



Dependence of the Structural Stability of MCM-41 on the Impregnating Iron Solution

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Abstract. The MCM-41 mesoporous material was chosen as support of very small iron oxide particles. To study the preparation conditions that allow to preserve the support structure four samples were prepared. The solids were characterized by atomic absorption spectroscopy (AAS), specific surface area (BET), X-ray diffraction (XRD) and Mössbauer spectroscopy at 298 and 22 K. The absence of water in the impregnation step is essential to avoid the collapse of the structure.

Key words: supported iron particles, Fe/MCM-41 preparation, Mössbauer Fe/MCM-41 characterization.

1. Introduction

MCM-41 belongs to the M41S mesoporous molecular sieve family [1], with a hexagonal arrangement of uniform channels of 15–100 Å diameter. Because of its very high surface area and its narrow size pore distribution [1], MCM-41 seems to be a good support material for iron oxide particles to be used as a catalyst in the ethanol hydrotreatment and for iron metallic particles to be used in hydrocarbon synthesis. The structure of this solid can collapse when is subjected to treatments with different solutions and/or temperatures [2], perhaps due to the very thin pore wall thickness.

To study the structure stability, we added the Fe^{3+} ions into the MCM-41 channels by different methods and obtained four catalyst precursors. The purpose of the present study is to demonstrate the importance of the control over the impregnation step to avoid the structure collapse of the MCM-41.

2. Experimental section

MCM-41 was synthesized according to Beck's recipe [1], using sodium silicate in acidic medium as silica source and cetyltrimethylammonium bromide as surfactant.

The support thus obtained was treated through the following methods:

- Sample 1. Dry impregnation with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ aqueous solution ($\text{pH} = 0.5$).
Sample 2. Dry impregnation with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ complexed with EDTA ($\text{pH} = 7.6$ with NaOH).
Sample 3. Mechanical mixing of MCM-41 with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, followed by thermal treatment at 320 K, in order to melt the iron salt.
Sample 4. Dry impregnation with iron acetyl acetonate ($\text{Fe}(\text{AcAc})_3$) solution in benzene.

All samples were dried in air. Samples 1 and 2 were calcined in dry N_2 stream at $60 \text{ cm}^3/\text{min}$, from 298 to 598 K, at 0.2 K/min and kept at the last temperature for 1 h. Sample 3 was calcined in dry air stream at $60 \text{ cm}^3/\text{min}$, from 298 to 773 K at 0.2 K/min and kept at the last temperature for 1 h. Sample 4 was treated in the same conditions that Sample 3 but the final temperature was 648 K. A final iron concentrations of about 5% (w/w) were obtained in all samples.

MCM-41 and all the samples impregnated without calcination, and calcined were characterized by atomic absorption spectroscopy (AAS), specific surface area (BET) and X-ray diffraction (XRD). Sample 4, before and after calcination, was also characterized by Mössbauer spectroscopy (MS) at 298 and 22 K. The Mössbauer spectra were obtained in transmission geometry with a 512-channel constant acceleration spectrometer. A source of ^{57}Co in Rh matrix of nominally 100 mCi was used. Velocity calibration was performed against a $6 \mu\text{m}$ -thick α -Fe foil. All isomer shifts (δ) mentioned in this paper are referred to this standard. The temperature between 22 and 298 K was varied using a Displex DE-202 Closed Cycle Cryogenic System.

3. Results and discussion

The X-ray diffraction patterns of MCM-41 and the samples before calcination are shown in Figure 1. It can be seen that only Samples 3 and 4 have been able to preserve the mesoporous structure after the impregnation step. The maintenance of the structure after calcination was only observed for Sample 4 (Figure 2).

The behavior of Samples 1 and 2 indicates that the pH of the impregnating solution is not responsible for the structure collapse. Bearing in mind the very thin wall thickness (Table I) and that no thermal treatment was carried out, the structure destruction could be due to the presence of water that hydrolyzes the Si–O–Si bonds.

To eliminate the water presence in the impregnation step we prepared Sample 3. The MCM-41 structure was preserved before calcination (Figure 1). However, when this sample is calcined, to carry out the anion decomposition, the structure fell down again (Figure 2). We attribute this behavior to the water vapor presence belonging to the structural water of the iron salt. This would produce hydrolysis of Si–O–Si bonds and/or reaction with nitrogen oxides, coming from the ther-

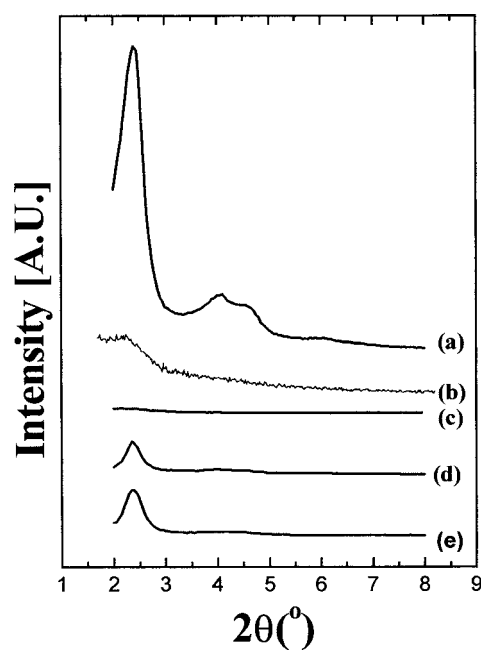


Figure 1. X-ray diffraction patterns of: (a) MCM-41, (b) sample 1 without calcination, (c) sample 2 without calcination, (d) sample 3 without calcination, (e) sample 4 without calcination (bc-Fe/MCM-41).

