; Ahmed, S. I.; Corrias, A., An X-ray absorption spectroscopy study of the inversion degree in zinc ferrite nanocrystals dispersed on a highly porous silica aerogel matrix. *J. Chem. Phys.* **2013**, 138, 054702.

55. Boubnov, A.; Lichtenberg, H.; Mangoldc, S.; Grunwaldt, J.-D., Identification of the iron oxidation state and coordination geometry in iron oxide- and zeolite-based catalysts using pre-edge XAS analysis. *J. Synchrotron Rad.* **2015**, *22*, 410-426.

56. Wilke, M.; Farges, F.; Petit, P.-E.; Brown, G. E.; Martin, F., Oxidation state and coordination of Fe in minerals: An Fe K-XANES spectroscopic study. *Am. Mineral.* **2001**, *86*, 714-730.

57. Waychunas, G. A.; Brown, G. E.; Apted, M. J., X-ray K-edge absorption spectra of Fe minerals and model compounds: II. EXAFS. *Phys. Chem. Miner.* **1986**, 13, 31-47.

58. Nilsen, M. H.; Nordhei, C.; Ramstad, A. L.; Nicholson, D. G.; Poliakoff, M.; Cabañas, A., XAS (XANES and EXAFS) Investigations of Nanoparticulate Ferrites Synthesized Continuously in Near Critical and Supercritical Water. *J. Phys. Chem. C* **2007**, 111, 6252-6262.

59. Scherrer, P., Bestimmung der Groesse und der inneren Struktur von Kolloidteilchen mittels Roentgenstrahlen. *Göttinger Nachrichten Math. Phys.* **1918**, 2, 98-100.

60. Sing, K. S. W.; Everett, D. H.; Haul, R. A. W.; Moscou, l.; Pierotti, R. A.; Rouquerol, J.; Siemieniewska, T., REPORTING PHYSISORPTION DATA FOR GAS/SOLID SYSTEMS with Special Reference to the Determination of Surface Area and Porosity. *Pure Appl. Chem.* **1985**, *57*, 603-619.

61. Bannwarth, M. B.; Camerlo, A.; Ulrich, S.; Jakob, G.; Fortunato, G.; Rossi, R. M.; Boesel, L. F., Ellipsoid-shaped superparamagnetic

nanoclusters through emulsion electrospinning. *Chem. Commun.* (*Cambridge, U.K.*)**2015,** 51, 3758-3761.

62. Zuo, X.; Yang, A.; Vittoria, C.; Harris, V. G., Computational study of copper ferrite (CuFe₂O₄). *J. Appl. Phys.* **2006**, 99, 08M909/1-3.

63. Jiang, J. Z.; Goya, G. F.; Rechenberg, H. R., Magnetic properties of nanostructured CuFe₂O₄. J. Phys.: Condens. Matter **1999**, 11, 4063.

64. Guo, P.; Cui, L.; Wang, Y.; Lv, M.; Wang, B.; Zhao, X. S., Facile Synthesis of ZnFe₂O₄ Nanoparticles with Tunable Magnetic and Sensing Properties. *Langmuir* **2013**, 29, 8997-9003.

65. Gonzalez-Sandoval, M. P.; Beesley, A. M.; Miki-Yoshida, M.; Fuentes-Cobas, L.; Matutes-Aquino, J. A., Comparative study of the microstructural and magnetic properties of spinel ferrites obtained by coprecipitation. *J. Alloys Compd.* **2004**, 369, 190-194.

66. Zi, Z.; Sun, Y.; Zhu, X.; Yang, Z.; Dai, J.; Song, W., Synthesis and magnetic properties of CoFe₂O₄ ferrite nanoparticles. *J. Magn. Magn. Mater.* **2009**, 321, 1251-1255.

67. Espinal, L.; Suib, S. L.; Rusling, J. F., Electrochemical Catalysis of Styrene Epoxidation with Films of MnO₂ Nanoparticles and H₂O₂. *J. Am. Chem. Soc.* **2004**, 126, 7676-7682.

 Kooti, M.; Afshari, M., Magnetic cobalt ferrite nanoparticles as an efficient catalyst for oxidation of alkenes. *Sci. Iran.* 2012, 19, 1991-1995.

69. Pardeshi, S. K.; Pawar, R. Y., SrFe₂O₄ complex oxide an effective and environmentally benign catalyst for selective oxidation of styrene. *J. Mol. Catal. A: Chem.* **2011**, 334, 35-43.

70. Pardeshi, S. K.; Pawar, R. Y., Optimization of reaction conditions in selective oxidation of styrene over fine crystallite spinel-type $CaFe_2O_4$ complex oxide catalyst. *Mater. Res. Bull.* **2010**, 45, 609-615.

71. Rayati, S.; Zakavi, S.; Koliaei, M.; Wojtczak, A.; Kozakiewicz, A., Electron-rich salen-type Schiff base complexes of Cu(II) as catalysts for oxidation of cyclooctene and styrene with tert-butylhydroperoxide: A comparison with electron-deficient ones. *Inorg. Chem. Commun.* **2010**, 13, 203-207.





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