

MCM-41 Ordered Mesoporous Molecular Sieves Synthesis and Characterization

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The aim of this work was to study the hydrothermal synthesis of Si and SiAlMCM-41 performed under both autogenic pressure and refluxing conditions. XRD data showed that the MCM-41 phase may be formed by both processes and that the synthesized material in the presence of Al and/or under reflux presents the hexagonal arrangement of less ordered mesopores. However, as verified by XRD and physisorption data, the order was improved with higher synthesis times. ²⁹Si and ¹H - ²⁹Si C/P MAS NMR spectra showed that a great part of the Si atoms exists as silanol groups which originate resonance peaks at -110, -100 and -91 ppm. The presence of Al atoms may generate Si(3Si, Al) and Si(2Si, 2Al) environments which might be contributing to resonance peaks at -100 and -91 ppm. The ²⁷Al MAS NMR spectrum of the as synthesized AlSiMCM-41 showed a resonance peak of tetrahedral framework aluminum close to 53 ppm and two others, one close to 14 ppm attributed to Al(H₂O)₆⁺³ species and the other a weak signal close to 32 ppm attributed to pentacoordinated Al. ²⁷Al MAS NMR spectra of the calcined sample showed a peak at 0 ppm corresponding to an hexacoordinated extra-framework aluminum formed during calcination.

Keywords: MCM-41, synthesis, characterization

1. Introduction

Molecular sieves with a zeolite structure and pore diameter < 15 Å exhibit a shape selectivity that enables them to be used as adsorbents or catalysts in a variety of processes. However, reactions involving bulky molecules require structures with channel diameters at mesopore scale. In the early nineties^{1,2}, scientists from *Mobil Oil Corporation* synthesized ordered mesoporous materials of the M41S type, family to which MCM-41 belongs. This material possesses a porous system consisting of hexagonally arranged channels with diameters varying from 15 to 100 Å. MCM-41 has attracted the attention of scientists due to its elevated specific surface area, high thermal and hydrothermal stability, possibility of controlling its pore size and its hydrophobicity and acidity. These characteristics have made MCM-41 a promising material as catalyst and/or support³ and to be used in industrial processes of adsorption⁴, ion exchange⁵ and environmental control⁶.

The scope of the current work was to investigate the hydrothermal synthesis of SiMCM-41 and AlSiMCM-41 performed under both autogenic pressure and refluxing conditions. The solids obtained were characterized by XRD, SEM, nitrogen physisorption TGA/DTG, ²⁹Si MAS NMR; ¹H - ²⁹Si CP/MAS NMR and ²⁷Al MAS NMR.

2. Materials and Methods

2.1. Synthesis of MCM-41

The molar compositions^{1,2,7} and synthesis times used are listed in Table 1. The used precursors consisted basically of amorphous silica (Aerosil-200/Degussa); sodium trisilicate (Aldrich); tetramethylammonium hydroxide (Aldrich); sodium aluminate (Riedel De Haën); cetyltrimethylammonium bromide (Merck) and distilled water. Part of the reaction mixture was placed in teflon cups inside of steel autoclaves being subsequently submitted to hydrothermal treatment under autogenic pressure in a oven at 100 °C. The remaining part was treated at the same tem-

Table 1. Molar compositions and synthesis time.

Samples	Composition	Reflux Y(h)	Aut Pres Y(h)
SiMCM-41	SiO ₂ :0.07Na ₂ O:0.27CTMA:0.14TMAOH:100H ₂ O	24; 108	48; 288
AlSiMCM-41	SiO ₂ :0.025Al ₂ O ₃ :0.07Na ₂ O:0.27CTMA:0.14TMAOH:100H ₂ O	24; 108	48; 288

perature under refluxing conditions. After the synthesis the solids were separated from the reaction mixture through centrifugation, washed and dried at 110 °C. Removal of the organic material occurred by calcination at 550 °C under nitrogen flow (100 cm³/min g) for 1 h and subsequently under synthetic air flow (100 cm³/min g) for 6 h. The samples were designated as SiMCM-41(X/Y) and AlSiMCM-41(X/Y), where X = P presents the samples obtained under autogenic pressure and X = R under refluxing conditions; Y corresponds to the synthesis time in hours.

