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SHORT COMMUNICATION

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Siliceous mesoporous material templated with hexadecyltrimethylammonium bromide–sodium dehydrocholate mixed micelles

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Abstract A mixture of sodium dehydrocholate (NaDHC) and hexadecyltrimethylammonium bromide (HDTAB) was employed as a template to produce mesoporous silica. The obtained material shows the same structure as common MCM-41 sieves, but the pore radius distribution is narrower than that of the material produced with the same concentration of pure HDTAB. The average pore radius is also larger than that of the pure HDTAB-templated material.

Keywords Mesoporous materials · Mesoporous sieves · Catanionic template · Hexadecyltrimethylammonium bromide-sodium dehydrocholate mixtures

Introduction

Porous materials containing interconnected microscopic to macroscopic cavities, such as sponges, clays, ceramics and different polymeric systems, are of outstanding importance in industry and everyday life. Their spectrum of applications range from many types of filtration, extraction, adsorption, catalyst carriers, drug delivery systems, environmental remediation materials [1], shape selective reactors for polymerisation [2], membrane separators, and stationary phases for chromatography [3].

In view of the extensive applications of these materials, the production of novel structures and novel synthesis procedures for them is of great interest.

In 1992, Mobil's scientists discovered that ionic surfactants could be used as templates for the synthesis of a family of mesoporous siliceous materials which they called M41S [4, 5]. One of the most studied of these structures is the MCM-41 material, with unidirectional mesopores ordered in an hexagonal array and a sharp pore size distribution, which is obtained using cationic surfactants in dilute (micellar) or liquid crystalline solutions. To modify the pore size, higher homologues of the surfactant series and inert oils (as swelling agents) are used.

The template strategy resembles macroscopic metal casting processes: geometrically well-defined structures ("templates"), which preform the shapes of the pores like casting-cores, are introduced into a liquid system and subsequently embedded by hardening of the solvent. After removal of these cores from the surrounding matrix, the shape of the remaining voids reflects the form of the templates.

Ultra-large pore hexagonal and cubic mesoporous products have been recently synthesized using non-ionic poly(ethylene oxide) triblock copolymers as structure-directing agents [6, 7, 8]. Recently a fibrous bacterium, *Bacillus subtilis*, was the substrate used for the deposition of a MCM-41-type material [9], obtaining materials with porosity in both the mesoscopic (2–10 nm) and macroscopic (0.5 μm) ranges after the bacteria were removed from the composite material by calcination.

Macromolecular templates have been used to produce organic mesoporous materials by polymerization of aqueous acrylamide solutions in the presence of xanthan or DNA fragments. Hydrogels containing non-oriented channels with diameters from 2 to 10 nm have been obtained [10]. Some cationic and anionic block copolymers with polyelectrolyte behavior were also utilized as structure-directing media in a sol-gel process to synthesize nanoporous silica [8].

In some cases, catanionic mixtures were employed as templates and it was found that different types of mesoporous molecular sieves may be obtained using these systems [11].

We have studied the interaction between sodium dehydrocholate (NaDHC) and hexadecyltrimethylammonium bromide (HDTMAB or CTAB). We have found that, even at very high NaDHC proportions, micelles have an excess of HDTAB, which behaves as a solvent. However, at the particular mole fraction of NaDHC $\alpha_{\mathrm{NaDHC}} = 0.4$, the micelles had the same composition: $X_{\mathrm{NaDHC}} = 0.4$. Both mole fractions were computed taking into account only the surfactants: $\alpha_{\mathrm{NaDHC}} + \alpha_{\mathrm{HDTAB}} = 1$ and $X_{\mathrm{NaDHC}} + X_{\mathrm{HDTAB}} = 1$ [12]. Then, this particular mixture was employed as a template to study the effect of the NaDHC addition to the HDTAB micelles on the obtained mesoporous material.

We also studied the NaDHC aqueous system and found that small micelles form [13, 14, 15]. Since NaDHC is soluble in basic solution, we supposed that their solutions might also be used as templates.

Experimental

Dehydrocholic acid (HDHC) was supplied by Dr. Theodor Schuchardt GMBH & Co. (München), and was of analytical grade. A concentrated sodium dehydrocholate (NaDHC) aqueous solution was prepared by weighing out a quantity of HDHC and then dissolving it in an appropriate amount of concentrated NaOH solution. Hexadecyltrymethylammonium bromide (HDTAB), analytical grade, was acquired from Sigma. Only double-distilled water was used.

