

The influence of synthesis conditions on the formation of high-ordered cubic mesoporous molecular sieve MCM-48

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High-ordered mesoporous silica molecular sieves MCM-48 were synthesized using the low surfactant (cetyltrimethylammonium bromide CTAB) to silica source (tetraethyl orthosilicate TEOS) ratio without other polar organic additives. The resulting materials were characterized using sorption of nitrogen, X-ray diffraction, FTIR-spectroscopy. The possibility of formation of Al- and Vinyl-MCM-48 on the basis of developed methods was shown. Synthesis of the structurally-ordered mesoporous carbon materials CMK-1 by matrix carbonization of sucrose inside silica MCM-48 confirmed high quality of the starting MCM-48.

1. INTRODUCTION

Mesoporous carbon molecular sieves (in particular CMK-1, synthesized by R. Ryoo [1]) due to their high surface areas and pore volume, hydrophoby, great stability can be used as adsorbents, hydrogen containers, separation materials, sensors and electrode materials. CMK-1 was synthesized by carbonization of sucrose, furfuryl alcohol or phenol resin as the carbon source inside the cubic mesoporous silica molecular sieve MCM-48 used as the exotemplate.

MCM-48 is nanoporous silica with a periodic, three-dimensional array of separate channels. Its structure is cubic bi-continuous and belongs to the space group Ia3d [2, 3]. Owing to its 3-D pore structure, MCM-48 may be an excellent inorganic exotemplate for synthesis of other nanostructures (for example, porous polymers). To receive the structurally ordered CMK-1 it is necessary to have high-ordered MCM-48. Although this exotemplate was obtained as long ago as

1992, there is no reliable, easily reproducible, low-cost method for preparing MCM-48 yet.

MCM-48 has first been obtained [4] by a self-assembling process of silicate species and alkyltrimethyl ammonium micelles under strongly determined conditions. The reliability of the synthesis of MCM-48 was improved by the use of gemini surfactants [5], mixtures of cationic and non-ionic surfactants [1], high surfactant to silica ratio [6], synthesis in several steps [7] etc.

The aim of this work was to determine the conditions and operate the method for synthesis of high-ordered silica mesoporous molecular sieves MCM-48 for the next usage as exotemplates to obtain mesoporous carbon materials.

2. EXPERIMENTAL

2.1. Preparation of MCM-48 and its derivatives

The Silica MCM-48 samples were obtained using tetraethyl orthosilicate (TEOS) as the silica source and cetyltrimethylammonium bromide (CTAB) as the structure-directing agent. The surfactant (CTAB) and alkali (NaOH) were dissolved in distilled water. The required amount of TEOS was then added to the template solution under stirring. The molar ratio of the resulting synthesis gel was 1 TEOS : 0.4 NaOH : 0.3 CTAB : 112 H₂O. After stirring for 2 h at 60 °C, the synthesis gel was transferred to a Teflon-lined autoclave and heated at 100 °C for 3 days. The autoclave was then cooled to room temperature and the solid product obtained by filtration and repeatedly washed with a large amount of distilled water. After air-drying at 100 °C, the obtained materials were calcined in air at 550 °C for 3 h (with the previously programmed temperature increase).

Al was included into MCM-48 in the quantity which was not destroying the silica framework. Aluminium isopropoxide was used as the source of Al. The maximal input content of Al responded to the ratio Si/Al of 20 (the range of the ratios Si/Al was from 30 to 10).

The possibility of MCM-48 formation in the presence of triethoxyvinylsilane was shown. 10% of TEOS were substituted on triethoxyvinylsilane without material structure change. Synthesis conditions for Al- and Vinyl-MCM-48 were the same as for silica MCM-48. Template from Vinyl-MCM-48 was removed by extraction with HCl-ethanol mixture.

2.2. Synthesis of CMK-1

Ordered mesoporous carbon molecular sieves (CMK-1) were synthesized using MCM-48 silica as exotemplate with sucrose as a carbon source and sulfuric acid as the carbonization catalyst. For synthesis of CMK-1 two-step

impregnation by sucrose and sulfuric acid was performed. The weight ratio of the initial substances per 1 g MCM-48 was as follows:

Tab.1. The weight ratio of sucrose, sulfuric acid and water per 1 g MCM-48 for the synthesis of CMK-1 in two steps.

