



**Synthesis of Mesoporous MCM-41 Materials
by Low Power Microwave Heating**

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Crystalline, high surface area, hexagonal mesoporous MCM-41 having uniform pore sizes and good thermal stability was successfully synthesized at 90-120°C in 30 minutes using low power microwave irradiation. This appears to be the first comprehensive and quantitative investigation of the comparatively rapid synthesis of mesoporous MCM-41 using low power microwave heating of 80W (90°C) and 120W (120°C). The influence of reaction temperature and the duration of heating were carefully investigated and the calcined MCM-41 materials were characterized by XRD, SEM, TEM, nitrogen adsorption, TGA and FTIR. The mesoporous MCM-41 product synthesized in 30 minutes at 120W and calcined at 550°C had a very high surface area of 1438 m²/g and was highly ordered, contained uniform pores with diameters in the range of 3.5-4.5 nm. The wall thickness of the materials highly depended on the power of the microwave energy used during the synthesis. Synthesis of the mesoporous MCM-41 products at 120°C resulted with a structure having thinner walls. The mesoporous MCM-41 materials synthesized in the present work had good thermal stability.

Keywords MCM-41; Mesoporous material; Microwave heating; Surface area; Pore size

Introduction

Since its first discovery by Mobil oil researchers, hexagonal MCM-41's possible use as catalyst and catalyst supports has attracted much attention (Kresge et al., 1992; Corma, 1997; Ying et al., 1999; Sayari, 2000). Pure siliceous mesoporous molecular sieves have a limited use as catalysts since it is necessary to incorporate metal centers as active sites in the silicate framework (Gates, 1992; Arends et al., 1997; Corma et al., 2002; Velu et al. 2002). Notably, mesoporous MCM-41 containing metal ions like Al, V, Fe, Mn, B, Ga, Ti, Zr or Cs have previously been synthesized and their catalytic properties have been explored (Tanev et al., 1994; Corma, 1997; Ying et al., 1999; Tuel, 1999; Lim et al., 1999; Bal et al., 2000; Wang et al. 2001).

Molecular sieves are usually synthesized with hydrothermal treatment of the raw gels in autoclaves. However, after the first application of microwave irradiation for the synthesis of zeolites (Chu et al., 1990) utilization of this new method for the production of such mesoporous materials have increased considerably (Arafat et al., 1993; Girmus et al., 1995; Lohse et al., 1996; Garcia et al., 1997; Zhao et al., 1997; Newalkar et al., 2001a; Newalkar et al., 2001b; Bonaccorsi and Proverbio, 2003; Zhou et al., 2010). Microwave irradiation has been successfully applied in chemistry and has become a widely accepted non-conventional energy source for performing organic synthesis. Spectacular accelerations, higher yields under milder reaction conditions and higher product purities have all been reported. For that reason microwave irradiation is now well established as a clean, cheap and rapid method for efficient heating providing phase purity in high yields, rapid kinetics and high reproducibility (Galema, 1997; Namboodiri and Varma, 2001; Komarneni, 2003; Tompsett et al., 2006; Wang et al., 2007).

This paper reports the determination of the optimum conditions for the microwave synthesis of highly ordered, mesoporous MCM-41 having high surface areas and uniform pore sizes. It was found that the microwave-assisted aging was a very efficient procedure to accelerate the crystallization. Successful synthesis required low power (80 W and 120 W) of microwave irradiation that heated the contents of the autoclave to 90°C and 120°C for not more than 30 minutes. The mesoporous MCM-41 has been characterized by XRD, SEM, TEM, nitrogen adsorption, TGA and FTIR. Subsequent papers will report the optimum conditions for the microwave synthesis of catalytic mesoporous MCM-41 possessing active sites containing selected concentrations of iron, cobalt, copper or nickel.

Experimental

Materials

An aqueous solution of sodium silicate, containing 27 wt. % SiO₂ (Aldrich) was used as the silica source and cetyl trimethylammonium bromide (CTABr, (C₁₆H₃₃)N(CH₃)₃Br), Merck 99% pure) was used as the surfactant.

Synthesis of MCM-41 with microwave heating

The synthesis of mesoporous MCM-41 was a modification of the procedure of Davis et al., (1988). 6.6g of CTABr was slowly dissolved in 43 ml of deionized water at 40°C and 5.65 ml of sodium silicate solution were added drop wise to the clear solution with continuous stirring for 1 hour at the same temperature. The pH of the mixture was reduced to 11 by the addition of 1M H₂SO₄. The resulting gel was again stirred for 1 hour before being transferred to a 120 ml Teflon autoclave. The autoclave was placed in a Delonghi EMD MW 311 adjustable power (<800W, 230V, 50Hz) microwave oven with a Velp Scientifica VTF Digital Thermoregulator. The aim of this study was synthesis of MCM-41 under low power microwave irradiation. The minimum adjustable power outputs for the utilized microwave oven were 80W and 120W. For that reason, these two power outputs were employed for the synthesis. Gels under autogenous pressure absorbed microwave energy of 80W or 120W to achieve desired reaction temperatures of 90°C or 120°C, respectively. Synthesis was carried out in a temperature-controlled mode. At 80W the temperature was ramped with a heating rate of 20°C/min and in approximately 2 minutes, the system reached 90°C. While for the synthesis at 120W the temperature was ramped with a heating rate of 35°C/min and again about in 2 minutes the system reached to 120°C. Two sets of experiments were conducted; in the first set, irradiation under an 80W of power for 10, 20, 30 and 60 minutes, and in the second one, irradiation under a 120W of power for 10, 20, 30 and 60 minutes. The prepared samples were labeled as follows: MCM41 X/Y. Where X indicates the power of microwave irradiation in watts and Y represents the duration of the experiment in minutes.

