

Synthesis of 3d-Hexagonal ($P6_3/mmc$) Mesoporous Material Using C_n TEABr-type Surfactants via Acidic Synthesis Route

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Mesoporous material having the 3d-hexagonal ($P6_3/mmc$) structure was synthesized under acidic condition using dodecyl- and tetradecyltriethylammonium bromides at low concentrations. The 3d-hexagonal structure was formed via the formation of the $Pm\bar{3}n$ structure.

Silica-based mesoporous materials have attracted intense interest due to their high potentials for catalytic application and environmental cleanup. Mesoporous materials can be synthesized via the alkaline route or the acidic route. A general method has been developed for the synthesis of a wide range of transition and main-group element oxide mesostructured materials under acidic conditions by using cationic, anionic, or nonionic surfactants with various concentrations and controlling the reaction temperatures.^{3-5,9} Although these materials have various structures,¹⁻⁸ much attention has been concentrated on the synthesis of the materials with the 2d-hexagonal structure, such as MCM-41 and SBA-15. Huo et al.⁹ reported that the silica mesophase of SBA-1 ($Pm\bar{3}n$) can be formed from a combination of cationic surfactant (S^+), halogen anion (X^-), and cationic silicic acid species (I^+). Large head-group surfactants favor the formation of cubic SBA-1 phase whereas small head-group surfactants are favorable to obtaining the SBA-3 hexagonal $P6mm$ phase.

Here we report that 3d-hexagonal ($P6_3/mmc$) material can be synthesized via the $S^+X^-I^+$ route by altering the alkyl chain length of surfactant having the triethylammonium head group. Moreover we have found that the synthesized 3d-hexagonal mesoporous material was not directly formed but generated from the once formed 3d-cubic phase. Using the reaction of triethylamine with 1-bromoalkanes, we synthesized dodecyl-, tetradecyl-, hexadecyl-, and octadecyltriethylammonium bromides, which were abbreviated as C_{12} TEABr, C_{14} TEABr, C_{16} TEABr, and C_{18} TEABr, respectively. In addition, cetyltrimethylammonium bromide [$CH_3(CH_2)_{15}N(CH_3)_2C_2H_5$]Br ($C_{16}M_2$ -EABr) and tetradecyltrimethylammonium bromide [$CH_3(CH_2)_{13}N(CH_3)_3$]Br ($C_{14}TMABr$) were synthesized in a similar manner. For the synthesis, surfactant, distilled water and hydro-

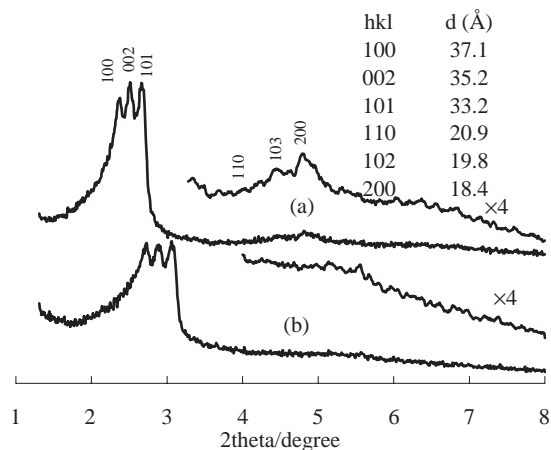


Figure 1. XRD patterns of materials obtained with (a) C_{14} TEABr and (b) C_{12} TEABr.

chloric acid were mixed to give a homogeneous solution, which was cooled to 0 °C prior to the addition of TEOS that was also precooled to 0 °C. TEOS was added while the mixture was vigorously stirred. The molar composition was TEOS:H₂O:HCl:surfactant = 1:125:5:x, where x was varied in the range of 0.03–0.09. The mixture was stirred for 3 min and then allowed to react at 0 °C under static conditions for 4 days. The resultant white precipitates were filtered, and dried at 100 °C overnight. Surfactants were removed by calcination in air at 630 °C for 4 h.

Figure 1 shows the XRD patterns of the as-synthesized samples using C_{12} TEABr and C_{14} TEABr as surfactants with the molar ratios of surfactant/TEOS = 0.03–0.09 and 0.03, respectively. The three well-resolved peaks in the range of $2\theta = 2.4$ to 2.7° and the additional three weak peaks in the range of 4.0 to 4.8° are the characteristics of the 3d-hexagonal $P6_3/mmc$ mesophase with unit cell parameters $a = 42.8 \text{ \AA}$ and $c = 70.3 \text{ \AA}$ for the material synthesized with C_{14} TEABr. The c/a ($c = 2d_{002}$, $a = 2d_{100}/\sqrt{3}$) ratios are 1.65 and 1.64 for the as-synthesized samples with C_{12} TEABr and C_{14} TEABr respectively. These values are very close to the ideal c/a ratio of 1.633 for the hexag-

