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# Synthesis of mesoporous MCM-48 using fumed silica and mixed surfactants

Fen-Yan Wei [b,c], Zhong-Wen Liu [a,b,*], Jian Lu [b], Zhao-Tie Liu [a,b]

[a] *Key Laboratory of Applied Surface and Colloid Chemistry, Shaanxi Normal University, Ministry of Education, Xi'an 710062, China*
[b] *School of Chemistry and Materials Science, Shaanxi Normal University, Xi'an 710062, China*
[c] *Department of Chemistry and Chemical Engineering, Baoji University of Arts and Sciences, Baoji, Shaanxi 721007, China*

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ABSTRACT

With mixed surfactants of cetyltrimethylammonium bromide (CTAB) and Triton X-100 (TX-100) as template agents and fumed silica as a silica source, mesoporous molecular sieves MCM-48 were hydrothermally synthesized under various conditions. Results indicate that high-quality MCM-48 was successfully prepared by substituting fumed silica for the traditional silica source of tetraethylorthosilicate. The effects of synthesis parameters such as quantity and composition of template agent(s), crystallization temperature, crystallization time, and the solution temperature to which fumed silica being added on the structure, morphology, relative degree of crystallization, and thermal stability of the resultant material were quantitatively investigated based on the analyses of XRD, $N_2$ sorption/desorption, and SEM. The optimized conditions for a high-quality MCM-48 were crystallization time of 60–84 h, crystallization temperature of 100 °C, and $n$(TX-100)/$n$(CTAB) of 0.2. Moreover, it was found, for the first time, that the solution temperature to which fumed silica being added plays an important role for the synthesis of MCM-48, and $n$(TX-100)/$n$(CTAB) ratio is crucial for the formation of pure MCM-48 structure.

## 1. Introduction

Inorganic porous materials have been used extensively in the area of catalysis and separation for their high specific surface area and high adsorption capacity. Since the introduction of the M41S mesoporous molecular sieves by Mobil scientists in 1992 [1,2], synthesis, characterization, and potential applications of these structure-ordered materials have been the subjects of progressive research growth [3–27]. The main members of the M41S family are MCM-41, MCM-48 and MCM-50, which have hexagonal, cubic, and unstable lamellar structures, respectively, although some other forms have also been reported [5–7]. In the M41S family, MCM-48 is widely concerned for its characteristics of three-dimensional double-helix channel structure, favorable long-range order, along with high thermal stability. Compared to MCM-41 and SBA-15 with one-dimensional channel structure, MCM-48 may be a more potent candidate as adsorbent, catalyst support, and template for the synthesis of the advanced nanostructure because that its cubic structure can provide three-dimensional channels and the pores can hardly be blocked by host molecules. Thus, a promising prospect of wide applications will be reasonably expected.

Compared to other mesoporous materials, the conditions for the synthesis of MCM-48 are more severe, i.e., using high-purity materials, a great deal of surfactants, and strong alkali condition for crystallization. Moreover, the synthesis conditions must be strictly controlled for high-purity MCM-48 because that minor variances of the synthesis factors such as silica source, temperature, alkalinity, reactant ratio and so on may have great effects on the resultant material. Thus, under the similar reaction system, MCM-41 mesoporous molecular sieve may be synthesized and even products with greatly different property may be obtained [8–10]. Some investigations have been carried out in an attempt to figure out the synthesis conditions and formation mechanism of MCM-48 materials. It has firstly been believed that a high molar ratio of surfactant/Si and a high concentration of surfactant are the prerequisite conditions for making MCM-48 [1,11]. Later, MCM-48 synthesized with much less amount of surfactant has been reported [9]. Recently, there are some reports dealing with the effects of synthetic conditions, such as surfactant/Si ratio, pH value, composition, and the utilization of cosolvents, etc. on the self-assemble behavior of MCM-48 [9,10,12–17]. But in these reports, a single surfactant as template or tetraethylorthosilicate (TEOS) as silica source is exclusively used for the synthesis of MCM-48. Moreover, systematic investigations on the effect of composite surfactants and the replacement of organic silica with inorganic silica on the synthesis of high-purity MCM-48 are very scarce in the published literatures [18–20].

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[*] Corresponding author. Address: Key Laboratory of Applied Surface and Colloid Chemistry, Shaanxi Normal University, Ministry of Education, Xi'an 710062, China. Tel./fax: +86 29 85303200.
*E-mail address:* zwliu@snnu.edu.cn (Z.-W. Liu).

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In the present paper, the combination of cetyltrimethylammonium bromide (CTAB) and Triton X-100 (TX-100) as a template and industrial fumed silica (FS) as silica source were used to synthesize high-quality MCM-48. The effects of the synthesis parameters such as the temperature of solution to which silica source being added, crystallization temperature, time, and the amount of TX-100 on the synthesis of molecular sieves were fully investigated and discussed. It was found that the high-quality MCM-48 can be successfully synthesized with FS, and the *n*(TX-100) to *n*(CTAB) ratio is a key parameter for the synthesis of high-purity MCM-48. Moreover, we report for the first time on the important effect of the temperature of solution to which silica source being added on the formation of MCM-48, and the reason is tentatively explained.

## 2. Experimental

### 2.1. Materials

The tetraethylorthosilicate (TEOS) and cetyltrimethylammonium bromide (CTAB) were purchased from the Tianjin Kermel Chemical Reagents Development Center. The nonionic surfactant Trition X-100 (TX-100) was obtained from Beijing Dingguo Biochemical Technology Co., Ltd. The sodium hydroxide (NaOH) was purchased from Xi'an Chemicals Co., Ltd. All chemicals were in AR grades, and used without any further purification. The industrial-grade fumed silica was used directly as a silica source. The EDAX analysis revealed that potassium and aluminium are the main impurities (less than 0.5 wt.%).

