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Synthesis of MCM-48 with a high thermal and hydro-thermal stability

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Abstract

High thermal and hydro-thermal stable MCM-48 was synthesized by a mixed nonionic–cationic surfactant templating pathway. The sample retains its cubic structure when at 1000 $^{\circ}$ C for 2 h and when calcined in air with 100% water vapor at 600 $^{\circ}$ C for 2 h.

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1. Introduction

Recently, mesoporous molecular sieves designated M41s have attracted much attention because of their possible uses as supports for catalysts, a host for nanosize materials, and other applications such as in chromatographic separation and membrane-based gas separation [1–3]. MCM-48, one member of these new materials contains two independent three-dimensional pore systems, which are interwoven and situated in a mirror-plane position to each other [4]. This special pore system provides favorable mass transfer kinetics in catalytic and separation applications than MCM-41 with a one-dimensional hexagonal directional pore system. However, both the critical synthesis condition and the disappointing hydro-thermal stability restrained the advantage of MCM-48 greatly. Although there are some reports of the improvement of the hydro-thermal stability of MCM-48 [5,6], but these methods make the synthesis procedure more complex and only study the hydro-thermal stability of MCM-48 in boiling water. In this paper, we introduced a simple and convenient method to synthesize the high quality MCM-48 and studied the thermal and hydro-thermal stability of this sample under the condition near to the industrial

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application. It is noted that the obtained MCM-48 sample can retain its cubic mesoporous structure even after calcination in air at 1000 °C for 2 h. This result has not been reported.

2. Experimental

A typical synthetic procedure is as follows: the aqueous solution of water glass (Na₂O: 7.4%, SiO₂: 25.4%) was drop wise added under constant stirring to the mixed solution of poly(ethyleneglycol) isooctylphenyl ether (Tx-100) and cethyltrimethylammonium bromide (CTAB). This solution was then stirred at 30 °C for 1 h. The molar composition of the resultant mixture was 1.0 SiO₂:xCTAB:yTx-100:0.282 Na₂O:58H₂O, where 0.12 < x < 0.16, 0.02 < y < 0.04 (the molar composition of the blank test is similar to this except leaving off the Tx-100). 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. At last, this material was calcined in air at 650 °C for 5 h followed by in air at 800 °C for another short time (designated as MCM-48 (o)). For the thermal and hydro-thermal stability studies, 0.5 g MCM-48 (o) was calcined in air at 1000 °C for 2 h (designated as MCM-48 (h)) in a quartz tube.

3. Results and discussion

The powder X-ray diffraction patterns of the resultant materials corresponded well to those reported for purely siliceous MCM-48 [7]. As shown in Fig. 1, the (420), (332) diffraction line are well resolved in the case of MCM-48 (o) sample. In the TEM image of this sample (Fig. 2), the channel like appearance in the [1 1 0] direction looks very orderly. These facts indicate that MCM-48 (o) has excellent textural uniformity. Both MCM-48 (t) and MCM-48 (h) still exhibited two obvious peaks (2 1 1 and 2 2 0) at



Fig. 1. XRD patterns of (a) MCM-48 (o), (b) MCM-48 (h), and (c) MCM-48 (t).



Fig. 2. HRTEM image of MCM-48 (o) on the (1 1 0) cubic plane.

d = 31.9, 28.5 Å and two weak peaks (420 and 332) at d = 18.0, 17.3 Å. It means that these two samples also keep the textural uniformity of cubic (Ia3d) structure even following the critical disposal of thermal and hydro-thermal, although the long-range structure order of them are somewhat decreased. All of above show that the textural uniformity, thermal stability and hydro-thermal stability of MCM-48 have been improved markedly by the improved synthesis route of mixed cationic and nonionic surfactant and the novel calcinations method.

The N₂ adsorption-desorption isotherms and the corresponding BJH pore size distributions based on the desorption branch for the MCM-48 samples are shown in Fig. 4. All of the isotherms are typical irreversible IV adsorption isotherm with two separate H1 and H4 hysteresis loops as defined by IUPAC [8]. The first well-defined step in the adsorption curve between partial p/p_0 of 0.2 and 0.35 is indicative of the filling of framework-confined mesoporous. The second condensation step on the isotherm between p/ $p_0 = 0.4$ and 1.0 exhibits a substantial hysteresis loop which may be due to the inter particle capillary condensation. Both H1 hysteresis loops of the disposed MCM-48 samples shift toward low p/p_0 slightly. And among them, the hysteresis loop of the MCM-48 (t) not only shifts further toward low p/p_0 , but also looked smoother than that of the MCM-48 (h). It suggests the pore structure of MCM-48 (t) was damaged more seriously than that of MCM-48 (h), although their X-ray diffraction patterns are similar. This is in good agreement with the TEM results (Fig. 3) and the distribution of pore diameter of these two samples (Table 1). In the wide range, both the TEM images of MCM-48 (t) and MCM-48 (h) keep their order of the channel, so their X-ray diffraction patterns are similar. While in the narrow range, some pores of MCM-48 (t) are damaged more seriously than that of MCM-48 (h) (arrow shows in Fig. 3). As a result, the FWHM of MCM-48 (t) is wider than that of MCM-48 (h), while the BET and pore volume of MCM-48 (t) decrease sharply. In addition, the H4 hysteresis loop of MCM-48 (t) (Fig. 4) is larger than that of the MCM-48 (h). This suggests that the large inter-particle pores of MCM-48 (t) may be damaged. This change may also partly contribute to the decrease of BET and pore volume of MCM-48 (t) sample.