The siliceous mesoporous materials were prepared by a technique obtained by comparing different literature procedures [16, 17, 18, 19, 20]: 11.6 ml of 99% tetramethylorthosilicate (TEOS) (Aldrich) was dissolved in 2 ml of water and stirred for 10 minutes at 500 rpm. Then, a solution of 1.1 g of NaOH in 20 ml of water was added drop-by-drop to the TEOS solution whilst stirring. A minute later, 38 ml of the surfactant solution was poured into the mixture and stirred for 5 mins. The system was put in an autoclave and heated at 100 °C for 48 h. The gel was then filtered and washed with distilled water. The resulting gel was dried at room temperature for 4 days, and then calcined at 540 °C under air flux.

This technique was employed with the following surfactant solutions: a) HDTAB 0.55 mol dm^{-3}; b) HDTAB-NaDHC mixture, with $\alpha_{\mathrm{NaDHC}} = 0.4$, $C = 0.55$ mol dm^{-3}; c) NaDHC 0.03 mol dm^{-3}.

Transmission electron microscopy was performed using a JEOL 100 CX II transmission electron microscope, operated at 100 kV with magnification of 100,000×. Observations were made in bright field. Powdered samples were placed on copper supports of 2000 mesh.

The nitrogen adsorption isotherms at 77.6 °K were measured with an Micrometrics Model Accusorb 2100 E instrument. Each sample was degassed at 373 K for 720 mins at a pressure of 10^{-4} Pa.

Results and discussion

The sample with pure NaDHC produced a very small amount of solid. When observed in the electron microscope, the material showed a homogeneous, non-porous structure. Several runs with varied synthesis procedures (including acidification with acetic acid after mixing the surfactant solution with the TEOS one) gave the same results. We were not able to obtain a mesoporous material templated with pure NaDHC solution.

Both HTAB and HTAB-NaDHC solutions gave well-developed mesoporous materials. The uniform mesopore structure of both samples is evident in the transmission electron microscope lattice images shown in Figs. 1 and 2. TEM of the calcined samples shows the regular hexagonal array of uniform channels that is characteristic of MCM-41. When viewed in the direction

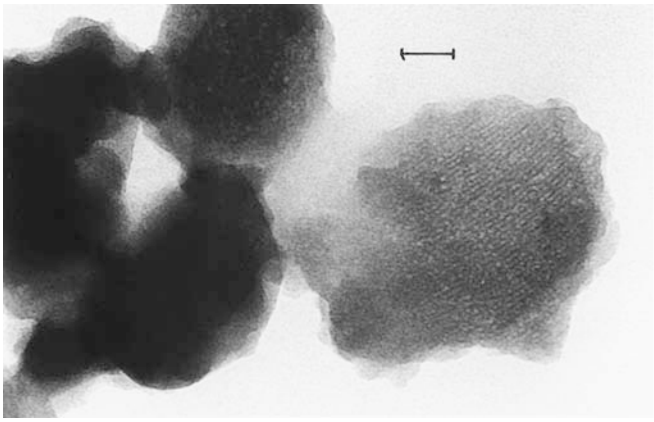


Fig. 1 Transmission electron microphotography of HDTAB-templated mesoporous material, showing patches composed of regular rows viewed perpendicular to the mesopores axis. The bar represents 312 nm

Fig. 2 Transmission electron microphotography of the mixed HDTAB-NaDHC micelles-templated material. The bar represents 312 nm

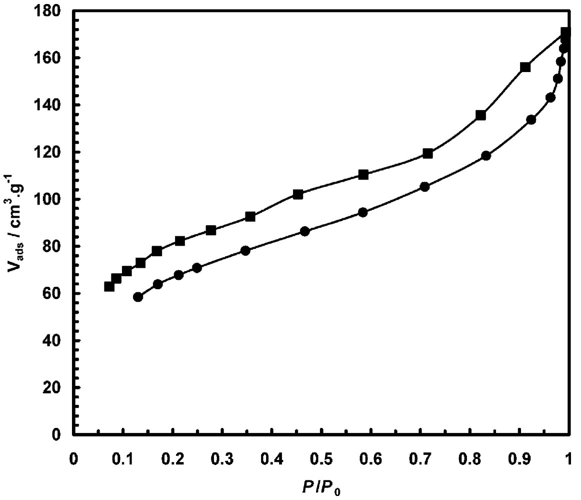


Fig. 3 Adsorption (circles)-desorption (squares) of nitrogen on HDTAB-templated mesoporous material

