Synthesis and Pore Size Control of Cubic Mesoporous Silica SBA-1

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The formation of silica−surfactant mesostructures has been studied under various acidic conditions using tetraethyl orthosilicate and hexadecyltriethylammonium bromide. The synthesis conditions have been optimized in order to obtain the cubic ($Pm3n$) mesoporous molecular sieve designated as SBA-1 of high quality. The pore diameter of the SBA-1 material has been controlled within the range of 1.4−2.7 nm by expanding the surfactant micelles with 1,3,5-trimethylbenzene or substituting the hexadecyl group of the surfactant with other *n*-alkyl groups ($C_{12}H_{25}$ to $C_{18}H_{37}$).

Introduction

Mesoporous molecular sieves have attracted much attention as a catalyst support, adsorbent, and host for nanometer-scale quantum objects.[1−3] Recently, Huo et al. reported the synthesis of a mesoporous molecular sieve referred to as SBA-1 using tetraethyl orthosilicate (TEOS) as a silica source and hexadecyltriethylammonium bromide (HTEABr) as the surfactant under strongly acidic synthesis conditions.[4−7] The SBA-1 material is characterized by its X-ray powder diffraction (XRD) pattern, which is analogous to that of the cubic $Pm3n$ assemblage of globular micelles in amphiphilic surfactant solutions. Its structure has been suggested to be of a cage type with open windows, following the clathrate-like model proposed for the surfactant mesophase by Charvolin and Sadoc.[8] The cage-type pore structure of SBA-1 is unique among mesoporous molecular sieves known hitherto. The three-dimensional channel connectivity is considered to be suitable for its applications as a catalyst support and adsorbent. The cage-like mesopores can also be considered as a unique host for quantum dots.

Despite interesting structural and synthetic aspects, SBA-1 has not been so widely investigated as other well-known mesoporous silica molecular sieves such as MCM-41 (hexagonal structure) and MCM-48 (cubic $Ia3d$). We believe that this is probably because details of the synthesis procedure to reproduce SBA-1 are not reported. As mentioned above, Huo et al. have already reported the synthesis of SBA-1.[4−7] However, the previously published procedure for SBA-1 was very sketchy and incomplete. We have therefore investigated synthesis conditions for reproducing high-quality SBA-1 materials. In addition, we have studied control of the pore diameter using 1,3,5-trimethylbenzene (TMB) and choosing surfactants with various chain lengths.

Experimental Section

Surfactant Preparation. Hexadecyltrimethylammonium chloride (HTMACl, 25% in aqueous solution) was used as received from Acros. HTEABr was synthesized by the reaction of 1-bromohexadecane with an equimolar amount of triethylamine in ethanol solution under reflux conditions. The resulting product was purified by recrystallization from a chloroform/ethyl acetate mixture. Details of the synthesis procedure are as follows: 3.15 g of 1-bromohexadecane (97%, Acros) was dissolved in 25 mL of absolute ethanol; 1.02 g of triethylamine (99%, Aldrich) was combined with the ethanol solution at room temperature. The resultant mixture was heated while being stirred for 12 h under reflux conditions. The solvent was evaporated until a brown viscous liquid was obtained, using a rotary evaporator at 353 K. The brown liquid turned to a solid upon cooling to room temperature. A minimum amount of chloroform (98%, Junsei) was added to dissolve the solid. To this solution was added ethyl acetate (99.9%, JT Baker) slowly while the mixture stirred until the precipitation of the HTEABr reached a maximum. The mixture was cooled in a refrigerator in order to increase precipitation. The resultant precipitate was filtered, washed with ethyl acetate, and dried in a vacuum oven at room temperature. The product was identified as HTEABr by ^{1}H NMR spectrum after dissolution in chloroform-*d*.

Other alkyltriethylammonium bromides (ATEABr), i.e., the C_{10}, C_{12}, C_{14}, C_{18} and C_{20} surfactants, were also synthesized by the reaction of triethylamine with 1-bromoalkanes.

