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# Development of iron modified MCM-41 as promising nano-composites with specific magnetic behavior

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### ABSTRACT

MCM-41 type mesoporous silica materials were synthesized and modified with different iron loadings by the wet impregnation method and exhaustively characterized by different instrumental techniques, including XRD, TEM, N<sub>2</sub> adsorption, UV–Vis DRS, XPS, TPR and Mössbauer spectroscopy. The relation between the iron loadings in the samples and their structural, textural and magnetic properties were studied. The curves of room temperature magnetization vs. field were measured using a maximum magnetic applied field of  $\mu_0$ Ha = 1 T. Depending on the dispersion and size of the different iron species, the nanocomposites showed different magnetic behaviors. Thus, a predominant superparamagnetic behavior was found for the samples with the lower iron loadings; this feature was assigned to oxide species finely dispersed such as the oligonuclear (FeO)<sub>n</sub> clusters and nanoparticles, both of very small size and located preferably inside the channels. Meanwhile, a lineal behavior was observed for the samples with the higher Fe loadings, attributed to the hematite nanoparticles of larger size, located on the external surface. © 2014 Elsevier Inc. All rights reserved.

## 1. Introduction

The new family of mesoporous silica compounds, called M41S [1-4], was one major discovery in the area of inorganic nanostructured materials with controlled pore size distribution. Particularly, MCM-41 is one of the most attractive porous materials because of its characteristic well-ordered structure with a hexagonal arrangement of mesopores [2,3]. The thermal stability, the large specific area (>900  $m^2/g$ ) and the uniform mesopores with controllable diameter of 2-10 nm, have made these materials highly desirable in multiple application fields. However, pure siliceous mesoporous materials have not sufficient intrinsic activities as catalysts neither interesting magnetic properties. In this sense, it has been found that metal ions can also be implanted into MCM-41 by different synthesis methods. Thus, the application field of these materials has been extended to catalysis, adsorption and separation, lasers, sensors, solar cells, host-guest chemistry, environmental technology as well as to biomedical field [5–11]. In this last field, a limitation of traditional therapies is that the therapeutic drugs are

administered intravenously leading to general systemic distribution, resulting in harmful side-effects. However, if such treatments could be localized only at the specific site required of the body then the continued use of therapeutic drugs very potent and effective could be possible. This fact, combined with the intrinsic penetrability of magnetic fields into human tissue, opens up many applications involving the transport of magnetic nanoparticles, or of magnetically tagged biological entities [12]. Therefore, drug delivery has been presented as a potential use of these mesoporous materials, because of their features: a suitable pore size to host biomolecules/drugs, superior adsorption capacities, and low cytotoxicity [10–15]. In this context, it is pertinent to mention the synthesis of mesoporous composites having magnetic elements embedded in the nanochannels or in the porous framework as an alternative to the controlled release of drugs.

Two main factors regulate material magnetic properties at the nanometer scale: the size and the surface effects. At even smaller sizes (tens of nanometers or less), a superparamagnetic behavior is observed, in which the particle magnetic moment as a whole freely fluctuates in response to thermal energy [12]. This regime, similar to the paramagnetic one but involving the total magnetic moment of the particles  $(10^3 \text{ mB})$  instead those of the individual atoms, is detected in systems containing small, non-interacting







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single domain particles. The single-domain critical size, above which particles develop domain walls and become multidomain, is an upper bound above which no superparamagnetism is observed.

Nanosized magnetic particles are extremely difficult to synthesize because they tend to aggregate and/or coalesce, losing the specific properties associated to non-interacting superparamagnetic particles. However, when nanoparticles are fabricated into porous solid supports, offering high specific surface, magnetic particles agglomeration may be completely inhibited and the stability of small sized metal and metal oxide nanoparticles enhanced. Recognition of these effects led to propose the use of porous substrates to design magnetic carriers for drug delivery to specific sites within the body [16,17]. In this sense, Debrassi et al. [18] have recently reported advancements about magnetic materials synthesis for the controlled release of indomethacin. They obtained materials with high drug loading efficiency and adequate magnetic properties. Meanwhile, Limnell et al. [19] have researched about the application of mesoporous materials as hosts for therapeutic drugs as well as their chemical stability.