The resultant solid from each experiment was recovered by filtration, washed thoroughly with distilled water until the pH was neutral and dried at room temperature and

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3 stored at 40°C for 24 hours. The dried solid was finally calcined inside a quartz tube (120 cm
4 long x 1 cm diameter) fitted with quartz filters to obtain MCM-41. The tube was placed in a
5 furnace and heated from ambient temperature to 550°C at a rate of 10°C/min and kept at
6 550°C for 6 hours in a flow of dry air.
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10 11 *Characterization*

12 13 *N₂ Sorption analysis*

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18 The surface areas and porosities of the produced mesoporous MCM-41s were determined
19 using a NOVA 2200e Surface Area and Pore Size Analyzer (Quantachrome Instruments Co.,
20 USA). Measurements were performed in boiling liquid nitrogen (77 K). Samples were
21 outgassed at 150°C overnight. BET surface areas were determined by the multipoint method
22 using adsorption data in the relative pressure (P/P_0) with a range of 0.05-0.3. The pore volume
23 and pore size distributions were estimated from the adsorption branch of the isotherms by the
24 Barrett-Joyner-Halenda (BJH) method.
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30 31 *XRD*

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35 A Bruker AXS-D8 advanced powder diffractometer fitted with a Siemens X-ray gun and
36 equipped with Bruker axs Diffrac Plus software provided XRD data at room temperature.
37 Measurements were performed in the 2θ range of 2°-7°, at 40 kV and 40 mA, using Cu-K α
38 1.5406 Å radiation. The step size was always 0.01° and data collection was in 1 second steps.
39 All samples were outgassed before XRD measurements.
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44 45 *SEM*

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48 A Leo G34-Supra 35VP field emission scanning electron microscope (SEM) coupled to
49 energy dispersive spectrometer software was used for image and elemental analysis. Samples
50 were first coated with carbon by an Emitech T950 Turbo Evaporator to provide a conducting
51 surface layer. The gun chamber pressure was $\sim 10^{-11}$ mbar. The SEM electron column was
52 equipped with a secondary electron detector, a back-scattering electron detector, and an in-
53 lens detector for secondary electron detection. Imaging was done at the extractor voltage of
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3 5.2 keV and accelerating voltages ranging between 2 and 5 keV using the secondary electron
4 detector.
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7 8 *FTIR*

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11 A Nicolet iS10 Fourier transform infrared spectrometer with the KBr pellet technique was
12 used in the range of 400-4000 cm^{-1} to determine structural information of the MCM-41
13 materials produced.
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16 17 18 *TGA*

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21 Thermal stabilities of the samples were determined by a Netsch 449C thermal gravimetric
22 analyzer. The samples were heated from room temperature to 1000°C at 10°C/min under a
23 nitrogen atmosphere in pure alumina crucibles.
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27 28 29 *TEM*

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31 High Resolution transmission electron microscopy (TEM) analyses were performed by JEOL
32 2100 LaB6 HRTEM.
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36 **Results and Discussions**

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39 Figure 1 and 2 presented the low-angle (2θ value ranging from 2° to 7°) XRD patterns
40 of the MCM-41 samples prepared at 80W and 120W for various reaction times. The
41 characteristic Bragg peaks of the calcined MCM-41s can be indexed as the (100), (110),
42 (200), (210), and (300) members of a hexagonal lattice (Beck et al., 1992). The diffractograms
43 of the MCM-41 produced in the present work, show three Bragg peaks which can be indexed
44 as (100), (110) and (200). MCM-41 prepared at 80W microwave power (90°C) for up to 20
45 minutes gave a characteristic (100) Bragg peak at $2\theta = 2.70^\circ$. It appears that the reaction time
46 was insufficient to initiate the formation of ordered structure. MCM-41 prepared at 120°C
47 (120W of microwave power) for 20 minutes, however, gave three Bragg peaks at $2\theta = 2.50^\circ$
48 (100), $2\theta = 4.20^\circ$ (110) and $2\theta = 4.80^\circ$ (200). Thus, the relatively higher microwave power
49 was effective in synthesizing MCM-41 even with relatively short reaction times. When the
50 duration of microwave heating was 30 minutes, ordered structures formed and three Bragg
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peaks were detected at $2\theta = 2.48^\circ$ (100), $2\theta = 4.20^\circ$ (110) and $2\theta = 4.80^\circ$ (200) (90°C, 80W microwave power) and $2\theta = 2.50^\circ$ (100), $2\theta = 4.26^\circ$ (110) and $2\theta = 4.82^\circ$ (200) (120°C, 120W microwave power). Even greater intensities were observed at same 2θ values for 60 minutes of microwave heating duration.

Representative SEM images (using the secondary detectors) of MCM-41 samples 120/30 (prepared at 120W microwave power in 30 minutes), 80/30 (prepared at 80W microwave power in 30 minutes) and 80/60 (prepared at 80W microwave power in 60 minutes) were shown in Figure 3. The morphology of agglomerated particles in MCM-41 sample 120/30 (Figure 3a) showed smaller particles of about 70 nm as compared to MCM-41 sample 80/30 and 80/60 (Figure 3b and 3c). The reason for this observation can be attributed to the faster reaction rate and nucleation of crystallization of MCM-41 production in 120 W power output. As shown in Figure 4, the TEM image of calcined MCM-41 sample 120/30 illustrates that the sample has highly ordered regular channels with a pore diameter of approximately 3.9 nm.

Figures 5 and 6 illustrate the N_2 sorption isotherms at 77 K and the pore distributions of MCM-41 which was synthesized under various experimental conditions. Table 1 summarizes the parameters derived from nitrogen sorption and XRD.

Figures 5a and 6a show the nitrogen isotherms of MCM-41 prepared at 90°C (80W microwave power) and 120°C (120 W microwave power), respectively. All of the isotherms can be classified as type IV according to the IUPAC nomenclature. Thus, all the isotherms indicate a linear increase of adsorbed volume at low pressures due to monolayer adsorption on the pore walls, followed by a steep increase in nitrogen uptake at a relative pressure of $0.25 < P/P_0$ due to capillary condensation inside the mesopores, highly characteristic of MCM-41 (Nalbant et al. 2008). The steep adsorption starting from $P/P_0 < 0.25$ and the narrow hysteresis loops that occurred at $0.40 < P/P_0 < 0.65$ are characteristic features of mesoporous materials having a narrow range of uniform and cylindrical pores (Zhao et al., 1996; Beck et al., 2001; Selvam et al., 2001). The long plateau at higher relative pressures indicates that after capillary condensation of the mesopores, multilayer adsorption continued on the surface of the material.

Table 1 includes the specific surface area (BET), the pore volume and average pore diameter (D_{pore}) evaluated from the desorption branch of the N_2 isotherms by BJH theory, the d_{100} , lattice parameter (a), and the pore wall thickness (δ) of the calcined MCM-41.