First step		
Sucrose	H ₂ SO ₄	H ₂ O
1.25	0.14	5
Second step		
0.75	0.08	5

Carbonization was carried out in the argon flow at 900 °C. The obtained carbon-silica composite was stirred with 10% HF for 4–5 hours in order to dissolve the silica template. The carbon samples received after the silica removal were filtered, washed with ethanol and dried at 100 °C.

2.3. Characterization

Powder X-ray diffraction (XRD) studies were performed using the diffractometer DRON-3M with Cu-K_α radiation. Nitrogen adsorption-desorption isotherms were measured with Sorptomatic 1990. IR-spectra were recorded using a FTIR spectrometer Perkin-Elmer Spectrum One.

3. RESULTS AND DISCUSSION

The MCM-48 samples were synthesized with a different molar composition of the initial reaction mixture (distinctions in the amount of CTAB and NaOH). From the XRD patterns presented in Figure 1 it can be seen that highly ordered MCM-48 mesoporous materials were obtained. All sharp diffraction peaks observed in MCM-48 can be indexed by cubic system, and reflection conditions are consistent with the space-group symmetry Ia3d. It was shown that the quantities of surfactant and alkali may vary in some limits without change of material quality.

Powder XRD patterns of both the as-synthesized and the calcined MCM-48 samples are shown in Figure 2. Upon calcination, the intensity of the XRD peaks increases significantly compared to the as-synthesized sample, indicating that the degree of ordering improves by the removal of the surfactant. The ordering of the structure takes place because of development condensation processes of silicate-anions (up to complete removal of surfactant) and formation of rigid high-ordered framework.

Synthesis of mesoporous carbon materials is performed with the sulfuric acid as a catalyst of carbonization [1]. Such a role can be played by acidic centers in the structure of silica template. XRD patterns Al-MCM-48 are shown in Figure 3. The values of 2θ , the interfacial spacings d_0 and the unit cell parameters a_0 for Al-MCM-48 are the same as for silica MCM-48.

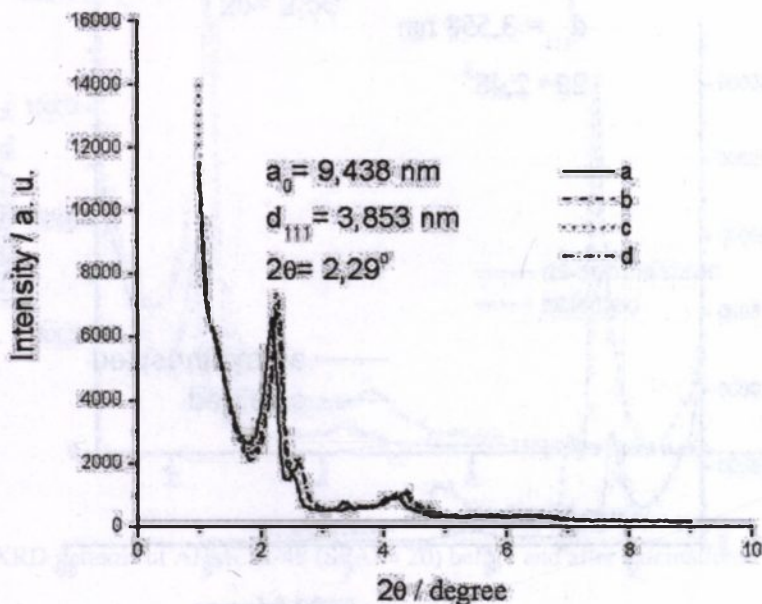


Fig. 1. X-Ray diffraction patterns of MCM-48 samples obtained with different molar composition of the initial reaction mixture: a – 1 TEOS : 0.55 NaOH : 0.5 CTAB : 112 H₂O; b – 1 TEOS : 0.4 NaOH : 0.5 CTAB : 112 H₂O; c – 1 TEOS : 0.4 NaOH : 0.4 CTAB : 112 H₂O; d – 1 TEOS : 0.4 NaOH : 0.3 CTAB : 112 H₂O.

