

Synthesis of hematite nanowires using a mesoporous hard template

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Abstract The influence of the impregnation media (ethanol or water) and the calcination atmosphere (air and NO/He) on the hematite nanowires production embedded on a hard template (MCM-41) was studied. The solids were characterized by X-ray diffraction, Mössbauer spectroscopy and magnetic measurements. The results obtained indicate that the more appropriate conditions for the iron oxide nanowires to get inside the MCM-41 hard template seem to be reached using water as a solvent and air as calcination atmosphere.

Keywords Nanoarrays · Nanoparticles · Hematite · Fe/MCM-41

1 Introduction

The properties exhibited by arrays of nanowires and nanotubes are currently intensively investigated because of the new phenomena that they give rise and the wealth of applications that these systems offer, like potential applications in high-density magnetic recording media and other nanodevices [1]. Several methods have been used to obtain nanowires with specific physical properties, for example: laser ablation [2], electrodeposition [3] or supercritical fluid phase inclusion [4]. However, these techniques have the common disadvantage of their complexity.

Aiming at overcoming this difficulty, a highly ordered mesoporous template could be used as a host, where the material of interest can be embedded. MCM-41 is an almost perfectly ordered mesoporous material suitable for this purpose. It has been reported that conveniently magnetic compounds [5, 6] can be confined in a quasi

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one-dimensional array due to its particular topology of regular hexagonal parallel channels with usual average diameters of less than 5 nm.

In a previous work [7] we have obtained nanowire geometry by embedding hematite nanoparticles in the hexagonal array of the very narrow channels of MCM-41. Hematite was chosen as the first step of the preparative methods because its handling is easier than the magnetic iron oxides, maghemite and magnetite. Notwithstanding, the magnetic oxides are more interesting due to their potential applications [1]. Currently we are carrying out alternative experiments to induce the structural transformations that lead from hematite nanowires to maghemite and magnetite nanowires.

In this work, we report the synthesis of three samples prepared in different conditions by incipient wetness impregnation of MCM-41 with iron nitrate to yield an iron nominal concentration of 15 wt.%. The aim of the present work is to study the effect of the nature of the impregnating solution and the calcination atmosphere on the structural properties of the iron oxides nanowires.

2 Experimental section

The MCM-41 matrix was prepared according to the methodology proposed by Ryoo and Kim [8]; firstly 40 g of sodium silicate (26.1% SiO₂) is dissolved into 74 g of water. The solution was then slowly added to 38 ml of cetyltrimethylammonium chloride and 0.65 ml of NH₃ with vigorous stirring at room temperature. This mixture was heated in a polypropylene bottle, without stirring to 373 K for 24 h, afterwards, it was cooled to room temperature. The pH was adjusted to approximately 11 by drop wise addition of acetic acid with vigorous stirring. The reaction mixture was heated again to 373 K for 24 h. This procedure for pH adjustment and subsequent heating was repeated twice. The resulting solid was filtered, washed and dried in air at room temperature. It was then calcined at 813 K for 1 h in flowing N₂ (150 cm³/min) followed by 6 h in flowing air (150 cm³/min).

Three solids were obtained treating MCM-41 in the following ways in order to obtain iron concentrations of about 15 wt.%:

- | | |
|-----------------------|--|
| Fe/MCM-41 (alc-air) | incipient wetness impregnation with Fe(NO ₃) ₃ ·9H ₂ O in ethanolic solution. The sample was dried at room temperature in atmospheric air, calcined in dry air stream (100 cm ³ /min) from 298 to 723 K at 1 K/min and kept at 723 K for 4 h. |
| Fe/MCM-41 (alc-NO/He) | impregnated in the same way that Fe/MCM-41 (alc-air). The sample was dried at room temperature in atmospheric air, calcined in a dry mixture of 1% (V/V) of NO in He (100 cm ³ /min) from 298 to 723 K at 1 K/min and kept at 723 K for 4 h following the methodology proposed by Sietsma et al. [9]. |
| Fe/MCM-41 (aq-air) | incipient wetness impregnation with Fe(NO ₃) ₃ ·9H ₂ O aqueous solution. The sample was dried at room temperature in atmospheric air, and calcined in the same way than Fe/MCM-41 (alc-air). |

The resulting solids were characterized by X-ray diffraction (XRD), Nitrogen adsorption (BET), Mössbauer spectroscopy and magnetic measurements.

All XRD patterns were measured using a standard automated powder X-ray diffraction system Philips PW 1710 with diffracted-beam graphite monochromator using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Nitrogen adsorption isotherms were recorded at the temperature of liquid nitrogen (77 K) using a Micromeritics ASAP 2020 apparatus.