The characteristic lattice parameter a , defined as the repeating distance between two pore centers, was evaluated from equation (1) (Fenelonov et al., 1999):

$$a = (2/\sqrt{3}) d_{100} \quad (1)$$

and the pore wall thickness (δ) was evaluated from equation (2) (Fenelonov et al., 1999):

$$\delta = a - 0.95 D_{pore} \quad (2)$$

BET surface area values of the MCM-41 prepared at 90°C (80W microwave power) increased from 558 m²/g to 1211 m²/g, 1385 m²/g and 1390 m²/g at heating durations of 10, 20, 30 and 60 minutes respectively, Table 1. Wu and Bein, (1996), reported that, microwave treatment at 150°C for 60 minutes with cethyltrimethyl ammonium bromide as surfactant resulted in the formation of mesoporous MCM-41 having specific surface areas of 800-1000m²/g. MCM-41 prepared at 100-120°C within 40 minutes with microwave irradiation in ethylene glycol solution using the same surfactant possessed BET surface areas and pore volumes of 700-1150 m²/g and 0.60-0.78 cm³/g, respectively (Kim et al., 1999). Mesoporous MCM-41 prepared at 90°C (80W) microwave irradiation for 60 minutes, possessed a specific surface area of 1390 m²/g and a pore volume of 1.10 cm³/g, which is higher than any previously reported values (Kim et al., 1999; Wu and Bein,1996).

The BET surface area of MCM-41 synthesized at 120°C (120W microwave power) and calcined at 550°C increased from 688 m²/g to 1438 m²/g as the duration of heating was increased from 10 to 30 minutes. Pore volumes increased from 0.28 cm³/g to 0.58 cm³/g as the duration of heating was increased from 10 to 60 min. Pore diameters of the products obtained at 120°C (120 W microwave power) were 4.46 nm, 4.02 nm, 4.00 nm and 4.02 nm for MCM-41s which were prepared at 10, 20, 30 and 60 minutes, respectively. These values are about 15% larger than those obtained at 90°C (80W microwave power). Pore diameter of MCM-41 prepared at 120°C (120W microwave power) for 30 minutes were close to those of MCM-41 prepared at 80W microwave power for 60 minutes. This suggests that, providing the same surfactant is used, one obtains very similar pore diameters after ordered hexagonal mesoporous structures form. This is consistent with the work of Jana et al. (2004) who prepared MCM-41 using a mixture of surfactants with alkyl chain lengths ranging from C₈ to C₂₂. They obtained BJH pore diameters of 3.2 nm at 25°C using 80W microwave power with a C₁₆ surfactant which is quite close to 3.49 nm value that we obtained. When compared with other MCM-41s produced in this work and also the materials reported in the literature, MCM-41 prepared at 120°C (120 W microwave power) in 30 minutes had the highest specific surface area value of 1438 m²/g.

While wall thickness of the MCM-41 mesoporous materials produced at 90°C (80 W microwave power) was in the range of 0.78-0.90 nm, the wall thickness of those produced at 120°C (120 W microwave power) was in the range of 0.34-0.38 nm. It seems that the wall

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3 thickness of the materials highly depends on the power of the microwave energy used during
4 the synthesis. As it is suggested in the literature (Carrott et al., 2007), increase in the
5 temperature causes an expansion of the micelles and as a consequence pore diameter
6 increases. Also, since the reaction rates are very high with microwave synthesis, condensation
7 of the walls occurred very fast and the lattice parameters remained almost constants for both
8 power outputs. From this observation, it can be interpreted the increase in microwave oven
9 power output from 80W to 120W resulted in decrease in pore wall thickness values. So it can
10 be suggested that synthesis of the mesoporous MCM-41 materials at relatively higher
11 temperature of 120°C (120 W power microwave) produce materials with thinner walls. The
12 effect of microwave irradiation in the synthesis of MCM-41 materials in the present work at a
13 relatively low reaction temperature, 120°C, might be due to a combination of thermal effects,
14 arising from the heating rate, superheating or “hot spots” and the selective absorption of
15 radiation by polar substances present in the reaction mixture. According to the studies
16 reported in the literature, advantages like higher yields, milder reaction conditions and shorter
17 reaction times do not occur by conventional heating (Hoz et al., 2005). This appears to be the
18 first comprehensive and quantitative investigation of the comparatively rapid synthesis of
19 mesoporous MCM-41 by low power microwave (80 W and 120 W) heating in the relatively
20 low temperature range of 90°C and 120°C.
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33 Thermal stabilities of the calcined samples were characterized by thermal gravimetric
34 methods. Thermogravimetric analysis of the 120/30 MCM-41 sample (120W microwave
35 power for 30 minutes) from room temperature to 1000°C with a 10°C/min heating rate in air
36 (Figure 7) revealed a weight loss of only 13.89 % by weight at 170.0°C. At the end of the
37 analysis total weight loss was measured as 22.76 % by weight which is in good agreement
38 with the literature (Koh et al., 1997; Araujo and Jaroniec, 2000). According to Jaroniec et al.
39 (2000) desorption of water occurs until 170°C. After that temperature up until 600°C
40 decomposition of residual surfactants and condensation of silanol groups was observed.
41 Finally the last 1.50 % weight loss from 600°C to 1000°C is attributed to condensation of
42 residual silanol groups occur. The results indicated that the mesoporous MCM-41 materials
43 produced in the present work had good thermal stability.
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51 Figure 8 shows the FTIR spectra of uncalcined and calcined 120/30 MCM-41 sample
52 (120 W microwave power for 30 minutes). Uncalcined MCM-41 (Figure 8a), gave bands at
53 2922 cm⁻¹, 2852 cm⁻¹ and 1478 cm⁻¹, characteristic of surfactant alkyl chains. These bands
54 were not present after calcination, showing calcinations to be effective (Zholobenko et al.,
55 1997; Holmes et al., 1998). In Figure 8b the band at 3407 cm⁻¹ is characteristic of the
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3 vibrations of Si–OH and adsorbed water molecules; the band at 1632 cm^{-1} is another
4 characteristic vibration of adsorbed water molecules. The band at 1065 cm^{-1} is the asymmetric
5 extension vibration of Si–O–Si.
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8 The high specific surface areas, pore volumes and the uniformity of the ordered pore
9 diameters and pore wall thicknesses suggested that MCM-41 materials synthesized with low
10 power microwave irradiation might have invaluable applications as molecular sieves and in
11 the production of catalysts. This will be considered in the subsequent paper.
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14 15 16 **Conclusion**