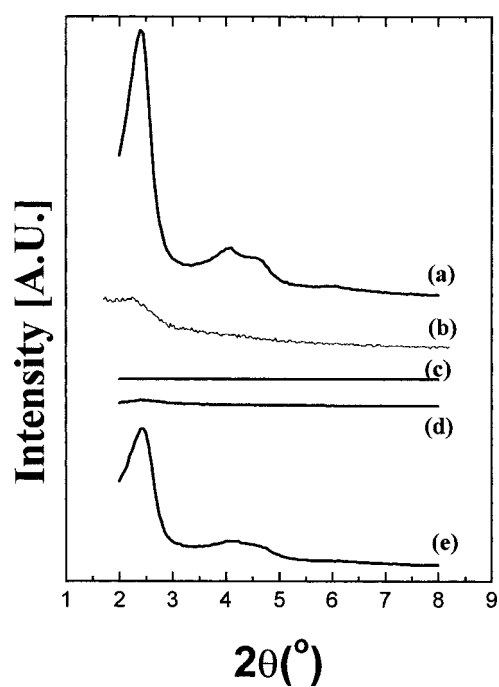


Figure 2. X-ray diffraction patterns of: (a) MCM-41, (b) sample 1 calcined, (c) sample 2 calcined, (d) sample 3 calcined, (e) sample 4 calcined (ac-Fe/MCM-41).

Table I. Textural properties

	MCM-41	ac-Fe/MCM-41
S_g [m ² /g]	1148	1022
V_p [cm ³ /g]	1.9	4.9
\bar{r}_p [nm]	1.5	1.4
L [nm]	1.0	1.4

S_g : specific surface area, V_p : specific pore volume, \bar{r}_p : average pore radii, L : wall thickness.

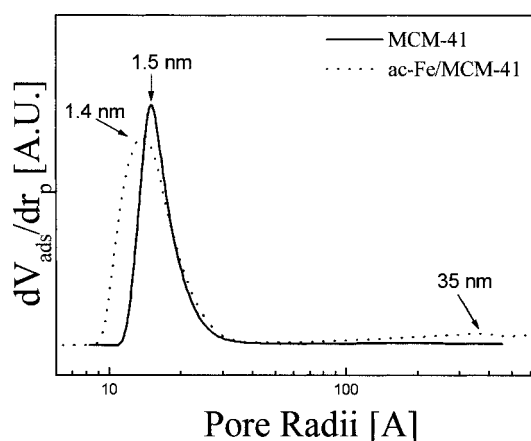


Figure 3. Pore size distribution of MCM-41 and ac-Fe/MCM-41.

mal decomposition of the anion, yielding nitric acid. This acid can also produce hydrolysis and destruction of the support structure.

According to the above results, we decided to use an iron salt without structural water, soluble in a non-polar organic solvent. In this way Sample 4 was prepared. As it can be seen from Figures 1 and 2, the structure was maintained before and after calcination.

Comparing the XRD results of Sample 4, before calcination (bc-Fe/MCM-41) and after calcination (ac-Fe/MCM-41), an increase of the peak intensity of ac-Fe/MCM-41 can be observed. This behavior is attributed to the organic compound elimination.

As Sample 4 was the only one, able to preserve the MCM-41 structure, a more exhaustive characterization was performed on bc-Fe/MCM-41 and ac-Fe/MCM-41.

Table I displays the N₂ absorption results. The ac-Fe/MCM-41 has approximately the same S_g as MCM-41, while its average pore radii are slightly lower. Figure 3 shows the pore radii distribution; ac-Fe/MCM-41 presents a wider and less intense distribution curve with a displacement of the maximum. This is in

