

Sorption Properties of MCM-41 Mesoporous Materials

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Abstract: Synthesis of siliceous MCM-41 mesoporous materials has been performed. Cethreelmethylammonium bromide has been employed as structure-directing agent (surfactant), tetraethyl-orthosilicate as silica source, concentrate ammonia solution as mineralizing agent and distilled water or mixture water-ethylen glycol, water-glycerine as solvent was used. The synthesis was carried out for four days at 80 °C. The obtained mesoporous materials were proved by XRD examination and the specific surface area and average pore diameter were measured by nitrogen physisorption.

Keywords: MCM-41; Synthesis; Adsorptive characterization.

Introduction

According to IUPAC¹ definition, porous materials are classified in three categories: 1. microporous materials (pore diameter ≤ 2 nm); 2. mesoporous materials (pore size 2 – 50 nm); 3. macroporous materials (pore size > 50 nm). The porous materials with pore size < 100 nm are named as

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nanoporous materials. Microporous, mesoporous and macroporous materials are based on silica (SiO_2), (aluminum) silicates and other metal oxides and are technological materials. An important subclass of the microporous materials are molecular sieves, such as zeolites and zeotypes which have a narrow and uniform micropore size distribution and pore diameter within the 0.4 – 1.4 nm range.

The first synthesis of an ordered mesoporous material was described in the patent literature in 1969² but, due to a lack of analysis, the product was not recognized. In 1992, similar ordered mesoporous materials with pores larger than 2 nm were obtained by scientists from Mobil Oil Corporation (termed M41S, family) to which MCM-41 belongs.³⁻⁵

The main characteristic of M41S materials (MCM-41-hexagonal, MCM-48-cubic and MCM-50-lamellar) are their high pore volume ($\sim 1 \text{ cm}^3/\text{g}$), very narrow pore-size distribution (1.8 to 10 nm in diameter, depending on the surfactant used as template) and large specific surface area ($\sim 1000 \text{ m}^2/\text{g}$ or more).

The pore size distribution for different porous silica materials is shown in Figure 1.

Silica and other mesoporous materials or micelle-templated silica materials are typically synthesized with surfactant micelles as templates via a “liquid-crystal templating” mechanism,^{7,8} where the structures can be formed by interaction of organic template molecules and inorganic species (Figure 2).

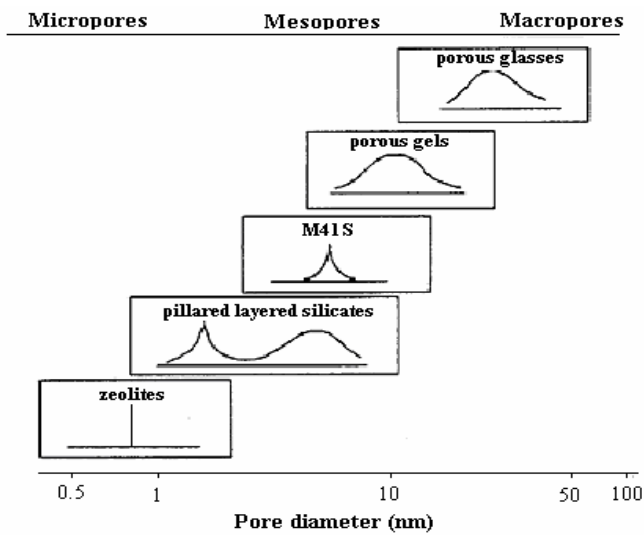


Figure 1. Pore size distribution for micro-, meso- and macroporous silica materials.⁶