It is possible to carry out carbonization of some organic substances inside the organic-silica MCM-48. Besides, polymerization of some monomers can be performed inside such templates due to possible extension of graft unsaturated organic chains by monomer molecules. The XRD pattern of Vinyl-MCM-48 is demonstrated in Figure 4. The first diffraction peak (211) shifts to smaller angles 2θ that indicates increasing of interfacial spacing and lattice expansion due to participation of CH₂-CH – radical in the formation of silica framework.

Figure 5 shows the XRD patterns of the initial MCM-48, obtained carbon-silica composite, CMK-1 and resultant silica after removal of carbon. The silica framework of infiltrated MCM-48 shrinks during the preparation of the carbon/silica composite [8,9]. Consequently, the available pore volume is observed to be lower than that expected from the original silica matrix. Carbon

from the composite was removed via calcination and the received silica had a unit cell similar to that of the carbon/silica composite but significantly smaller than initial MCM-48 before sucrose impregnation.

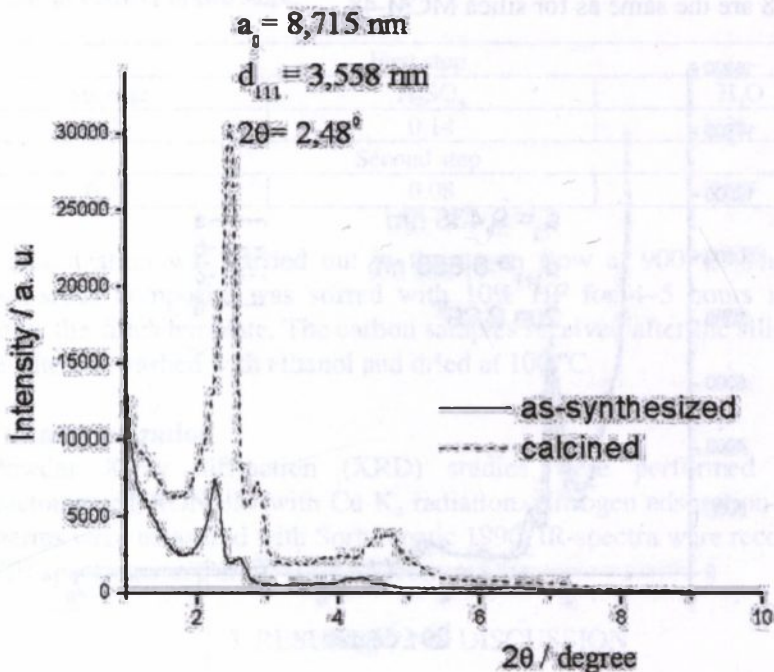


Fig. 2. XRD patterns for MCM-48 before and after calcinations.

The course of some processes during the multi-stage synthesis of ordered porous carbon materials was clarified by means of intermediate products' investigation using IR-spectroscopy. Figure 6 shows the IR-spectra of MCM-48 in the preparation process in the matrix synthesis of ordered mesoporous carbon materials in the consecutive stages of sucrose carbonization and formation of carbon MMS.

Calcination at 550 °C leads to complete clearing of the porous structure MCM-48 from the surfactant CTAB (absorption bands of stretching vibrations ν_{CH} in the range 2800–3000 cm^{-1} disappear).

Infiltration of silica matrix with sucrose and carbonization catalyst (H_2SO_4) results in appearance of the absorption band at 1720 cm^{-1} in the spectrum that characterizes the presence of carboxylic groups ($\nu_{\text{C=O}}$). The result of carbonization is great abnormality of silica structure, the absorption band at

1580 cm^{-1} appears in the spectrum that characterizes unsaturated carbon structures.