Fig. 3. HRTEM image of MCM-48 (h) (a) and MCM-48 (t) (b) on the (1 1 0) cubic plane.

The excellent hydro-thermal and thermal stability of the obtained MCM-48 sample may be due to three factors: (1) the amount of CTA⁺ cationic is much lower in the mother liquor (CTAB/SiO₂ = 0.15), so, the number of compensation anionic (the silicate species) will decrease in order to keep the electric charge balance. Then, the rearrangement and polymerization of the silicate species themselves proceed further. As a result, the formation of highly connected silicate polyanions is achieved (the ratio of Q^4/Q^3 is 3.31, where Q^4 corresponds to the Si(SiO)₄ units; Q^3 corresponds to the (SiO)₃–SiOH units). (2) As a small amount of Tx-100 in the as-synthesized MCM-48 is advantageous for the Hoffman elimination and combustion of CTAB at low temperature (see next discussion); so, upon calcination, the defects of the structure, which seem to induce the collapse of the framework at high temperature and easy to be attacked by water molecules in hot water, will decrease. Fig. 5 is the DTG spectra of the as-synthesized MCM-48 (bottom) and the blank sample (top). For the spectra of as-synthesized MCM-48, the peak b can be assigned to the Hoffmann elimination (giving C₁₆H₃₂ and (CH₃)₃N) and subsequent trimethylamine desorption; the peak c can be assigned to the desorption and subsequent oxidization of hexadecane and its decomposition products; and the peak d probably can be assigned to the water loss relating to the Tx-100 and the condensation of silanol group. Compared to the blank sample (without Tx-100), both the peak b

Sample Unit cell BET surface Pore volume Pore size (Å)	
parameter $(\text{\AA})^{\text{b}}$ area $(\text{m}^2 \text{g}^{-1})$ $(\text{cm}^3 \text{g}^{-1})$	FWHM (Å) ^c
MCM-48 ^a 83.1 1.40 24.3	5.1
MCM-48 (o) 82.8 1148.7 1.37 23.5	3.5
MCM-48 (h) 78.3 (5.4%) 1037.8 1.16 21.2	4.7
MCM-48 (t) 78.3 (5.4%) 762.8 0.68 20.9	5.3

Physical characteristics of MCM-48 samples under investigation

 $^{\rm a}$ MCM-48 sample that can only be calcined in air at 650 $^{\circ}{\rm C}$ for 5 h.

^b The values in parentheses are the lattice contraction upon disposal with respect to the MCM-48 (o).

^c The full-widths at half-maximum for the pore size distribution curves.

Table 1



Fig. 4. N₂ adsorption-desorption isotherms and pore size distribution of (a) MCM-48 (o), (b) MCM-48 (h), and (c) MCM-48 (t).

and c of the as-synthesized MCM-48 shift toward the low temperature region. This can be explained as follows: the hydrogen bond between the CTA^+ and Tx-100 can weaken the static interaction between CTA^+ and the initially solidified mesoporous silica wall with the negative charge, and then cause the thermal desorption or decomposition of CTA^+ easily. Further, the O atom of Tx-100 can decrease the formation of coke, and then, favor the burning off the decomposition products of CTA^+ at low temperature. 3. Since the FWHM of MCM-48* (sample only calcined in air at 650 °C for 5 h, see Table 1) is 5.1 Å which is 1.6 Å wider than that of MCM-48 (o), we believe that the calcination procedure



Fig. 5. DTG spectra of the as-synthesized MCM-48 (bottom) and the blank sample (top).

at 800 °C probably can cause a local reconstruction process of the framework which can optimize the pore structure of MCM-48.

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References

- [1] R. Ryoo, S. Jun, J. Phys. Chem. B 101 (1997) 317.
- [2] X.S. Zhao, G.Q. Lu, A.K. Whittaker, G.J. Millar, H.Y. Zhu, J. Phys. Chem. B 101 (1997) 6525.
- [3] K. Moller, T. Bein, Chem. Mater. 10 (1998) 2950.
- [4] H. Kosslick, G. Lischke, H. Landmesser, B. Parlitz, W. Storek, R. Fricke, J. Catal. 176 (1998) 102.
- [5] J. Xu, Z. Luan, H. He, W. Zhou, L. Kevan, Chem. Mater. 10 (1998) 3690.
- [6] R. Ryoo, S.H. Joo, J.M. Kim, J. Phys. Chem. B 103 (1999) 7435.
- [7] F. Chen, L. Huang, Q. Li, Chem. Mater. 9 (1997) 2685.
- [8] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscon, R.A. Pierotti, J. Rouquerol, T. Siemieniewska, Pure Appl. Chem. 57 (1985) 603.

1780