Synthesis of MCM-48 Silica Using a Gemini Surfactant with a Rigid Spacer

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Gemini surfactant *p*-phenylenedimethylenebis(*n*-hexadecyldimethylammonium) dibromide (abbreviated C_{16}-DMB-C_{16}, with DMB = *p*-$CH_2C_4H_6CH_2$) with a rigid spacer was found to produce cubic MCM-48 silica mesophase by temperature-induced phase transition from the MCM-41 hexagonal phase. The synthesis involved two steps, a precipitation stage at room temperature for a period of time t_1, followed by an aging step at higher temperature for a period of time t_2. The synthesis was optimized for particular combinations of t_1 and t_2 periods. The phase transformation was studied under various pH and temperature conditions. Although it was observed that ethanol partitioning induced, at least partially, the formation of the cubic structure, the transformation was also shown to be influenced by the degree of silicate polymerization. The MCM-48 silica prepared under optimized conditions exhibited a type IV nitrogen adsorption isotherm, a BET surface area of 1164 m^2/g, and a narrow pore size distribution with a maximum at 2.5 nm.

Introduction

The synthesis of periodic nanoporous materials templated by surfactant supramolecular assemblies has attracted considerable interest in recent years. Much attention has been focused on the 2D hexagonal mesophase (MCM-41) due to its wide stability domain and thus ease of synthesis. However, cubic phases such as MCM-48, SBA-1, SBA-16, and FDU-1 with 3D pore systems are more compelling candidates as adsorbents or catalyst supports.[1−4] By using MCM-48, potential pore blockage can be avoided due to its highly interwoven pore structure.

Introduction of Gemini surfactants for the consistent preparation of MCM-48 cubic mesophase by Huo et al.[5] and further development of a postsynthesis treatment improving the pore size distribution and order greatly facilitated the synthesis of MCM-48.[6] Since then, the emphasis has been placed on optimizing the chain and spacer length of the surfactant and the duration of hydrothermal treatment during the synthesis.[6,7] Alami et al.[8] noticed that variations of the size of the spacer group bring about changes of the surface area occupied by the surfactant headgroup at the interface. The area initially increases and then decreases as the length of the alkyl spacer increases. Formation of good-quality MCM-48 was reported to occur in the presence of Gemini surfactants with spacers having 2, 10, and 12 carbon atoms and long alkyl tails with 12, 16, 18, and 22 carbon atoms. As the length of the surfactant tail increases, the spontaneous curvature remains nearly the same, although significant deviations are observed as the carbon number becomes larger than 20 and the chain coils. By adjusting the synthetic parameters, surfactants with long chains can be used to produce materials with larger pores.[5−7,9]

Although, cubic MCM-48 was shown to occur at room temperature using a Gemini surfactant, the synthesis was tedious and had a low yield.[5] Therefore, some workers focused on the restructuring of surfactant−silicate mesophases to synthesize MCM-48 through a phase transformation process.[5,9−11] The transformation was performed by initially generating the MCM-41 mesophase, followed by heating at higher temperature to induce the structural change. In situ X-ray diffraction was utilized by Laundry et al.[12] to illustrate the change of the mesophase and show that it proceeded in an epitaxial manner without dissolution of the original MCM-41 phase. It has been claimed that the gradual release of ethanol from the synthesis gel during the hydrolysis of TEOS drives the transformation by altering the surfactant packing parameter $g = V/a_0l$, where V is the total volume of the surfactant chain plus any cosolvent molecules, a_0 is the effective area of the headgroup, and l is the kinetic surfactant chain length.[11] The g value, and hence MCM-48 formation, however depends on other parameters besides the presence

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of organic additives. The first approach for the control of the silica mesophase structure in the presence of surfactants was through adjustment of the surfactant to silica molar ratio.[13] MCM-48-type materials were usually prepared by using high surfactant to silica ratios.[14] At lower ratios, extended aging periods are required to produce well-organized materials,[5] while Gemini surfactants with very low critical micelle concentration are an exception. Siliceous MCM-48 was also shown to be formed under high pH conditions and at elevated temperature. Another parameter shown to play an important, but not yet fully understood, role is the silica polymerization rate.[12]

In this study, the importance of synthetic parameters, such as precipitation time or base to surfactant molar ratio, was investigated for the synthesis of MCM-48 silica using for the first time a Gemini surfactant with a bulky rigid spacer, i.e., *p*-phenylenedimethylenebis(*n*-hexadecyldimethylammonium) dibromide (abbreviated C_{16}-DMB-C_{16}, with DMB = *p*-$CH_2C_4H_6CH_2$), as template.