The modification of mesoporous materials with iron by different methods has already been widely discussed in the literature [20–22]. Many works describing the magnetic properties of MCM-41 with some particular iron compositions can be found [23–27]. In this sense, Ursachia et al. [23] and Marchetti et al. [24–26] have studied magnetic properties of iron oxide nanoparticles dispersed inside the mesopores of silica matrix, prepared by impregnation using an Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O aqueous solution, but they have presented only some iron contents. Gervasini et al. [27] have reported a magnetic study about silica like mesoporous materials with high iron content using Fe-acetylacetonate as metal source; they obtained materials with loads from  ${\sim}6\%$  to about  ${\sim}17\%$  but with low specific area (lower than  $300 \text{ m}^2/\text{g}$ ). Nevertheless, up to now, thorough and systematic investigations on the nature of the iron species in terms of the metal loading and its influence on the magnetic behavior are scarce. In this sense, beyond studying a post-synthesis method to functionalize MCM-41 silicates, the main differentiating criterion of the present work is the study of the evolution in the iron speciation, depending of the metal loading and associated with a particular magnetic behavior, through an exhaustive multi-technique characterization including XRD, TEM, N<sub>2</sub> adsorption, UV-Vis RD, XPS, TPR, Mössbauer spectroscopy and magnetization measurements. Thus, the nature of the different iron species obtained as consequence of anchoring and clustering processes on the MCM-41 surface, depending of metal loading, have been described and closely related with their magnetic behavior, in searching nanocomposites potentially suitable as drug carriers.

### 2. Experimental

#### 2.1. Synthesis

The metal-free MCM-41 mesoporous molecular sieve was synthesized as previously reported [28] following the method B, using cetyltrimethylammonium bromide (CTAB) as template and tetraethoxysilane (TEOS) as silicon source. The synthesis mixture (pH = 11.25) was stirred at room temperature for 4 h. Then, this gel was heated at 70 °C under stirring in a closed flask. The obtained solid was then filtered off, washed with distilled water, and dried at 60 °C overnight. To remove the template, the samples were heated, under N<sub>2</sub> flow, up to 500 °C maintaining this temperature for 6 h and subsequently calcined at 500 °C under air flow for 6 h. This solid, previously calcined for 5 h in oven at 500 °C, was modified with iron by the wet impregnation method. Different concentrations of an aqueous solution of the metal precursor Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, were used to reach the desired metal loadings (0.0036, 0.009, 0.019, 0.040, 0.063 M corresponding to 1, 2.5, 5, 10 and 15 wt.%, respectively). The MCM-41 host (0.75 g) was dispersed in 37.5 mL of the precursor solution at room temperature and then, the solvent (water) was slowly removed by rotary evaporation at 60 °C for 30 min. The resulting powder was dried at 60 °C and calcined in air atmosphere for 9 h at 500 °C. The samples were designated as Fe/M(*x*) where M indicates the MCM-41 mesoporous structure and *x* indicates the nominal metal loading in wt.%.

## 2.2. Characterization

The X-ray diffraction patterns (XRD) were recorded in a Philips PW 3830 diffractometer with Cu K<sub> $\alpha$ </sub> radiation ( $\lambda$  = 1.5418 Å). Diffraction data were recorded in the  $2\theta$  range of  $1.5-7^{\circ}$  at an interval of 0.01° and a scanning speed of 0.6°/min and 20-80° at an interval of 0.04° and a scanning speed of 0.5°/min. The specific surface, the pore size distribution, and the total pore volume were determined from N<sub>2</sub> adsorption-desorption isotherms obtained at -196 °C using a Micromeritics ASAP 2010. The surface was determined by the Brunauer-Emmett-Teller (BET) method in the pressure range of  $P/P_0$ : 0.01–0.21. The pore size distribution curves were determined by the NLDFT method. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-1200 EX-II transmission electron microscope. Samples were prepared by suspending the catalyst in ethyl alcohol 99.5% and casting a drop of the suspension onto a lacey carbon copper grid. UV-Vis diffuse reflectance (UV-Vis DR) spectra in absorbance mode were recorded using a Jasco V 650 spectrometer with an integrating sphere, in the wavelength range of 200–900 nm. The original spectra obtained were fitted by three Gaussian-Lorenz bands using the conventional least squares method. Curve-fitting calculations were useful in determining each band location and relative area, with confidence levels given by  $R^2 \ge 0.99$ . The Fe content was determined by inductively coupled plasma optical emission spectroscopy (ICP) using a VISTA-MPX CCD Simultaneous ICP-OES-VARIAN. XPS analyzes were performed on a computer equipped with a Multitechnique Specs Dual X-ray source Mg/Al model XR50 and hemispherical analyzer 150 PHOIBOS Fixed transmission mode analyzer (FAT). Spectra were obtained with a power passage 30 eV and Al anode operated at 100 and 150 W when conditions in the main chamber were adequate. The pressure during the measurement was less than  $2 \times 10^{-8}$  mbar. The samples were supported on double-sided tape of Cu and then subjected to ultrahigh vacuum evacuation for 12 h prior to the readings. The reducibility of the catalysts was measured by Temperature Programmed Reduction (TPR) experiments in a Quantachrome Chembet 3000. In these experiments, the samples were heated at a rate of 10 °C/min in the presence of H<sub>2</sub> (5% H<sub>2</sub>/N<sub>2</sub> flow, 20 mL/min STP), and the reduction reaction was monitored by the H<sub>2</sub> consumption. <sup>57</sup>Fe Mössbauer spectra were taken in transmission geometry at room temperature with a nominal 20 mCi <sup>57</sup>Co source in the Rh matrix with a linear velocity waveform. The spectra were fitted with Voigtian line shapes (Lorentzian lines of constant width = 0.21 mm s<sup>-1</sup> and Gaussian distributions of variable dispersion  $\sigma$ ). Isomer shifts (IS) are referred to metallic  $\alpha$ -Fe at room temperature. The curves of room temperature magnetization vs. field were measured in a Quantum Design SQUID magnetometer MPMS XL7 with static field up to  $\mu_0$ Ha = 1 T.