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19 This appears to be the first comprehensive and quantitative investigation of the
20 comparatively rapid synthesis of mesoporous MCM-41 materials with low power microwave
21 heating in the relatively low temperatures of 90°C and 120°C . Highly crystalline ordered
22 mesoporous MCM-41 was produced reproducibly with uniform pore size distributions and
23 good thermal stability. The effect of microwave irradiation in the synthesis of MCM-41 at
24 such a low reaction temperature might be due to a combination of thermal effects, arising
25 from the heating rate, superheating or “hot spots” and the selective absorption of radiation by
26 polar substances present in the reaction mixture. Microwave-assisted heating caused
27 spectacular accelerations in the reactions as a consequence of the heating rate, which cannot
28 be reproduced by thermal heating. Higher yields, milder reaction conditions and shorter
29 reaction times were thus attained. It was found in the experiments that using 120 W of
30 microwave irradiation increased the reaction temperature to only 120°C , and highly ordered
31 mesoporous MCM-41 materials were produced only in 30 minutes. The MCM-41 material
32 obtained in this experiment had a specific surface area of $1438\text{ m}^2/\text{g}$, a pore volume of 0.53
33 cm^3/g with a rather uniform pore diameter of 4.00 nm ; values that compare favorably to those
34 of MCM-41s reported in the literature. It seemed that the wall thickness of the materials
35 highly depended on the power of the microwave energy used during the synthesis. Synthesis
36 of the mesoporous MCM-41 materials at 120°C using relatively higher microwave power of
37 120 W, appeared to produce materials with thinner walls ($0.34\text{--}0.38\text{ nm}$).
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Table captions

Table 1 Physical and structural properties of MCM-41 synthesized by microwave irradiation.

Figure Legends

Fig. 1 Representative XRD patterns of MCM-41 irradiated at 80W microwave power

Fig. 2 Representative XRD patterns of MCM-41 irradiated at 120 microwave power

Fig. 3 SEM images of MCM-41 a) Sample 120/30, a) Sample 80/30 a) Sample 80/60 with the secondary electron detector.

Fig. 4 TEM image of MCM-41 sample 120/30.

Fig. 5 a) Nitrogen sorption isotherms obtained at 77 K and b) pore size distributions of MCM-41 prepared at 80W microwave power for 20, 30 and 60 minutes

Fig. 6 a) Nitrogen sorption isotherms obtained at 77 K and b) pore size distributions of MCM-41 prepared at 120W microwave power for 20, 30 and 60 minutes

Fig. 7 Thermogravimetric trace of MCM-41 120/30 sample

Fig. 8 FTIR spectra of MCM-41 synthesized at 120 W microwave power for 30 minutes

a) uncalcined, b) calcined

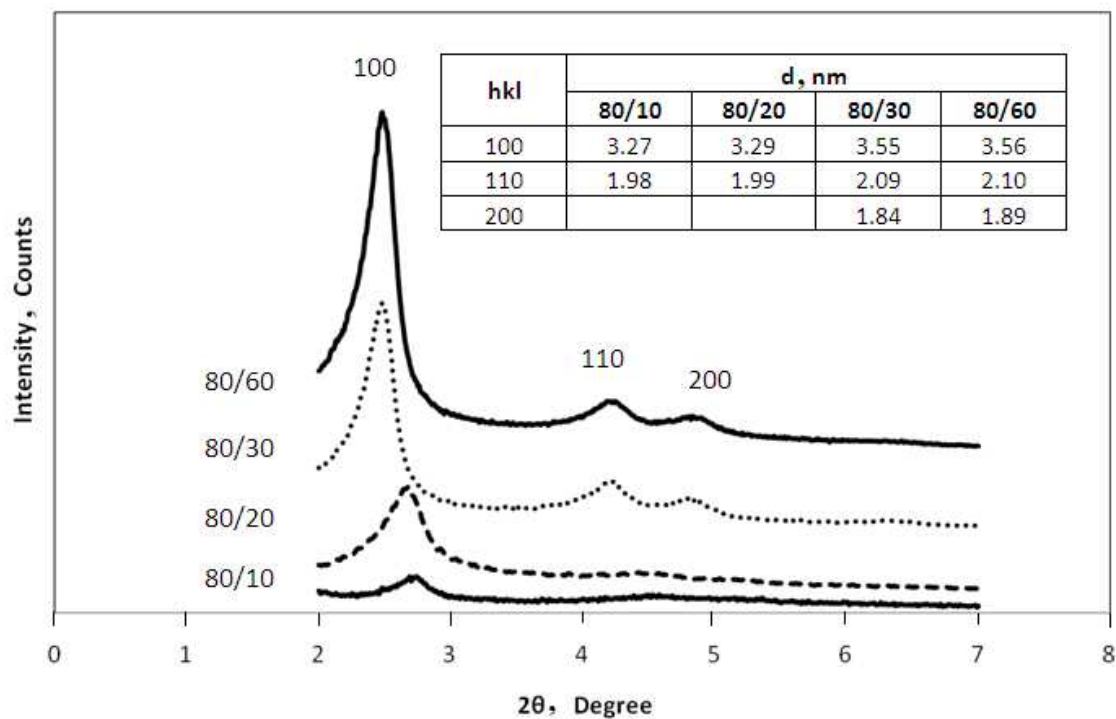


Fig. 1 Representative XRD patterns of MCM-41 samples 80/10, 80/20, 80/30 and 80/60

