# Synthesis of MCM-48 Using Mixed Cationic−Anionic Surfactants as Templates

Fengxi Chen, Liming Huang, and Quanzhi Li*

*Department of Chemistry, Fudan University*
*Shanghai 200433, P.R. China*

*Received May 28, 1997*
*Revised Manuscript Received October 17, 1997*

Using the mixture of cetyltrimethylammonium bromide and carboxylate anionic surfactant ($C_nH_{2n+1}$-COONa, $n = 11, 13, 15, 17$) as templates, siliceous MCM-48 is synthesized with low molar ratio (0.168:1) of mixed surfactants to silica and low concentration (5 wt %) of mixed surfactants. The material is characterized by X-ray powder diffraction, transmission electron microscopy, TGA/DTA, and $N_2$ adsorption/desorption isotherm. In the synthesis systems, the carboxylate anionic surfactant functions as a polar organic cosolvent and cosurfactant. The MCM-48 is formed via the electrostatic templating routine. Its formation is facilitated by the unique structure of the micelles of mixed surfactants with a thick palisade layer and a small effective headgroup area when the carboxylate anionic surfactant is added.

Since Mobil researchers reported the discovery of a novel family of silica-based mesoporous molecular sieves (M41S) in 1992,[1−2] there has been a growing interest in synthesizing the mesoporous materials with alkyltrimethylammonium surfactant cations ($C_nH_{2n+1}Me_3N^+$, $n > 6$). The M41S family contains MCM-41, MCM-48, and other species whose structures have not yet been elucidated. MCM-41 has a hexagonal arrangement of unidimensional mesopores. MCM-48 exhibits cubic structure of three-dimensional mesopores which can be indexed to an *Ia*3*d* unit cell. Among the M41S materials, since the unidimensional mesopores of MCM-41 make it sensitive to blockage and limit its use as catalysts, adsorbents, and host matrixes, more attention was recently paid to the synthesis and characterization of MCM-48.[3−11] But the synthesis of MCM-48 requires more specific conditions than that of MCM-41. With the common alkyltrimethylammonium surfactants, MCM-48 will not be formed until the surfactant/silica molar ratio is beyond 1.[1−3] A representative synthesis of MCM-48 was presented by Monnier et al.[4] According to their method, MCM-48 was synthesized from a reaction mixture with a molar composition of TEOS:$0.25Na_2O$:0.65CTMACl:$62H_2O$ at 373 K for 3 days. In this system the CTMACl:Si molar ratio and the concentration of CTMACl were 0.65:1 and 13 wt %, respectively. Here, we report the first synthesis of MCM-48 using mixed cationic−anionic surfactants (i.e., the mixture of cetyltrimethylammonium cationic surfactant and carboxylate anionic surfactant [$C_nH_{2n+1}COONa$, $n = 11, 13, 15, 17$]) as templates under low molar ratio (0.168:1) of mixed surfactants to silica and low concentration (5 wt %) of mixed surfactants.

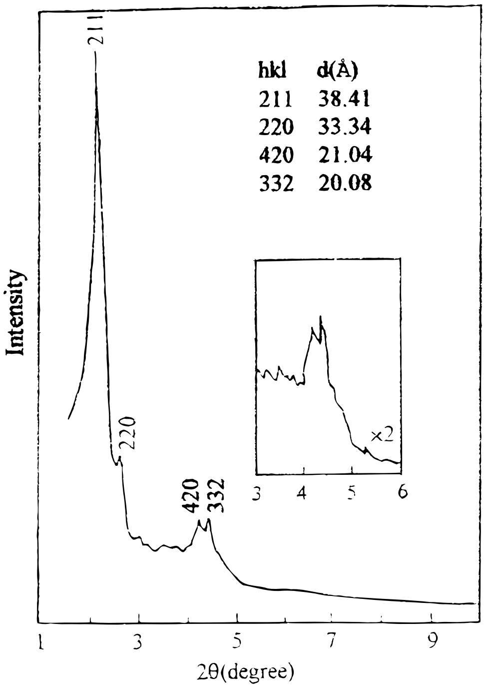

**Figure 1.** Representative XRD pattern of calcined MCM-48. Inset is expansion of $2\theta = 3−6°$. This pattern was collected on a Rigaku D/MAX-IIA equipment using the Cu Kα radiation at 40 kV and 20 mA.

A typical synthetic procedure is outlined as follows: The aqueous solution of sodium silicate (25.42 wt % $SiO_2$, 7.4 wt % $Na_2O$) was dropwise added under constant stirring to the mixed solution of cetyltrimethylammonium bromide ($C_{16}H_{33}Me_3NBr$, CTMAB) and sodium laurate ($C_{11}H_{23}COONa$, SL). This solution was then stirred at 30 °C for 1 h. The molar composition of resultant mixture was $SiO_2$:$x$CTMAB:$y$SL:$0.282Na_2O$:$58H_2O$ with $0.147 < x < 0.154$ and $0.013 < y < 0.025$. After that, this mixture was placed in a static autoclave at 100 °C for 4 days. The solid product was recovered and calcined as described by Beck et al.[2]

Using the above procedure, MCM-48 can be generated with low molar ratio (0.168:1) of mixed surfactants to silica and low concentration (5 wt %) of mixed surfactants. The XRD powder pattern of a typical calcined MCM-48 is depicted in Figure 1. The pattern consists of several distinguishable Bragg peaks which can be indexed to different (*hkl*) reflections. These reflections verify the presence of cubic phase (*Ia*3*d*) with unit-cell dimension of ca. 94 Å. The TEM image of the calcined MCM-48 is given in Figure 2, which is in good agreement with the results reported in the literature.[3,6] After

---

* To whom correspondence should be addressed.

