

# Synthesis of Nanosize MCM-48 with High Thermal Stability

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Received July 2, 2003

Revised Manuscript Received September 22, 2003

Recently, a family of periodic mesoporous silica materials, PMSs,<sup>1</sup> has received much attention because of their useful catalytic properties and their potential as adsorbents and hosts for nanocluster synthesis. MCM-48, the cubic phase of the M41s mesoporous family, has a system of two disconnected enantiomeric network of mesoporous channels that exhibit three-direction pore branching.<sup>2</sup> Such a structure not only is less prone to pore blocking<sup>3</sup> but also has higher structure symmetry<sup>4</sup> than the one-dimensional hexagonal phase of MCM-41. Now the micrometer size MCM-48 with a different controlling morphology has been prepared successively, such as large crystals,<sup>5</sup> uniform sphere,<sup>6</sup> membrane,<sup>7</sup> and faceted particle.<sup>8</sup> In contrast, the nanosize or near nanosize MCM-48 has not been reported. It is well-known that the nanomaterial has some novel properties that differ from the bulk material. These unique properties are of considerable importance in the development of advanced quantum-confined electronic and optoelectronic devices such as laser, switches, transistor, and information storage processes.<sup>9</sup> At present, some reports<sup>10,11</sup> dealing with the nanostructure zeolites have appeared. However, similar reports of PMS are very few.<sup>12</sup> Here, we first report the synthesis of the nanosize MCM-48 (the uniform particle size of 125 nm). The structure characterization and the thermal stability of this material were also studied. It is worth mentioning that this nanosize MCM-48 shows excellent thermal stability that can retain its cubic structure even after calcination at 1000 °C in air for 2 h.

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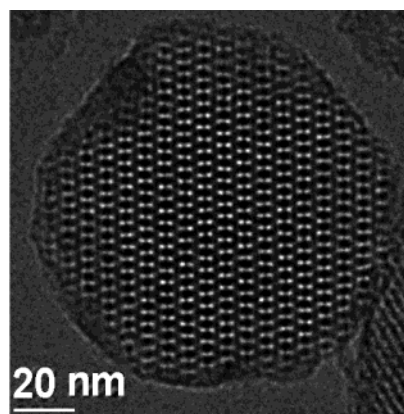


Figure 1. TEM image of MCM-48 taken in the [311] direction.

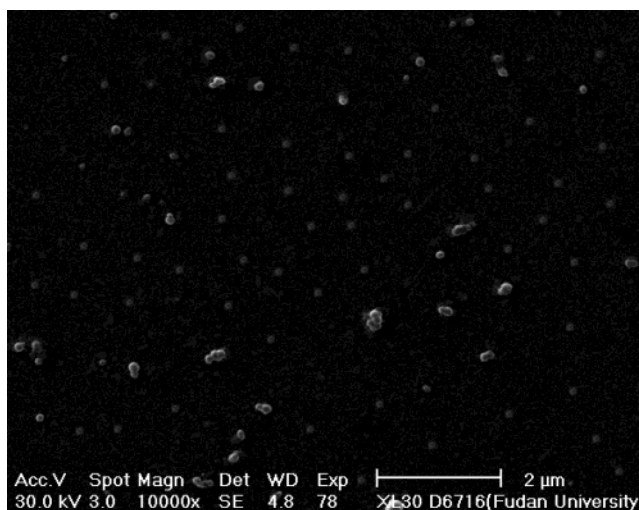
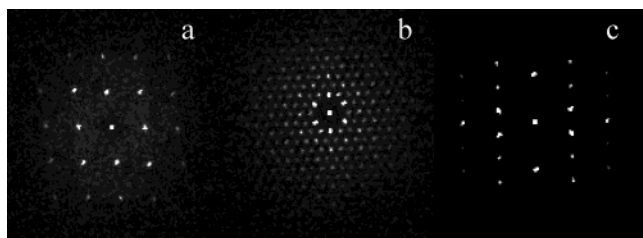


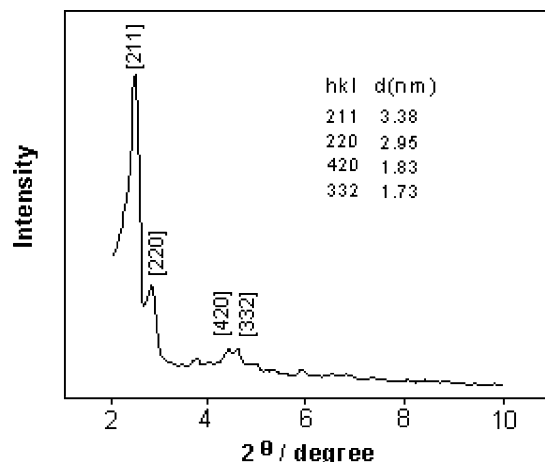
Figure 2. SEM image of MCM-48 sample.