Experimental Section

***p*-Phenylenedimethylenebis(*n*-hexadecyldimethylammonium) Dibromide [$CH_3(CH_2)_{15}N^+(CH_3)_2(p\text{-}CH_2C_4H_6CH_2)(CH_3)_2N^+(CH_2)_{15}CH_3$].** C_{16}-DMB-C_{16} cationic Gemini surfactant was prepared by quaternization of hexadecylamine with 1,4-bis(bromomethyl)benzene in anhydrous acetone.[15] An 2.5 g (0.947 mmol) sample of *p*-xylylene dibromide was dissolved in 60 mL of warm acetone. Then 6.3 g (2.36 mmol) of *N,N′*-dimethyl-*n*-hexadecylamine was dissolved in 2 mL of acetone and the resulting solution introduced into the previous solution. A white, fine precipitate appeared within 5 min of stirring. Acetone (30 mL) was added, and the solution was allowed to stir overnight. The solid was filtered out, washed with 10 mL of acetone, and recrystallized from an acetone/chloroform mixture to obtain 6.574 g (86.4%) of C_{16}-DMB-C_{16} as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (s, 4H), 5.31 (s, 4H), 3.53 (m, 4H), 3.24 (8, 12H), 1.83 (m, 4H), 1.38 (m, 12H), 1.26 (m, 40H), 0.88 (t, 6H). ^{13}C NMR (100 MHz, $CDC1_3$): δ 134.1, 130.1, 66.2, 64.9, 49.4, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 26.4, 23.0, 22.7, 14.1. MS (EI, ethanol/acetonitrile): *m/z* 723(M − ^{81}Br)$^+$, 721(M − ^{79}Br)$^+$.

Material Synthesis. Mesoporous silica was prepared using C_{16}-DMB-C_{16} and TEOS as a silica source in a basic medium. The molar ratio of the reactants TEOS/C_{16}-DMB-C_{16}/NaOH/H_2O was 1/0.064/0.74/185. Typically the surfactant (0.513 g) was dissolved in water (33.3 g), NaOH (0.296 g) was then added under stirring, and after 20 min, the silica source (2.08 g) was introduced to the solution. A white, fine precipitate appeared within 5 min of stirring. After a certain time (t_1) of room-temperature precipitation, the mixture was transferred to a Teflon-lined steel autoclave, the temperature was raised to 100 °C, and the mixture was aged for another period of time (t_2). The solid product separated by filtration was dried at ambient conditions and calcined in air at 550 °C for 5 h (36.4% yield). Materials with NaOH to TEOS ratios of 0.64 and 0.84 were also prepared, and fumed silica was investigated as a silica source.

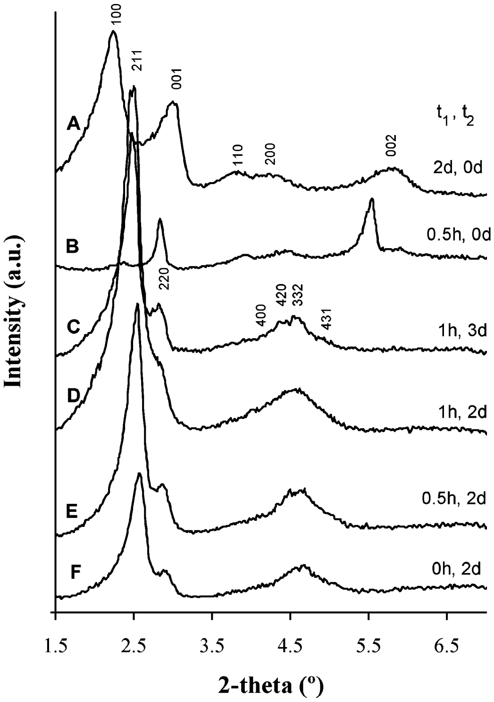

Figure 1. X-ray diffraction patterns of solid materials prepared after various reaction times (t_1, t_2) as indicated.