## 3. Results and discussion

The low-angle XRD patterns of all of the materials synthesized in this study are shown in Fig. 1A. All the samples exhibit, besides an intense low-angle reflection at 2.27–2.44° corresponding to the



Fig. 1. (A) Low-angle XRD patterns and (B) high-angle XRD patterns of the synthesized samples.

distance between (100) planes, other two weak peaks at about 4.23° and 4.88° corresponding to reflections from (110) and (200) planes, typical of the MCM-41 mesoporous structure [29]. All these peaks gradually decrease in height and are slightly broaden when the metal loading increases. In this sense, a reduction in the peak intensities is expectable as result of the reduction in the electron density contrast due to the presence of the iron oxide within the pores; moreover, the mentioned feature is also giving account of some structural deformation occurring when the loaded Fe atoms begin to form small oxide clusters or nanoparticles, filling some pores or being located on the external surface. Anyway, all of the Fe modified samples have XRD patterns comparable to that of bare MCM-41 indicating that the mesoporous structure of the support is sustained after applying the impregnation and calcination processes.

No well-defined diffraction peaks characteristic of iron oxide crystalline phases were detected in the high-angle XRD patterns for the samples with Fe nominal loadings between 1 and 10 wt.% (Fig. 1B). Thus, if iron oxide species are present in these samples, they are clusters or nanoparticles with crystal domain size below the XRD detection limit (<4–6 nm). Then, the broader peaks scarcely hinted at around  $2\theta = 33^{\circ}$ , 35.6° and 63° for the Fe/M(15) sample, are probably indicative of Fe<sub>2</sub>O<sub>3</sub> finely dispersed on the external surface with crystal domain size close to XRD detection limit.

The N<sub>2</sub> adsorption–desorption isotherms of all the samples and their corresponding pore size distribution curves are shown in Fig. 2. All the solids exhibit type IV isotherms, typical of welldefined mesoporous structures, which is in agreement with those previously reported by us [30,31]. Table 1 summarizes the chemical composition and the structural properties of all the resulting materials. All of the materials show average pore sizes around 3.5 nm, high areas and pore volumes typical of MCM-41 structures. These last parameters are slightly decreased with Fe nominal loading increasing up to 5 wt.%, while a meaningful reduction in these values was observed for the Fe nominal loadings of 10 and 15 wt.%. This behavior can be attributed to the increase in amount and size of the iron oxide species formed both inside the channels and on the external surface, which is also contributing to certain loss of mesostructuration degree.