Synthesis of Mesoporous Silica. The mesostructures between silica and the surfactant were allowed to form under various conditions using ATEABr (typically HTEABr) or HTMACl as the surfactant and TEOS (98%, Aldrich) as a silica source in aqueous solutions of HCl, HBr, H_2SO_4, and HNO_3. The molar composition of the reaction mixture was varied in the range of 1 surfactant:(1−12) TEOS:(20−1600) acid:(500−20000) H_2O. Reaction temperatures were varied from 273 to 353 K.

Reactants were mixed as follows: surfactant, acid, and distilled water were combined to obtain a homogeneous

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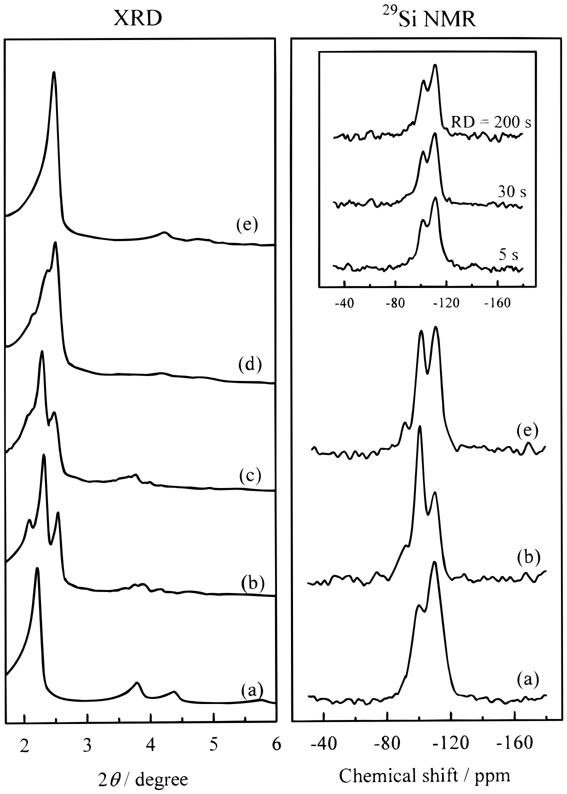

Figure 1. XRD patterns and MAS ^{29}Si NMR spectra for surfactant−silica mesophases: (a) MCM-41 (hexagonal, *P*6*m*) synthesized using 1 HTMACl:4 SiO_2:1 Na_2O:250 H_2O at 373 K; (b−e) materials synthesized by 4 h reaction using 1 HTEABr:5 TEOS:280 HCl:3500 H_2O. Results in b−e show a transition from SBA-1 (cubic, *Pm*3*n*) to SBA-3 (hexagonal, *P*6*m*) as the reaction temperature increases: (b) 273 K, (c) 298 K, (d) 318 K, (e) 353 K. All MAS ^{29}Si NMR spectra presented in this work were taken after samples were completely wet in distilled water, to decrease the spin−lattice relaxation times. It is known that the spin−lattice relaxation times in mesoporous silica molecular sieves were very long (30−70 s for Q^3 and 70−125 s for Q^4).[10] However, we have found that the relaxation times can be decreased tremendously by wetting samples in water. Spectra in inset were taken from a calcined SBA-1 sample with the relaxation delay times of 5, 30, and 200 s, respectively. The same peak intensities in these spectra justify our use of the short relaxation delay time of 5 s.