2.2. Characterization

X-ray powder diffraction patterns were recorded on a Siemens D500 diffractometer using a monochromated CuK_α radiation in the angular range from 1 to 10° (2θ); the 2θ scanning speed was 0.6°/min. The scanning electron micro-analysis was performed on a Zeiss DSM 960 Scanning Electron Microscope operated at 30 kV. Thermogravimetric analysis was carried out on a Thermal Analyst 2100 TA Instruments equipment in the temperature range from 30 to 900°C (heating rate 3 °C/min) in O₂ flow (30 cm³/min). Nitrogen physisorption measurement at -196 °C was conducted on a NOVA 1200 TGA Quantachrome Corporation analyzer. Solid state ²⁹Si MAS NMR spectra were recorded on a Varian 400 MHz spectrometer at 79.5 MHz with 50° pulses (4.3 μs) and 5 kHz spinning rates. The recycle delay was 100 s. The ¹H - ²⁹Si C/P MAS NMR spectrum was recorded with 4.5 μs ¹H (90°) pulses with a contact time of 5 ms and 5 s of recycle delay. The ²⁷Al MAS NMR spectra were recorded on a Bruker MSL 400P spectrometer operating at 104.2 MHz with 0.6 s (π/18) pulses and a recycle delay of 0.8 s.

3. Results and Discussion

3.1. X-ray powder diffraction

XRD analysis of the as synthesized samples indicated that the mesoporous MCM-41 molecular sieve may be obtained by both processes and allowed identification of the peaks relative to the (100), (110), (200) and (210) planes corresponding to an hexagonal structure with symmetry P6 for the reflection planes (hk0), indicating that there are no planes for $l \neq 0$ ^{1,2}. The values of the parameter a₀ of the hexagonal pore arrangement for different samples are sum-

marized in Table 2. These values are seen to be very representative compared to those presented by other authors who used the same surfactant⁸. The parameter a₀ is also seen to show a tendency to increase with synthesis time for both processes, which has been attributed to the increase in the wall thickness of the mesopores⁹.

Figure 1 shows X-ray diffraction patterns for samples SiMCM-41 and AlSiMCM-41 synthesized in 48 h. The diffraction peak related to the (100) plane is seen to be more

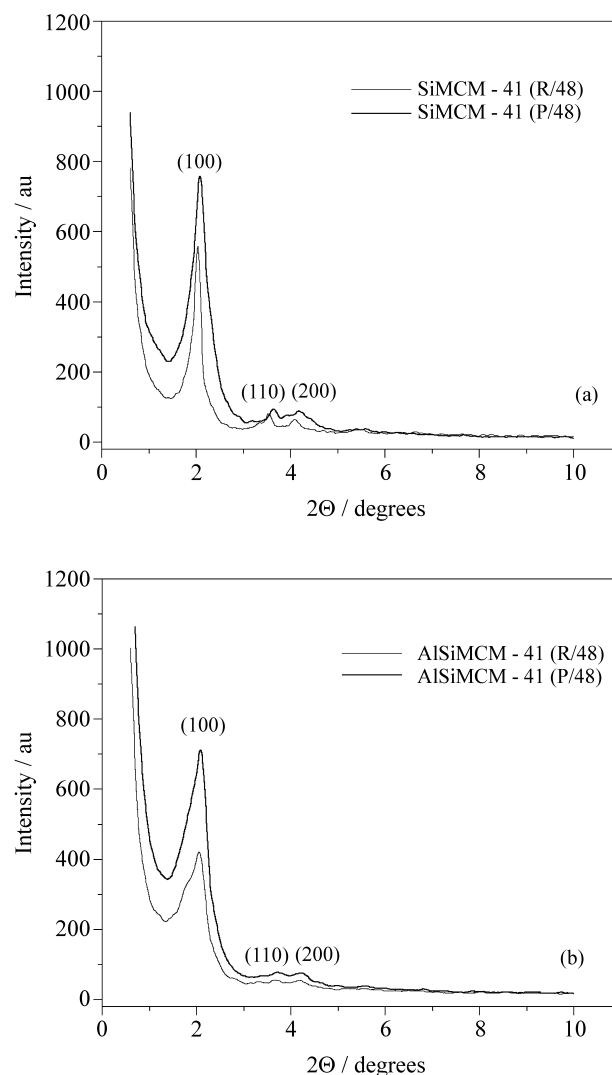


Figure 1. XRD of the as synthesized: a) SiMCM-41, and b) AlSiMCM-41 samples.

