

Preparation of spherical large-particle MCM-41 with a broad particle-size distribution by a modified pseudomorphic transformation

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ABSTRACT

Large-particle MCM-41 with spherical morphology and broad particle-size distribution was synthesized using a modified pseudomorphic transformation. The MCM-41 sample exhibited well-defined mesophase porosity characterized by X-ray diffraction (XRD), nitrogen physisorption, and transmission electron microscopy (TEM). Broad particle-size distribution of parent silica presented a great challenge during the synthesis because small particles may suffer grain fragmentation, whereas large ones were unchanged. In order to maintain the spherical shape of the parent silica particles with broad particle-size distribution, over-hydrolysis of silica source had to be avoided with optimized preparation time, moderately basic synthesis condition, and introducing an appropriate amount of 3-(2-aminoethyl aminopropyl) trimethoxysilane (ATMS). The ATMS had significant effect on preserving the morphology of the parent silica particles characterized by field emission scanning electron microscopy (FESEM) and particle-size analyzer, the optimal molar ratio ATMS/SiO₂ = 0.1 was required in this study for obtaining the perfectly spherical shape and well-ordered mesostructure. Solid state ²⁹Si NMR confirmed that the incorporation of ATMS did not affect the silanol group condensation during synthesis.

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1. Introduction

Significant research on mesoporous silicas has occurred since the discovery of M41s type materials in 1992 [1,2]. The synthesis of MCM-41, one of the most popular mesoporous molecular sieves in the family of M41S, has attracted more awareness because of its high thermal and hydrothermal stability, narrow pore size distribution with size controllable pores, and uniform shape of the pores over micrometer length scales. Many potential applications of MCM-41 required controlled nanoporous structures and macroscopic morphologies, therefore, exploring the novel formulation to produce morphology and particle-size controlled mesoporous silicas was the critical step to achieve their extensive applications of MCM-41 material [3,4]. Many groups have dedicated to the simultaneous and independent control of both textural and morphological properties of MCM-41 by tuning the evolution of mesoporous structure formation [5–8]. Based on a modified Stöber's method, Unger's group firstly prepared the sub-micrometer-size spherical MCM-41 and successfully applied as stationary phase in HPLC [6]. Subsequently, several research groups have devoted to the synthesis of mesoporous silicas with spherical morphology by tuning their evolution as a function of time and experimental conditions, such as the addition of necessary co-solvent and/or

co-surfactant. However, the main drawback of these approaches was that the particle size of obtained products was usually less than 2 μm and the formation of mesostructure usually took long time (>24 h) [6–8]. Furthermore, the resultant products were aggregates of weakly stacked spherical particles in SEM images [7,8]. As a result, it was still a great challenge to obtain the mono-dispersed spherical particles of mesoporous materials with large-particle size. Martin et al. initially introduced the concept of pseudomorphism to synthesize large particles (more than 5 μm) of silica-based mesoporous materials with controlled spherical morphology [9]. Subsequently, Galarneau et al. reported the synthesis of large-particle MCM-41 with a variety of less expensive parent silica sources, such as Davicat 1700 (spheroid of 50 μm), Fractosil 60 (60 μm) and W432 (800 μm). It offered new opportunities in chromatography applications [10,11]. They have found that the amount of water and sodium hydroxide content are crucial to maintain the particle morphology. However, the silica sources in their method were pre-shaped silica gel with uniform particle-size distribution, they did not explore the feasibility of fabricating spherical MCM-41 samples with pre-shaped silica gel of a broad particle-size distribution.

Besides the large number of applications in biological separation technologies, MCM-41 materials also extended the range of catalytic reaction engineering beyond the micropore domain. It was highly desired to apply the MCM-41 type materials to a fluidized-bed reactor (FBR) because the fluidized-bed reactor could be

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used to carry out a variety of multiphase catalytic reactions. However, conventional MCM-41 materials prepared by hydrothermal approach were not suitable due to the major barrier of their small particle size (less than 1 μm) and low bulk density. Therefore, large-particle mesoporous materials with spherical morphology are demanded. The above-mentioned pseudomorphic transformation method may be an appropriate synthesis approach for large-particle MCM-41 catalyst applications. Nevertheless, a certain degree of particle-size distribution of MCM-41 particles is greatly preferred in order to successfully apply MCM-41 materials in the fluidized-bed reactor because a recent study showed that the fluidization behavior is strongly correlated to the particle-size distributions. The addition of 10% of fine particles decreases the solids holdup in the emulsion phase due to the breakup of large bubbles which dramatically enhances the gas–solid contact [12,13].

In this contribution, applying a modified pseudomorphic transformation, the attempt to synthesize mesoporous MCM-41 using parent silica with a broad particle-size distribution was reported. This modified method was developed by introducing 3-(2-aminoethyl aminopropyl) trimethoxysilane (ATMS) during the MCM-41 synthesis. The spherical morphology and particle-size distribution of parent silica particles were well-retained. The preparation time was shortened to less than 8 h in order to avoid the over-hydrolysis of silica source.

2. Experimental

2.1. Materials

The following materials, pre-shaped silica with a broad particle-size distribution (99.99% SiO_2 , particle size: 20–45 μm , product number: S10020C, Silicycle), cetyltrimethylammonium bromide (CTAB, Sigma–Aldrich), 3-(2-aminoethyl aminopropyl) trimethoxysilane (ATMS, TCI), were used as received without further treatment.