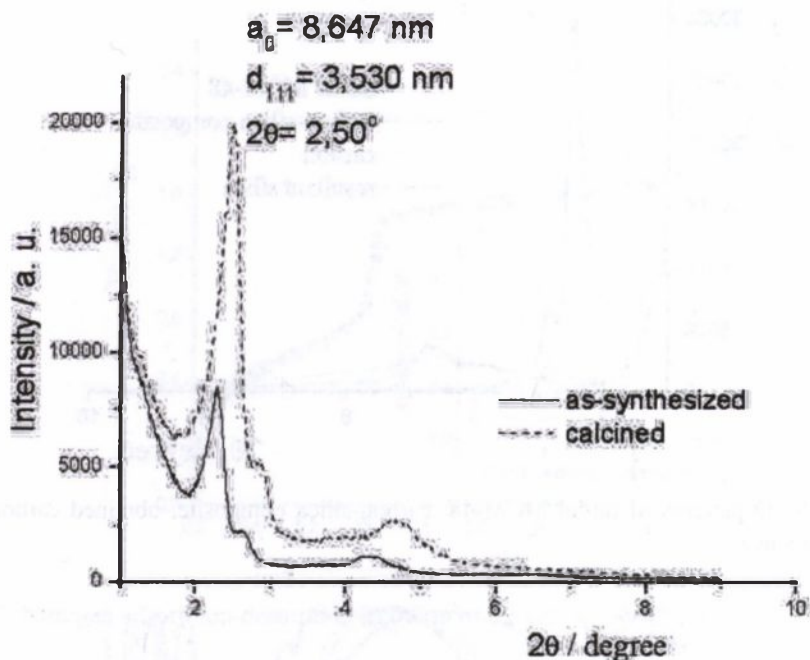


Fig. 3. XRD patterns of Al-MCM-48 (Si/Al = 20) before and after calcinations.

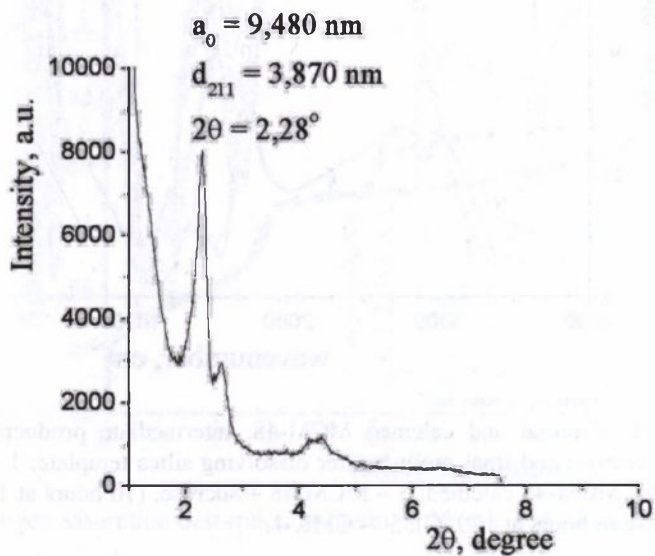


Fig. 4. XRD pattern of vinyl-MCM-48.

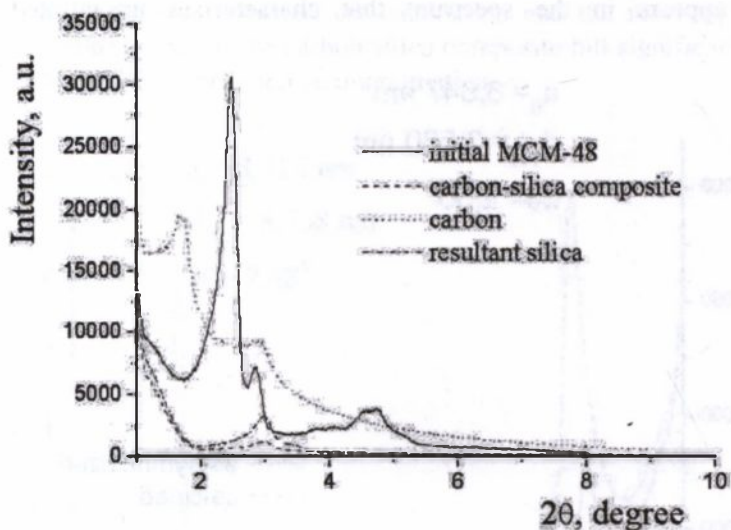


Fig. 5. XRD patterns of initial MCM-48, carbon-silica composite, obtained carbon and resultant silica.