Some transmission electron microscopy images (TEM) of the synthesized samples (taken as representative) are shown in

Fig. 3. The images exhibit well-ordered parallel straight mesochannels, characteristic of the regular and hexagonal pore arrangement of MCM-41 type materials, which was already, inferred from the XRD patterns. Fig. 3A<sub>2</sub>, C<sub>2</sub>, E<sub>1</sub> and E<sub>2</sub> mainly correspond to views perpendicular to the direction of the pore arrangement, where it can be observed unidirectional straight channels arranged along the long axis; meanwhile frontal views of the arrangement of mesopores can be evidenced in some zones of Fig. 3A<sub>1</sub>, B and C<sub>1</sub> [25]. Then, the pore size estimated from these TEM images is about 3.2 nm (see Fig.  $3E_1$ ), which is close to that obtained from N<sub>2</sub> adsorption-desorption isotherms. Since the darker areas in TEM images represent the electronically more dense phases, metal oxide is considered to be present when irregular contrasts in the images are observed. Therefore, some pores seem to be filled with the iron oxide species (as very small clusters or nanoparticles) judging by the darker regions along the mesopores seen in Fig.  $3A_2$ , B and C<sub>2</sub>. Moreover, the incorporation of the Fe species inside the mesochannels is also evidenced by the small black spots, with a size of the pore order, mainly observed in Fig. 3B [32]. It should be noted that although the iron oxide species located within the channels are increased with the metal loading increasing, their maximum size cannot overcome 3.5 nm (the channel size) and therefore they cannot be detected by XRD. However, the Fig. 3E corresponding to the sample with highest Fe loading (Fe/M(15))shows a scarce number of larger iron oxide nanoparticles (of about 6 nm) segregated on the external surface of the silicate; but their small size and amount could be the reason why these are hardly observed by XRD.

Finally, on the basis of the structural characterization, we can claim that there are evidences about the formation of iron oxides within channels. Moreover, it is logically expectable that the growth of larger species is favored on the external surface due to the lack of size constraint effects of the matrix.

UV–Vis DR spectroscopy is a useful method to characterize the coordination environment of transition metals in zeolite type frameworks [33,34]. The UV–Vis DR spectra of the investigated samples are shown in Fig. 4. The original spectra have been deconvoluted into three bands which can be assigned to the different Fe species. The first maximum at about 254 nm could be associated with the  $d\pi$ – $p\pi$  charge transfer between Fe and O respectively, indicating that some iron atoms are able to link to surface O atoms, being incorporated onto the host as isolated iron cations [35,36].



**Fig. 2.** (A) Nitrogen adsorption–desorption isotherms and (B) pore size distribution curves of the MCM-41 samples synthesized with different Fe contents: (a) MCM-41, (b) Fe/M(1), (c) Fe/M(2.5), (d) Fe/M(5), (e) Fe/M(10) and (f) Fe/M(15).

The formation of such specie can be explained taking account that after impregnation,  $Fe^{3+}$  ions are present in the mesoporous channels as hydrated ions. Then, upon calcination, the water molecules surrounding the Fe and adsorbed on the support are removed and the  $Fe^{3+}$  ions can be stabilized on the surface by an anchoring

reaction with oxygens of the structure [37]. For its part, the contributions detected at longer wavelengths evidence the presence of iron with octahedral coordination in extra-framework positions. Thus, the second maximum at about 378 nm may be attributed to small oligonuclear iron oxide clusters  $(FeO)_n$  [35,36,38] and iron oxide nanoparticles of very small size, whereas the third maximum at about 545 nm can be assigned to larger iron oxide nanoparticles [38,39]. It is known that the UV-Vis DR bands shift to shorter wavelengths when the iron species size (clusters or nanoparticles) decreases, indicating a quantum size effect. Then, the relative positions of the last two contributions are giving account for this effect. The overall metal content in the final solids as well as the relative distribution of the different iron species and an estimation of the iron percentage in these species, are presented in Table 2. As it is observed, the evolution of the speciation of iron is depending on the loading degree. Thus, the iron can be stabilized as isolated cations on the support surface until certain saturation coverage is reached. Beyond this limit, and mainly when the iron loading is increased, the silanol groups on the surface cannot stabilize more iron cations and an incipient oligomerization of iron species containing Fe-O-Fe bonds start to appear. Such clustering process would lead to the formation of very small oligonuclear (FeO)<sub>n</sub> clusters, probably with low oxygen coordination, and finally, to the iron oxide nanoparticles [31,40,41]. In our case, judging by the relative percentage of band areas, the oligonuclear  $(FeO)_n$  clusters and iron oxide nanoparticles of very small size seems to play a dominant role. Nevertheless, this contribution is slightly decreased for the samples with high iron loading due to the enhanced formation of larger iron oxide nanoparticles. In fact, the relative percentage of the band corresponding to this last specie increases up to  $\sim$ 32% for the Fe/M(15) sample.

