

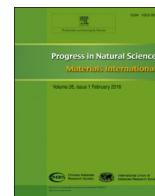
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Original Research

## Synthesis and characterization of silica mesoporous material produced by hydrothermal continues pH adjusting path way



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### ABSTRACT

Mesoporous silica molecular sieves MCM-41 were synthesized under hydrothermal conditions. For this purpose, a solution with a molar coefficient of water, cetyltri-methyl ammonium bromide surfactants as template and sodium silicate as the source of SiO<sub>2</sub> are used. Phase formation, morphology and gas absorption properties were investigated by XRD and BET analysis, respectively. The results showed that silica mesoporous material has been successfully synthesized. A favorable special surface and porosity volume together with regular arrangement of nano metric-hexagonal porosities were obtained from this synthesis. Thickness of the wall and average diameter of the pores are 0.8 nm and 4 nm, respectively.

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### 1. Introduction

Since the discovery of MCM-41 by the Mobil Co. scientists at 1992 [1,2], mesoporous molecular sieves (MMS) have aroused a great deal of interest in the field of catalysis due to their potential to overcome the drawback of zeolite—limited diffusion of molecules due to the small channels. Up to now, MMS with pores sizes ranging from 2 to 30 nm have been developed [3], and are being examined for their catalytic applicability in variable chemical reactions [4,5]. However, the general catalytic processes involve a hot water or high temperature condition, which makes the structure of MMS very weak and unstable due to the hydrolysis of the Si–O–Si bonds and the thin pore walls. Therefore, many studies have focused on improving the structural stability of MMS for catalytic applications [6–8]. This material opened a new field for more study about ideal materials to bridge the divide between microporous zeolites and meso/macroporous metal oxide supports with respect to physical and chemical properties. For a systematic study of this new material, highly ordered physical structure is necessary. Especially, for some catalytic applications, highly ordered metal incorporated M41S needs to be synthesized, e.g. MCM-41, one of M41S group, has been a major research focus for scientists interested in high surface area solids. MCM-41 can be considered the most important mesoporous material of a class of materials, known as MCM (Mobil Composition of Matter). Compared to microporous crystalline zeolites, these materials can be

regarded as amorphous oxides with an array of regular mesopores. Also, it can be depicted as an array of cylindrical pores having diameter in the range between 2 and 50 nm, surrounded by amorphous silica and organized in a hexagonal long-range structure; cylinders length results in the range of microns [2,3]. The prominent features of MCM-41, whose pores can be tailored and finely tuned, are: very high surface area and reactivity, well-defined pore shape with a narrow size distribution, large amounts of internal hydroxyl groups, ease modification of the surface properties, enhanced catalytic selectivity, and excellent thermal, chemical and mechanical stability. These features have allowed using MCM-materials as catalysts of many petro-chemical [3–5] and redox process in liquid phase [6,7], as heteropoly acid support [8], as highly efficient adsorbents [9,10] and as molecular hosts [11–16].

The objective of this study, mesoporous MCM-41 material with different content pH was synthesized using a hydrothermal method. The obtained material characterized by XRD, Nitrogen adsorption, and TEM methods.

### 2. Experimental methods

Hydrothermal method with regulation of pH of solution was used for the synthesis of mesoporous. An aqueous solution with a molar ratio of 5SiO<sub>2</sub>:0.16CTAB:300H<sub>2</sub>O was first prepared. pure Cetyltrimethylammonium bromide (CTAB) was used as surfactant factor and sodium silicate was used as SiO<sub>2</sub> resource. The conditions of synthesized and corresponding parameters are listed in Table 1.

In order to synthesis the mesoporous sample, 55 g of CTAB was

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**Table 1**  
Condition of synthesized mesoporous samples.