Table 2. Parameter a_0 for SiMCM-41 and AlSiMCM-41 samples.

Samples	a_0 (Å)
SiMCM-41(R/24)	45.85
SiMCM-41(R/108)	46.07
SiMCM-41(P/48)	45.54
SiMCM-41(P/288)	47.59
AlSiMCM-41(R/24)	45.75
AlSiMCM-41(R/108)	45.32
AlSiMCM-41(P/48)	45.95
AlSiMCM-41(P/288)	48.16

intense for samples obtained under autogenic pressure when compared to those obtained under reflux, which can be interpreted as an indication of higher ordering of the mesopore channels¹⁰. The materials synthesized in the presence of aluminum exhibit broader and slightly less intense diffraction peaks, indicating that within 48 h synthesis, the hexagonal arrangement of the mesopores in these materials is less ordered compared to SiMCM-41

3.2. Nitrogen physisorption

The adsorption/desorption isotherms of N₂ (Fig. 2) and the values of specific surface area (S_{BET}), mean diameter of the mesopores (d_{mp}), total volume of pores (V_t) and wall thickness (ϵ) obtained for calcined SiMCM-41 (Table 3) are in agreement with those published by other authors¹¹. Curves in Fig. 2 and data from Table 3 show an increase in the adsorption capacity of N₂ with time for the SiMCM-41 samples synthesized under reflux, indicating an improvement in the order of the mesopore phase, already observed by the increase in the XRD peak intensity (Fig. 3). However, as it has been observed from the data in Fig. 1, the MCM-41 phase is formed more readily under autogenic pressure, showing a small dependence with synthesis time, as it can be seen in Fig. 4 and from the data in Table 3.

3.3. TG/DTG analysis

Thermogravimetric analysis of the as synthesized Al-SiMCM-41(P/288) sample presented a DTG curve typical of MCM-41 (Fig. 5). The as synthesized material presents approximately 50 wt% of the MCM-41 phase. The remaining part corresponds to organic material whose mass loss is related to three exothermal stages: (a) between 100–285 °C: decomposition of the surfactant²; (b) between 285–400 °C: breaking of the hydrocarbon chain, and (c) between 500–700 °C: combustion of the surfactant and water loss associated with condensation of silanol groups¹².