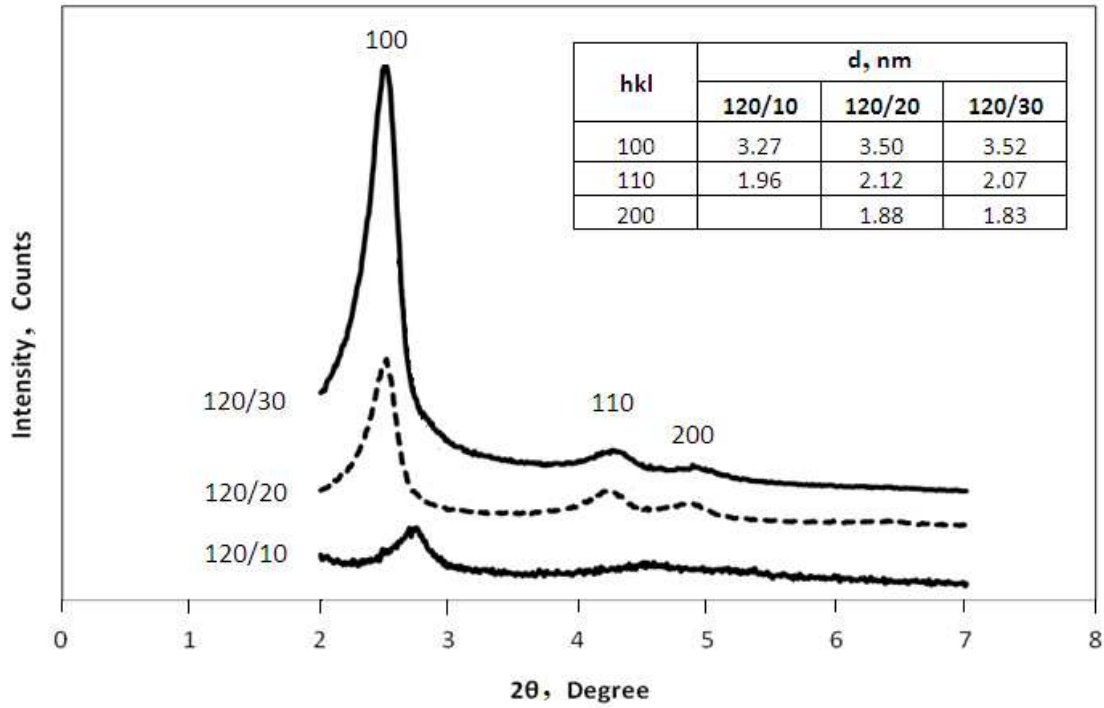


Fig. 2 Representative XRD patterns of MCM-41 samples 120/10, 120/20 and 120/30

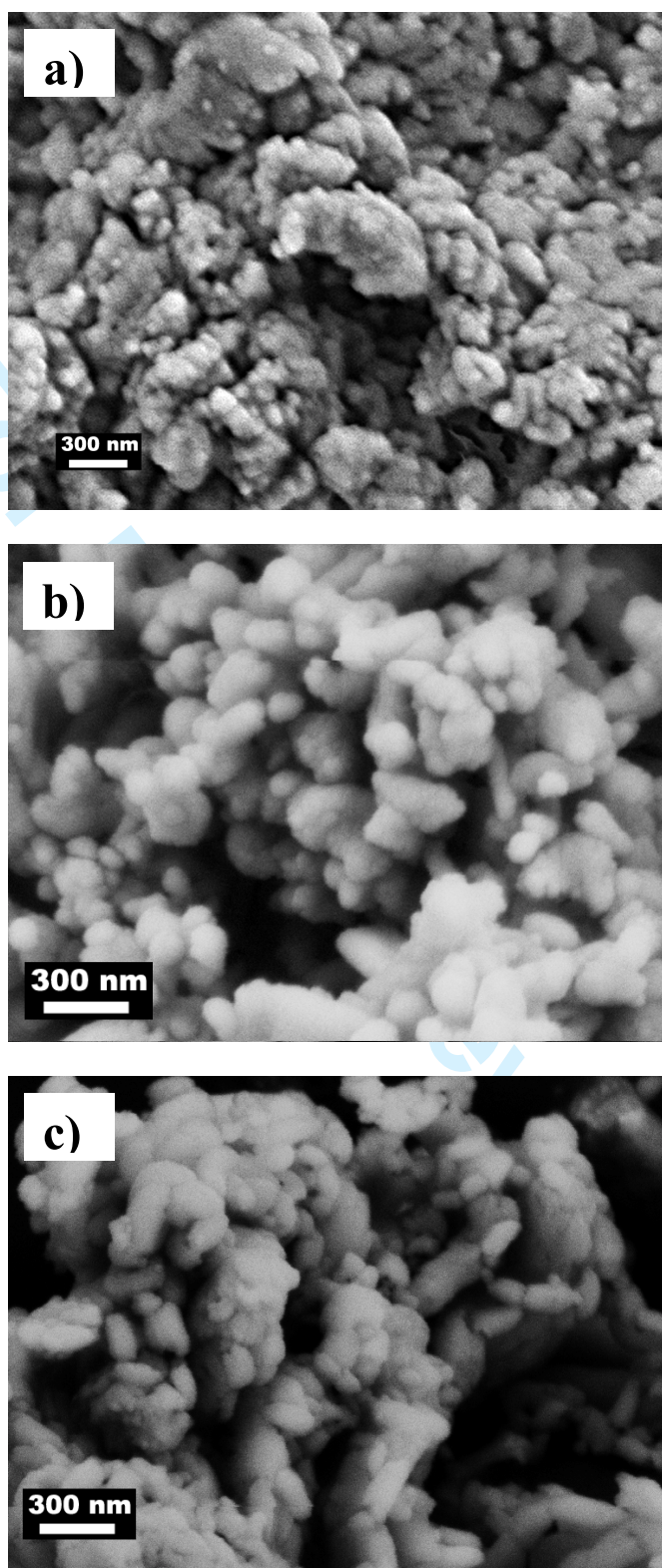


Fig. 3 SEM images of MCM-41 a) Sample 120/30, a) Sample 80/30 a) Sample 80/60 with the secondary electron detector.