(1) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.

(2) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.

(3) Vartuli, J. C.; Schmitt, K. D.; Kresge, C. T.; Roth, W. J.; Leonowicz, M. E.; McCullen, S. B.; Hellring, S. D.; Beck, J. S.; Schlenker, J. L.; Olson, D. H.; Sheppard, E. W. *Chem. Mater.* **1994**, *6*, 2317.

(4) Monnier, A.; Schüth, F.; Huo, Q.; Kumar, D.; Margolese, D.; Maxwell, R. S.; Stucky, G. D.; Krishnamurty, M.; Petroff, P.; Firouzi, A.; Janicke, M.; Chmelka, B. F. *Science* **1993**, *261*, 1299.

(5) Alfredsson, V.; Anderson, M. W. *Chem. Mater.* **1996**, *8*, 1141.

(6) Schmidt, R.; Stöcker, M.; Akporiaye, D.; Tørstad, E. H.; Olsen, A. *Microporous Mater.* **1995**, *5*, 1.

(7) Morey, M.; Davidson, A.; Stucky, G. *Microporous Mater.* **1996**, *6*, 99.

(8) Zhang, W.; Pinnavaia, T. J. *Catal. Lett.* **1996**, *38*, 261.

(9) Huo, Q.; Margolese, D. I.; Stucky, G. D. *Chem. Mater.* **1996**, *8*, 1147.

(10) Zhao, D.; Goldfarb, D. *J. Chem. Soc., Chem. Commun.* **1995**, *8*, 875.

(11) Kim, J. M.; Ryoo, R. *Bull. Korean Chem. Soc.* **1996**, *17*, *7*(1), 66.

S0897-4756(97)00394-3 CCC: $14.00 © 1997 American Chemical Society

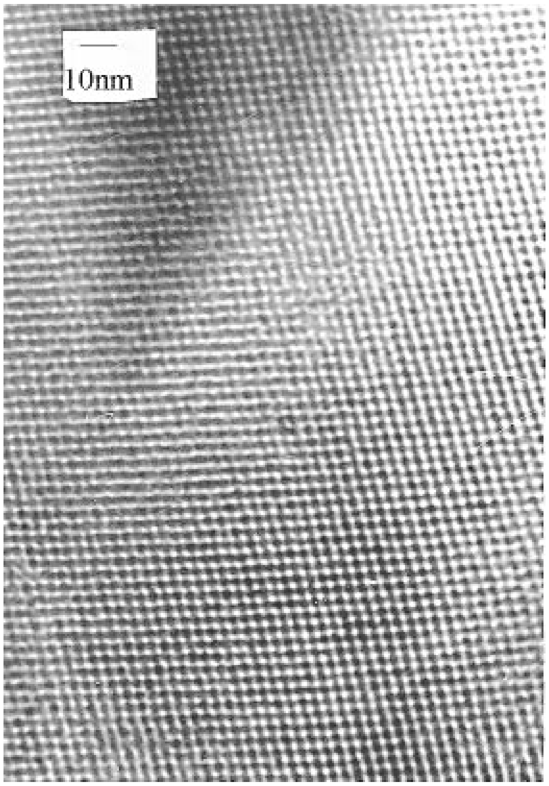

**Figure 2.** Representative HREM image of calcined MCM-48 showing the mesopores on the (110) cubic plane. This image was obtained with a JEM-200CX transmission electron microscope operating at 200 kV from a thin section prepared by ultramicrotomy.

the TGA/DTA experiment of the calcined MCM-48, the XRD pattern of the residue shows that the cubic structure of the calcined MCM-48 is thermally stable at 1200 K. The calcined MCM-48 is further characterized by a $N_2$ adsorption−desorption isotherm, which gives a BET surface area of 1055.8 $m^2\ g^{-1}$ and pore volume of 0.98 $cm^3\ g^{-1}$. The pore size distribution, calculated from the desorption curve using BJH model, shows an average pore size of about 29.4 Å and half-height width of 4 Å. It corresponds to the hysteresis loop in the 0.3−0.4 $p/p_0$ region of the isotherm, which exhibits the presence of the typical mesoporosity of the calcined MCM-48.