2.2. Synthesis

MCM-41 samples were prepared in a stainless steel autoclave with Teflon liner. The molar composition of reaction mixture was $1\text{SiO}_2:0.1\text{CTAB}:0.25\text{NaOH}:20\text{H}_2\text{O}:x\text{ATMS}$, where x varied from 0 to 0.4. Typically, 1.82 g of CTAB and 0.5 g of NaOH were dissolved in 18 g of H_2O with vigorous magnetic stirring at room temperature for 1 h. After adding the parent silica (particle size: 20–45 μm), the mixture was magnetically mixed for another 30 min under low-shear stirring, and then ATMS was added to the mixture and stirred for 30 min. The resultant mixture was transferred into an autoclave and kept at 388 K for 7 h under static condition. The solid was then filtered, washed with deionized water, and dried at 363 K overnight. The pre-dried solid was heated at a constant rate from room temperature to 813 K over 20 h under He and held for 1 h under the same condition, then the sample was held at 813 K for 5 h in air to remove the residual surfactant.

2.3. Characterization

Powder X-ray diffraction patterns of calcined MCM-41 samples were recorded with a Bruker AXS D8 diffractometer (under ambient conditions) using filtered $\text{Cu-K}\alpha$ radiation. Diffraction data were recorded from 0.5° to 8° (2θ) with a resolution of 0.02° (2θ). Nitrogen adsorption/desorption isotherms were measured at 77 K with a static volumetric instrument Autosorb-6b (Quanta Chrome). Prior to each measurement, the samples were outgassed at 473 K up to a residual pressure below 10^{-4} Torr. A Baratron pressure transducer (0.001–10 Torr) was used for low-pressure measure-

ments. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method [14]. The pore size distributions (PSD) were calculated from desorption isotherm branch using the Barrett–Joyner–Halenda (BJH) method [15]. The BJH method underestimates the PSD, but this mathematical algorithm will not significantly affect the systematic comparison in this study [16]. The FESEM images were obtained with a JEOL Field Emission Scanning Electron Microscope (JSM-6700F-FESEM). Prior to the analysis, the samples were deposited on a sample holder using an adhesive carbon tape and then sputtered with gold. Transmission electron microscopy (TEM) images were obtained on a JEOL 2010, operated at 200 kV. The samples were suspended in ethanol and dried on holey carbon-coated Cu grids. Particle-size distributions were measured on MASTERSIZER 2000 (Malvern Instruments). The given amount of sample was added to anhydrous ethanol and ultrasonicated for 10 min before analysis. The particle-size distributions were also estimated by counting characteristic particles from more than 500 randomly chosen particles in the SEM images. Thermogravimetric (TG) analysis was carried out on a SDT Q600 thermogravimetric analyzer with heating rate of $10^\circ\text{C}/\text{min}$ under air flow of 200 ml/min. About 10 mg of sample was used in each experiment. The ^{29}Si NMR experiments were carried out at frequency of 400 MHz on a Bruker NMR spectrometer. All spectra were measured at room temperature and the magic-angle spinning frequency was set at 5 kHz. Chemical shifts were externally referenced to tetramethylsilane (TMS).

3. Results and discussion

It has been found that it is not applicable to directly employ the pseudomorphic transformation to synthesize spherical silica-based mesoporous materials with broad particle-size distributions. This is mainly due to small-size particles of pre-shaped silica may suffer grain fragmentation, whereas large particles are unchanged. In fact, it has been found that the morphology of resultant product is shattered with the increase of aging time, even when a parent silica with a narrow particle-size distribution is used. As clearly shown by the SEM image displayed in Fig. 1a, right, a substantial amount of fragments exists in the final MCM-41 product after an aging treatment of 24 h. When starting silica material with a broad particle-size distribution is used, a similar fragmentation is observed even though the aging time is reduced to 7 h (Fig. 1b, right). Nevertheless, both samples exhibit four well-resolved X-ray dif-

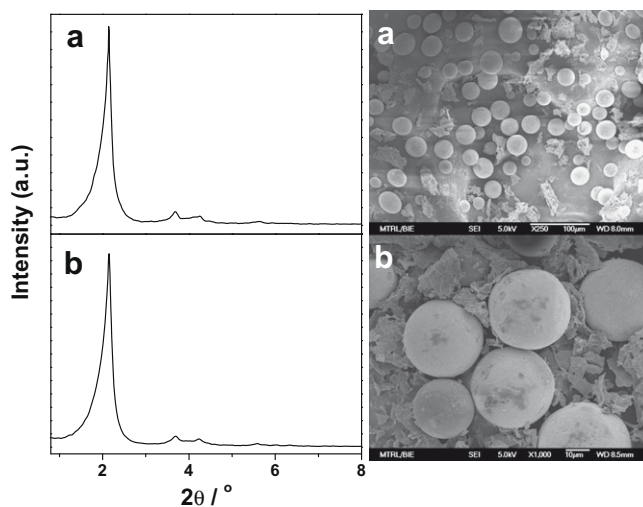


Fig. 1. (a) XRD pattern of the calcined sample (right: SEM image of this sample) with the aged time of 7 h. (b) XRD pattern of the calcined sample (right: SEM image of this sample) with the aged time of 24 h.

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