Usually, XPS is a powerful technique to obtain information concerning to composition at superficial level and to explore the oxidation state of the transition metal compounds with localized valence d orbitals, due to the different energies of the photoelectrons. Thus Si 2p spectrum for the Fe/M(x) samples is shown in Fig. 5A. This spectrum can be fitted with a single peak, centered at BE = 103.8 eV, which is characteristic of silicates. The spectrum of O 1s (Fig. 5B) is also composed of a single peak centered at 533.3 eV corresponding to oxygen of the SiO<sub>2</sub>. Other peaks of oxygen attributable to iron oxides such as Fe<sub>2</sub>O<sub>3</sub> (at about 530 eV) and to adsorbed --OH groups (at about 531.5 eV) were not observed, probably due to that their low signal is masked by the intense signal corresponding to the oxygen of the SiO<sub>2</sub> [35]. The Fe 2p spectra of the samples prepared with different Fe contents are shown in Fig. 6. In addition, Table 3 summarizes the binding energy values, the surface and bulk Fe/Si atomic ratios and the surface iron atomic percentage in the samples. These spectra can be fitted with four peaks which can be assigned to Fe<sup>3+</sup> chemical state. These peaks are broader compared with the narrow lines of bulk oxides, which is taken as evidence of presence of the highly dispersed metal species on the silica. According to the literature, the binding energy of

 Table 1

 Structure properties and chemical composition of the synthesized samples.

Sample	Area <sup>a</sup> (m <sup>2</sup> /g)	$a_o (nm)$	Dp <sup>b</sup> (nm)	$V_{\rm TP}({\rm cm}^3{\rm g}^{-1})$	Fe content (wt.%) <sup>c</sup>
MCM-41	996	4.21	3.5	0.70	-
Fe/M(1)	996	4.22	3.5	0.72	0.92
Fe/M(2.5)	948	4.32	3.5	0.71	2.56
Fe/M(5)	923	4.47	3.5	0.69	4.24
Fe/M(10)	801	4.23	3.5	0.59	8.33
Fe/M(15)	747	4.28	3.5	0.54	12.55

<sup>a</sup> Determined by BET.

<sup>b</sup> Pore diameter determined by the NLDFT method.

<sup>c</sup> Determined by ICP method.



Fig. 3. Transmission electron microscopy images of: (A<sub>1</sub> and A<sub>2</sub>) Fe/M(1), (B) Fe/M(2.5), (C<sub>1</sub> and C<sub>2</sub>) Fe/M(5), (D) Fe/M(10), and (E<sub>1</sub> and E<sub>2</sub>) Fe/M(15).



Fig. 4. UV-Vis DR spectra of the MCM-41 samples synthesized with different Fe contents.

 Table 2

 Chemical composition and iron species relative distribution in Fe/M(x) samples.

Sample	Fe content (wt.%)	Distribution of Iron species							
		Isolated cation		Iron oxide cluste	ers and smaller nanoparticles	Larger iron oxide nanoparticles			
		% area	Fe (wt.%)	% area	Fe (wt.%)	Fe (wt.%)	% area		
Fe/M(1)	0.92	13.6	0.12	77.30	0.72	9.10	0.08		
Fe/M(2.5)	2.56	13.33	0.34	77.52	1.98	9.15	0.23		
Fe/M(5)	4.24	12.8	0.54	69.61	2.95	17.50	0.74		
Fe/M(10)	8.33	9.89	0.82	66.06	5.50	24.05	2.00		
Fe/M(15)	12.55	7.14	0.89	61.16	7.67	31.7	3.98		



Fig. 5. XPS spectra of (A) Si 2p and (B) O 1s for the Fe/M(1) sample (taken as representative).