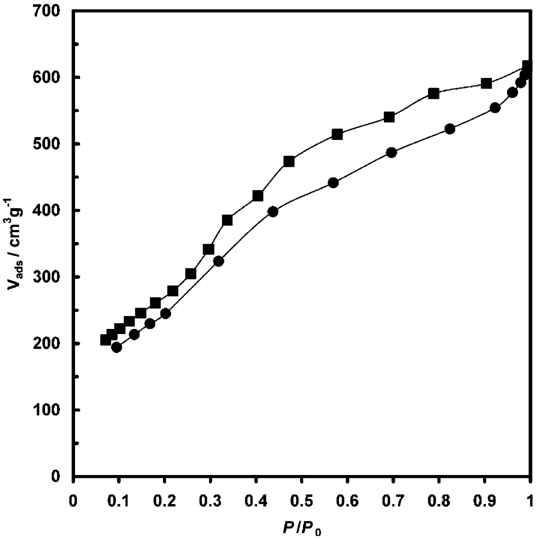
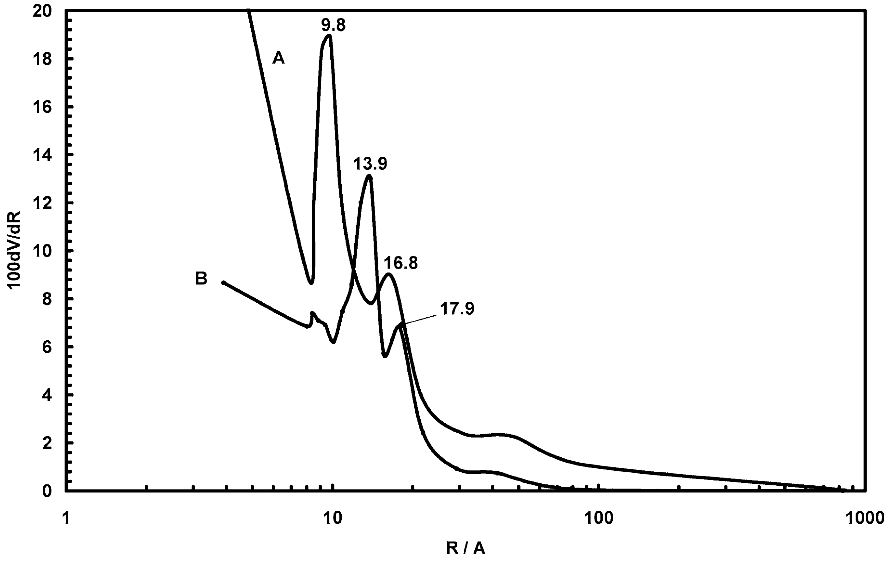


Fig. 4 Adsorption (circles)-desorption (squares) of nitrogen on the mixed HDTAB-NaDHC micelles-templated material

perpendicular to their axes, the pores were seen to be arranged in patches composed of regular rows. The hexagonal structure, with each pore surrounded by six neighbors, is present in both samples. This is consistent with the conclusion found in a previous work [12] that HDTAB micelles act as a solvent for NaDHC, and that the general structure of micelles is not changed with the inclusion of the bile salt derivative compound.

The adsorption-desorption isotherm and the mesopore size distribution of each sample are presented in Figs. 3 and 4. Both samples show a type II isotherm, which is obtained in mesoporous-macroporous adsorbents [21]. The inflection in the adsorption isotherm indicates the mesopore filling. The co-ordinate of the inflection point depends on the pore size. Hysteresis loops of type *H2* may be seen in the figures, which are associated with capillary condensation taking place in the mesopores [22] with both ends open [23]. According to de Boer [24], this type of hysteresis loop appears when the capillaries are regular or irregular cylinders or prisms open at both ends. Furthermore, the desorption hysteresis at low p/p_0 values indicates micropore filling. According to Cohan [24] no pores of actual radii less than about a molecular diameter could be effective in causing hysteresis (actually, the critical radius was taken to be two molecular diameters), and Cohan showed that for a number of systems, the desorption branch rejoined the adsorption one at p/p_0 values corresponding to pore radii close to twice the estimated