As an estimation we explored the use of surfactant packing parameter, $g = V/a_0l$,[12] to explain the phase behavior in surfactant mixtures, as described in the literature.[9,13] There are two kinds of force between cationic and anionic surfactant, which are (1) van der Waals force between hydrocarbon chains in the mixed micelles and (2) electrostatic attraction between quaternary ammonium ion and carboxyl ion. The electrostatic attraction at the micelle surface decreases $a_0$[14] and makes our systems different from the $C_{n-3-l}/C_m$-TMA, $C_{16-12-16}/C_{16-3-1}$ and CPCl/CTMCl systems reported by Stucky et al.[9,13,15] and Khushalani et al.,[16] respectively, which can be classified into mixed cationic−cationic surfactant systems. As a result of the balance between the two forces, the hydrocarbon chains of SL may not enter the micelle core, but are located at the hydrophobic−hydrophilic portion of the micelles and therefore form a thick palisade layer, which increases $V$. Since $a_0$ decreases and $V$ increases, the $g$ value increases in the micelles of mixed CTMA-SL as SL is increasingly added. This was verified by our experimental results. At a constant concentration (i.e., 5 wt %) of mixed surfactants and the constant molar ratio (i.e., 0.168:1) of mixed surfactants to silica, the as-synthesized products were correspondingly MCM-41 (hexagonal), MCM-48 ($Ia3d$), MCM-50 (lamellar), and gels when the SL/CTMA molar ratio was 0, $^1/_{12}$−$^1/_6$, $^1/_6$−$^1/_3$, $^1/_3$−1, respectively. It should be noted that the mixed surfactants/inorganic composite materials cannot be formed when the SL/CTMA molar ratio is beyond $^1/_3$ because both the charge density at the micelle interface of the mixed surfactants and counterion binding capacity decrease as the SL/CTMA molar ratio increases.[17] This suggests that the MCM-48 is formed via the electrostatic templating routine in our synthesis systems, as also reported by Huo et al.[18,19] The above phase transitions may be viewed as a variation of $g$ in the liquid-crystal-like solid phase.[9,13] So, it can be considered that SL functions as a polar organic cosolvent. In addition, it has been shown that the addition of anionic surfactants can increase the surface activity of cationic surfactant aqueous solutions (i.e., lower the surface tension and critical micelle concentration) and thus facilitate the mixed micelle formation.[17,20] In this sense SL can also be considered as a cosurfactant. It is the bifunction of SL that favors the formation of MCM-48 under mild conditions used in this study. According to the above description of the micelles of mixed CTMA-SL, it would be probable to use the mixtures of CTMA and other types of anionic surfactants (e.g., alkyl sulfates, alkyl sulfonates, alkyl phosphates, etc.) in appropriate molar ratio regions as templates to synthesize MCM-48 under similar conditions. This is being studied in our laboratory.[21]

**Acknowledgment.** This work is supported by NSFC under Project 29733070.

CM9703942

---

[12] In classical micelle chemistry, the expected mesophase sequence is a function of the local effective surfactant packing parameter, $g = V/a_0l$, where $V$ is the local volume of the surfactant chains plus any cosolvent organic molecules between the chains, $a_0$ is the effective headgroup area at the micelle surface, and l is the kinetic surfactant tail length or curvature elastic energy. According to this treatment, cubic ($Pm3n$) will form if $g < {}^1/_3$, hexagonal ($P6m$) if ${}^1/_3 < g < {}^1/_2$, cubic ($Ia3d$) if ${}^1/_2 < g < {}^2/_3$, and lamellar or inverted micelles if $g > 1$.

(13) Stucky, G. D.; Huo, Q.; Firouzi, A.; Chmelka, B. F.; Schacht, S.; Voigt-Martin, I. G.; Schüth, F. *Stud. Surf. Sci. Catal.* **1996**, *105*, 3.

(14) Zhao, G.; Huang, J. *Acta Phys. Chim. Sin.* **1992**, *8*, 583.

(15) Huo, Q.; Leon, R.; Petroff, P. M.; Stucky, G. D. *Science* **1995**, *268*, 1324.

(16) Khushalani, D.; Kuperman, A.; Coombs, N.; Ozin, G. A. *Chem. Mater.* **1996**, *8*, 2188.

(17) Zhang, L.; Qiao, J.; Ding, H.; Zhao, G. *Acta Phys. Chim. Sin.* **1993**, *9*, 478.

(18) Huo, Q.; Margolese, D. I.; Ciesla, U.; Feng, P.; Gier, T. E.; Sieger, P.; Leon, R.; Petroff, P. M.; Schüth, F.; Stucky, G. D. *Nature* **1994**, *368*, 317.

(19) Huo, Q.; Margolese, D. I.; Ciesla, U.; Demuth, D. G.; Feng, P.; Gier, T. E.; Sieger, P.; Firouzi, A.; Chmelka, B. F.; Schüth, F.; Stucky, G. D. *Chem. Mater.* **1994**, *6*, 1176.

(20) Zhao, G. X.; Cheng, Y.; Ou, J.; Tian, B.; Huang, Z. *Acta Chim. Sin.* **1980**, *38*, 409.

(21) Chen, F.; Chen, H.; Yan, X.; Li, Q. CN Patent Application Number 971066159.