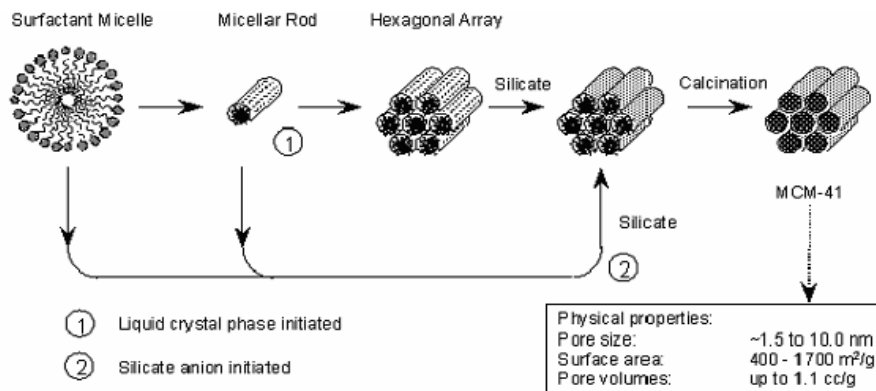


Figure 2. Liquid-crystal templating (LCT) mechanism for the formation of MCM-41.⁴

Surfactants are amphiphilic molecules which consist of a hydrophobic non-polar tail and a hydrophilic polar head group. The nature of the polar head group imparts the surfactants in four groups: anionic, cationic, zwitterionic and non-ionic surfactants.

The structure and properties of mesoporous materials are affected by the length of the hydrophobic chain and pH of system that are responsible for the pore size and by surfactant: solvent ratio, which determines the symmetry. The geometry of the surfactant aggregates formed in solution depends on the values of dimensionless surfactant packing parameter g ,⁹ defined as $g = v/a l$, where v is the volume of the hydrophobic chain, a is the aggregate surface area of the hydrophilic head group and l is the hydrophobic chain length (Figure 3).

Much attention has been concentrated on these highly ordered structures for applications in a wide variety of industries as catalysts, catalyst supports, photocatalysts, in adsorption, gas separation and bioseparation, in ion exchange, nanocomposite host materials and in environmental control.¹⁰⁻²²

The aim of this paper was the synthesis and adsorptive characterization of high quality mesoporous MCM-41 silica material.

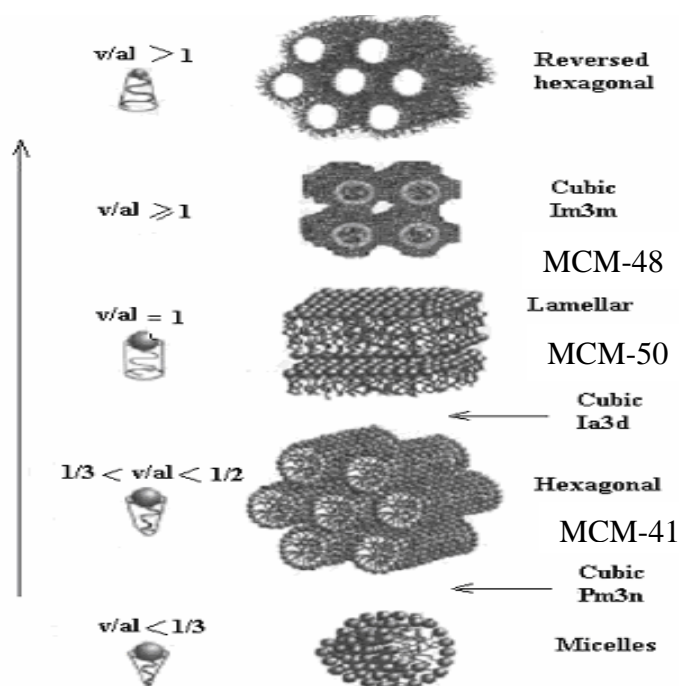


Figure 3. Geometry of aggregates as a function of the surfactant packing parameter.¹⁰

Experimental

Synthesis

The siliceous MCM-41 mesoporous materials were synthesized using tetraethyl-orthosilicate (TEOS) as silica source, cetylthreemethylammonium bromide ($C_{16}TMAB$) as structure-directing agent (surfactant), concentrated ammonia solution as mineralizing agent and distilled water or water-ethylen glycol, water-glycerine mixtures as solvent.

The syntheses were carried out according to the following procedure. $C_{16}TMAB$ is added to water (or mixture) while stirring a half hour at room temperature until the solution become clear. The concentrated ammonia solution was added to the solution of $C_{16}TMAB$ while stirring a

half hour. The silica source (TEOS) was added to the alkaline solution while stirring and aged for 3 h. Gel mixtures were reacted for four days at 80 °C. The reaction product was filtered, washed with distilled water, dried in air at 80 °C and finally calcined at 550 °C for 6 h. Three MCM-41 samples with presumably uniform pore structure denoted MCM-41_w, MCM-41_{EG} and MCM-41_{Gly}, were prepared.