Fig. 5 d*V*/d*R* versus pore radius for **A** HDTAB-templated mesoporous material, and **B** mixed HDTAB-NaDHC micelles-templated material. Numbers indicate the average pore radius in Å



size of the adsorbate molecules. The plot of the derivative of the pore volume per unit weight with respect to the pore radius (d*V*/d*R*) is shown in Fig. 5. Some micropores (with radius is less than 1 nm) are present in all samples, as can be seen in the pore size distribution plots. The sharp pore size distribution confirms that the mesopores are exceptionally uniform. The BET surface area is 240.7 m^2g^{-1} for the pure HDTAB-templated material, and 923.7 m^2g^{-1} for the NaDHC-HDTAB mixture-templated material. Both materials show bimodal pore size distributions. HDTAB-templated material has a broad distribution with maximums at R≈0.98 and 1.68 nm. The mixture-templated system shows a narrower distribution with maximums at R≈1.39 and 1.79 nm.

MCM-41 prepared with CTAB as a template by the hydrothermal synthesis typically have pore radii of about 1.5–1.8 nm and surface areas of about 1000 m^2g^{-1} [25, 26]. The MCM-41 prepared using the method described above has a similar pore radius but smaller specific area.

The comparison between both materials shows that the inclusion of NaDHC into the HDTAB aggregates matrix produced a slight but significant increase in the pore radius.

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References

1. Mercier L, Pinnavaia TJ (1997) Adv Mater 9:500
2. Llewelyn PL, Ciesla U, Decher H, Stadler R, Schuth F, Unger KK (1994) Stud Surf Sci Catal 84:2013
3. Grun M, Kurganov AA, Schacht S, Schuth F, Unger KK (1996) J Chromatogr A 740:1
4. Beck JS, Vartuli JC, Roth WJ, Leonowicz ME, Kresge CT, Schmitt KD, Chu CT-W, Olson DH, Sheppard EW, McCullen SB, Higgins JB, Schlenker JL (1992) J Am Chem Soc 114:10834
5. Kresge CT, Leoniwics ME, Roth WJ, Vartuli JC, Beck JC (1992) Nature 359:710
6. Zhao DY, Yang PD, Huo QS, Chmelka BF, Stucky GD (1998) Curr Opin Colloid Interface Sci 3:174
7. Zhao DY, Feng JL, Huo QS, Melosh N, Freddrickson GH, Chmelka BF, Stucky GD (1998) Science 279:548
8. Krämer E, Förster S, Götner C, Antonietti M (1998) Langmuir 14:2027
9. Davis SA, Burkett, SL, Mendelson NH, Mann S (1997) Nature 385:420
10. Beginn U (1998) Adv Mater 10(16):1391
11. Chen F, Yan X, Li Q (1998) Stud Surf Sci Catal 117:273–279
12. Schulz PC, Messina P, Morini MA (2003) Colloid Polym Sci (submitted)
13. Messina P, Morini MA, Schulz PC, Ferrat G (2002) Colloid Polym Sci 280:328
14. Schulz PC, Messina P, Morini MA, Vuano B (2002) Colloid Polym Sci 280:1104 15
15. Messina P, Morini MA, Schulz PC (2003) Colloid Polym Sci 281:695
16. Lee YS, Surjadi D, Rathaman JP(2000) Langmuir 16:195
17. Chen CY, Li HX, Davis ME (1993) Microporous Mater 2:17
18. Whitehurst DD (1992) US Patent 5,143,879
19. Tanev PT, Piunnavai T (1995) Science 267:865
20. Hartman M, Bischof C (1999) J Phys Chem B 103:6230
21. Sing KSW, Everett DH, Haul RAW, Moscou L, Pierotti RA, Rouquérol J, Siemieniewska T (1985) Pure Appl Chem 57(4):603
22. Cohan LH (1938) J Am Chem Soc. 60:433
23. de Boer JH (1958) The structure and properties of porous materials (Proc X Symp Colston Research Soc Univ Bristol). Butterworths Sci, London, p 68
24. Cohan LH (1944) J Am Chem Soc 66:98
25. Namba S, Mochizuki A, Kito M (1998) In: Bonneviot L, Béland F, Danumah C, Giasson S, Kaliaguine S (eds) Mesoporous molecular sieves. Elsevier, Amsterdam, p 257–264
26. Sonwane CG, Bhatia SK, Calos NJ (1999) Langmuir 15:4603