Sample	Time Calcinations (hr)	Time drying (hr)	Time Temp. (k)	Drying Temp. (k)	pH
Me <sub>1</sub>	6	24	873	352	11
Me <sub>2</sub>	6	24	873	352	10.5
Me <sub>3</sub>	6	24	873	352	10

first heated in 1 liter of distilled water so that the color of the solution be clear. Then, 56 g of sodium silicate was added to it. Next, the solution was poured into a poly-ethylene bottle. The crystalline phase identification and phase purity determination of the calcined MCM-41 samples were carried out by XRD (Philips, Holland) using nickel filtered CuK $\alpha$  radiation ( $L=0.15406$  nm). The samples were scanned from  $0.5^\circ$  to  $10^\circ$  ( $2\theta$ ) angle in steps of  $0.5^\circ$ . The characteristic lattice parameter was calculated from the following equation  $a_0=2d_{100}3^{1/2}$  [2,13,14]. Absorption/Desorption analysis of nitrogen at the temperature of 77 k. was done using a nitrogen absorption device (germini2375 model), after drying the samples at  $100^\circ\text{C}$  and  $300^\circ\text{C}$  under nitrogen atmosphere. The area of specific surface was obtained by the BET method. The total volume of the holes was calculated through- the absorbed nitrogen volume under the pressure of  $p/p_0=0.95$ . The structures of the samples were investigated by transmission electron microscopy (TEM, Hitachi H200 model). In order to preparation of the samples of TEM, the powder of MCM-41 and was first suspended in ethanol using ultrasonic device. The particles were then put between glass slide and carbon film. The carbon film was located on a tough sub-layer of copper.

### 3. Results and discussion

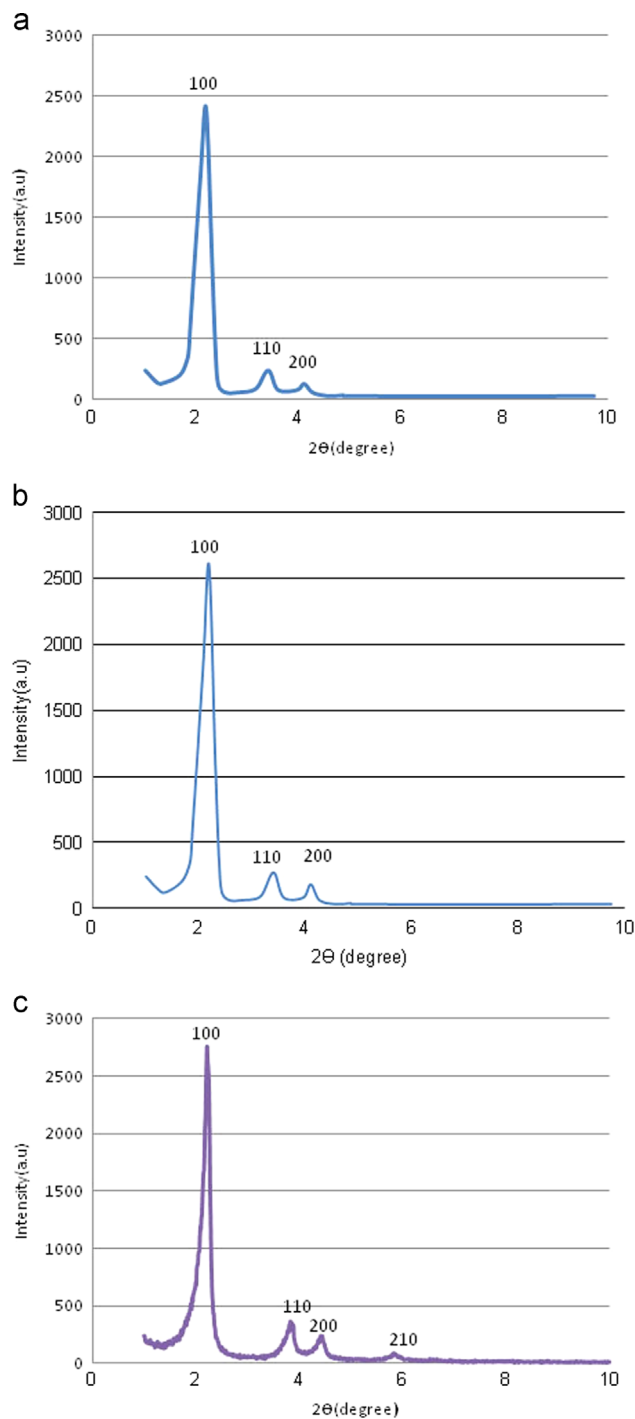
The results of the low angle range of XRD patterns of all samples are briefly summarized in Fig. 1. In Fig. 1, three reflections can be observed. Intensity of the first peak, which is stronger than the two others, is related to index to the (100), while the two others are related to (110), (200) reflections, respectively. All samples shows the (100), (110) and (200) reflections. The interpretation can be made that MCM-41 is formed with hexagonal structure.