In a typical synthesis of nanosize MCM-48, the aqueous solution of water glass ( $\text{Na}_2\text{O}:\text{SiO}_2$  7.4:25.4%) was dropwise added under constant stirring to the mixed solution of poly(ethylene glycol) monooctylphenyl ether (OP-10) and cetyltrimethylammonium bromide (CTAB). This solution was then stirred at 30 °C for 1 h. The molar composition of the resultant mixture was 1.0:  $x:y:0.282:58$   $\text{SiO}_2:\text{CTAB}:\text{OP-10}:\text{Na}_2\text{O}:\text{H}_2\text{O}$ , where  $x$  is 0.12–0.16 and  $y$  is 0.02–0.04. After that, this mixture was placed in a static autoclave at 100 °C for 2 days. The product was recovered by filtration, washed with distilled water, and dried at 80 °C. Then, this material was calcined in air at 650 °C for 5 h and then in air at 800 °C for 1 h; a heating rate of approximately 15 °C  $\text{min}^{-1}$  was applied. For the thermal stability study, 0.5 g of solid product was calcined in air at 1000 °C for 2 h in a quartz tube.

The high-resolution transmission electron microscopy (HRTEM) images (Figure 1) and the scanning electron microscopy (SEM) images (Figure 2) reveal that the sample is composed of relatively uniform particles both in size (ca. 120–150 nm) and shape (faceted octahedral). The electron diffraction (ED) pattern, where 110, 111, and 311 reflections were observed (Figure 3) and the power X-ray diffraction (XRD) pattern (Figure 4) confirm that the sample is high-quality MCM-48 silica with