### 2.2. Experimental procedure

MCM-48 was synthesized by using CTAB and TX-100 as the template and FS as a silica source with the molar ratio of 1.0 FS:0.468 NaOH:*x* CTAB:*y* TX-100:54.7 $H_2O$, where $0.12 \leqslant x \leqslant 0.139$, $0.160 \leqslant y \leqslant 0.267$. Typically, 1.4 g sodium hydroxide, 3.6 g CTAB, and 0.36 g TX-100 were dissolved in 74 g deionized water, and the mixtures were vigorously stirred at 36 °C for 4 h. After the mixtures were cooled to the stated temperature, FS was added to this solution, and stirred for 0.5 h to give a white gel. Then, the gels were transferred into a PTFE-lined stainless steel autoclave, and the temperature was raised to 90–120 °C for aging under static conditions for a certain period of time. A white precipitate was recovered by filtration and washed extensively with deionized water. After drying at 120 °C for 12 h, the sample was calcined in a flowing air at 540 °C for 6 h to yield MCM-48. For the comparison purpose, in several cases, MCM-48 was prepared by substituting TEOS for FS while keeping the remaining conditions the same.

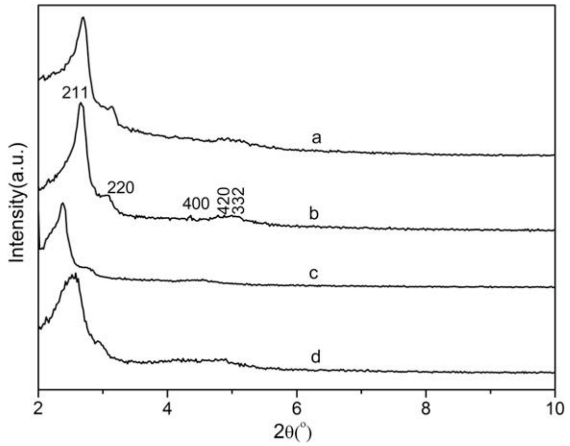

**Fig. 1.** The XRD patterns of MCM-48 samples (the synthesis conditions are listed in Table 1).

### 2.3. Characterization

The X-ray powder diffraction (XRD) measurements of samples were carried out on a Rigaku D/Max-3c X-ray diffractometer with a Cu*Kα* radiation and operated at 40 kV, 50 mA. The XRD patterns were recorded at $2\theta$ from 2° to10° with a step size of 1°/min.

$N_2$ adsorption–desorption isotherms were measured on an AutoChem 2920/ASAP 2020 M analyzer at 77 K. Surface areas were calculated using the BET equation and pore size distributions were obtained using the Barrett–Joyner–Halenda (BJH) method.

For SEM analysis, the samples were shadowed with gold, and then the surface microtopographies were examined with a Philips-FEI Model Quanta 2000 Field Emission Scanning Electron Microscopy (FESEM).

### 2.4. Thermal stability test

To test its thermal stability, the synthesized MCM-48 sample was heated to 700 °C at a temperature rate of 2 °C/min, and kept at 700 °C for 5 h.

## 3. Result and discussion

### 3.1. The effects of silica source

MCM-48 mesoporous molecular sieves were synthesized using TEOS or FS as silicon source, and mixed surfactants of CTAB and TX-100 as template. The XRD patterns (Fig. 1) for the prepared mesoporous silica showed three peaks at $2\theta = 2.5°$, 3.1°, and 4.9°, respectively. These peaks were indexed as (2 1 1), (2 2 0), and (3 3 2) crystal facets, which belong to a bicontinuous $Ia\overline{3}d$ cubic space group. According to the formula of $a_0 = (h^2 + k^2 + l^2)^{1/2} d_{211}$ [21], the unit cell $a_0$ of cubic system was calculated and listed in Table 1. The results show that MCM-48 mesoporous molecular sieve was obtained no matter TEOS or FS was used. Moreover, by changing the silica source from TEOS to FS while keeping the remaining synthesis conditions the same, the relative crystallinity (the peak intensity of 211 facet of the sample relative to that of

**Table 1**
The textural properties of MCM-48 synthesized under different conditions[a].

| Samples | *n*(CTAB)/ *n*(Si) | *n*(Tx-100)/ *n*(Si) | *n*(Total template)/ *n*(Si) | Silica source | Unit cell $a_0$ (nm) | Pore size *D* (nm) | Crystallinity $\phi$ (%) | $S_{BET}$ ($m^2/g$) | Pore volume ($cm^3/g$) |
|---|---|---|---|---|---|---|---|---|---|
| a | 0.139 | 0.028 | 0.167 | TEOS | 8.846 | 2.624 | 108 | 1014 | 0.94 |
| b | 0.139 | 0.028 | 0.167 | FS | 8.865 | 2.639 | 100 | 999 | 0.93 |
| c | 0.120 | 0.028 | 0.148 | TEOS | 8.741 | 2.451 | 64.4 | 618 | 0.70 |
| d | 0.120 | 0.028 | 0.148 | FS | 8.538 | 2.582 | 68.1 | 570 | 0.78 |
| S1 | 0.415 | 0 | 0.415 | FS | 7.890 | 2.673 | 87 | 1102 | 0.86 |

[a] Reaction conditions: samples a, c and S1: 1.0 TEOS:0.468 NaOH:*x* CTAB:*y* TX-100:54.7 $H_2O$ at 110 °C for 3 days. Samples b and d: 1.0FS:0.468 NaOH:*x* CTAB:0.028 TX-100:54.7 $H_2O$ at 100 °C for 3 days.