# Synthesis of MCM-48 Single Crystals with Cube Morphology

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MCM-48 single crystals with cube morphology were synthesized by using a new ternary surfactant templating route and controlling the rate of the hydrolysis of Si source.

As is known to all, mesoporous materials synthesized using supramolecular templating method have no true crystalline order, their pore walls are constructed by amorphous materials with short-range order, but their channel structures are in highly long-range order on the mesoscopic scale. Recently, mesoporous materials with unique crystal-like morphology have been reported, they are corresponding to different space group *Ia*3*d*,[1,2,8–10] *Pm*3*n*,[3–6] *Im*3*m*.[7]

Cubic phase MCM-48, a member of M41s, has attracted much attention for its 3D-bicontinuous cubic structure, and can be used as a promising material in chiral catalysis, biological molecules separation, hosts for the synthesis of nanostructures, optical material, and so on. However, its synthesis is not easy because of the seriously restricted synthesis condition, and even more difficult for synthesis of MCM-48 single crystal. This may be the reason why only a few reports of MCM-48 with crystal shapes have been presented. Ryoo et al.[1] have first reported the synthesis of MCM-48 crystals with truncated rhombic dodecahedral shape by a hydrothermal procedure using alcohol as an additive. Sayari et al.[2] have reported the synthesis of high-quality MCM-48 with truncated rhombic dodecahedral shape from synthetic gels composed of cetyltrimethylammonium bromide (CTAB), fumed silica, trimethylammonium hydroxide, and water. Terasaki et al.[10] have presented the synthesis of MCM-48 crystals with rhombic dodecahedral morphology by use of the method reported by Ryoo et al.[1] More recently, Xia et al.[9] have also synthesized MCM-48 crystals with rhombic dodecahedral morphology from CTAOH–$SiO_2$–$H_2O$ system. However, the synthesis of MCM-48 single crystal with cube morphology has not been reported up to now.

Herein, we present the first synthesis of cube morphology of MCM-48 single crystals, using a ternary surfactant template route $S^+s^-s^0I^-$ through adjusting the amount of ethanol produced by the hydrolysis of TEOS to control the hydrolysis rate of Si source under basic condition. This is performed at an extremely low total molar ratio of surfactant to silicon (0.07:1) and extremely low surfactant concentration (2.4 wt %) owing to the synergistic effects in the mixture of the ternary surfactants.

In a typical synthesis of cube crystals of MCM-48, 1.458 g of CTAB (purified by recrystallization from acetone), 0.095 g of sodium laurate (SL, purified by recrystallization from a mixture of ethanol and acetone), 0.173 g of poly(ethylene glycol) monooctylphenyl ether (OP-10) and 1.504 g of NaOH were dissolved in 70 g of distilled water by stirring at 38 °C to give a clear solution, 15.2 mL of TEOS was then added dropwise to the solution. After further stirring for 1.5 h, the resulting mixture was then loaded into a Teflon-lined stainless steel autoclave and heated at 100 °C for 110–118 h. The molar composition of the resulting synthesis gel was $1.0SiO_2$: 0.06CTAB: 0.004OP-10: 0.0064SL: $0.282Na_2O$: $58H_2O$. The solid products were recovered by filtration, extensively washed with warm distilled water and ethanol, and dried at 80 °C. The as-synthesized powders were calcined in a flow of $N_2$ at 550 °C for 1 h followed by 5 h in air to give calcined sample.

Powder X-ray diffraction (XRD) patterns for as-synthesized and calcined MCM-48 single crystals are shown in Figure 1. The synthesized samples show excellent structural order, whose fine diffraction peaks assigned to (321), (400), (420), (322), (422), and (431) reflections are clearly observed. The corresponding unit cell parameters calculated from XRD data are 93.9 and 80.8 Å, respectively.

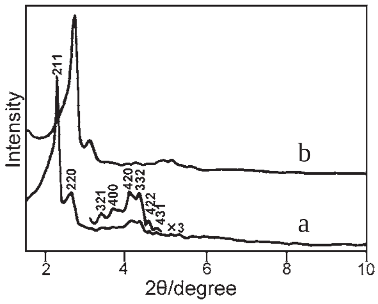

**Figure 1.** XRD patterns of the as-synthesized (a) and calcined (b) MCM-48 single crystals.

The calcined MCM-48 single crystals give a typical type IV $N_2$ adsorption–desorption isotherm. Sharp increase in volume of adsorbed nitrogen are observed at relative pressure of $P/P_0 =$ 0.15–0.3. The BET surface area, pore volume, pore diameter and wall thickness of the studied material are 966 $m^2/g$, 0.74 $cm^3/g$, 2.35 and 1.41 nm, respectively. The pore diameter is calculated from the adsorption branch of the $N_2$ isotherm using the BJH method. Wall thickness calculated by the equation, is $a_0/$3.0919-pore/2.