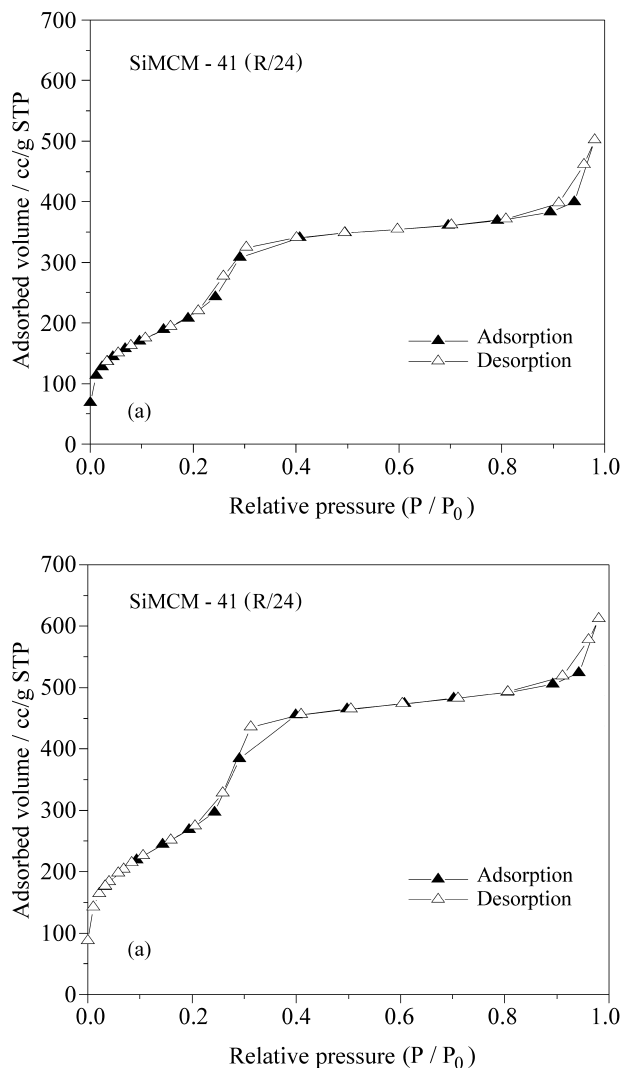
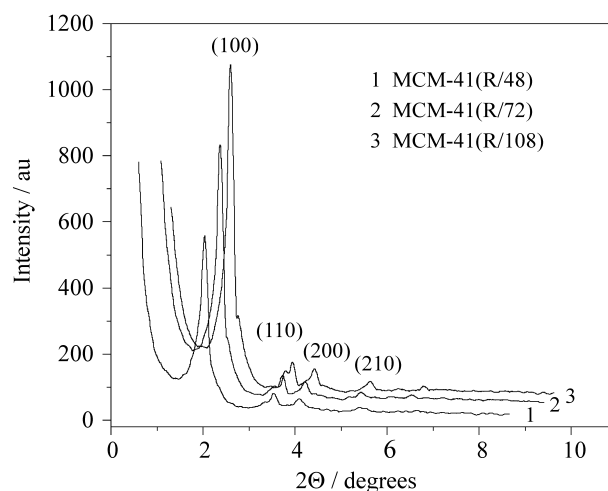
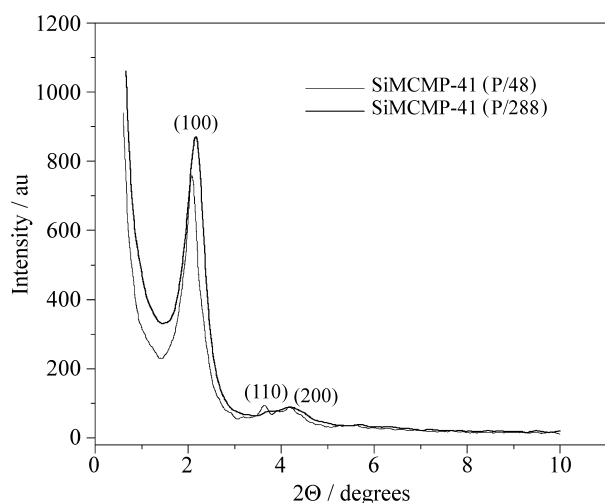
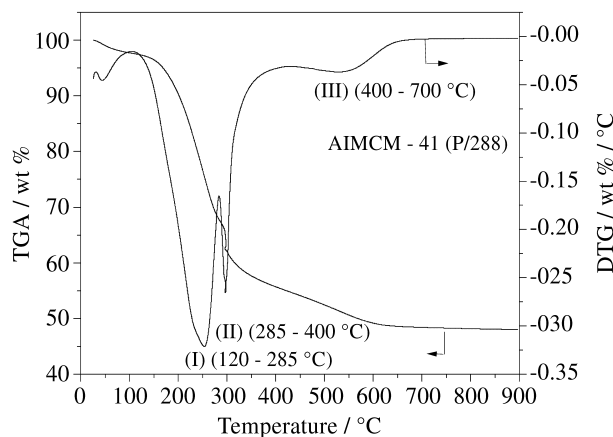
**Figure 2.** Adsorption/desorption isotherms of N₂ for calcined SiMCM-41 samples.**Figure 3.** XRD of the as synthesized SiMCM-41(R/Y) samples.

Table 3. Textural characteristics of the calcined SiMCM-41 samples.