Fe<sup>3+</sup> 2p3/2 at 711.5 eV, accompanied by a satellite line visible at 720 eV, and the binding energy of Fe<sup>3+</sup> 2p1/2 at 725 eV (Fig. 6), are indicative of the presence of Fe<sup>3+</sup> in oxide environment [27,42]. However, judging by the very low oxygen signal attributed to iron oxides such as Fe<sub>2</sub>O<sub>3</sub> (spectrum of O 1s in Fig. 5B), it is possible infer the presence of Fe<sup>3+</sup> in oxide environment as oligonuclear (FeO)<sub>n</sub> clusters with lower oxygen coordination evidenced by

UV–Vis DR spectroscopy. Meanwhile, the presence of the peak around 714.0 eV, between the peak corresponding to  $Fe^{3+} 2p3/2$  and its satellite peak, could be related to the presence of isolated  $Fe^{3+}$  cations linked to surface O atoms in the matrix, which were also evidenced by UV–Vis DR spectroscopy [43–46]. In this sense, a decrease in the crystal field energy of the  $Fe^{+3}$  ions located at the surface compared with those found within an oxide



Fig. 6. XPS spectra of Fe 2p for the MCM-41 samples synthesized with different Fe contents.

environment could be the reason for the presence of this peak. Thus, with a decrease in the coordination, the surface  $Fe^{+3}$  ions would be surrounded by a lower electron density requiring this energy (714 eV) to be used to produce a photoelectron [47]. On the other hand, the surface Fe/Si ratios, considered as a measurement of the relative dispersion of metallic ions on the mesoporous structure, were compared with the bulk Fe/Si ratios (both values shown in Table 3). As it can be seen, these surface Fe/Si ratios are notably lower than the corresponding bulk Fe/Si ratios. This feature is indicating that the iron species are not homogeneously dispersed in the total volume of particles but they would be largely incorporated inside the mesopores, as it has been evidenced by TEM images.

In this work the Temperature Programmed Reduction (TPR) was used in order to study the interaction between the loaded metal species and the support. It is important to note that, unlike the bulky oxides for which it is expected an increase in the reduction temperature with the particle size, the metal oxides particles deposited on inert supports have a more complex reduction

XPS hinding	energies	(RF)	for	Fe 2	n c	nectra	and	surface	iron	comr	ositions
APS Diliuling	energies	(DC)	101	re z	ps	респа	dIIU	Suilace	11011	comp	JOSILIOIIS.

Table 3



Fig. 7. TPR profiles of (a) Fe/M(2.5), (b) Fe/M(5) and (c) Fe/M(10).

behavior. In this sense, the reduction profile of the iron species loaded on the MCM-41 support would be the result of the competition between two factors: the faster reduction of smaller size particles due to the increase in the surface/volume ratio, and the slower reduction of these smaller particles due to the higher interaction with the support [48]. Thus, analyzing the TPR profiles of the Fe/M(x) samples allow to estimate the reducibility of the iron species present in them. Fig. 7 shows the profiles corresponding to Fe/ M(2.5), Fe/M(5) and Fe/M(10) samples taken as representatives. For the higher Fe loading three TPR peaks, although some overlapping, appear at around 430, 470 and 550 °C. These can be related to the Fe<sup>3+</sup>  $\rightarrow$  Fe<sup>3+/2+</sup>; Fe<sup>3+/2+</sup>  $\rightarrow$  Fe<sup>2+</sup> and Fe<sup>2+</sup>  $\rightarrow$  Fe<sup>0</sup> processes respectively, which are frequently observed in iron oxides [49]. Therefore, the complete reduction of iron oxide species to the zero-valence state can be reached for the high loading of iron (8.33 wt.%) probably due to presence of larger size iron oxide species with lower interaction with the matrix which makes easier the reduction to the minor oxidation state (zero valence) [50,51]. For the Fe/M(5) sample, two well-resolved TPR peaks appear at around 425 and 500 °C. which may be related to the first two mentioned reduction processes. Therefore, at this iron content, the Fe<sup>3+</sup> species are reduced only to Fe<sup>2+</sup> species, which are stabilized in the MCM-41 structure with high resistance to the reduction to metallic state. Meanwhile, for the lower Fe loading, only a single peak corresponding to the first reduction process ( $Fe^{3+} \rightarrow Fe^{3+/2+}$ ) is observed, indicating that the resistance to the reduction is even greater due to the higher stabilization of the oxidized iron species in the matrix. Moreover, it is notable a shift to lower temperature for this reduction which could be attributed to the faster reduction of smaller size iron oxides species due to the increase in the surface/volume ratio. Finally, the hydrogen consumption at

