# Morphology Control of Organic–Inorganic Hybrid Mesoporous Silica by Microwave Heating

Dong-Jun Kim, Jin-Seong Chung, Wha-Seung Ahn,* Gyoung-Won Kang,[†] and Won-Jo Cheong[†]
*School of Chemical Science and Engineering, Inha University, Inchon 402-751, Korea*
[†]*Dept. of Chemistry, Inha University, Inchon 402-751, Korea*

(Received December 9, 2003; CL-031209)

A periodic ordered mesoporous organosilica containing uniform ethane groups in the pore walls was prepared using microwave heating to produce 1.5–2.5-μm uniform particles with spherical morphology.

Organically functionalized mesoporous silicas have been attracted much attention because new catalytic and adsorptive functions can be imparted by introducing various organic groups to the silica host.[1–6] Recently, periodic mesoporous organosilicas (PMOs) containing bridge-bonded organic groups ($-CH_2-CH_2-$,[1] $-CH{=}CH-$,[2] $C_6H_4$,[4] $(C_6H_4)_2$[5]) directly integrated into the silica framework were reported by several groups. One of the attractive points of the PMOs is that in addition to the large surface area and narrow pore size distribution, it can be prepared to multi-faceted crystal-like particles. Furthermore, a large fraction of organic component in its composition can prove useful in achieving hydrophobicity necessary for the effective adsorption of non-polar organic molecules. Even though the potential of inorganic M41S type mesoporous silica as a column packing material has been proposed,[7,8] irregular particle shape and inadequate particle size remain as problems for practical applications so far. In this regard, PMOs with uniform particle morphology can be a promising candidate to consider as a column packing material. Improvements of synthesis, which can lead to smaller particles with spherical morphology are, however, still highly desirable for chromatographic application of PMOs.

A preliminary investigation of the reported recipes for PMOs by us established that the materials prepared by Inagaki et al.[1] exhibit the best resolved XRD patterns with crystal-like particle morphologies. In this work, a hybrid mesoporous material containing homogeneous ethane groups designated as HMM-3 by Inagaki group[1] was prepared using microwave heating and its particle morphology was compared with the one prepared by conventional hydrothermal method. As was reported, synthesis of inorganic materials using microwave heating can reduce the synthesis time significantly in comparison with general hydrothermal reaction conducted in a conventional oven.[9] In addition, uniform internal heating achieved by rapid rotation of water molecules induced by the microwave irradiation may result in particles with more uniform particle morphology.

PMO sample was prepared in molar ratio of 1 BTME: 0.91 $C_{16}$TMACl: 2.28 NaOH: 336 $H_2O$. $C_{16}$TMACl and BTME are hexadecyltrimethylammonium chloride and 1,2-bis(trimethoxysilyl)ethane, respectively. The substrate mixture was stirred for 19 h at 25 °C. This mixture was then transferred to a 200-mL-Teflon vessel for microwave heating. The microwave instrument used was CEM MDS-2100 equipped with a fiber optic temperature probe and pressure controller, and was capable of an adjustable power output. Synthesis was conducted at temperature range of 95 to 135 °C for 4 h. Heating time was also varied between 2 and 6 h at a fixed temperature of 115 °C. After refluxing 1-g sample of the as-synthesized material in 3.8 g of 37 wt % HCl in 150 mL ethanol for 6 h at 50 °C to remove the surfactant, it was filtered and dried for later use.

The XRD patterns and TEM micrographs of the samples prepared by conventional (PMO-C) and microwave heating (PMO-M) are shown in Figure 1. Both exhibited characteristic diffraction peaks assignable to a cubic symmetry similar to the mesoporous silica, SBA-1; major (120) peak accompanied by two minor (200) and (112) peaks between $2\theta = 1.5$–$2.0$,[10] but PMO-C showed somewhat better crystallinity. TEM images of the both PMO samples demonstrated a clear arrangement of pores with uniform size. $^{29}$Si MAS NMR and $^{13}$C CP MAS NMR of the hybrid mesoporous material synthesized at 95 °C for 4 h confirmed that Si–C covalent bond was the basic unit of framework structure and ethane fragments of the precursor remained intact during hydrolysis process.[1] TGA showed that decomposition of $CH_2$–$CH_2$ groups in their framework gradually took place above 200 °C and its weight decreased by ca. 20% after thermal treatment to 800 °C.

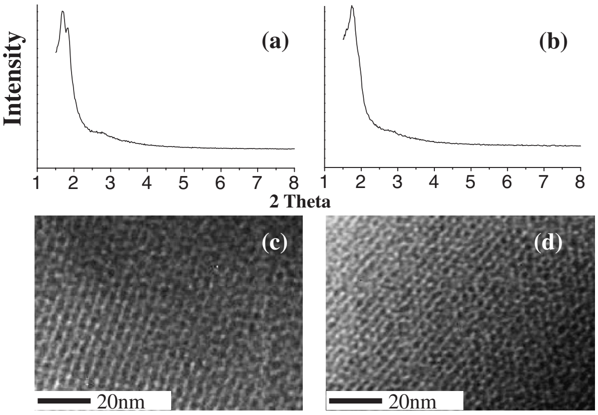

**Figure 1.** XRD patterns and TEM micrographs of PMO-C (a,c) and PMO-M (b,d).

SEM images of the solvent-extracted PMOs are shown in Figure 2. PMO-C prepared by conventional method was composed of ca 8.0-μm particles with decaoctahedron shape. PMO-M prepared by microwave heating, on the other hand, was composed of much smaller particles with spherical morphology. Average particle size of the samples prepared was 2.2 μm at 95 °C and 1.5 μm at 115 °C, and remained almost the same at 135 °C. All the materials synthesized showed narrow