Table 1. Phases of products with various surfactants

Surfactant/TEOS	C_{12} TEABr	C_{14} TEABr	C_{16} TEABr	C_{18} TEABr	C_{16} DMEABr	C_{16} TMABr	C_{14} TMABr
0.03	3d – h ^a	3d – h	C ^b	C	C	2d – h	C
0.05	3d – h	C	C	C	C	2d – h	2d – h ^c
0.07	3d – h	C	C	C	C + 2d – h	2d – h	2d – h
0.09	3d – h	C	C	C	C + 2d – h	2d – h	2d – h

^a3d – h: 3d hexagonal $P6_3/mmc$ structure, ^bC: cubic $Pm\bar{3}n$ structure, ^c2d – h: 2d hexagonal $P6mm$ structure.

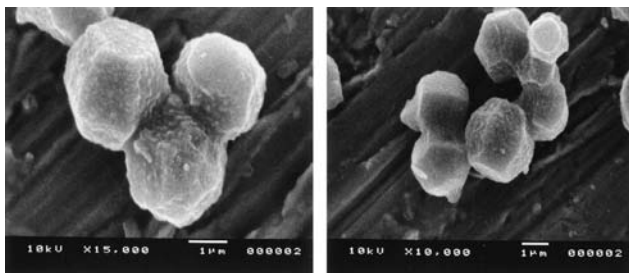


Figure 2. SEM images of the material synthesized with $C_{14}TEABr$.

onal close-packed (hcp) structure. Table 1 shows that 3d-hexagonal mesostructured materials can be synthesized with $C_{12}TEABr$ and $C_{14}TEABr$, at a low concentration of the latter, although an increase in the alkyl chain length and concentration of the surfactants gave rise to the cubic $Pm\bar{3}n$ structure. Only the surfactants with the small size of head group could lead to the formation of the 2d-hexagonal $P6mm$ structure.

Figure 2 shows the SEM images of the material synthesized with $C_{14}TEABr$ (surfactant/TEOS = 0.03). This material has 20 distinct crystal faces with one six-fold axis, as have already been reported¹⁰ for the silica synthesized by using $C_{16}TEABr$ and H_2SO_4 . From N_2 adsorption-desorption isotherms and pore size distribution curve (the BJH method) of the material, it has been found that this material has a BET surface area of $958\text{ m}^2\text{ g}^{-1}$, with a narrow distribution of pore diameter centered at 2.3 nm and a pore volume of $403\text{ mm}^3/\text{g}$.

To observe the phase transition of the material obtained with molar ratio of $C_{14}TEABr/TEOS = 0.03$ during synthesis, a portion of the gel was sampled in the period from 1 h to 72 h. The XRD patterns are shown in Figure 3. For the sample collected at 1 h after the start of the synthesis, the peaks of 200, 210, and 211 of the $Pm\bar{3}n$ structure were observed. These peaks gradually disappeared, when synthesis time was extended, and the peaks characteristic of the $P6_3/mmc$ structure appeared after 8 h. The XRD patterns clearly indicate that the once formed $Pm\bar{3}n$ structure was transformed into the $P6_3/mmc$ one. Che et al.¹¹ have reported that with $C_{16}TEABr$ the initially formed $P6mm$ structure was reconstituted to the $Pm\bar{3}n$ structure with increasing time of synthesis as a result of the condensation of silica.

It was suggested that the mesophase with a large g value was formed shortly after the addition of silica source, and then converted to the one with a small g value. Therefore, the g value³ of surfactants used in this work is considered to be increased in the order of $C_{12}TEABr < C_{14}TEABr < C_{16}TEABr < C_{18}TEABr < C_{16}DMEBr < C_{14}TMABr < C_{16}TMABr$. Products were changed from 3d-hexagonal to 3d-cubic and further to 2d-hexagonal with increasing g value of the surfactant under the same conditions. Since the 3d-hexagonal phase was generated from the 3d-cubic structure, presumably the 3d-hexagonal phase is smaller than the 3d-cubic one in g value.

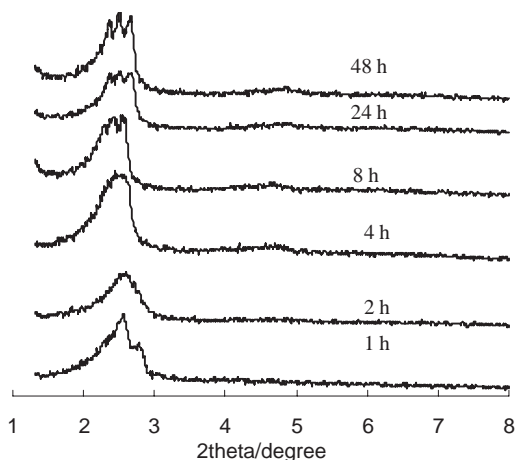


Figure 3. XRD patterns of the as-synthesized materials synthesized with $C_{14}TEABr$ for various times.

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