Similar results have already been reported by other researchers [2,14–19].

By comparing Fig. 1a with that of Fig. 1b, it can be conclude that the peaks intensity of Me<sub>2</sub> sample is higher than that obtained for Me<sub>1</sub> sample. Also, X-ray diffraction patterns of parent Me<sub>3</sub> sample is presented in Fig. 1c. As seen, Me<sub>3</sub> exhibits four main peaks. It is clear that the peak intensity of (100) index for all sample are higher than the other reflections. Similar patterns have been obtained on the whole series of Me<sub>1</sub> and Me<sub>3</sub>.

Fig. 1c display four reflection peaks, that can be indexed to the (100), (110), (200), and (210) diffraction lines. The peak of index (210) was not shown in Fig. 1a and b. As can be seen in Fig. 1, the appearance of three peaks in all diagrams, related to (100), (110) and (200) reflections, is specified. These planes certify the creation of mesoporous with regular and hexagonal structure of pore particles, an indication of silicate MCM-41 of type mesoporous. As the final result, it is concluded that silicate mesoporous with hexagonal porosity was created in all three samples synthesized under the condition of pH=11, pH=10.5 and pH=10.

The observed (210) reflection in Me<sub>3</sub>, can be related to decreasing of pH. This reflection did not appear in the diffraction pattern of the two other samples. The appearance of the (210) reflection in sample Me<sub>3</sub> indicated that the hexagonal structure of this sample is more amorphous in structure with respect to the



**Fig. 1.** Low angle range of XRD patterns of the samples a) Me<sub>1</sub> b) Me<sub>2</sub> and c) Me<sub>3</sub>.

other samples [3,7,9].

The hexagonal structure of the pores had also lesser change and displacement in comparison with two other samples. The hexagonal structure of MCM-41 finds a better solidarity and a longer order. The appearance of the high peak related to the (100) reflection is an indication of perfect order of the hexagonal structure of mesoporous. Other researcher obtained similar result in this regard [3,7,9,19]. The broad XRD peaks indicate that the particles and pores are nanosized.

The hexagonal unit cell parameter ( $a_0$ ) was calculated using the formula as  $a_0=2d_{100}/\sqrt{3}$ . Value of  $d_{100}$  was obtained from the peak in the XRD pattern by Bragg's equation ( $2d \sin X=L$  where  $L=1.54060^\circ\text{A}$  for the CuK $\alpha$  line). The value of  $a_0$  was equal to the

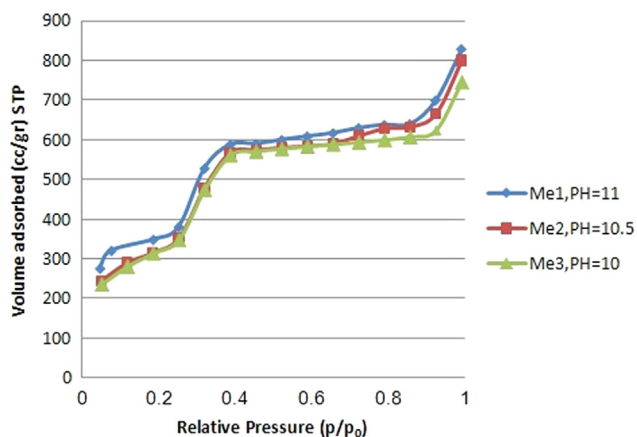


Fig. 2. Low temperature nitrogen adsorption-desorption isotherms of Me<sub>1</sub>, Me<sub>2</sub> and Me<sub>3</sub> samples.

Table 2  
Structural properties of samples.