Table 1. Typical Syntheses Conditions and Product Mesophases

	composition[a]			temp	product
surfactant	acid	*x*	*y*	(K)	mesophase[b]
$C_{16}H_{33}N(C_2H_5)_3Br$	HCl	40	500	273	cubic
$C_{16}H_{33}N(C_2H_5)_3Br$	HCl	280	3500	273	cubic
$C_{16}H_{33}N(C_2H_5)_3Br$	HCl	1600	20000	273	cubic
$C_{16}H_{33}N(C_2H_5)_3Br$	HCl	280	3500	298	cubic
$C_{16}H_{33}N(C_2H_5)_3Br$	HCl	280	3500	353	hexagonal
$C_{16}H_{33}N(C_2H_5)_3Br$	H_2SO_4	80	1000	298	cubic
$C_{16}H_{33}N(C_2H_5)_3Br$	HBr	80	1000	298	hexagonal
$C_{16}H_{33}N(C_2H_5)_3Br$	HNO_3	80	1000	298	hexagonal
$C_{16}H_{33}N(CH_3)_3Cl$	HCl	210	3500	273	hexagonal
$C_{16}H_{33}N(CH_3)_3Cl$	HCl	420	3500	273	cubic
$C_{10}H_{21}N(C_2H_5)_3Br$	HCl	280	3500	273	disordered
$C_{12}H_{25}N(C_2H_5)_3Br$	HCl	280	3500	273	cubic
$C_{14}H_{31}N(C_2H_5)_3Br$	HCl	280	3500	273	cubic
$C_{18}H_{37}N(C_2H_5)_3Br$	HCl	280	3500	273	cubic
$C_{20}H_{41}N(C_2H_5)_3Br$	HCl	280	3500	273	hexagonal

[a] Starting materials, consisting of 1:5:*x*:*y* surfactant:TEOS:acid:H_2O, were stirred for 4 h at the given temperatures. [b] "Cubic" indicates the SBA-1 material with cubic *Pm*3*n* structure, and "hexagonal" the *P*6*m* SBA-3.

solution. The solution was cooled or heated to a desired reaction temperature prior to the addition of TEOS, using an ice or hot water bath. TEOS was precooled or heated to the same temperature. The TEOS was then added to the surfactant solution while the mixture was being vigorously stirred. Stirring was continued for 4 h until the precipitation of the silica−surfactant assemblies was completed. The reaction mixture was then heated to 373 K rapidly (about 10 min) and maintained there for 1 h. The resultant precipitate was filtered, dried (without washing) in a vacuum oven at room temperature, and subsequently heated for 30 min at 433 K using a drying oven. Products after these treatments were washed with an ethanol−HCl mixture by the same method used previously for the synthesis of other mesoporous silica. After subsequent drying at 433 K for 30 min, the products were calcined in air under static conditions at 823 K.

When TMB was used as a pore-swelling organic agent, surfactant and TMB were homogeneously mixed by the addition of a small amount of ethanol. This ethanol solution was added to a HCl−H_2O mixture while the reaction mixture stirred at room temperature. The remainder of the synthesis procedure was the same as described above.

Characterization. XRD patterns were recorded using a Rigaku D/MAX-III (3 kW) instrument with a Cu Kα X-ray source. Solution ^1H NMR for surfactants and magic angle spinning (MAS) ^{29}Si NMR spectra for the mesostructured materials were recorded on a Bruker AM 300 instrument at 296 K. Measurement conditions for the MAS ^{29}Si NMR were as follows: ^{29}Si resonance frequency = 59.6 MHz, pulse width = 3 μs (30° pulse), relaxation delay = 5 s, and spinning speed = 3.5 kHz. Tetramethylsilane was used as a reference. All samples were completely wet in distilled water before taking the NMR spectra, to decrease the spin−lattice relaxation time. The use of the short relaxation delay of 5 s is justified by the NMR signal intensity, which is independent of the relaxation delay times in the range of 5−200 s (Figure 1, inset). N_2 adsorption/desorption isotherms at 77 K were measured using a Micromeritics ASAP 2010 instrument. Pore-size distribution was obtained with the N_2 adsorption branch, using the BJH (Barrett−Joyner−Halenda) method.[9]