The Mössbauer spectra at 298 and 30 K were taken in transmission geometry with a constant acceleration spectrometer. A source of ^{57}Co in Rh matrix of nominally 50 mCi was used. Velocity calibration was performed against a metallic 12 μm -thick $\alpha\text{-Fe}$ foil at room temperature. All isomer shifts (δ) are referred to this standard. The temperature between 30 and 298 K was varied using a Displex DE-202 Closed Cycle Cryogenic System. The Mössbauer spectra were fitted using the Recoil program [10]. At 30 K the Blume and Tjon's dynamic line shape site analysis option was used [10]. Lorentzian lines with equal linewidths were considered for each spectrum component in a complete superparamagnetic regime.

Magnetic measurements of Zero Field Cooling (ZFC) and Field Cooling (FC), recorded between 5 and 300 K, were carried out using a commercial superconducting quantum interference device magnetometer from Quantum Design with a field of $H_{\text{FC}} = 500 \text{ Oe}$.

3 Results and discussion

The typical structural properties of an ordered mesoporous solid MCM-41, used as template, were confirmed by XRD and by their textural properties measured by N_2 adsorption using the BET method. Because of the lack of space, the results are not shown here. The XRD measurements allowed verifying that the impregnation and calcination treatments did not modify the solid structure.

The Mössbauer spectra of all samples at 298 K only display a doublet (Fig. 1). The hyperfine parameters obtained by the fitting procedure (Table 1) are identical, within the experimental errors, for all solids. They can be assigned to superparamagnetic $\alpha\text{-Fe}_2\text{O}_3$ or paramagnetic Fe^{3+} ions. Taking into account our previous results, the absence of a sextuplet at room temperature, is an indication that nearly all the iron species are inside the MCM-41 channels [7].

When the temperature decreases down to 30 K, the spectrum of Fe/MCM-41 (aq-air) shows a magnetic splitting with a very intense central peak and four additional peaks (Fig. 1). One relaxing sextet and a very broad singlet were used in the fittings. The hyperfine parameters of the sextuplet can be assigned to small $\alpha\text{-Fe}_2\text{O}_3$ crystals [11] (Table 1). Therefore, from the thermal evolution of the spectra we conclude that iron species in Fe/MCM-41 (aq-air) consists of $\alpha\text{-Fe}_2\text{O}_3$ constituted by crystallites of very small size, which are in a superparamagnetic relaxation regime at room temperature. Since at 30 K the magnetic signal area is about 58%, we can consider that the blocking temperature is not far from this value.

The Fe/MCM-41 (alc-air) spectrum at 30 K displayed a central doublet and a curved background typical of a superparamagnetic signal belonging to a magnetic system that is close to its blocking temperature (Fig. 1). It was fitted with a doublet and a relaxing sextet. Following the same reasoning that in the sample impregnated