Samples	$Fe^{3+}2p^{3/2}$ (eV)	Peak II (eV)	Satellite (eV)	Fe <sup>3+</sup> 2p1/2 (eV)	Surface Fe/Si (XPS)	Bulk Fe/Si (ICP)	Fe <sup>3+</sup> 2p <sup>3/2</sup> (at.%)
Fe/M(1)	711.60	714.20	719.01	725.30	0.003	0.010	0.10
Fe/M(2.5)	711.57	714.14	719.02	725.29	0.005	0.028	0.17
Fe/M(5)	711.20	713.98	719.35	725.20	0.006	0.047	0.19
Fe/M(10)	711.65	713.85	718.90	725.24	0.009	0.097	0.28
Fe/M(15)	711.70	714.31	719.40	725.25	0.012	0.154	0.38



**Fig. 8.** Mössbauer spectra of samples synthesized with different Fe contents, where D1, D2 and S correspond to doublet 1, doublet 2 and the sextet signals in the spectra.

temperatures higher than 700 °C can be ascribed to framework  $Fe^{3+}$  species of difficult reducibility [52]. This high reduction temperature is indicative of the shielding effect of the mesoporous framework, which protects the isolated  $Fe^{3+}$  cations from H<sub>2</sub> attack [52]. In addition, the smaller hydrogen consumption above 700 °C for the Fe/M(10) sample indicates the lower reduction of isolated  $Fe^{+3}$  species likely less accessible.

Mössbauer spectroscopy is a very useful tool to study the iron oxide species supported in molecular sieves like MCM-41. The room temperature Mössbauer spectra for the Fe/M(2.5), Fe/M(5), Fe/M(10), Fe/M(15) samples are shown in Fig. 8 and the corresponding hyperfine parameters obtained by fitting the spectra are listed in Table 4. The sample with the lowest loading presents two doublets which could be assigned to superparamagnetic iron oxide species, as well as to paramagnetic Fe<sup>+3</sup> ions. Thus, the doublet (D1) with isomeric shift ( $\delta$ ) and quadrupole splittings ( $\Delta Q$ ) of 0.360 and 0.76 mm/s respectively, characteristic of trivalent iron ions (Fe<sup>3+</sup>) in octahedral coordination, is associated to superparamagnetic iron oxide nanoparticles of very small size, which are expectable to be located inside the pores [53]. Meanwhile, the doublet (D2) with  $\delta$  = 0.28 mm/s and  $\Delta Q$  = 1.6 mm/s is attributed to the presence of superparamagnetic  $(FeO)_n$  clusters with lower oxygen coordination, judging by its lower isomeric shift value [38], also located inside the channels [53]. The spectrum corresponding to the Fe/M(5) sample shows, besides the two doublets already



Fig. 9. Magnetization curves at room temperature of samples synthesized with different Fe contents.

present in the lower loading sample, a sextet (S) (H = 51.1 T,  $\delta$  = 0.37 mm/s and quadrupole shift ( $\varepsilon$ ) = -0.23 mm/s) which is typical of Fe<sup>3+</sup> species magnetically blocked assigned to hematite nanoparticles of larger size but close to XRD detection limit. The spectra corresponding to the Fe/M(10) and Fe/M(15) samples also show the mentioned sextet and the two doublets: however, these doublets have isomeric shifts close and higher than 0.3 mm/s, probably due to an increase in the oxygen coordination of the clusters. This feature would be giving account for a more advanced clustering process that finally lead to formation of iron oxide nanoparticles as consequence of the higher iron loading. It is worth to note that, for all the samples, the higher area percentages (Table 4) correspond to the doublet signals that are characteristic of systems with superparamagnetic relaxation. On the other hand, since  $\delta$ . were very different of 1 mm/s it could be exclude the presence of Fe<sup>2+</sup> in the synthesized samples.

It is known that the bare silica support is diamagnetic, however it is expected that the modified iron silica matrix shows different magnetic behaviors depending on the size and dispersion of the metal species loaded. Fig. 9 shows the magnetization vs. applied field at room temperature for all the samples. Given that the Fe is the only possible source of magnetic signal, the units of magnetization are

Table 4	
Fitted Mössbauer parameters for spectra recorded at room temperature.	