Results and Discussion

We performed the synthesis of mesoporous silica using TEOS as a silica source and HTEABr as a surfactant under various acidic conditions. Typical synthesis results are given in Table 1. Among the synthesis conditions, the SBA-1 mesophase was best formed from a mole composition of 1 HTEABr:5 TEOS:*x* HCl:12.5*x* H_2O at 273 K, where *x* can be varied over 240−400. The reactant composition and reaction temperature have been chosen as an optimized synthesis condition for the formation of the SBA-1 mesophase. Under this condition, the surfactant−silica assembly began to precipitate in about 10 min after the initial mixing of the reactants. The precipitation was completed in about 4 h. The mesophase, after filtration without washing at room temperature, showed an XRD pattern with three well-resolved lines in the region of $2\theta = 1.5−3°$, which are indexed to the (200), (210), and (211) diffraction, characteristic of the cubic *Pm*3*n* mesostructure ($a_o = 8.3$ nm). However, the XRD lines were merged to a single broad peak after the precipitate was washed with distilled water, acetone, or ethanol after the filtration.

The structure of the silica−surfactant mesophase was investigated with XRD patterns and MAS ^{29}Si NMR spectra after treatments in various ways, after the

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formation under the optimized synthesis condition. The XRD patterns and MAS ^{29}Si NMR spectra are compared in Figure 1 with those for MCM-41 synthesized under a basic condition at 373 K. The NMR spectrum of the SBA-1 mesophase formed at 273 K shows much more intense Q^2 and Q^3 silicon peaks than those for MCM-41. The difference indicates that the SBA-1 mesophase was constructed with a silica framework of a very low cross-linking degree, compared with the MCM-41 sample. The loosely cross-linked framework of SBA-1 was damaged while being washed with distilled water. We therefore tried to enhance the cross-linking by increasing the reaction temperature. The XRD patterns and MAS ^{29}Si NMR spectra of the resultant mesophases are displayed against the synthesis temperature in parts b−e of Figure 1. As the result shows, the cross-linking degree of the framework increased with the synthesis temperature. However, the synthesis at high-temperature resulted in the formation of a silica−surfactant mesophase with a hexagonal structure. The transition from cubic to hexagonal occurred in a broad temperature range around 313 K. Low temperatures were favorable for the formation of the cubic mesophase. The XRD patterns show a distinct improvement in the structural order of the cubic mesophase with the decrease of the synthesis temperature from room temperature to 273 K.

The synthesis of MCM-41 under strong basic conditions is known to be controlled reversibly so that the formation of the hexagonal mesophase is energetically favored. However, the formation of the SBA-1 mesophase under the present acidic condition is controlled by the initial condition for the reactants mixing. As described above, an excellent $Pm3n$ mesophase was formed from a reaction mixture 1 HTEABr:5 TEOS:x HCl:12.5x H_2O, where x can be varied over 240−400, during the initial stirring period of 4 h at 273 K. This reaction mixture containing the $Pm3n$ mesophase was heated to 373 K over 10 min and maintained for several hours at 373 K while being stirred. The XRD patterns and MAS ^{29}Si NMR spectra of the resultant surfactant−silica mesophase are shown in parts b and c of Figure 2. These figures show that heating for 1 h at 373 K resulted in a significant enhancement in the framework cross-linking while the cubic mesostructure was maintained. However, excessively long heating resulted in a gradual loss of the XRD resolution. The kinetic stability of the mesostructure exhibited by this experiment was useful for stabilization of the framework to a certain degree, but the heated mesostructure was still lost by washing with distilled water at room temperature. The product heated at 373 K may be calcined in air without any additional treatments, to obtain pure silica SBA-1. However, such calcination is often undesirable, due to coke formation, particularly when a large amount of the sample is calcined. It is convenient to remove most of the surfactant by washing with ethanol−HCl mixtures prior to the calcination. The washing is known to be effective for MCM-41.[11] In addition, aluminum can be grafted onto the silica framework using $AlCl_3$ solutions after washing. It is reported that the resulting aluminosilicate MCM-41 materials after subsequent calcination contained tetrahedral aluminum, which exhibited acidity, cation exchange capacity, and catalytic activity.[12] However, unlike the case of MCM-41, our SBA-1 product heated at 373 K was not stable enough to maintain the structure during its washing with the ethanol−HCl mixture. We then stabilized the structure by heating the product for 30 min at 433 K in a drying oven or N_2 atmosphere. The material after this treatment was stable enough to maintain the SBA-1 mesostructure after the surfactant removal with ethanol−HCl and subsequent incorporation of aluminum using $AlCl_3$ (Si/Al > 7).

