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Morphology control of the hybrid mesoporous silica by microwave heating

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1. Introduction

Hybrid organic-inorganic mesoporous materials have been attracted much attention because new catalytic and adsorption functions can be assigned to the inorganic mesoporous molecular sieves [1-6]. Recently, hybrid mesoporous materials with organic groups (-CH₂-CH₂-[1], -CH=CH-[2], C₆H₄[4], (C₆H₄)₂[5]) incorporated to their framework was synthesized by many groups. The potential of the mesoporous material as a separate medium was proposed by recent publications [7,8]. The attractive point of the hybrid mesoporous material as a separation medium is that on top of the large surface area, narrow pore size distribution of the M41S type mesoporous material, it has a large fraction of organic component, which can prove useful in controlling hydrophobicity needed for the adsorption of organic molecules.

Synthesis using microwave heating can reduce the synthesis time in comparison with general hydrothermal synthesis in a conventional oven. Its rapid heating rate primarily promotes the nucleation process and crystal growth is also accelerated. Another advantage of microwave heating is uniform morphology of the particles formed as can be expected through equal heating in all areas inside a reactor compared with thermal conduction from external heating source. In this work, hybrid mesoporous material containing ethane groups designated as HMM-3[1] was synthesized at various synthesis time and temperature using microwave heating to produce smaller and uniform particles with spherical morphology to apply as a reverse phase HPLC column.

2. Experimental

2.1 Synthesis of hybrid mesoporous materials by microwave heating

C₁₆TMACl (hexadecyltrimethylammonium chloride) were used as a structure binder and BTME (1,2-bis(trimethoxysilyl)ethane) used as a silicon precursor. Synthesis of hybrid mesoporous material was carried out in molar ratio of 1 BTME: 0.91 surfactant: 2.28 NaOH: 336 H₂O according to Inagaki et al [1]. For the preparation of hybrid mesoporous materials by microwave heating, the precursor was added to the surfactant solution and stirred for 19h at 25 °C. This mixture was transferred to a 200ml Teflon autoclave for microwave heating. At the first stage, the sample was quickly heated to intended temperature in 1min using maximum power of microwave equipment, which was subsequently adjusted to constant half power to maintain isothermal condition. Initially, synthesis of hybrid mesoporous materials were tried at temperature of 95 °C, 115 °C and 135 °C for 4h then tried at a fixed temperature of 115 °C, varying the heating time between 2h and 6h. Precipitates were filtered, washed with distilled water, and dried at room temperature. After refluxing 1g sample of as-synthesized mesoporous material in 3.8g of 37 wt%HCl in 150ml ethanol for 6h at 50°C to remove the surfactant, it was filtered and dried for use. The microwave instrument used was CEM MDS-2100 equipped with a fiber optic temperature probe and pressure controller, which was capable of an adjustable power output.

The crystallinity of samples was measured by X-ray diffraction using Ni-filtered CuK α radiation

(Rigaku model D/Max-3C), and the morphology of the samples was examined by TEM (Jeol model JEM-200CX) and SEM (Hitachi, X-650). It was confirmed that the organic groups are homogeneously distributed in the framework through solid state NMR analysis (Varian Unity INVOA400 model). The specific surface area and average pore diameters were determined by N₂ physisorption at liquid nitrogen temperature using a Micromeritics ASAP 2000 automatic analyzer. The surface area was determined by BET method and the pore size distribution was calculated by the Barrett-Joyner-Halenda (BJH) method using the desorption branch of the isotherm. TGA (Mettler Toledo TGA/SDTA 851) was performed at a heating rate of 10 °C /min up to 1000 °C in a flow of nitrogen.

2.2 HPLC column test

A microcolumn (0.5mm I.D. X 300mm) was packed with the samples and examined for its chromatographic performance in HPLC. C-18 modification of the samples was carried out for reverse phase application. 1g of hybrid mesoporous material, 0.6ml pyridine, and 6ml xylene were put into a small round bottom flask with a reflux condenser and stirred. Subsequently, 0.40g of chlorodimethyloctadecylsilane was added and stirred at 100 °C for 5 h. The product was filtered and washed with toluene, THF, and methanol, and dried. For trimethylsilylation, 1g of the dried product, 0.6ml pyridine, 6ml xylene, and 0.20ml chlorotrimethylsilane were mixed and stirred at 100 °C for 3 h, followed by filtering, washing, and drying as before.