Analyses. Powder X-ray diffraction (XRD) analysis was performed using a Philips PW3710 diffractometer with Cu Kα radiation (45 kV, 40 mA), a 0.02° step size, and 2.5 s of accumulation per step. Nitrogen sorption isotherms were determined with a Coulter Omnisorp 100 gas analyzer at 77 K. Before analysis the samples were evacuated at 200 °C under vacuum. The BET specific surface area, S_{BET}, was obtained from the nitrogen adsorption data in the relative pressure range 0.05−0.15, and the total pore volume was determined from the amount of nitrogen adsorbed at P/P_0 = ca. 0.99. The pore size distributions were derived from the adsorption branches using the KJS method valid over a broad range of pore sizes.[16] Transmission electron micrographs were recorded on a Hitachi HD-2000 instrument operating at 200 kV. Before examination, specimens were embedded in cyanoacrylate and microtomed.

Results and Discussion

The XRD patterns displayed in Figure 1 show that the material prepared at room temperature in 2 days (t_1 = 2 days, t_2 = 0) consisted of a mixture of hexagonal (H) and lamellar (L) mesophases. Aging this mixture at 100 °C gave rise to a single cubic MCM-48 (C) mesophase. Samples prepared at room temperature for a much shorter time, e.g., 0.5 h, exhibited only a lamellar phase (Figure 1, sample B). The XRD patterns of the material obtained after t_1 = 0−1 h and t_2 = 2−3 days (Figure 1, samples C−F) are consistent with the occurrence of *Ia*3*d* symmetry and show intense (211) and (220) diffraction peaks. A more diffuse pattern observed in the 3−4° region can be attributed to 321, 400, 420, 332, 422, and 431 reflections. The ratio between the *d* spacing of the peaks assigned as (211) and (220) is 0.87, which is consistent with the cubic MCM-48 mesophase.[17] The lattice

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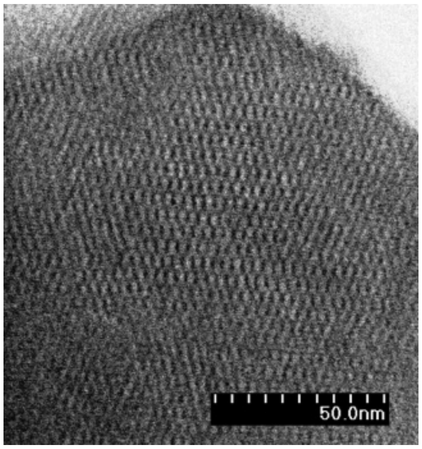

Figure 2. Transmission electron micrograph of mesoporous silica prepared from starting mixture 1TEOS/0.064C$_{16}$-DMB-C$_{16}$/0.74NaOH/185H$_2$O (t_1 = 0.5 h, t_2 = 2 days) recorded along the [110] direction.

parameter calculated from this pattern reflects a structural periodicity with a unit cell of 83 Å. The transmission electron microscopy (TEM) images confirm that the structure of the materials is consistent with the cubic MCM-48 mesophase. The image (Figure 2) of sample E viewed down the [110] zone axis of a cubic unit cell is consistent with literature data.[18] Along the [110] direction the electron density variation in projection in different regions creates the channel-like appearance.

It thus appears that the MCM-48 is generated from MCM-41 through a temperature transition. This was possible because the room-temperature precipitation time (t_1) was relatively short and the degree of condensation of the silica was still low enough that by further changing the synthesis conditions, e.g., increasing the temperature, it would be possible to induce the transition of one mesophase to another. It has been suggested in the literature that the transition from H to L is a reversible process whereas the transition into the cubic phase is more thermodynamically favorable and less reversible.[12] Consistent with this statement, the current work showed that the L phase appears when $t_2 = 0$, and as t_2 increases the L phase vanishes. Further, Pevzner et al.[18] suggested that the C phase results from a collapse of the H phase where the (100) plane stays intact and evolves into a (211) cubic plane of approximately the same interplanar spacing. Our data are consistent with this observation. Indeed, the interplanar spacing of the hexagonal phase present in the mixture at $t_1 = 0.5$ h and $t_2 = 0$ corresponds to the spacing of the cubic phase formed at $t_2 = 2$ days (Figure 1).