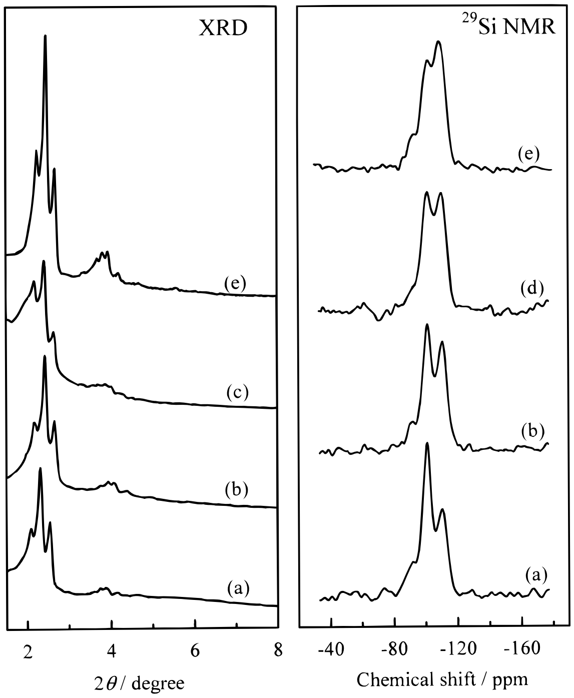

Figure 2. XRD patterns and MAS ^{29}Si NMR spectra for SBA-1 obtained using 1 HTEABr:5 TEOS:280 HCl:3500 H_2O (a) after reaction for 4 h in ice bath; (b) after heating the reaction mixture described in a for 1 h at 373 K; (c) after heating the reaction mixture described in a for 24 h at 373 K; (d) after subsequent drying of the product described in b at 433 K for 30 min; (e) after washing the product described in d with ethanol−HCl and then calcination in air under static condition at 823 K.

As shown in Figure 3a, the hexagonal SBA-3 mesophase is formed from a starting mixture with 1 HTMACl:5 TEOS:210 HCl:3500 H_2O at 273 K. The formation of the hexagonal mesophase with the HTMACl surfactant is consistent with recent synthesis reports.[7] However, after increasing the amount of the acid to 420 HCl, we obtained the SBA-3 cubic mesophase as shown in Figure 3b. Thus, the cubic SBA-1 mesophase can also be obtained using the HTMACl surfactant instead of HTEABr if acid concentration is increased. The transition of the mesophases from hexagonal to cubic, observed with the increase in the acid concentration, can be explained by the surfactant−silica assembly mechanism proposed by Huo et al.[4,5] According to the mechanism, the formation of the silica−surfactant mesophase under strong acidic conditions occurs through the formation of $S^+X^-I^+$ micelles, where

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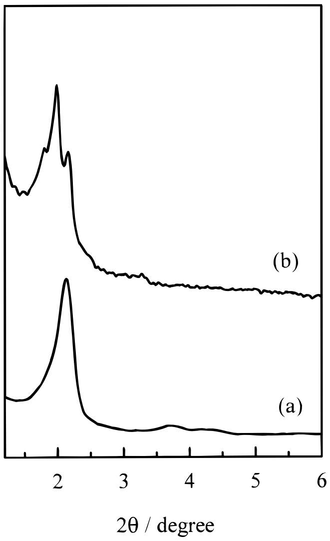

Figure 3. XRD patterns for silica−surfactant mesophases obtained by 4 h reaction at 273 K using 1 HTMACl:5 TEOS:*x* HCl:3500 H_2O. The XRD patterns show a transition from SBA-3 (hexagonal, *P*6*m*) to SBA-1 (cubic, *Pm*3*n*) as the molar ratio, *x*, between HCl and HTMACl increase: $x = $ (a) 210, (b) 420.