Characterization

X-ray diffraction

Small-Angle X-ray scattering (SAXS) pattern was recorded with a PANANALYTICAL X'PERT PRO MPD power diffractometer using CuK α radiation.

N₂ sorption measurement

The specific surface area, pore size distribution and the average pore diameter were measured by nitrogen physisorption on a Quantachrome Autosorb 1 MP automatic instrument at liquid nitrogen temperature with sample degassed at 200 °C under vacuum for 12 h.

Water and benzene sorption

Adsorption/desorption isotherms of non-polar molecules and polar molecules were measured gravimetrically using a CI Electronics MK 2 vacuum microbalance.

Results and discussions

Figure 4 shows the X-ray diffraction pattern of the calcined MCM-41_w sample. The diffraction pattern exhibits three clear diffraction peaks situated at low angles corresponding to the (100), (110) and (200) reflections. The fourth diffraction peak with a lower intensity corresponding to the (210) reflection can be sometimes present. The presence of diffraction

peaks above $2\theta = 3^\circ$ represents the very good long-range order of the mesoporous material. The lattice of MCM-41 can be indexed with a hexagonal unit cell, with $a = b = a_0$ and $c = \infty$ and reflection planes $(hk0)$.

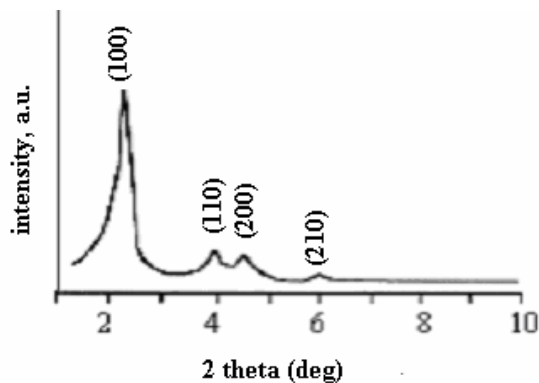


Figure 4. SAXS pattern of calcined MCM-41_w.

Based on $2\theta_{hkl}$ values we can calculate the lattice spacing d_{hkl} by Bragg's law and the unit cell parameter a by using the formula: $a = 2d_{hkl}/\sqrt{3}$. For the (100) reflection, $2\theta = 2.2$ degrees, the lattice spacing, $d_{100} = 4.01$ nm and the pore-to-pore distance $a_0 = 4.63$ nm.

Figure 5 shows the low-temperature nitrogen adsorption-desorption isotherms at 77 K for MCM-41_w, MCM-41_{EG} and MCM-41_{Gly} samples and Figure 6 the pore size distribution.

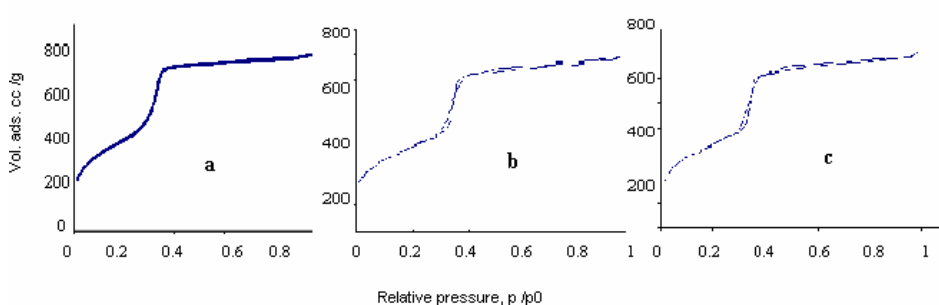


Figure 5. Nitrogen isotherms of calcined samples: a. MCM-41_w; b. MCM-41_{EG}; c. MCM_{Gly}