In surfactant systems, the addition of salt screens the electrostatic repulsive forces between neighboring polar headgroups, thus changing the spontaneous curvature. The addition of NaOH in microemulsion systems with ionic surfactants is therefore a means to control the mesophase, and thus, its concentration is often employed as an experimental control parameter. Pena et al.[20] provided evidence that, by adjusting the pH during the synthesis of mesoporous silica, various structures can be generated. Also in this work, to achieve the desired transition from the hexagonal to cubic structure, the amount of base added needed to be optimized to allow the packing parameter to reach a value associated with the cubic phase. It was observed that the NaOH to silica ratio required for the transition from the hexagonal to cubic structure to occur needs to be adequate (0.74), but excess base results mostly in the formation of the hexagonal phase. For example, the material obtained using a NaOH to silica ratio of 0.84 at a relatively short room-temperature precipitation period ($t_1 = 0.5$ h) and a long aging period ($t_2 = 2$ d) consisted mainly of the MCM-41 phase in addition to a small amount of MCM-48 (Figure 3B). However, when the synthesis gel reacts at room temperature for a longer period of time, only the hexagonal phase is obtained (not shown). Due to extended condensation of the silica during the precipitation stage, the hexagonal to cubic phase transition becomes much less favorable. At a lower NaOH to TEOS ratio (0.64), the XRD pattern obtained (Figure 3A) indicates the occurrence of a poorly ordered mesophase.

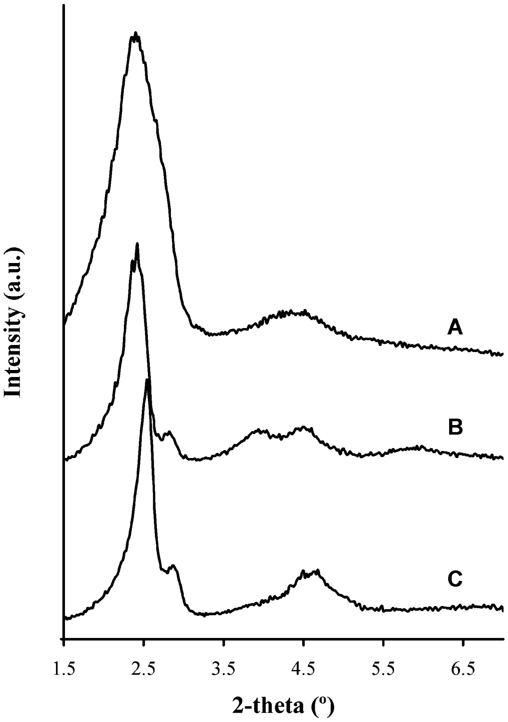

Figure 3. X-ray diffraction patterns of mesoporous materials obtained at $t_1 = 0.5$ h and $t_2 = 2$ days with the following 1TEOS/0.064C$_{16}$-DMB-C$_{16}$/xNaOH/185H$_2$O gel molar compositions: (A) $x = 0.64$, (B) $x = 0.84$, and (C) $x = 0.74$.

In all cases the time allowed for the formation of the hexagonal and lamellar phases at room temperature needs to be limited to prevent the framework from becoming too rigid before the cubic phase is formed. As the room-temperature precipitation period is extended to more than 1 h, due to an increased degree of condensation, the time required for the hexagonal to cubic transition to take place increases. As shown in Figure 1, the optimum conditions for obtaining cubic MCM-48 silica correspond to short precipitation periods (t_1) and long aging periods (t_2). Although the results (Table 1) indicate that cubic mesophases with higher surface areas and pore volumes are obtained with longer precipitation (t_1) and aging (t_2) times, a shorter t_1 leads