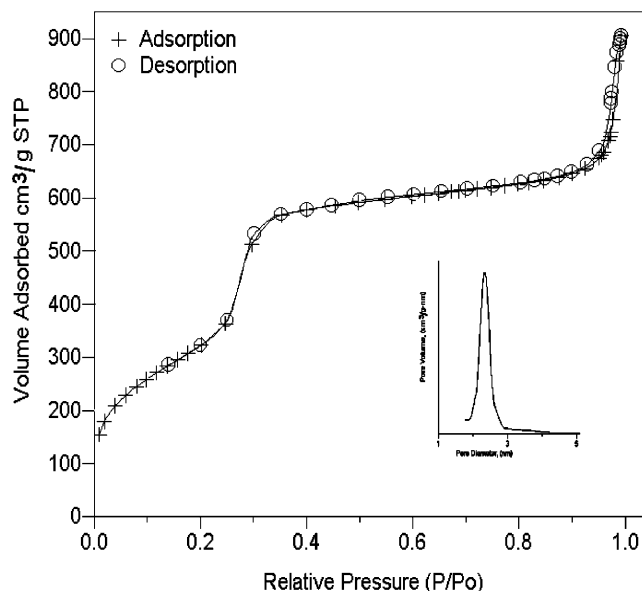


**Figure 3.** ED patterns for MCM-48 along [110] (a), along [111] (b), and along [311] (c).

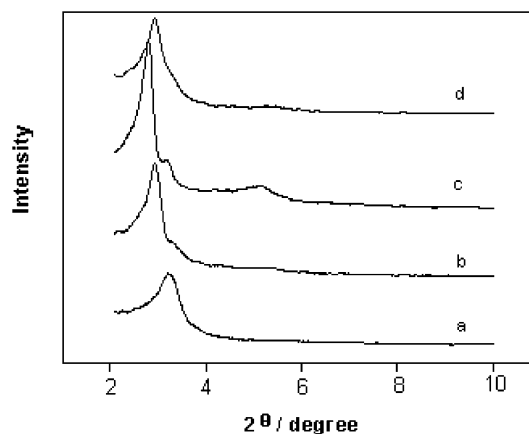


**Figure 4.** Powder XRD pattern of MCM-48 sample.

the cubic  $Ia3d$  space group. The reason for the forming of the nanosize MCM-48 in this system can be tentatively explained as follows: (1) The polar end of nonionic surfactant  $t\text{-C}_8\text{H}_{17}\text{-C}_6\text{H}_4\text{-O-(CH}_2\text{CH}_2\text{O)}_{10}\text{H}$  (OP-10) is a clumsy polymer, which can combine with the micelle of cationic  $\text{CTA}^+$  through hydrogen bonding, so the effective headgroup area ( $a_0$ ) of the polar headgroup of the  $\text{CTA}^+$  cationic will be decreased. (2) As the reason that the hydrogen bonding between the OP-10 and the polar headgroups of  $\text{CTA}^+$  micelle is weaker than the electrostatic attraction between anion and cation and the another reason that OP-10 (whose hydrophobic chain contains benzene ring with  $\pi$  electron) has more powerful dispersion force than the straight chain paraffin, OP-10 thus will not be subjected to the binding of strong electrostatic attraction and its hydrophobic chain can combine with the hydrophobic chain of  $\text{CTA}^+$  micelle by strong van der Waals forces; then it will probably stretch into the void of the  $\text{CTA}^+$  micelle rather than only stay in the palisade region (the border area between the hydrophobic and hydrophilic portion of the micelle). As a result, the local effective surfactant packing parameters  $g^{43}$  ( $g = V/a_0l$ ) will increase and the silicate anions at the interface of the inorganic/organic phase are well-dispersed; then the cubic ( $Ia3d$ ) mesophase and the nanosize particles are likely to form in this system. The regular morphological nature of the particles that tends to be faceted octahedral is a result of excellent organization of the wall structure in the MCM-48 right across the particles and the cubic mesophase is the predominant phase in the system, which can also be seen in the nitrogen adsorption-desorption isotherm and BJH pore size distribution (calculated



**Figure 5.**  $\text{N}_2$  adsorption and desorption isotherm and the pore-size distribution (inset) for MCM-48 sample.



**Figure 6.** XRD patterns of different samples after calcination of 1000 °C for 2 h. (a) Sample calcined in air at 550 °C for 5 h. (b) Sample calcined in air at 650 °C for 5 h. (c) Sample calcined in air at 650 °C for 5 h and then in air at 800 °C for 1 h. (d) Sample calcined in air at 750 °C for 5 h.

from the adsorption isotherm) for this sample (Figure 5). The nitrogen adsorption isotherm of type IV,<sup>14</sup> with a sharp nitrogen condensation step at  $P/P_0 = 0.25\text{--}0.35$  and the extremely narrow pore size distribution with a maximum at ca. 2.35 nm and a width at half-height of only 2.94 Å clearly indicate that the material has a high-order pore system. Especially, the pore volume of this sample is  $1.40\text{ cm}^3\text{g}^{-1}$ , which is almost the highest value, to our knowledge, compared to that of similar other mesoporous materials. When this sample was calcined at 1000 °C in air for 2 h, it still can retain its cubic structure, although its pore diameter is in contrast to the 1.75 nm and its nitrogen adsorption-desorption isotherm is similar to type I isotherm characteristic for microporous materials (see Supporting Information). This result corresponds well to the result of mesoporous zirconium oxophosphate with the pore size in the upper

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micropore range or lower mesopore range.<sup>15</sup> On the basis of the above data and in reference to the TEM images, we further conjecture that the wall thickness of this sample may be very uniform; thus, the framework can equally disperse the distorted strain caused by the thermal disposed procedure. In addition, the special high-temperature calcination method originated from the results of Huo et al.,<sup>16</sup> from which they found that high-temperature calcination can increase the hydrothermal stability of the MCM-41 materials. From our results (Figure 6), one can see as the calcination temperature increase, the thermal stability increases also. However, if the calcination temperature is much higher ( $\geq 750$  °C), the burning off of the decomposition products of CTAB will be intensified; so the forming of coke and the faults of structure will be unavoidable, and then the thermal stability will be decreased. These similar results suggest to us that high-temperature calcination will be an effective path for improving the

thermal and hydrothermal stability of mesoporous material.

In the end, we believe that this novel material will have bright application prospects in the area of nano-reactors and microelectronics.

**Acknowledgment.** This work was supported by the National Natural Science Foundation of China (NSFC, Grant No: 29733070).

**Supporting Information Available:** TEM images of MCM-48 taken in the [110] and [111] directions, scheme of a possible self-assemble procedure for this synthesis system, powder XRD patterns of MCM-48 samples, and N<sub>2</sub> adsorption and desorption isotherms and the pore-size distribution for thermal disposed MCM-48 sample (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

#### Note Added after ASAP Posting

This communication was released ASAP on 10/10/2003 with a minor error in Figure 4. The correct version was posted on 10/XX/2003.

CM034570K

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