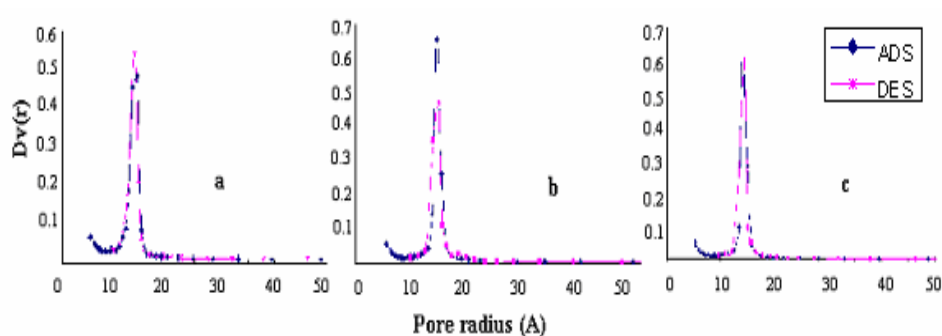


Figure 6. Pore size distribution of calcined samples: a. MCM-41_w; b. MCM-41_{EG}; c. MCM_{Gly}.

The shape of the isotherms is characteristic of the pore structure. In the case of MCM-41, low temperature nitrogen adsorption-desorption isotherm exhibits a sharp step which occurs at $0.25 < P/P_0 < 0.34$, associated with capillary condensation and hysteresis loop in mesopores. The sharpness of the step is related to the pore size heterogeneity expressed by pore size distributions. High ordered mesoporous materials MCM-41 typically have isotherms of Type IV, according to IUPAC classification²³ (Figure 7a). Occurrence of the hysteresis loop depends on the adsorbate, pore size and temperature. For MCM-41 with small pore diameter no hysteresis is observed. Usually, mesoporous MCM-41 display a hysteresis loop of Type H₁ (Figure 7b)²³ characteristic for porous materials with cylindrical pores and a high degree of pore size uniformity.

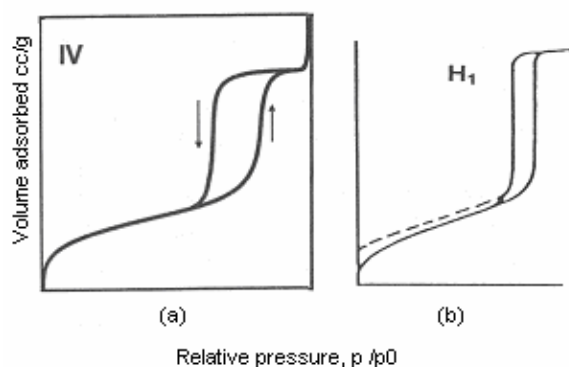


Figure 7. The adsorption-desorption isotherms type IV (a) and H₁ (b) type of hysteresis loop according to IUPAC.²³

The specific surface area theoretically estimated by Brunauer, Emmett and Teller (BET) was calculated using the BET equation based on the adsorption data in the relative pressure range of 0.05 – 0.3. Pore size distributions were determined from adsorption-desorption isotherms according to the method of Barrett – Joyner – Halenda (BJH method). A very narrow pore size distribution is specific for the MCM-41 nanoporous material.

The physical properties of the calcined mesoporous silica-MCM-41 materials are listed in Table 1.

Table 1. Characterization of MCM-41 calcined samples.

Sample	d_{100} , nm	a_o , nm	S_{BET} , m ² /g	D_p (BJH), nm	V_p , cm ³ /g; $p/p_o = 0.98$
MCM-41 _w	4.01	4.63	983	2.76	0.82
MCM-41 _{EG}	3.91	4.42	1224	2.81	0.98
MCM-41 _{Gly}	3.39	3.92	1118	2.82	0.89

Considerable interest has been shown in the development of shape selective porous adsorbents. Pore dimensions, the nature of adsorbent-adsorbate and adsorbate-adsorbate interactions are of great importance for such materials. The adsorbent surface can be hydrophilic or hydrophobic and the adsorbate molecules can be polar, non-polar or polarizable. Due to the surface heterogeneity and mesoporosity, MCM-41 materials exhibit different organophilic properties for polar (methanol, ethanol) and non-polar (benzene, hexane, cyclohexane, carbon tetrachloride) organic compounds and for water.