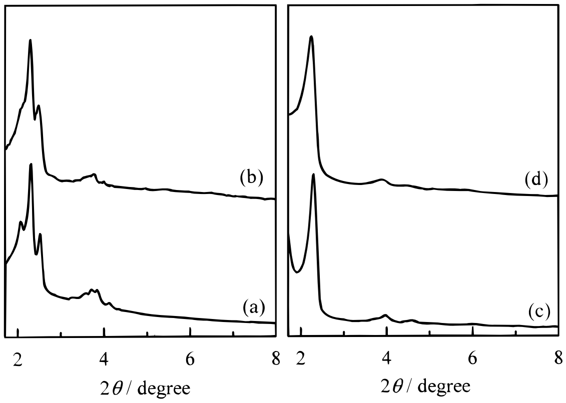

Figure 4. XRD patterns for silica−surfactant mesophases obtained by 4 h reaction at 298 K using 1 HTEABr:5 TEOS:80 acid:1000 H_2O. SBA-1 (cubic, *Pm*3*n*) or SBA-3 (hexagonal, *P*6*m*) was obtained depending on the acid used: (a) H_2SO_4; (b) HCl; (c) HBr; (d) HNO_3.

S^+ denotes surfactant cation, X^- the acid anion, and I^+ the inorganic (silica) species. Since the I^+ species is positively charged by the proton adsorption, the concentration of I^+ participating in the formation of the surfactant micelle is believed to increase at high acidity. The high concentration of HCl in the starting materials is therefore believed to cause an increase in the head-to-tail volume ratio for the $S^+X^-I^+$ micelle. The result of the change can be a transition from hexagonal micelles to spherical, leading to the formation of the cubic SBA-1 mesophase.

The effect of the counteranion, X^-, has also been investigated in the present work, keeping the same mole ratios of the starting materials at 1 HTEABr:5 TEOS:80 acid:1000 H_2O at 273 K. The acid was varied from HCl to H_2SO_4, HBr, and HNO_3. The XRD patterns of the resultant mesophases are presented in Figure 4. The SBA-1 mesophase was obtained when H_2SO_4 and HCl were used. The XRD lines obtained with H_2SO_4 were better resolved than those with HCl. However, the XRD lines from the use of H_2SO_4 were broadened upon calcination of the mesophase. It appears that the surfactant was decomposed at a relatively low temperature during calcination in the case where the $S^+X^-I^+$ assembly was formed with the oxidizing SO_4^{2-} anions. The loss of the surfactant during the calcination, before the silica framework was sufficiently cross-linked, seemed to result in the structure loss. Huo et al. reported on the formation of an amorphous solid instead of SBA-1 using H_2SO_4 at room temperature.[5] It thus seems that the mesophases were sensitive to the variation of the mixing ratios of the same starting materials. Parts c and d of Figure 4 show that the hexagonal mesophase was obtained when HBr and HNO_3 were used.

The acid anions may affect the mesophase formation in various ways, but the main effect of the X^- anions should be through their adsorption on the headgroups of the surfactant micelle. The adsorption in high concentration increases the volume of the headgroups and therefore contributes to a significant increase in the surface curvature. The SBA-1 mesophase is obtained under the conditions where the surface curvature increases until spherical micelles are formed. The X^- ions are more or less hydrated in the surfactant solution. Less strongly hydrated ions have in general smaller ionic radii and bind more strongly on the surface of the surfactant micelles. The adsorption ability or the aggregation number is reported to decrease in the following order: $\frac{1}{2}SO_4^{2-} > F^- > BrO_3^- > Cl^- > Br^- > NO_3^- > I^- > CNS^-$.[13,14] On the basis of this series, it is reasonable that H_2SO_4 and HCl lead to the formation of the cubic mesophase, whereas HBr and HNO_3 lead to the hexagonal phase. Further, the divalent anion SO_4^{2-} is believed to be more effective than the monovalent Cl^- for the formation of the $S^+X^-I^+$ assembly between the surfactant cations and the silicate cations.