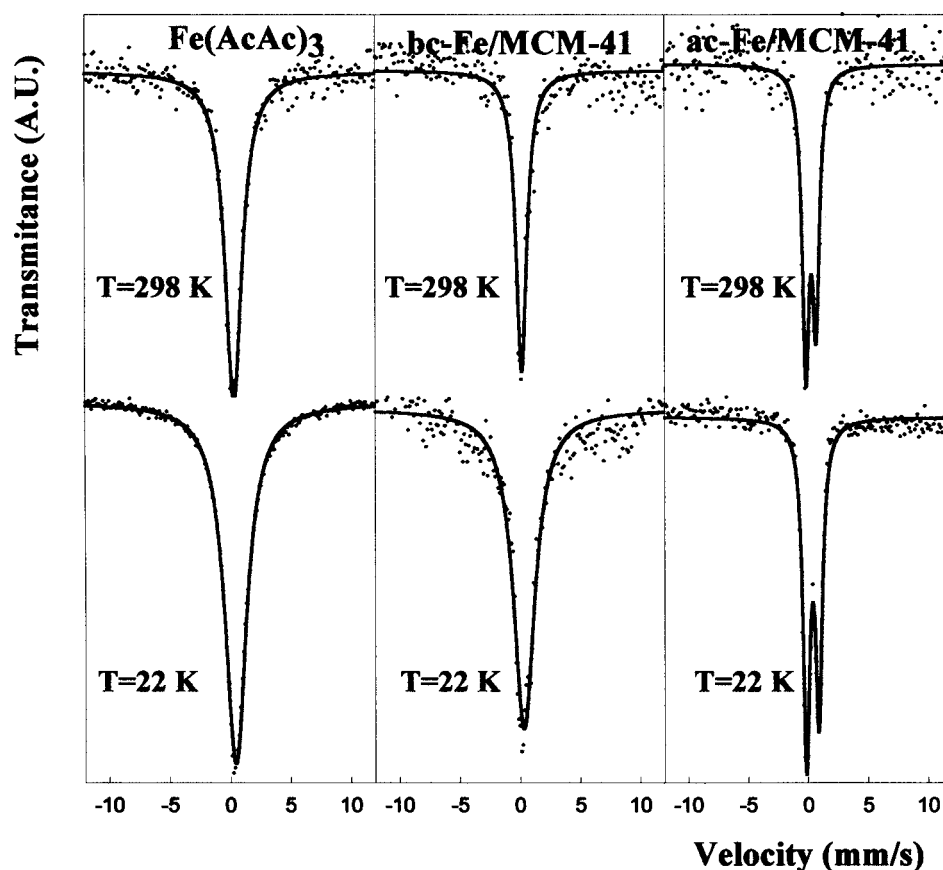


Figure 4. Mössbauer spectra at 298 and 22 K of $\text{Fe}(\text{AcAc})_3$, bc-Fe/MCM-41 and ac-Fe/MCM-41.

agreement with the partial recover of the channel walls with iron species. Besides, a very broad and low intense peak, centered at about 35 nm appears in ac-Fe/MCM-41. This fraction can be assigned to the joint of some channels with the consequently appearance of others of higher diameters. This is in agreement with the increase of the pore volume (Table I).

After verification the conservation of the structure and textural properties of MCM-41, we have obtained the Mössbauer spectra at 298 and 22 K of bc-Fe/MCM-41 and ac-Fe/MCM-41 (Figure 4). We have also measured the spectra at both temperatures of $\text{Fe}(\text{AcAc})_3$ (Figure 4) for comparative purposes obtaining a δ value comparable with that found by Klinedinst and Boudart [3]. The spectra of $\text{Fe}(\text{AcAc})_3$ and bc-Fe/MCM-41 display only one singlet at both temperatures, suggesting the maintenance of the salt structure in the impregnated sample but with an increase in the electronic density of Fe^{3+} nucleus, as can be inferred from the δ decrease (Table II) attributed to the salt-support interaction.

Table II. Mössbauer hyperfine parameters at 298 and 22 K of the iron species in the samples

Samples	Parameters	$T = 298$ K	$T = 22$ K
Fe(AcAc) ₃	δ [mm/s]	0.41 ± 0.01	0.53 ± 0.01
bc-MCM-41	δ [mm/s]	0.24 ± 0.02	0.40 ± 0.02
ac-MCM-41	δ [mm/s]	0.34 ± 0.01	0.45 ± 0.01
	Δ [mm/s]	0.85 ± 0.02	1.04 ± 0.01

The Mössbauer spectra of ac-Fe/MCM-41 at 298 and 22 K show an asymmetric doublet. The hyperfine parameters obtained by fitting can be assigned to superparamagnetic crystals of Fe₂O₃ and/or paramagnetic Fe³⁺ ions. Since MCM-41 has not exchangeable sites [4] and the impregnating solution is non-polar, we discarded the Fe³⁺ ions presence. However, it is remarkable to note that at 22 K the spectrum background is not curved yet, being far away from the beginning of the magnetic ordering. Therefore, the iron oxide crystallites must be very small.

Notwithstanding, through the Mössbauer results we could not discern between α - and γ -iron oxide due to the lack of the magnetic ordering. Considering that the conditions of the Fe(AcAc)₃ decomposition used yields to γ -Fe₂O₃ [5], it is possible to estimate the upper limit of particle size assuming that this oxide was obtained. Considering that the blocking temperature is lower than 22 K and using the Néel–Brown model [6] we have estimated a value of 3.8 nm for the oxide particle diameter.

4. Conclusions

- MCM-41 is a mesoporous material useful to be use as support of small iron oxide particles.
- The impregnation with the iron compound is a very important step to preserve the MCM-41 structure.
- The structure collapse depends on the water presence but not on the pH of the impregnating solution.
- It is possible to support small particles of iron oxide on MCM-41 using a non-aqueous solution of an iron salt without structural water as Fe(AcAc)₃ in benzene.

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