The adsorption of water over MCM-41 is characterized by a type V isotherm (Figure 8) and the amount of water adsorbed is between 40% and 80%.²⁴⁻²⁶ The isotherm reveals an initially repulsive character of the surface followed by a capillary condensation step of water at relative pressure $p/p_0 = 0.56 / 0.68$, indicating that MCM-41 posses both hydrophobic (organophilic) and hydrophilic (organophobic) properties.

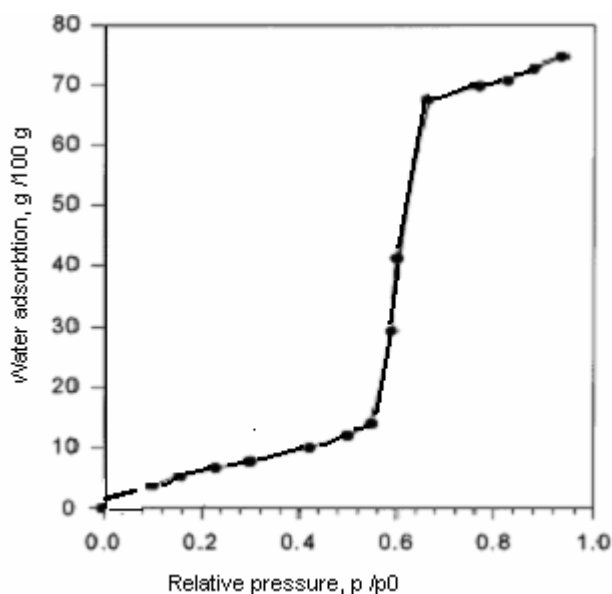
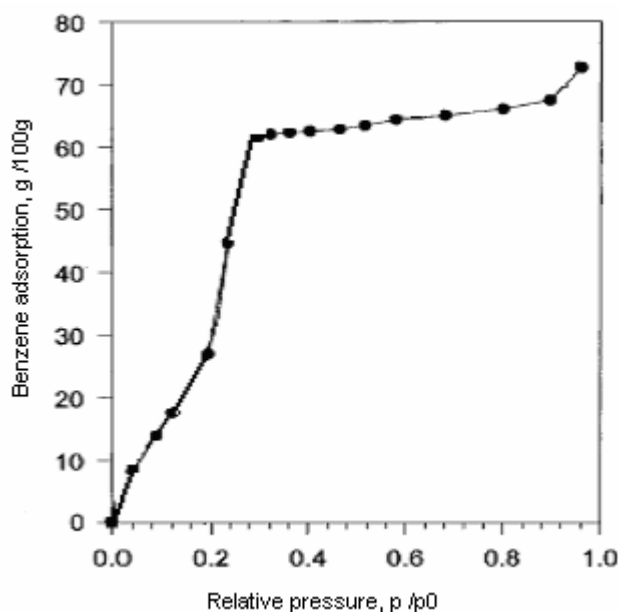


Figure 8. Water adsorption isotherm at 298 K on siliceous MCM-41_{EG}.

The benzene adsorption isotherm over MCM-41_{EG} is of type IV and the amount adsorbed is between 60% and 90% (Figure 9). At very low relative pressure ($p/p_0 = 0.0 - 0.2$) a monolayer adsorption takes place on the surface and then a multilayer adsorption revealing the organophilic property. Between relative pressure $p/p_0 = 0.2$ to 0.32 the amount of benzene increases suddenly because of capillary condensation.

**Figure 9.** Benzene adsorption isotherm at 298 K on siliceous MCM-41_{EG}.

Conclusions

The synthesized samples exhibit a MCM-41 mesoporous materials structure, proved by their SAXS pattern.

Low temperature nitrogen adsorption-desorption isotherm exhibits a sharp step which occurred at $0.25 < p/p_0 < 0.40$ associated with capillary condensation and hysteresis loop in mesopores.

The specific area values estimated from the BET theory are of 983 -1224 m²/g, characteristic for MCM-41 materials.

The water and benzene adsorption isotherms are indicating that the synthesized MCM-41 materials possess both hydrophobic and hydrophilic properties.

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