The XRD patterns obtained from our synthesis experiments using ATEABr surfactants with various alkyl chains are presented in Figure 5. The XRD patterns show that the use of the C_{10}-ATEABr surfactant gave a disordered material exhibiting a broad XRD peak centered at $2\theta = 3.1°$ instead of a cubic *Pm*3*n* mesophase. Thus, the decyl group in the surfactant seemed to be too short to have the hydrophobic interaction required for the formation of the ordered cubic mesophase. The cubic *Pm*3*n* mesophase was obtained when the alkyl group in the surfactant was varied between C_{12} and C_{18}. The XRD patterns obtained using these surfactants indicate that the structural order for the cubic mesophase increased with the increase of the size of the alkyl group in this range. However, when the alkyl group increased to C_{20}, there appeared a sudden transition to a well-ordered hexagonal mesophase. This transition indicates that the increase of the alkyl chain length caused the C_{20}-ATEABr surfactant to have a micelle packing parameter favoring the formation of the hexagonal mesophase.[4,6]

Figure 6 shows a N_2 adsorption−desorption isotherm for the calcined SBA-1 material obtained from C_{18}-ATEABr and its corresponding pore size distribution curve obtained by the BJH method.[9] The adsorption isotherm shows a large increase at $P/P_o = 0.2-0.3$ due to the capillary condensation in mesopores. The adsorp-

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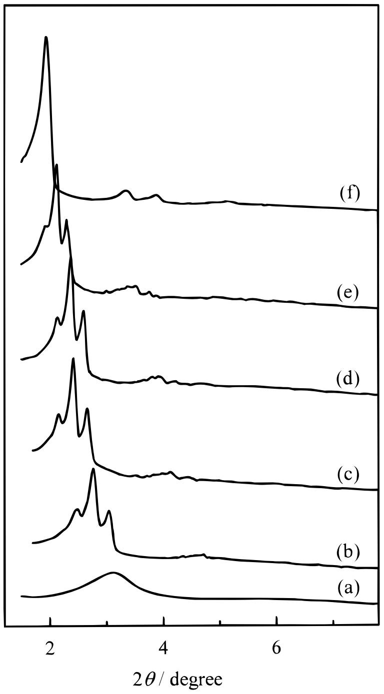

Figure 5. XRD patterns for silica−surfactant mesophases obtained by 4 h reaction at 273 K using 1 ATEBr:5 TEOS:280 HCl:3500 H_2O. The number of carbon atoms (n) in the linear alkyl group in ATEABr was varied: n = (a) 10, (b) 12, (c) 14, (d) 16, (e) 18, (f) 20.

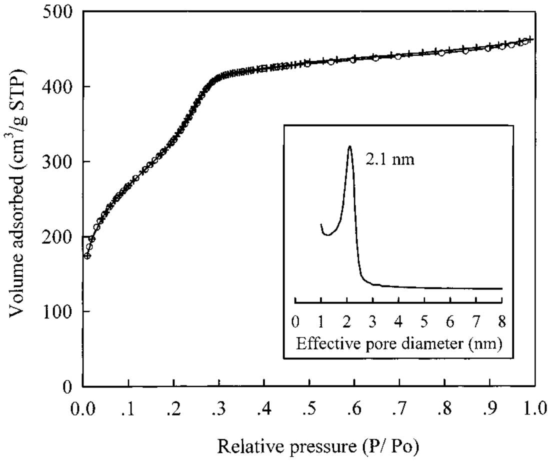

Figure 6. N_2 adsorption−desorption isotherm at liquid N_2 temperature for the calcined SBA-1 obtained from C_{18}-ATEABr: (○) adsorption and (+) desorption. (inset) The corresponding pore-size distribution curve obtained from adsorption branch using the BJH method.