Sample	BET Surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore Volume (cm <sup>3</sup> g <sup>-1</sup> )
Me <sub>1</sub>	1070	1.132
Me <sub>2</sub>	1056	1.124
Me <sub>3</sub>	1050	1.120

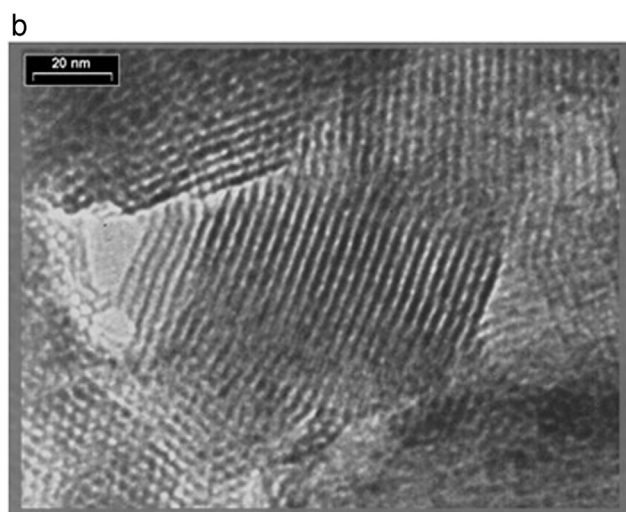
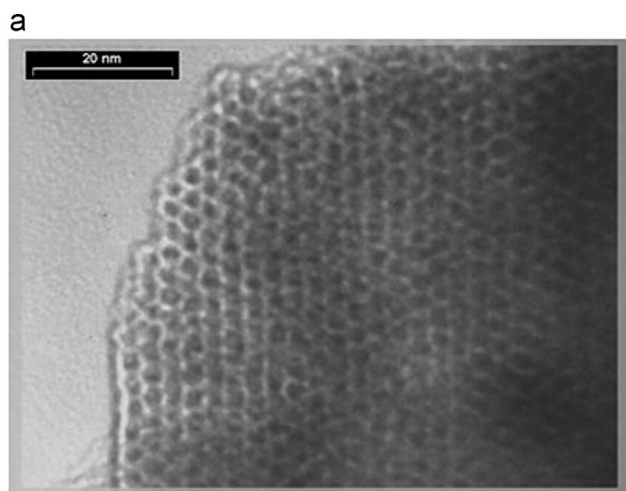


Fig. 3. TEM image of Si-MCM-41 silica (Me<sub>3</sub>), b) cells alongside the pore of mesoporous MCM-41 (Me<sub>3</sub>).

internal pore diameter plus one pore wall thickness [3,7,9–19]. Thickness of the wall and average diameter of the pores obtained 0.8 nm and 4 nm, respectively.

Absorption isotherm of the all synthesized samples with different of pH were shown in Fig. 2. In this figure, as it is expected all materials possess the well known type IV isotherms. According to IUPAC classification they are also of mesoporous solids [3,4,14,19–21]. All three samples of Me<sub>1</sub>, Me<sub>2</sub> and Me<sub>3</sub>, (in relative pressure of  $0.3 \leq P/P_0 \leq 0.5$ ) have a sudden at liner increase in the amount of nitrogen absorption. The reason of appearing this effect may be related to capillary condensation in mesoporous structure [3,19–21]. The sharpness of this step indicates to a uniform pore size distribution. Presented data in Fig. 2 and Table 2, clearly indicates that, when the amount of pH increases, the specific surface and volume of the pores increase too. With increasing in the specific surface and volume of the pores, the amount of nitrogen absorption increases.

The structure of MCM-41 is shown in Fig. 3. It is seen that both pore channels and hexagonal symmetry can be clearly identified. In the TEM image for the Me<sub>3</sub> sample, which indicates that the MCM-41 materials have only one uniform phase as inferred from the XRD results. The presence of internal sites in our compounds could be explained by a reorganization of the hexagonal tubular structure of MCM-41 upon hydrothermal treatment.

#### 4. Conclusions

The silica molecular sieves of MCM-41 mesoporous were synthesized successfully. It was carried out with a high regularity, different amounts of pH, using hydrothermal method and continuous regulation of the amount of pH. Results indicated that the regularity of MCM-41 is not satisfactory when a large amount of pH is used. The results of various investigations indicated that regularity of crystal structure of hexagonal increases by decreasing the amount of pH. The results of BET test indicate the composition of mesoporous with a regular and large distribution of the pores. The specific surface of created mesoporous is 1050–1070 m<sup>2</sup>/gr, indicating the large area of synthesized mesoporous. Thickness of the wall and average diameter of the pores are 0.8 nm and 4 nm, respectively.

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