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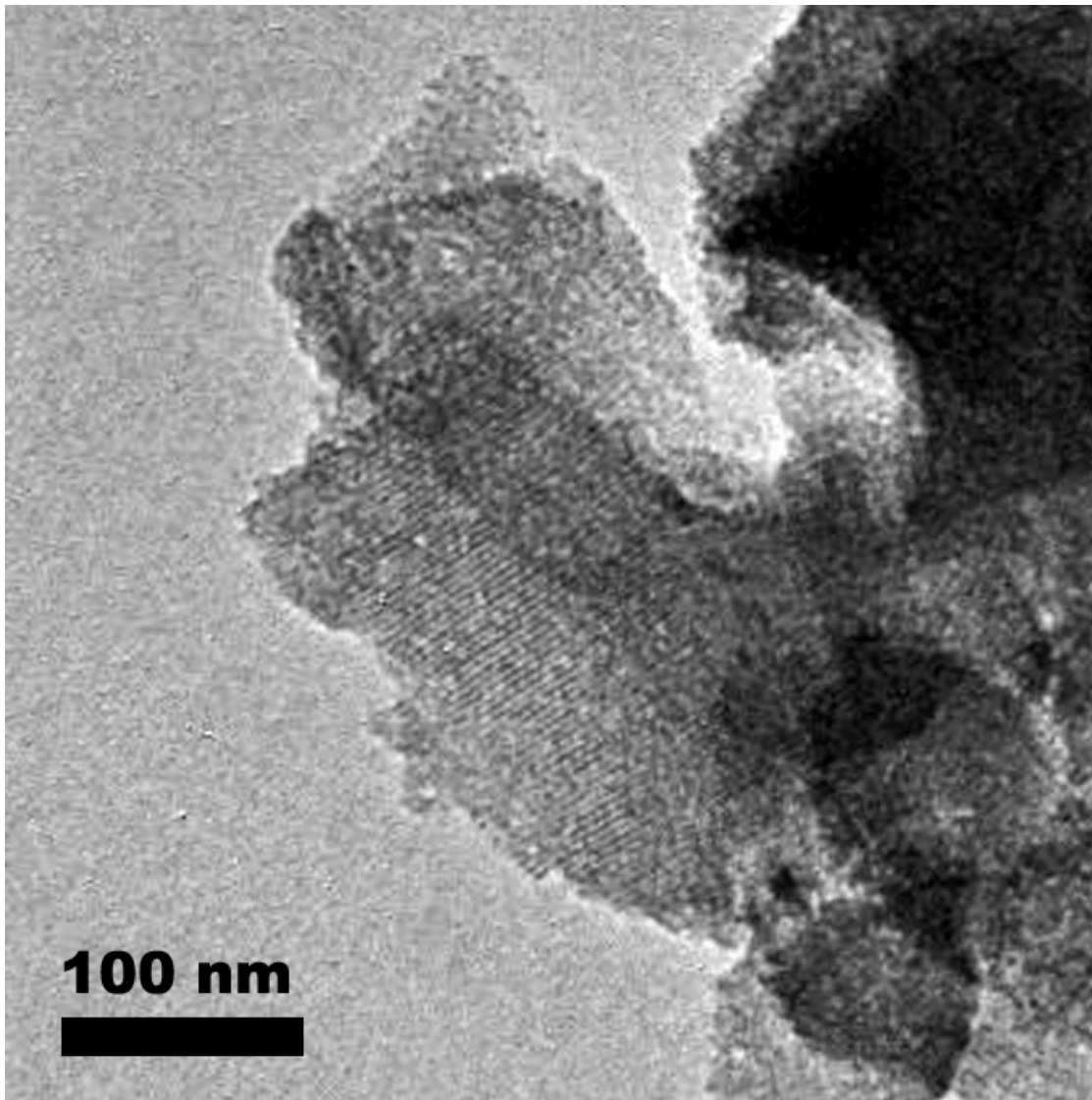


Fig. 4 TEM image of MCM-41 sample 120/30.

