Micron-Sized Phenyl-PMO Materials with a Crystalline Wall

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Received January 16, 2008

Key Words : Nanostructured materials, Periodic mesoporous organosilicas, Phenyl-PMO

The preparation of pure siliceous mesoporous materials with an atomic-scale crystalline wall is an illusive task even though the mesoporous material researches flourish recently because of their various intriguing applications.[1] Periodic mesoporous organosilica (PMO) materials are nanoporous hybrid materials containing organic and inorganic moieties on the pore wall simultaneously.[2] Single crystal-like PMO consisted of phenyl ($-C_6H_4-$) moieties was firstly reported by Inagaki *et al.*[3] However, it was claimed that very strict reaction conditions such as an alkaline condition and a narrow range of molar ratio of the reactants were mandatory to produce single crystal-like phenyl-PMO materials. This rather strict synthetic condition hampers further studies to control the particle morphology and size variation of the PMO materials with intrinsically hydrophobic interior because of the constituent phenyl moieties on the wall. For example, most phenyl-PMO derivatives were prepared *via* quite similar reaction conditions originally proposed by Inagaki *et al.*[4] Therefore, we have been interested in finding a reliable synthetic method to fine-tune their particle size and shape suitable for various advanced applications such as controlled drug delivery system, host materials for hydrophobic biomolecule encapsulation, and robust catalyst supports.[5]

We speculated that the $\pi\cdots\pi$ stacking interaction between two adjacent benzene moieties of different 1,4-bis(triethoxysilyl)benzene (BTEB) precursors might be strong enough to induce the single crystalline wall structure in a variety of reaction conditions unlike the original report.[3] Therefore, we investigated various synthetic conditions such as different reactant molar ratios and precursor concentrations to prepare phenyl-PMOs having different particle size and morphology with an aforementioned single crystalline nature of the pore wall. We were particularly interested in the size control of the particles without perturbing the crystallinity of the pore wall. Herein, we describe a preliminary result of the preparation of size-controlled phenyl-PMO material with molecularly ordered pore walls.

Our attempts closely relate to the literature method of preparing shape-controlled organic-functionalized micron-size MCM-41 type of hybrid silica materials.[6] For example, an optimized reactant molar ratio is C_{18}TMABr:BTEB:NaOH:H_2O = 1.0:1.2:6.1:5644 where C_{18}TMABr is an octadecyltrimethylammonium bromide, $CH_3(CH_2)_{17}N(CH_3)_3Br$. The low relative molar ratio of C_{18}TMABr to water was crucial to obtain small micron-size particles. The $C_{18}TMA^+$ templates of the as-made material were easily removed by an acid extraction in ethanol solution at 60 °C. TEM images of the template-removed samples are shown in Figure 1. Under the low C_{18}TMABr concentration, the products were formed as micron-size particles (average length or diameter < 3 μm) with the parallel pore direction relative to the longitudinal axis of the particle as shown in Figure 1. The mesopore orientation of the previously reported phenyl-PMO materials normally exhibited a perpendicular pore direction relative to the flat surface of the thin flake.[4,7] In our case, however, the low surfactant concentration as well as a short period of stirring after the addition of BTEB precursors might prevent surfactant-organosilica micelles from aggregating to form large flakes. As a result, small particles with a parallel pore orientation as well as a crystal-like wall structure have been successfully obtained. Interestingly, individual nanotube-like uniform mesochannels were clearly discerned from the TEM images of Figures 1(b) and 1(c). SEM images of Figure 1 indicate the shape of particles and their size distribution.

The powder XRD pattern of the template-free material, top trace of Figure 2, exhibited higher angle diffraction peaks at 2θ= 11.70°, 23.36°, and 35.48° which correspond to

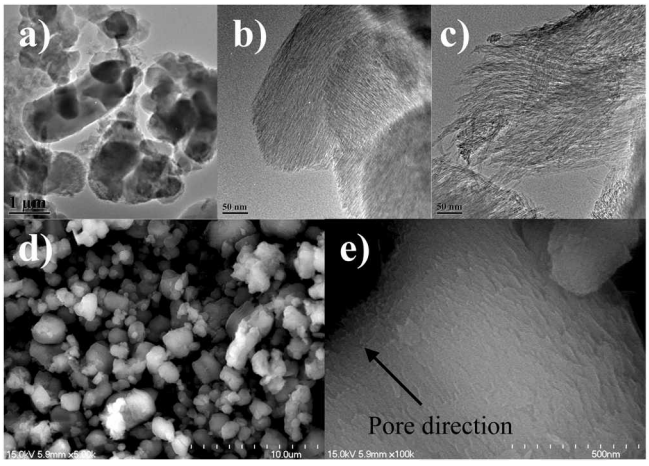

Figure 1. (a-c) TEM micrographs of the template-free phenyl-PMO material. (d, e) SEM images of the same sample with different magnifications.