Table 2. Lattice Parameter, Pore Diameter, and BET Surface Area of Calcined Materials

surfactant	TMB	a_o (nm)	pore size (nm)	surface area (m^2/g)
$C_{12}H_{25}N(C_2H_5)_3Br^a$	0	6.0	1.4	988
$C_{14}H_{31}N(C_2H_5)_3Br^a$	0	6.9	1.8	1276
$C_{16}H_{33}N(C_2H_5)_3Br^a$	0	7.6	2.1	1355
$C_{16}H_{33}N(C_2H_5)_3Br$	0.5^b	8.7	2.3	1324
$C_{16}H_{33}N(C_2H_5)_3Br$	1.0^b	10.4	2.7	1195
$C_{18}H_{37}N(C_2H_5)_3Br^a$	0	8.4	2.4	1187

^{a} The synthesis condition were described in Table 1. ^{b} Starting materials, consisting of 1 surfactant:5 TEOS:x TMB:950 HCl:7000 H_2O:400 EtOH, were stirred for 4 h at 273 K.

tion due to the capillary condensation exhibits a gentle slope compared to that of MCM-41, exhibiting no hysteresis loops.[15,16] Consequently, the BJH pore-size distribution for SBA-1 is much broader than that of high-quality MCM-41 materials. Why this is observed for the present SBA-1 sample despite its high structural order judged by the XRD pattern is an interesting problem. Further works are necessary for the adsorption−desorption behavior of SBA-1 to be fully understood. Other SBA-1 samples obtained using the C_{12}-, C_{14}- and C_{16}-ATEABr surfactants gave similar results, except that continuous shifts of the pore size distribution to a larger size occurred as the alkyl chain length increased. Similar changes were obtained in the pore size distribution and XRD pattern when less than or equal to 1 TMB/CTEABr was added to the starting materials for SBA-1 using the C_{16}-ATEABr surfactant. The results for the pore size changes and BET surface area obtained from these synthesis experiments are summarized in Table 2.

As given in Table 2, the pore size variation achieved in the present work was limited to within 1.4−2.7 nm. Attempts to increase the pore diameter for SBA-1 beyond 2.7 nm resulted in the formation of hexagonal materials or the separation of TMB from the starting materials. On the other hand, the use of short surfactants to decrease the pore diameters to below 1.4 nm resulted in the formation of disordered materials. Nevertheless, the lower limit of 1.4 nm for the present SBA-1 materials is considerably smaller than the pore size (~2.1 nm)[15] for MCM-41 obtained using dodecyltrimethylammonium bromide. The small pore diameter for SBA-1 may be due to its cage-type pores constructed with small windows. Therefore, the SBA-1 materials may contribute to a significant extension of the surfactant-templated porous silica to the microporous region. The porous materials may be suitable for the shape-selective catalytic applications between the microporous and mesoporous regions.

Conclusion

The optimized synthesis procedure for the cubic SBA-1 mesophase is as follows: precooled TEOS is added to a precooled solution of HTEABr−HCl−H_2O in an ice bath while the mixture is stirred vigorously using a magnetic stirrer. The resultant reaction mixture has a mole composition of 1 HTEABr:5 TEOS:x HCl:12.5x H_2O, where x can be varied from 240 to 400. The reaction mixture is stirred continuously in the ice bath for 4 h and subsequently for an additional 1 h at 373 K. Then, the resultant precipitate is filtered, washed, and dried. The dried precipitate is further heated in air or preferably N_2 atmosphere at 433 K. The mesophase is calcined after the surfactant is removed by washing in an ethanol−HCl mixture. An aluminosilicate form of the cubic molecular sieve can be obtained by using an ethanol solution of $AlCl_3$ between the calcination and the ethanol−HCl washing. High-quality SBA-1 samples exhibiting well-resolved XRD peaks can be obtained following the procedure. The SBA-1 materials may be considered for various applications in adsorption, separation, and catalysis.

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