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The synthesis of MCM-48 with high yields

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Abstract

Using tetraethyl orthosilicate as a silica source and cetyltrimethylammonium bromide as a template, MCM-48 mesoporous molecular sieves were synthesized with hydrothermal methods. Reducing the pH of the solution during synthesis improved the yield of MCM-48 and enhanced its stability. While the pH was adjusted to 5, a high yield of 98% was gained. XRD and N_2 adsorption–desorption isotherms were used to characterize the synthesized samples. These mesoporous molecular sieves showed high specific surface areas and ordered channel systems. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: A. Nanostructures; B. Chemical synthesis

1. Introduction

MCM-48 is a member of M41S mesoporous silicas. It has recently attracted much attention for its three-dimensional mesoporous channel systems, which can be used as a prospective catalyst, an adsorbent, and even a template for the synthesis of nanostructures. A lot of work has been done in the synthesis of pure silica MCM-48 [1–4] and the incorporation of its framework with various heteroatoms [5–7]. MCM-48 was usually synthesized using cationic surfactants as supramolecular template materials. Cationic-neutral or cationic-anionic surfactants were also used as its structure-directing agent [1,8]. With almost no exception, MCM-48 was prepared in basic solution, and its yields were usually low. The product yield was only ca. 50% using cetyltrimethylammonium bromide (CTAB) as a single surfactant [9]. Ryoo gained a yield of ca. 80% using cationic-neutral surfactant

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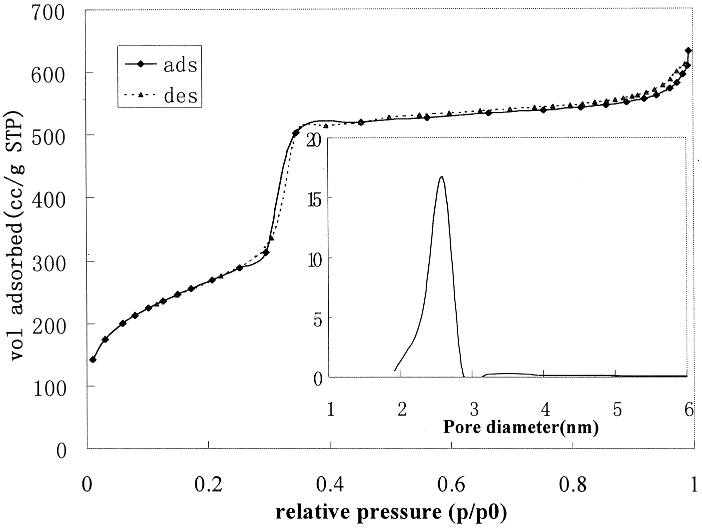

Fig. 1. N_2 adsorption–desorption isotherms and pore size distribution of the sample M2.

mixture and adjusting the pH of the reaction mixture to 10 during synthesis [3]. It is important to identify procedures suitable for a cost-efficient synthesis of MCM-48 with high yields. Herein, by adjusting the pH of the solution in a synthesis process, a high product yield of 98% was gained using CTAB as a surfactant.

2. Experimental

Sodium hydroxide and CTAB were dissolved in deionized water, and tetraethyl orthosilicate (TEOS) was added into it. The molar composition of the gel was TEOS/0.48 NaOH/0.48 CTAB/55 H_2O. The solution was stirred for about 1 h and then transferred into a Teflon bottle and heated up to 373 K. After 3 days the solution was cooled to room temperature and its pH was adjusted by adding HCl. Then it was heated at 373 K for 1 to 3 days. The product was filtered, washed, and dried in air at ambient temperature. The dried product was finally calcined at 823 K for 6 h. The obtained samples were characterized by XRD, which was performed using a D/max-rA X-Ray Diffractometer, and nitrogen adsorption, which was performed using ASAP2000M Accelerated Surface Area and Porosimetry at 77 K.

3. Results and discussion

When the pH of the solution was adjusted to 5–9 during synthesis, MCM-48 could be synthesized. But amorphous silica was gained when the pH was adjusted to 3.