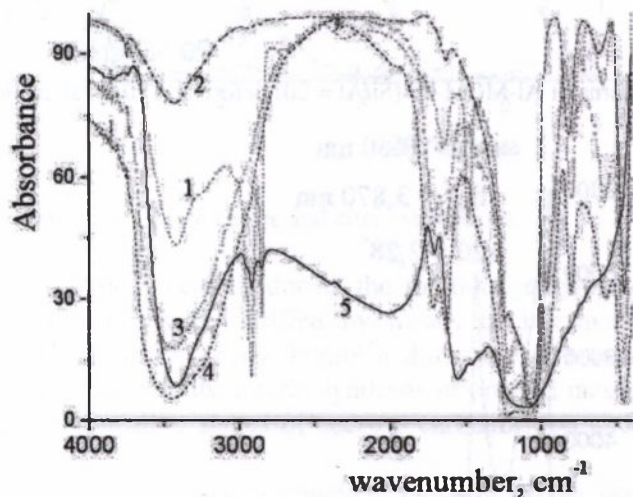


Fig. 6. IR-spectra of initial and calcined MCM-48, intermediate products of matrix carbonization of sucrose and final product after dissolving silica template: 1 – MCM-48 as-synthesized; 2 – MCM-48 calcined; 3 – MCM-48 + sucrose, (10 hours at 100 °C); 4 – MCM-48 + sucrose (6 hours at 170 °C); 5 – CMK-1.

The nitrogen adsorption-desorption isotherm of the calcined MCM-48 sample and the pore size distribution are illustrated in Figure 7.

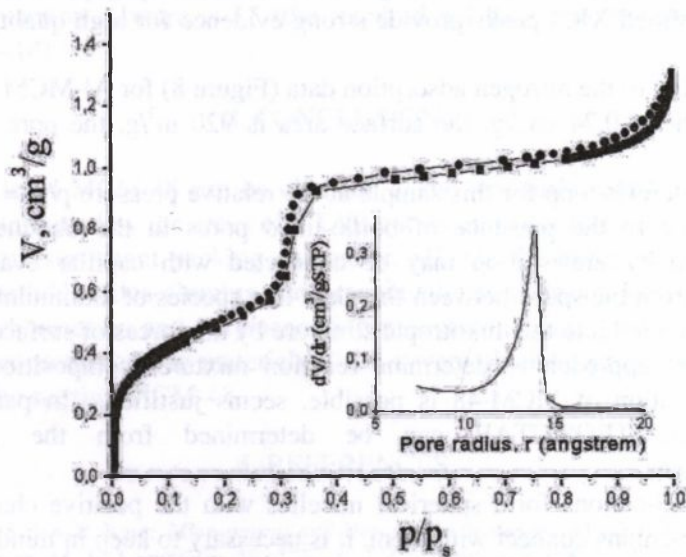


Fig. 7. Nitrogen adsorption-desorption isotherm of the calcined MCM-48.

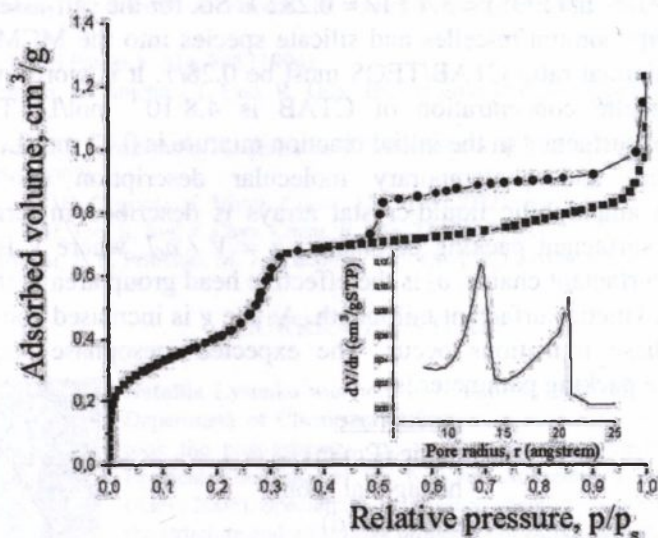


Fig. 8. Nitrogen adsorption-desorption isotherm of the calcined Al-MCM-48 (Si/Al = 20).