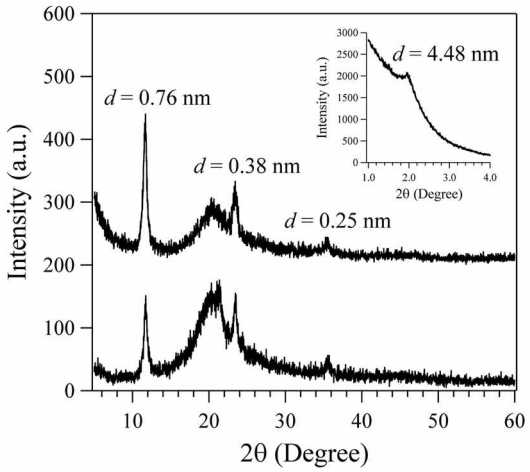

Figure 2. High angle region XRD patterns of the as-made (bottom trace) and the template-free (top trace) materials (inset: low angle XRD pattern).

d-spacing values of 0.76, 0.38, and 0.25 nm, respectively. These *d*-spacing values are indicative of the pore wall crystallinity from the molecularly ordered phenyl moieties according to the literature.[4] A small angle diffraction at $2\theta = 1.97^{\circ}$ can be assigned as 100 diffraction of hexagonal mesotructure with d_{100} spacing value of 4.48 nm (Figure 2 inset). However, higher ordering peaks were not observed. Therefore, the pore ordering is relatively poor compared with the conventional MCM-41 materials. The phenyl-PMO was further studied by using an N_2 sorption analysis at 77 K. The template-free material obtained from acid-extraction showed BET (Brunauer-Emmett-Teller) surface area of 658 m^2/g, pore volume of 0.50 cm^3/g and BJH (Barett-Joyner-Halenda) pore diameter of 3.77 nm from the desorption branch as shown in the supporting information. The original bulk phenyl-PMO was reported to have BET surface area of 818 m^2/g, pore volume of 0.66 cm^3/g and BJH pore diameter of 3.80 nm.[3] In order to confirm the presence of phenyl groups, the phenyl-PMO material was also investigated by solid-state ^{13}C CP-MAS NMR as shown in Figure 3. A singlet at δ = 133.9 ppm was observed. This chemical shift of the carbon atoms indicates our phenyl moieties have similar chemical environments to other bulk phenyl-PMO materials. It was also revealed that there were no residual $C_{18}TMA^+$ templates,[4b] and which could be attributed to the easiness of the ion exchange with protons during the acid-extraction process due to the small size of individual particles.

In summary, size-controlled single crystal-like hybrid phenyl-PMO material with uniform hydrophobic mesopores (*ca.* 3.8 nm) was successfully prepared by an efficient method. These materials can be used as a small hydrophobic drug container for biological applications. Therefore, smaller particle size would enable us to develop more efficient drug

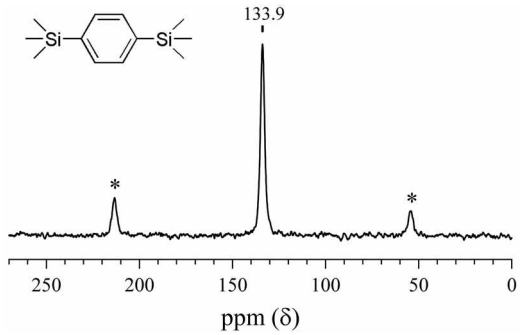

Figure 3. Solid state ^{13}C CP-MAS NMR spectrum of the template-free phenyl-PMO. Asterisk (*) indicates spinning side bands.

delivery systems. We will use these nanomateirals as containers for the guided delivery of various drug molecules, especially hydrophobic oligopeptide drugs[8] and a hydrophobic anticancer drug, paclitaxel.[9]

Acknowledgements. This work was supported by Hankuk University of Foreign Studies Research Fund of 2007.

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