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Table 1. Effect of Temperature and Precipitation and Aging Periods on the Characteristics of MCM-48

molar composition C_{16}-DMB-C_{16}/NaOH[a]	precipitation time (h)/aging time (days)/temp (°C)	S_{BET} ($m^2\,g^{-1}$)	$d_{KJS,ads}$ (nm)	V_{tot} ($cm^3\,g^{-1}$)	d_{211} (nm)	a (nm)
0.064/0.74	1/3/100	1164[b]	2.5	0.58	2.5	8.6
0.064/0.74	0.5/2/100	1023	2.4	0.48	2.6	8.3
0.064/0.74	0/2/100	941	2.3	0.47	2.6	8.3

[a] Where TEOS/H_2O = 1.0/185. [b] Broad pore size distribution.

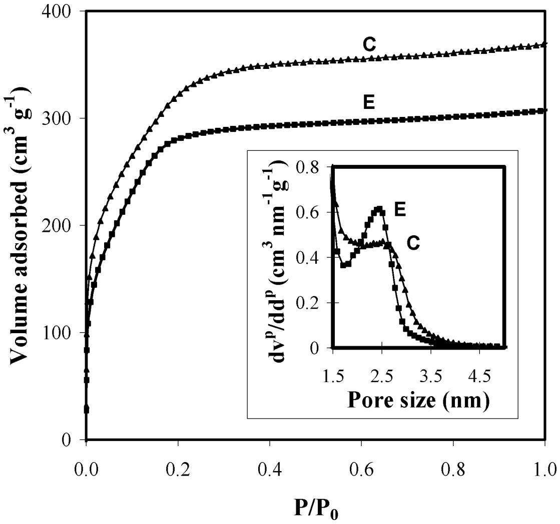

Figure 4. Adsorption isotherms and pore size distributions of products prepared after precipitation and aging for samples C ($t_1 = 1$ h, $t_2 = 3$ days) and E ($t_1 = 0.5$ h, $t_2 = 2$ days).

to materials with a narrower pore size distribution within a shorter t_2 period. In addition, the elevated temperature appears to be crucial as it provides heat to overcome the activation energy for the transition from hexagonal to cubic symmetry. Temperatures higher than 100 °C, however, lead to poor-quality materials.

The nitrogen adsorption isotherms of samples C ($t_1 = 1$ h, $t_2 = 3$ days) and E ($t_1 = 0.5$ h, $t_2 = 2$ days) are shown in Figure 4. The surface areas and pore volumes were, respectively, 1164 m^2/g, 0.58 cm^3/g and 1023 m^2/g, 0.48 cm^3/g. The isotherms were of type IV in the IUPAC classification,[21] showing capillary condensation at a relative pressure P/P_0 between 0.1 and 0.25, which is indicative of the occurrence of small-size mesopores. A narrower pore size distribution is usually indicative of better pore ordering. Although sample C exhibited a higher surface area than material E, its pore organization was inferior, which is also apparent in the shape of the adsorption isotherm that shows a broader condensation step.

As expected, when fumed silica was used as the silica source with $t_1 = 0.5$ h and $t_2 = 2$ days, no transition into the cubic phase was observed.[11] Under otherwise the same conditions ($t_1 = 0.5$ h, $t_2 = 2$ days), addition of 4 molar equivalents of ethanol with respect to fumed silica did not induce the phase transition. This shows that the presence of ethanol generated in situ by the hydrolysis of TEOS proved to be necessary for the formation of the cubic structure. It is thus inferred that the slow hydrolysis of TEOS during the polymerization of the silicate structure causes the micelles to adopt the cubic symmetry. This is consistent with the fact that a low-surface-curvature mesophase is the favored product when organic compounds of low polarity are present in the synthesis mixture.[11,22,23]

In conclusion, the MCM-48 silica mesophase has been successfully synthesized using a Gemini surfactant with a rigid spacer as template and TEOS as precursor. The effects of different reaction parameters, such as t_1, t_2, and NaOH/TEOS ratio, on the mesostructures obtained have been investigated and optimized. Heating to 100 °C was essential for the formation of the cubic mesophase, since MCM-48 is the thermodynamically favored product.

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