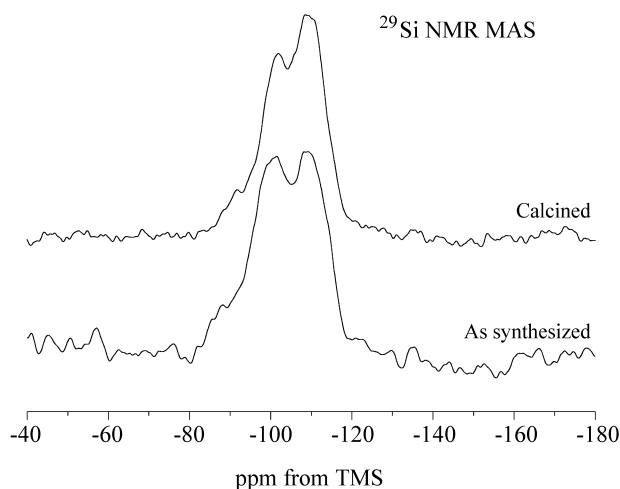
Sample	Average diameter of the mesopores d_{mp} (Å)	Wall thickness ϵ^* (Å)	Area S_{BET} (m ² /g)	Total pore volume (V _t) (cm ³ /g)
SiMCM-41(R/24)	35.34	10.51	876	0.77
SiMCM-41(R/108)	34.74	11.33	1087	0.94
SiMCM-41(P/48)	36.48	9.08	941	0.86
SiMCM-41(P/288)	34.90	12.69	978	0.85

$$\epsilon = a_0 - d_{mp}$$

**Figure 4.** XRD of the as synthesized SiMCM-41(P/Y) samples.**Figure 5.** TGA-DTG analysis of the as synthesized AISiMCM-41 (P/288) sample.

3.4. NMR spectra

The ²⁹Si MAS NMR spectra of the as synthesized and calcined AISiMCM-41(R/108) samples, shown in Fig. 6 bears much resemblance to that of amorphous silica, indi-

**Figure 6.** ²⁹Si MAS NMR spectra of the AISiMCM-41 (R/108) samples.

cating that the local arrangement of the Si-O-Si bonds at the pore walls is irregular and that the angle between these bonds vary over a wide range. The ¹H - ²⁹Si CP/MAS NMR spectrum (Fig. 7) of the calcined sample, shows that, similar to amorphous silica, part of the Si atoms exist as silanol groups which originate resonance peaks at -110, -100 and -91 ppm. These shifts have been attributed to the Si(4SiO), Si(OSi)₃OH and Si(OSi)₂(OH)₂ environments. Chemical analysis of this sample supplied a ratio Si/Al = 9. The presence of Al atoms in the MCM-41 network may generate Si(3Si, Al) and Si(2Si, 2Al) environments, which might be contributing to the resonance peak intensities at -100 and -91 ppm¹³.

The ²⁷Al MAS NMR spectra of the as synthesized and calcined AISiMCM-41(R/108) samples (Fig. 8), present a resonance peak close to 53 ppm which is attributed to structural tetrahedral coordinated aluminum. The as synthesized sample shows one peak close to 14 ppm and a weak signal at 32 ppm, which have been attributed to hexacoordinated aluminum, possibly forming Al(H₂O)₆³⁺ species within the pores and pentacoordinated species, respectively. These resonances were not detected in the calcined sample¹³. For the calcined sample the peak

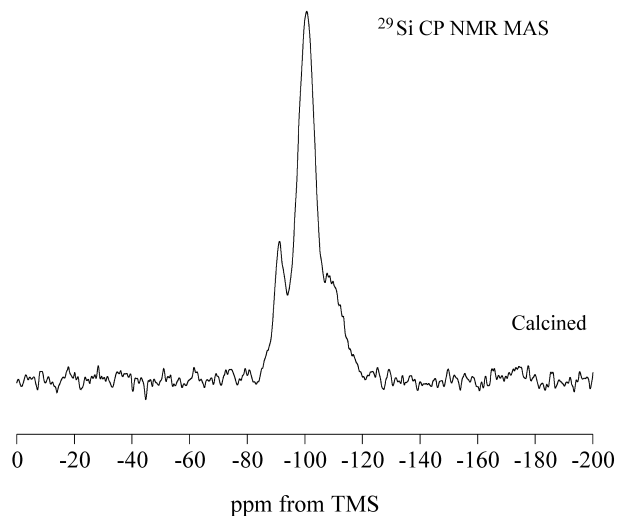


Figure 7. ^1H - ^{29}Si CP/MAS NMR spectrum of the AlSiMCM-41 (R/108) sample.

around 0 ppm is representative of hexacoordinated aluminum belonging to extra-structural species formed during calcination^{13,14}.