Parameters		Fe/M(2.5)	Fe/M(5)	Fe/M(10)	Fe/M(15)
D1	δ (mm/s) ΔQ (mm/s) A (%)	$\begin{array}{c} 0.360_8 \\ 0.76_2 \\ 86_1 \end{array}$	0.355 <sub>2</sub> 0.72 <sub>2</sub> 57 <sub>1</sub>	0.367 <sub>1</sub> 0.348 <sub>7</sub> 50 <sub>1</sub>	$0.348_7$ $0.67_2$ $52_1$
D2	δ (mm/s) ΔQ (mm/s) A (%)	0.28 <sub>5</sub> 1.6 <sub>2</sub> 14 <sub>1</sub>	0.29 <sub>2</sub> 1.2 <sub>2</sub> 26 <sub>1</sub>	$\begin{array}{c} 0.34_2 \\ 1.0_6 \\ 40_1 \end{array}$	0.32 <sub>1</sub> 1.1 <sub>1</sub> 34 <sub>1</sub>
S	$ \begin{array}{l} H \ (\mathrm{T}) \\ \delta \ (\mathrm{mm/s}) \\ \varepsilon \ (\mathrm{mm/s}) \\ A \ (\%) \end{array} $	- - -	51.1 <sub>1</sub> 0.37 <sub>1</sub> -0.23 <sub>2</sub> 17 <sub>1</sub>	51.2 <sub>1</sub> 0.39 <sub>5</sub> -0.21 <sub>1</sub> 10 <sub>1</sub>	$51.4_1$ $0.41_1$ $-0.26_2$ $14_1$

 $\delta$ : isomeric shift relative to  $\alpha$ -Fe,  $\Delta Q$ : quadrupole splitting,  $\varepsilon$ : quadrupole shift, A: relative subspectral area. D1, D2 and S correspond to doublet 1, doublet 2 and the sextet signals in the spectra.

Am<sup>2</sup> per kg of Fe. Thus, for the lower loaded samples a notable saturation magnetization appears, adjudicated to a superparamagnetic contribution attributed to the iron oxide species (clusters or nanoparticles) of very small size and finely dispersed located mainly inside the pores. This contribution could be caused by a surface phenomenon arising from a very high surface to volume ratio derived from the very small size and high dispersion of the oxides species, which lead to non-interacting single domains. Meanwhile, although it was expectable observe a paramagnetic contribution for these samples due to the presence of the isolated iron species, such contribution seems to have little relevance or be masked by the predominant superparamagnetic contribution. On the other hand, in the curves corresponding to the higher loading samples (Fe/M(10) and Fe/M(15)) the notable attenuation of the superparamagnetic signal can be arising from iron species magnetically blocked evidenced for Mössbauer spectroscopy and associated to the larger hematite nanoparticles grown up on the external surface, whose canted antiferromagnetic behavior at room temperature is known [54].

### 4. Conclusions

All the materials exhibited high specific surface, pore volume and good structural regularity, retaining the mesoporous structure even after the higher metal loading of around 13 wt.%. The incorporation of the iron oxide species inside the mesochannels was evidenced by TEM and XPS. Such species cannot have a size higher than 3.5 nm (pore diameter) and hence be detected by XRD. Meanwhile, the sample with highest Fe loading showed a scarce number of larger iron oxide nanoparticles segregated on the external surface of the silicate; but their small size and amount could be the reason why these were hardly observed by XRD. The evolution in the iron speciation, depending of the metal loading and associated with a particular magnetic behavior, was investigated through UV-Vis DRS, XPS, TPR, Mössbauer spectroscopy and curves of magnetization vs field. Several metallic species such as isolated iron species linked to surface oxygen, iron oxide clusters and nanoparticles of very small size, and larger nanoparticles were detected. The two last species increased in amount and size when the Fe loading was increased, although for all Fe contents, oligonuclear  $(FeO)_n$ clusters and iron oxide nanoparticles of very small size inside the channels (not detected by XRD) seems to play a dominant role. An incipient oligomerization of iron species on the surface, leads to the formation of these iron oxide clusters with low oxygen coordination and then to the oxide nanoparticles. Depending on the dispersion and size of the different iron species, the nanocomposites showed different magnetic behaviors. Thus, a predominant superparamagnetic behavior (searched for drug carriers materials) was found for the samples with the lower iron loadings; this feature was assigned to oxide species finely dispersed such as the oligonuclear (FeO)<sub>n</sub> clusters and nanoparticles, both of very small size and located preferably inside the channels. Then, the notable attenuation of the superparamagnetic signal for the two highly loaded samples, which could be attributed to the hematite nanoparticles of larger size, located on the external surface and evidenced by Mössbauer spectroscopy. Finally, the wet impregnation method employed in this study results a good synthesis pathway, simple and inexpensive, for prepare iron modified MCM-41 nanocomposites with the structural and magnetic properties required for a successful application of these materials as drug carrier.

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