The nitrogen adsorption data show that for the obtained MCM-48 samples the total pore volume is $1.3 \text{ cm}^3/\text{g}$, surface area (BET) is $1200 \text{ m}^2/\text{g}$, pore diameter is 2.60 nm . The sharpness of the nitrogen condensation step ($p/p_s = 0.28\text{--}0.36$) and the well-defined XRD peaks provide strong evidence for high quality of MCM-48 sample.

According to the nitrogen adsorption data (Figure 8) for Al-MCM-48 the total pore volume is $0.74 \text{ cm}^3/\text{g}$, the surface area is $920 \text{ m}^2/\text{g}$, the pore diameter is 2.58 nm .

The hysteresis loop for this sample at the relative pressure $p/p_s = 0.45\text{--}1.0$ is possible due to the presence of bottle-like pores in the obtained material. Besides the hysteresis loop may be connected with capillar evaporation of adsorbate from the space between the plate-like species of aluminum hydroxide, which is directed into the thixotropic structure by the forces of surface strain.

The next approach to determine reaction mixtures composition range, in which formation of MCM-48 is possible, seems justified. In particular, the molar ratio TEOS/CTAB can be determined from the geometrical considerations.

As CTAB-cations form spherical micelles with the positive charge surface and silicate-anions connect with them, it is necessary to keep in mind the area of surfactant head (12 \AA^2) and the space occupied by one silicate-anion (the landing platform of $\text{Si}(\text{OH})_3\text{O}^-$ is 3.4 \AA^2).

Then $n(\text{CTAB}) : n(\text{TEOS}) = 3.4 : 12 = 0.28 : 1$. So, for the self-assembling of cetyltrimethyl ammonium micelles and silicate species into the MCM-48 cubic structure the minimal ratio CTAB/TEOS must be $0.28/1$. It is worth noting that the critical micelle concentration of CTAB is $4.8 \cdot 10^{-4} \text{ mol/L}$. The molar concentration of surfactant in the initial reaction mixture is 0.12 mol/L .

The classical and contemporary molecular description of surfactant arrangement in amphiphilic liquid-crystal arrays is described in terms of the local effective surfactant packing parameter, $g = V / a_0 l$, where V is the total volume of the surfactant chains, a_0 is the effective head group area at the micelle surface, l is the kinetic surfactant tail length. As the g is increased above critical values, mesophase transitions occur. The expected mesophase sequence as a function of the packing parameter is

g	mesophase
1/3	cubic (Pm3n)
1/2	hexagonal (p6m)
1/2–2/3	cubic (Ia3d)
1	lamellar

These transitions reflect a decrease in surface curvature from cubic through vesicular and lamellar. For surfactants to associate in a spherical structure, the surface area occupied by the surfactant polar head group should be large. If the

head groups pack tightly, the aggregation number will increase, and rod or lamellar packing will be favored. The values of g (between 1/2 and 2/3) for the cubic (Ia3d) phase depend upon the volume fraction of surfactant chains. pH of the initial reaction mixture is 13 (the required pH for condensation of silicate species is 9–14).

4. CONCLUSIONS

High-ordered MCM-48 can be obtained at the low surfactant to TEOS ratio which is determined by the areas of CTAB-cation and silicate-anion, surfactants' concentration, surfactant packing parameter, pH. On the basis of the MCM-48 synthesis methods silica-alumina and organic-silicate matrices were obtained in the next carbonization and polymerization processes. Using the silica MCM-48 ordered mesoporous carbon materials CMK-1 were obtained that confirmed high quality of the starting MCM-48.

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