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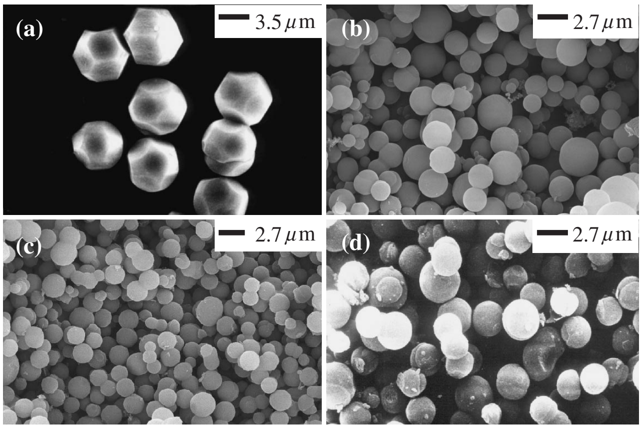

**Figure 2.** SEM images of the hybrid mesoporous materials;
(a) at 95 °C for 21 h by conventional method,
(b) at 95 °C for 4 h by microwave heating,
(c) at 115 °C for 4 h by microwave heating, 100% power,
(d) at 115 °C for 4 h by microwave heating, 25% power.

particle size distributions. For materials prepared at 115 °C, crystallinity of the hybrid material improved with time; 16% (0.5 h), 35% (1 h), 88% (2 h), 100% (4 h). Substantial reduction in synthesis time was achieved from the usual 24 h in hydrothermal synthesis. Textual properties of the samples prepared at 95 °C indicated that pore diameter and volume of PMO-M are larger (32 Å, 0.94 $cm^3/g$) than those of PMO-C (28 Å, 0.79 $cm^3/g$). The material synthesized at 115 °C for 6 h looks partially collapsed.

Particle size of the PMO was also found affected by microwave power level. While hardly changed above 50% full power, average particle size grew to ca. 2.8 μm at 25% power (Figure 2d), and even bigger with 15% at 115 °C. Uniformity in morphology, however, deteriorated fast and particle size distribution became broad.

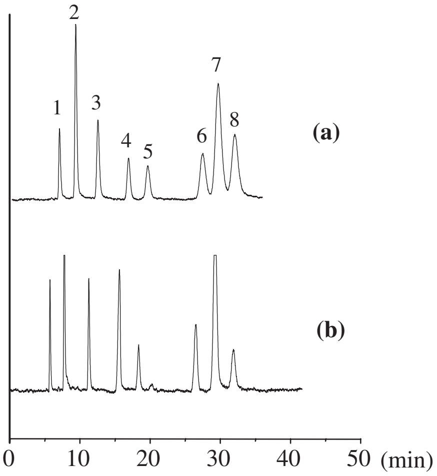

**Figure 3.** Chromatograms obtained with different stationary phases; hybrid mesoporous material synthesized (a) by hydrothermal method, and (b) by microwave heating; Solutes, 1;4-Methoxyphenol, 2;Acetophenone, 3;Ethylbenzoate, 4;Ethylbenzene, 5;Acenaphthylene, 6;Acenaphthene, 7;Phenanthrene, 8;Anthracene (Mobile phase: 80/20 v/v % $MeOH/H_2O$ at the flow rate of 10 μL/min).

The separation performances of hybrid mesoporous materials in HPLC were compared in Figure 3. PMO-M demonstrated clear separation improvement of acenaphthene, phenanthrene, and anthracene over the hydrothermally prepared sample, PMO-C as a consequence of the morphology changes. Further work is in progress to control the particle size to ca. 3–5 μm by using a seed or adjusting the substrate composition to improve its separation performance.

In conclusion, organic–inorganic hybrid mesoporous materials composed of 2.5-μm uniform particle size with spherical morphology was synthesized using microwave heating in substantially reduced synthesis time. The material demonstrated improvements as HPLC column material over the conventionally prepared PMO sample.

This work was supported by grant R01-2000-000-00325-0 from basic research program of the Korea Science & Engineering Foundation.

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11 A microcolumn (0.5 mm I.D. × 300 mm) was packed for chromatographic performance in HPLC. 1 g of hybrid mesoporous material, 0.6 mL pyridine, and 6 mL xylene were put into a small round bottom flask with a reflux condenser and stirred. Subsequently, 0.4 g 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, 1 g of the dried product, 0.6 mL pyridine, 6 mL xylene, and 0.20 mL chlorotrimethylsilane were mixed and stirred at 100 °C for 3 h, followed by filtering, washing, and drying as before.

Published on the web (Advance View) March 6, 2004; DOI 10.1246/cl.2004.422