3. Results and Discussion

The XRD pattern of as-synthesized material exhibited a single intense peak at 2θ about 2.0, and its intensity increased significantly after solvent-extraction. Solvent-extracted hybrid mesoporous material had characteristic peak, indicating cubic symmetry similar to mesoporous silica SBA-1 as reported[9], and the d-spacing of the most intense peak(120) is 49.5 Å, which was almost the same as the as-synthesized material. TEM images of the hybrid mesoporous materials confirmed a clear arrangement of pores with uniform size. BET surface area, BJH average pore diameter and pore volume of these hybrid mesoporous materials are summarized in Table 1. The properties of these materials proved good mesopore structure and their pore diameter and pore volume were larger than the sample prepared by hydrothermal method. The material synthesized at 115 °C for 6h is believed to be partially collapsed considering the significant reduction in BET surface area accompanied by the enlarged average pore size. ²⁹Si MAS NMR of the hybrid mesoporous material synthesized at 95 °C for 4h confirmed that Si-C covalent bond was the basic unit of framework structure; T² [SiC(OH)(Osi)₂] and T³ [SiC(Osi)₃] resonance appeared at -57 and -65ppm. ¹³C CP MAS NMR confirmed that the ethane fragments of the precursor were not cracked during hydrolysis process by peak at 5.4ppm, which is assigned for Si-CH₂-CH₂-Si covalent bond. TGA analysis of these materials was conducted in a nitrogen flow from room temperature to 1000 °C. The decomposition of hybrid mesoporous material gradually appeared at temperature over 200 °C due to CH₂-CH₂ groups in their framework and reduced its weight about 20%.

Material	Pore size (Å)	Pore vol. (cc/g)	Surface area (m ² /g)
95 °C – 21h (H-T)	28	0.79	799
95 °C – 4h	32	0.94	769
115 °C – 2h	33	1.13	905
115 °C – 4h	36	0.99	776
115 °C – 6h	56	0.93	490
135 °C – 4h	39	1.09	741

Table 1. List of pore size, pore volume and surface area of the hybrid mesoporous materials synthesized at each synthesis time and temperature condition by microwave heating method; (H-T) : hydrothermal method.

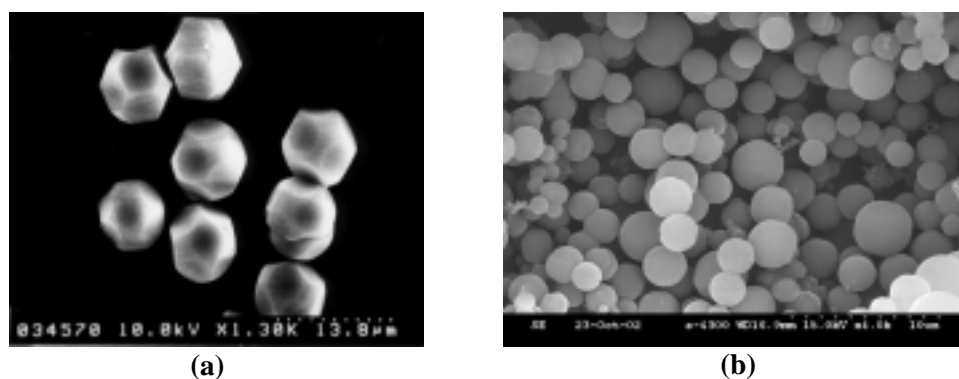
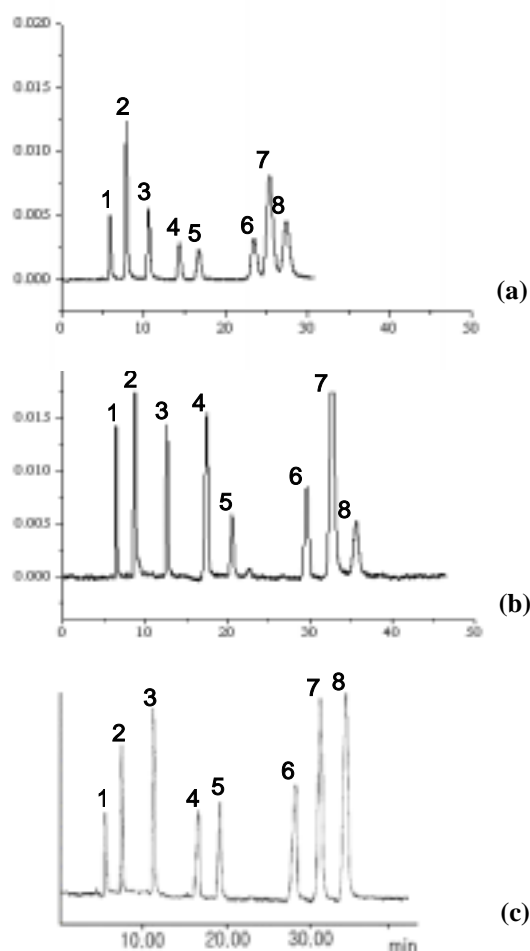