The N_2 adsorption–desorption isotherm of a typical MCM-48 (the sample M2) synthesized by pH adjustment is shown in Fig. 1, which gives a BET surface area of 921 m^2/g and

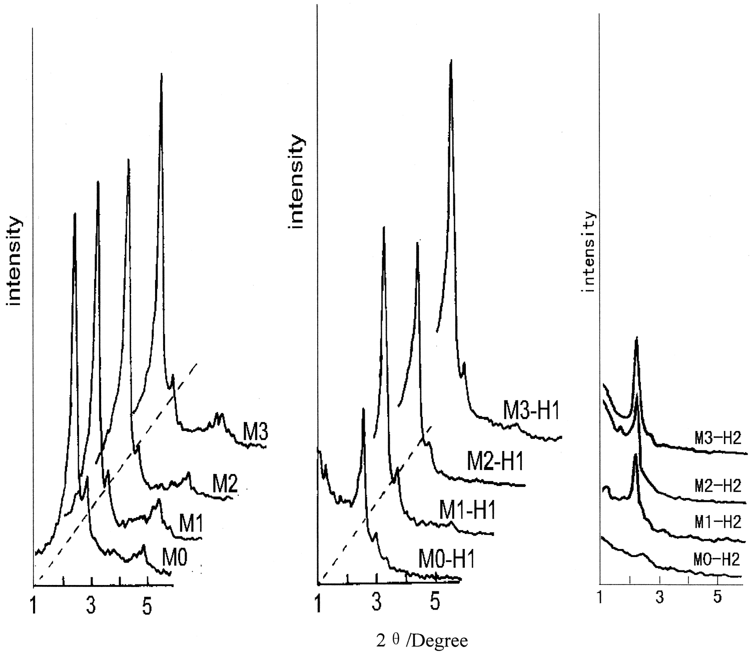

Fig. 2. XRD pattersn of MCM-48 (H1-heated in boiling water for 8 h; H2 for 16 h).

shows a pore size of 2.6 nm (BJH model). A sharp increase in the volume of N_2 adsorbed is observed at a relative pressure of $p/p_0 = 0.3–0.4$. The XRD patterns in Fig. 2 indicate excellent structure order for the products.

Adjusting the pH to a relatively low value drastically improved the yields of the synthesized molecular sieves (see Table 1). A product yield as high as 98% was gained when the pH was adjusted to 5; however, the yield of MCM-48 was not more than 60% before the pH adjustment (pH = 12), which was consistent with literature [10]. The stability of MCM-48 was also enhanced. After heating in boiling water for 8 h, the structure of the sample M0 was damaged more apparently than that of M1, M2, and M3; for 16 h, the mesostructure of the sample M0 collapsed thoroughly, but that of M1, M2, and M3 still remained (see Fig. 2).

Table 1
The synthesis conditions and characteristics of MCM-48

Sample	pH adjusted	t**/day	Yield/%	d_{211}/nm		Unit cell a_0/nm
				As-synthesized	Calcined	
M0	no	0	58	4.08	3.50	8.57
M1	7	1	95	4.09	4.02	9.85
M2	7	2	97	4.09	3.98	9.75
M3	7	3	96	4.10	3.98	9.75
M4	9	2	85	4.10	4.02	9.85
M5	5	2	98		3.82	9.36
M6	3	2	amorphous			

t**: the time heated for after pH adjustment.

In the solution, anionic silicate species associated at the micelle interface and then polymerized into extended framework that led to the formation of mesoporous structure. When a part of anionic silicate species dissolved in strong basic solution, the yield of the synthesized material was low. When the pH was reduced, the dissolved silicate would aggregate, and might further condense with the hydroxyl on the wall surface, then the yield of synthesized MCM-48 increased and its wall became thicker, so the unit cell shrunk less during calcination, which could be seen in Table 1. MCM-48 became more stable because of the thicker wall. When the pH was reduced to 3, in moderate acid solution, a part of surfactant cations would go out of the channel of MCM-48 and the mesoporous structure was destroyed because of its low hydrothermal stability, so amorphous silica was gained.

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