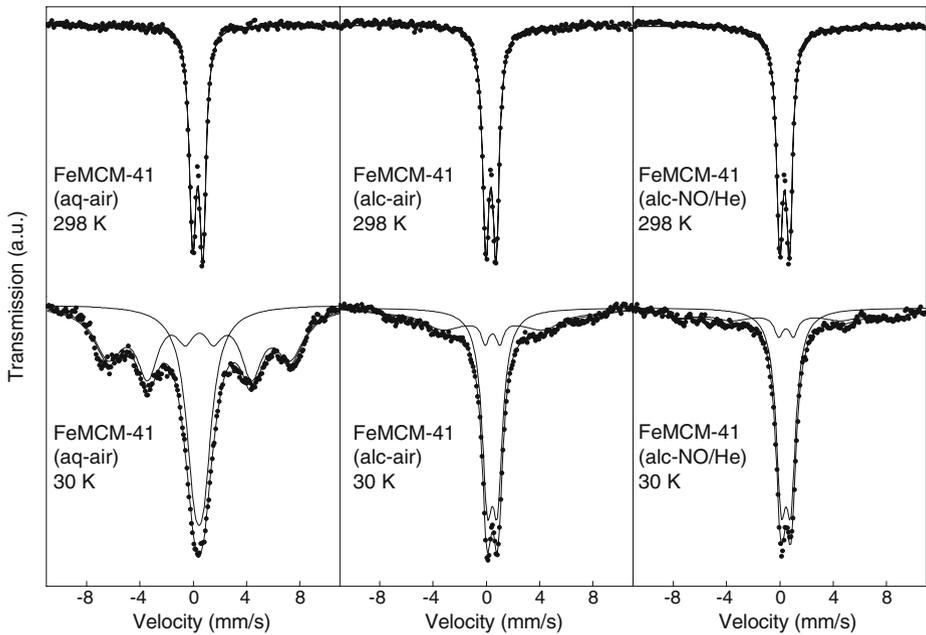


Fig. 1 Mössbauer spectra of all solids at 298 and 30 K

Table 1 Hyperfine parameters and blocking temperatures of the samples

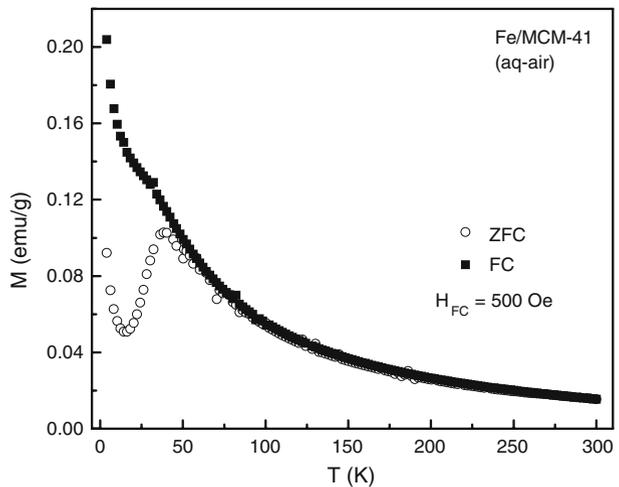
Temperature	Parameters	Fe/MCM-41 (aq-air)	Fe/MCM-41 (alc-air)	Fe/MCM-41 (alc-NO/He)
298 K	Δ (mm/s)	0.75 ± 0.01	0.75 ± 0.01	0.72 ± 0.01
	δ (mm/s)	0.35 ± 0.01	0.35 ± 0.01	0.36 ± 0.01
	%	100 ± 2	100 ± 2	100 ± 2
30 K	H (T)	54.2 ± 0.3	53^a	53^a
	δ (mm/s)	0.46 ± 0.03	0.47^a	0.47^a
	2ε (mm/s)	-0.02 ± 0.05	0^a	0^a
	%	58 ± 2	39 ± 2	36 ± 5
	δ (mm/s)	0.44 ± 0.01	–	–
	%	42 ± 1	–	–
	Δ (mm/s)	–	0.77 ± 0.01	0.73 ± 0.03
	δ (mm/s)	–	0.46 ± 0.01	0.46 ± 0.01
	%	–	61 ± 1	64 ± 1
ZFC-FC blocking temperature (K)		40 ± 2	15 ± 2	< 6

H hyperfine magnetic field in Tesla, δ isomer shift (all the isomer shifts are referred to α -Fe at 298 K), 2ε quadrupole shift, Δ quadrupole splitting

^aParameter held fixed in fitting

with aqueous solution, the only species present would be α -Fe₂O₃. However, in this sample the blocking temperature is lower than 30 K, since only 39% is magnetically blocked at that temperature. Therefore, the nature of the solvent has produced a difference on the α -Fe₂O₃ crystallite sizes. Perhaps, the lower surface tension of

Fig. 2 ZFC-FC curves for Fe/MCM-41 (aq-air)



the ethanolic solution has favoured the “spreading” of the iron species on the wall channels of the MCM-41 template leading to smaller crystallite sizes.

To study the influence of the calcination atmosphere, a sample impregnated in ethanolic solution was calcined in NO/He flow, as proposed by Sietsma et al. [9]. According to these authors, this procedure enables the preparation of high loading of Co_3O_4 (15–18 wt.%) inside the pores of SBA-15 with high dispersion. In our system (Fe/MCM-41 (alc-NO/He)) the Mössbauer spectrum at 30 K is very similar to that obtained by Fe/MCM-41 (alc-air; Fig. 1). There is only a slight difference between the percentages of the magnetically blocked signal (Table 1). Therefore, the blocking temperatures of both samples must be very similar.

The values of the blocking temperatures obtained from ZFC-FC magnetization results are in good agreement with the estimations from Mössbauer spectroscopy, taking into account the different sampling times of both techniques. These values are displayed in Table 1. Besides, at temperatures higher than the corresponding blocking temperatures, the ZFC-FC curves are coincident, confirming the superparamagnetic state of the iron species. As an example, in Fig. 2 it can be seen the ZFC-FC curves for Fe/MCM-41 (aq-air).

4 Conclusions

In the present work, we have demonstrated that in Fe/MCM-41 (15% wt of Fe) system, the effect of the solvent on the structural properties of the iron species is more important than that of the calcination atmosphere. Considering that in all samples the maximum diameter of the iron oxide particles is determined by the channel diameter of the MCM-41, the higher blocking temperature in Fe/MCM-41 (aq-air) would indicate a higher shape anisotropy magnetic constant. Therefore, the more appropriate conditions for the iron oxide nanowires to get inside the MCM-41 hard template seem to be reached using water as a solvent and air as calcination atmosphere.

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