Fig. 1. SEM images of the hybrid mesoporous materials synthesized at 95°C
 (a) by hydrothermal method for 21h
 (b) by microwave heating method for 4h

SEM images of solvent-extracted hybrid mesoporous materials are shown Fig. 1. The material prepared by hydrothermal method has same morphology of dodecahedron shape as reported earlier [1]. The material prepared by microwave heating at 95°C for 4h had well-defined morphologies with spherical shape and much smaller particle size. Average particle size of samples prepared at various temperature was 2.2 μm when synthesized at 95°C and 1.5 μm at 115°C and remained almost the same at 135°C. The materials synthesized at 115°C and 135°C had very narrow particle size distribution, somewhat improved compared with the data at 95°C showing a broader pore size distribution. The synthesis time did not largely affect the morphology of the synthesized materials. For materials prepared at different synthesis time, its particle size was 1.8 μm in diameter and it had very narrow particle size distribution curve and spherical shape.



Since the material with very small particle size makes it necessary to apply high inlet pressure when it is used as a column material in HPLC, packing medium with appropriate particle size is desired. To synthesize material with larger particle size close to 3-5 μm , heating rate of microwave equipment at the first step was adjusted. It takes longer to reach the final target temperature by decreasing the microwave heating power. At first step, the microwave heating power (maximum 950 W at 2450MHz) was applied to 100%, 50%, 25%, 15%,

Fig. 2. Chromatograms obtained in 80/20 v/v % MeOH/H₂O at the flow rate of 10 $\mu\text{l}/\text{min}$ with different stationary phases ; hybrid mesoporous material (a) by hydrothermal method, (b) by microwave heating and (c) commercial silica (Lichrospher Si60).

Solutes

1 : 4-Methoxyphenol, 2 : Acetophenone,
 3 : Ethylbenzoate, 4 : Ethylbenzene,
 5 : Acenaphthylene, 6 : Acenaphthene,
 7 : Phenanthrene, 8 : Anthracene.

5% of maximum power. When the microwave heating power was 100% or reduced to 50% of full power, particle size of the hybrid material was hardly affected. However, particle size was gradually enlarged when it came to the samples that were synthesized under 50% of full power. But uniformities in morphologies deteriorated fast and particle size distribution became broad.

The separation performance of hybrid mesoporous materials in HPLC was shown in Fig. 2. Hybrid material prepared by microwave heating demonstrated separation capability almost equivalent to the performance of commercial silica, and performed better than the one prepared by hydrothermal method. In the case of the hybrid material synthesized by hydrothermal method, total retention time was shortest among the three but the separation of nonpolar big molecules like acenaphthene, phenanthrene and anthracene was not achieved to high standard. Separation might be hindered by the smaller pore size of column packing material for hydrothermally prepared sample, especially large non-polar solutes are expected to have increasing difficulty in diffusion. In separation of small polar solutes like o,m,p-nitroaniline, the separation ability of hybrid mesoporous material at 95 °C for 4h by microwave heating was even superior to the performance of commercial silica.

4. Conclusions

Organic-inorganic hybrid mesoporous materials were synthesized using microwave heat system and found to have uniform and smaller particle size with a spherical morphology. Particle size of these hybrid mesoporous materials could be controlled between 1.5 μm and 2.2 μm by adjusting the synthesis parameters. The synthesis time of these materials was largely reduced by microwave heating method. The materials synthesized by microwave heating was used as separation medium for HPLC and showed high separation ability compared to commercial silica, demonstrating short analysis time, relatively low inlet pressure demanded, and clear resolution of the separation. This improvement in HPLC performance of the hybrid material prepared by microwave heating is believed to be a consequence of smaller uniform particles with enlarged pores in spherical morphology induced by the rapid and uniform heating. Separation ability could be further improved by controlling the particle size of column material closely by using different heating rate.

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