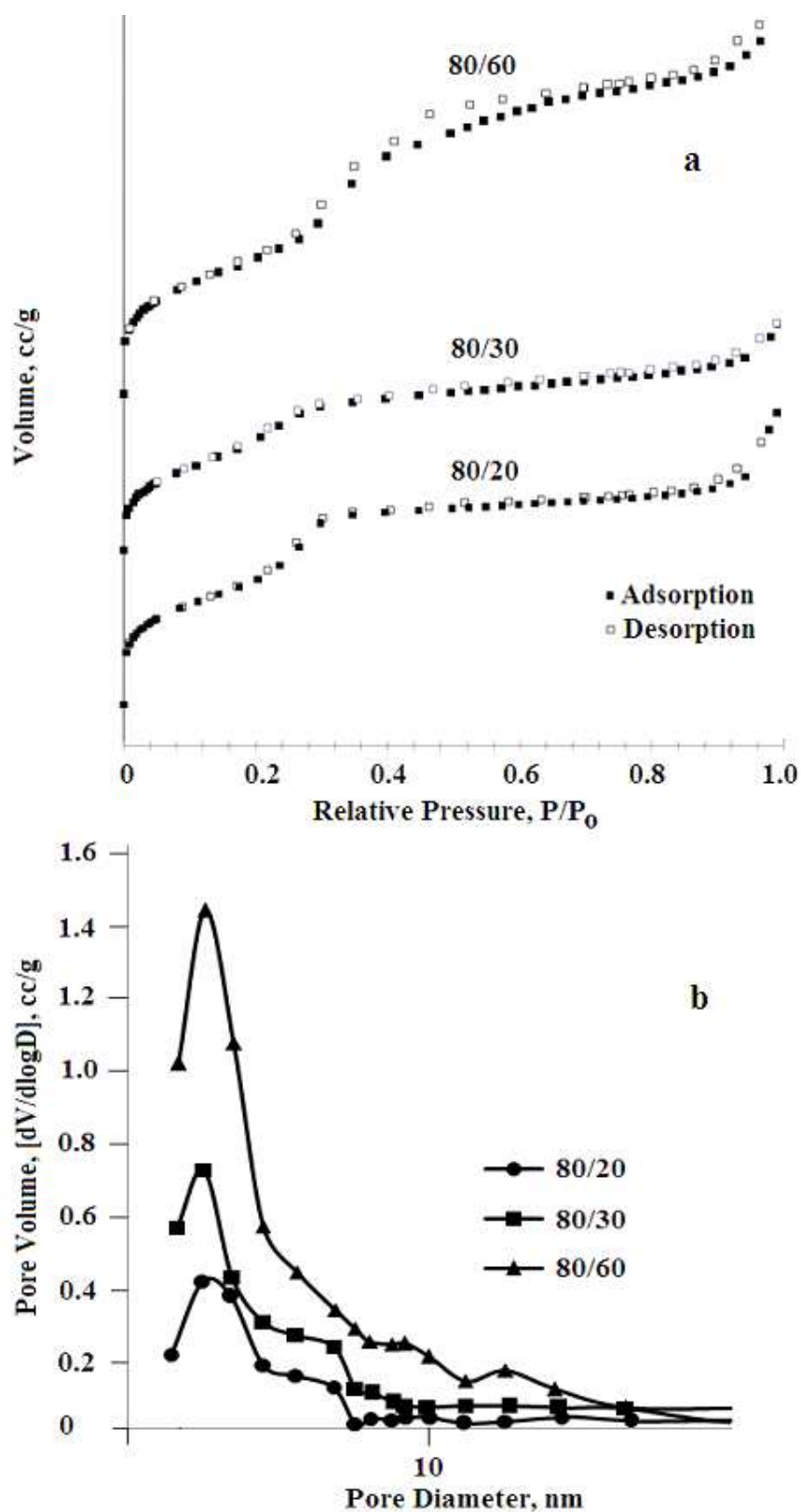


Fig. 5 a) Nitrogen sorption isotherms obtained at 77 K and b) pore size distributions of MCM-41 samples 80/20, 80/30 and 80/60

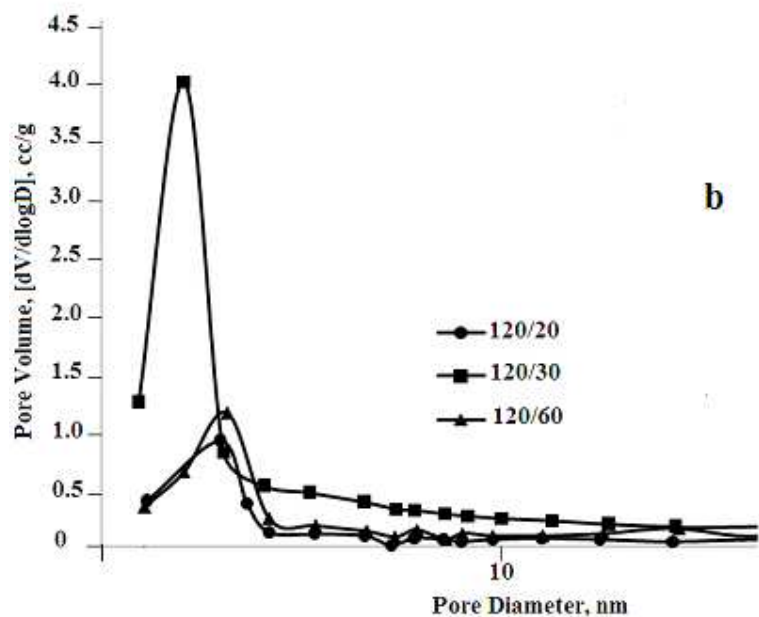
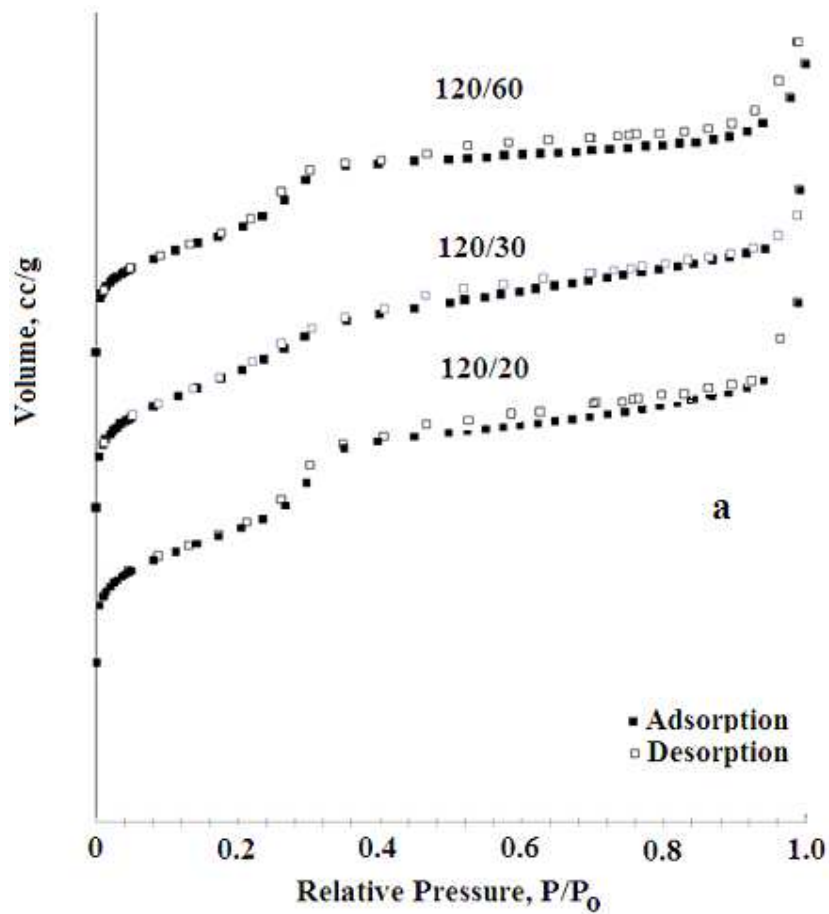


Fig. 6 a) Nitrogen sorption isotherms obtained at 77 K and b) pore size distributions of MCM-41 samples 120/20, 120/30 and 120/60