The SEM images of the as-synthesized MCM-48 crystals are shown in Figures 2a and 2c. As can be seen from it, the morphology of the as-synthesized sample possesses crystal-like cube shapes, consisting of 6 well-defined crystal faces (Figure 2d). This is the first synthesis of periodic mesoporous material possessing such less crystal faces, which belongs to the cubic *Ia*3*d* space group of *m*3*m* point group. The size of the crystals varies between 0.3–0.9 µm in diameter. The calcined MCM-48 crystals retain the same morphology, as shown in Figure 2b. It is noteworthy that the MCM-48 crystals possess eight round corner angles, and this can be observed more clearly by HRTEM images shown in Figure 2b, the reason may be that the surface

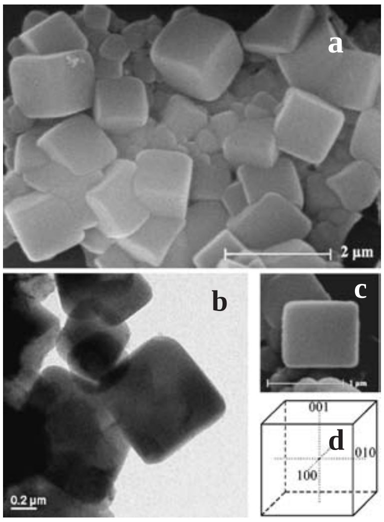

**Figure 2.** SEM images of the as-synthesized MCM-48 (a), (c), TEM image of the calcined MCM-48 (b) and schematic drawing of morphology (d).

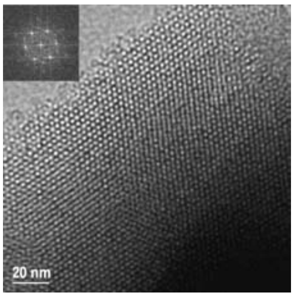

**Figure 3.** TEM image and corresponding Fourier diffractogram of the calcined sample viewed along the [111] direction.

energy of round corner angles is lower than that of pointed corner angles. Moreover, the well-ordered pore channels at the edge of the crystal-like particle, corresponding to the [111] plane of cubic MCM-48, as shown in Figure 3, are clearly observed.

The effects of the amount of ethanol produced by the hydrolysis of TEOS and the different surfactant systems on the synthesis of MCM-48 single crystal are also studied. It is found that MCM-48 single crystal is not obtained when increasing or decreasing the amount of ethanol, or when using the single cationic surfactant (CTAB) system and binary mixed surfactants (CTAB-SL and CTAB-OP-10) system under our experimental conditions. In these cases, the spherical, irregular or hollow-shell particles can be observed for MCM-48.

Generally, the morphologies of ordered mesoporous materials depend on the balance between the rate of polymerization of inorganic species and the formation rate of liquid crystal-like phase.[11] If the rate of the former is slow relative to the rate of the latter, the silicate wall is still poorly condensed and flexible, there is time to develop a highly ordered mesostructure, favoring the formation of mesoporous materials with specific crystal morphologies. In our experimental conditions, on the one hand, the synergistic effects of the ternary mixed surfactants can effectively decrease the "cmc" of forming micelles, promoting the formation of liquid crystal-like phase. On the other hand, the residual ethanol produced by the hydrolysis of TEOS through adjusting the hydrolysis time of mixture gel at 38 °C before crystallization at 100 °C would slow the rate of hydrolysis TEOS left to some extent, delaying the condensation of silicate–surfactant aggregates. Thus, the rate of the formation of the liquid crystal-like phase is faster than that of the condensation of Si species, which promote the formation of single crystal with cube shape during the crystallization. In other words, the use of ternary mixed surfactant template and the control of the amount of ethanol can offer an ideal dilute hydrothermal reaction environment in which the development of morphology, the further assembling and perfection of mesostructure for MCM-48 can be carried out simultaneously. In this case, the formed MCM-48's macroscopic cube morphology would reflect MCM-48's mesostructure on mesoscopic scale. In addition, the ternary mixed surfactants system has the ability to strongly decrease surface tension, even lower than that of single surfactant system or binary mixed surfactants system, which also benefits to the formation of MCM-48 single crystal and the growth of integral crystal.

In conclusion, both the ternary surfactant templating route and controlling the amount of ethanol coming from the hydrolysis of TEOS are the key factors for the synthesis of high-quality MCM-48 cube single crystals. The single crystals may be of considerable importance in development of advanced materials, especially in electrical devices, nonlinear optical and electrooptic materials.

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