3.5. SEM micrographs

Figure 9 presents typical micrographs of the calcined SiMCM-41(R/108) and SiMCM-41(P/48) samples. Formation of the SiMCM-41 phase at hydrothermal conditions under autogenic pressure is seen to result, in shorter time, in a solid consisting of small agglomerates (Fig. 9a). The SiMCM-41 obtained under autogenic pressure, synthesized under reflux conditions (Fig. 9b) presents agglomer-

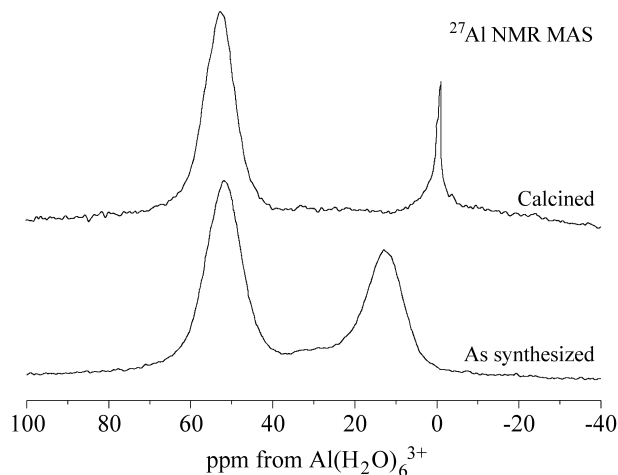


Figure 8. ^{27}Al MAS RMN spectra of the AlSiMCM-41(R/108) samples.

ates, similar to those obtained under autogenic pressure, and worm-like particles; this morphology practically did not change with synthesis time. The AlSiMCM-41 samples exhibit agglomerates with sizes between 3 and 200 μm , independent of the used synthesis method (Fig. 10). These samples did not show a tendency to form particles with a particular morphology.

4. Conclusion

XRD analysis of SiMCM-41 and AlSiMCM-41 samples showed that the MCM-41 phase may be formed by both processes and that the synthesized material in the presence of aluminum and/or under refluxing conditions