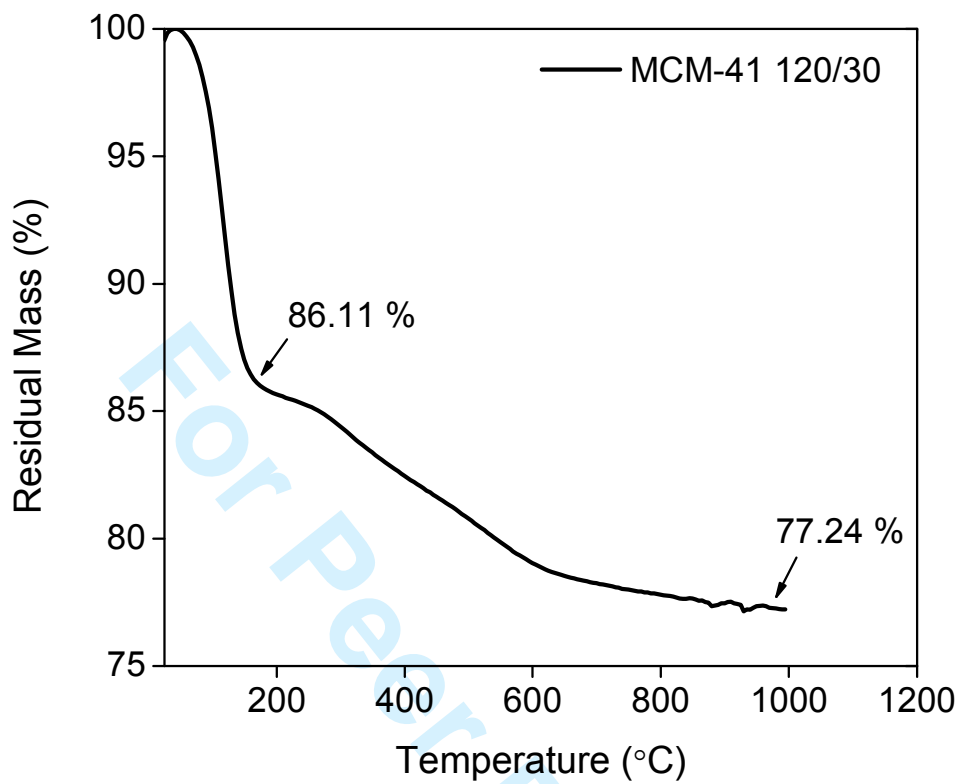


Fig. 7 Thermogravimetric trace of MCM-41 120/30 sample

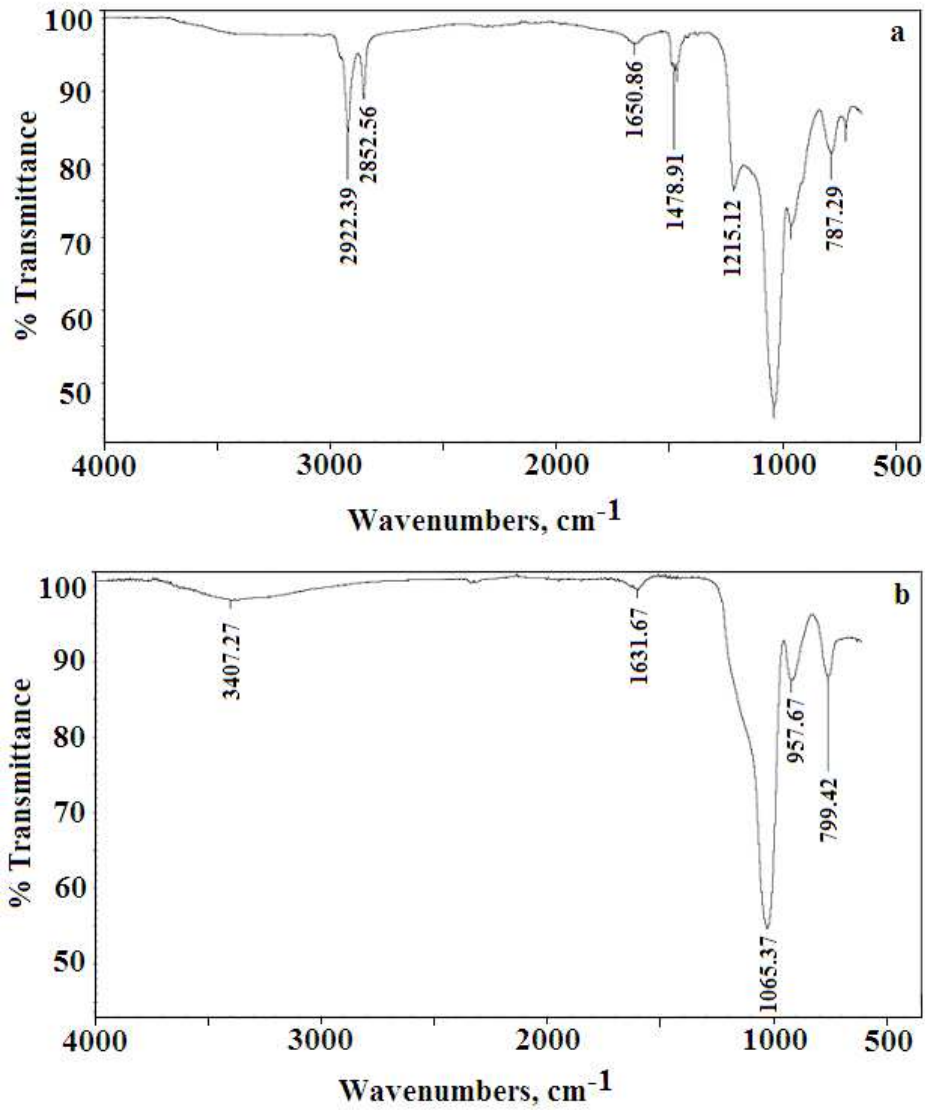


Fig. 8 FTIR spectra of MCM-41 synthesized at 120 W in 30 minutes a) uncalcined, b) calcined

Table 1 Physical and structural properties of MCM-41 type catalytic materials synthesized by microwave assisted direct synthesis method

Sample ID (Power/Time) (W/Min.)	BET Surface Area (m ² /g)	BJH Des. Pore Volume (cm ³ /g)	BJH Des. Pore Diameter (nm)	Interplanar Spacing, d ₁₀₀ , (nm)	Lattice Parameter “a” (nm)	Pore Wall Thickness “δ” (nm)
MCM-41 (80/10)	558	0.18	3.48	3.54	4.09	0.78
MCM-41 (80/20)	1211	0.45	3.47	3.54	4.09	0.79
MCM-41 (80/30)	1385	0.39	3.50	3.65	4.21	0.89
MCM-41 (80/60)	1390	1.10	3.50	3.65	4.22	0.90
MCM-41 (120/10)	688	0.28	4.46	3.54	4.09	0.34
MCM-41 (120/20)	1343	0.71	4.02	3.63	4.19	0.37
MCM-41 (120/30)	1438	0.53	4.00	3.64	4.20	0.38
MCM-41 (120/60)	1210	0.58	4.02	3.61	4.16	0.34