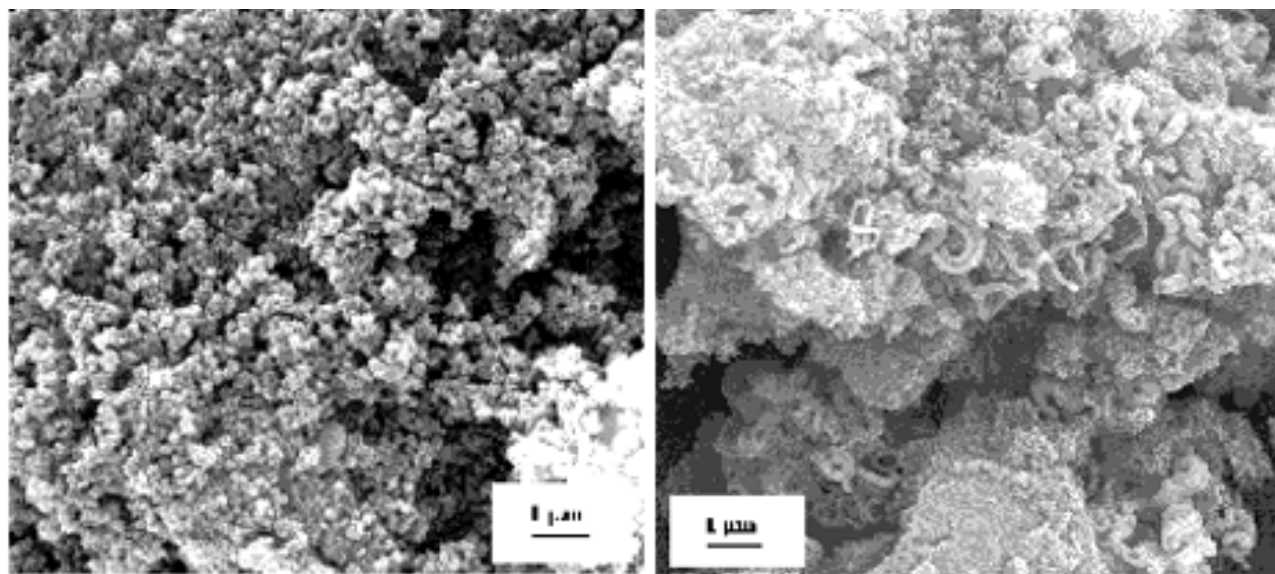
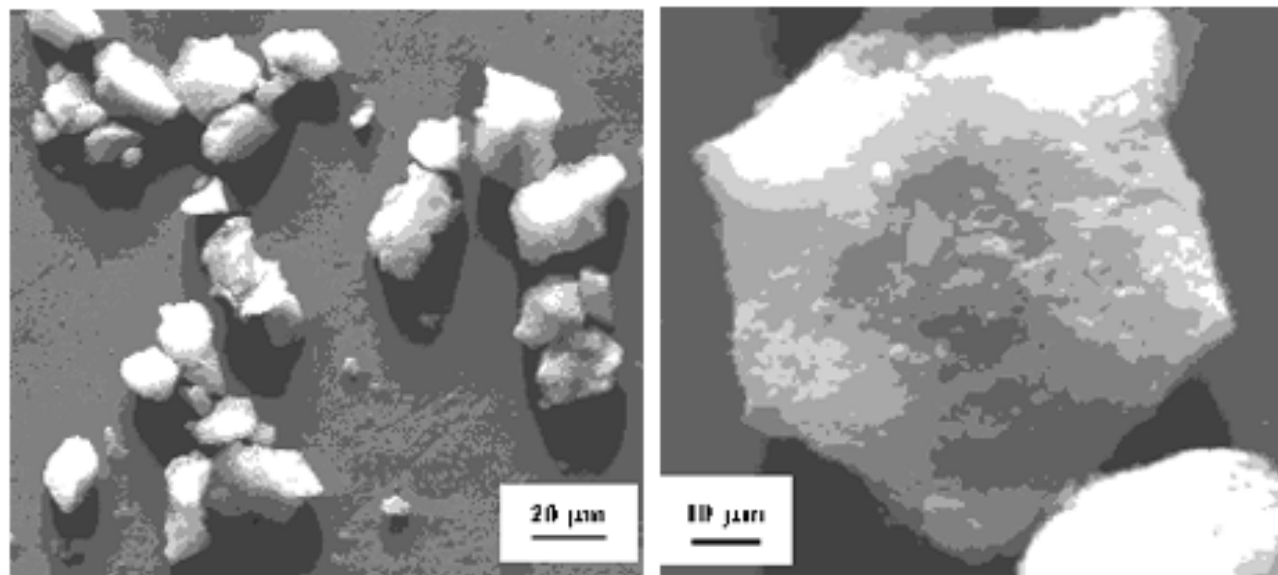


Figure 9. SEM micrographs of the SiMCM-41 samples. (a) Si MCM-41 (p/48), (b) Si MCM-41 (R/108).



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Figure 10. SEM micrographs of the AlSiMCM-41 samples. (a) AlSi MCM-41 (R/24), (b) AlSi MCM-41 (P/288).

presents a hexagonal arrangement of less ordered mesopores. However, in the latter case, as verified by XRD and physisorption data, improvement in order was observed with higher synthesis times.

^{29}Si MAS NMR and ^1H - ^{29}Si C/P MAS NMR spectra showed that a great part of the Si atoms exist as silanol groups which originate resonance peaks at -110, -100 and -91 ppm. The presence of Al atoms may generate Si(3Si,Al) and Si(2Si, 2Al) environments which might be contributing to resonance peaks at -100 and -91 ppm. The ^{27}Al MAS NMR spectra of the as synthesized AlSiMCM-41(R/108) confirm a strong resonance peak of tetrahedral framework aluminum close to 53 ppm and two others resonances, one close to 14 ppm attributed to $\text{Al}(\text{H}_2\text{O})_6^{+3}$ species within the pores and the other, a weak signal close to 32 ppm attributed to pentacoordinated aluminum species. ^{27}Al MAS NMR spectra of the calcined sample showed the peak at 53 ppm and another at 0 ppm corresponding to an hexacoordinated extra-framework aluminum species formed during the calcination process.

Acknowledgments

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