A Self-template Method for Mesoporous Organosilica Particles

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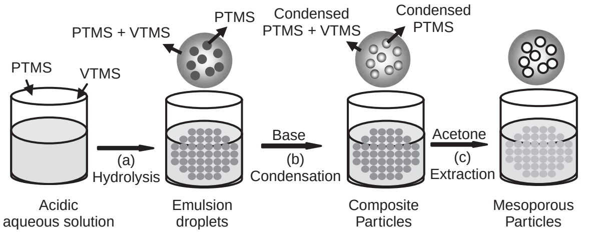
Mesoporous organosilica particles with large internal pores were prepared by a self-template, self-assembly process using homo- and heterocondensation of silane mixture, and extraction of highly soluble, homocondensed PTMS. This method not only provides a simple synthetic route without using an expensive template but also endows chemical flexibility to mesoporous particles owing to alkyl and aryl functional groups in organosilanes.

Mesoporous materials have received great attention because of their potential for scientific and industrial applications since the discovery of mesoporous silicates by Mobil's researchers.[1,2] With attractive novel properties such as high surface areas and controllable internal pores, mesoporous materials are the most promising candidates for nano- and microreactors, catalysts, absorbents, and drug delivery vehicles. Various synthetic approaches have been employed including surfactant templating, colloidal templating, and layer-by-layer self-assembly.[3–5] There have been recent efforts to enhance the chemical flexibility of mesoporous materials in order to tailor their chemical and physical properties for specific applications such as microelectronics and biosensors.[6] Organically modified mesoporous materials have been especially investigated as the chemical flexibility can be greatly enhanced by the introduction of organic groups into the framework of mesoporous materials. By carefully choosing the organic pendant groups, the porosity as well as mechanical strength of mesoporous materials can be easily controlled. Among the various types of organically modified mesoporous materials, periodic mesoporous organosilicas (PMOs) have been studied extensively.[7,8] Recently, Lu et al. reported a dual templating (vesicle and liquid crystal templating) process for the preparation of PMO hollow spheres.[9] The spherical morphology gives mesoporous materials further advantages such as low density, higher surface area, and ease of fabrication. However, these methods also require the use of external templates and multiple processes.



Scheme 1. Schematic representation of template-free, self-assembly process for mesoporous particles.

In this communication, we report a novel strategy for preparing monodisperse mesoporous organosilica spheres with large internal pores using a self-assembly process without using any templates. This method yields mesoporous silica particles having controlled size and porosity through cocondensation of an organoalkoxysilane mixture and subsequent extraction of the highly soluble network made of phenyltrimethoxysilane (PTMS) with a solvent.[10] The typical synthetic procedure of mesoporous spheres includes the addition of a mixture of PTMS (an excess amount) and alkyltrimethoxysilane (ATMS; VTMS for vinyl and MTMS for methyl) into an acidic solution for hydrolysis (Step a in Scheme 1). Next, a basic solution is added to induce homo- and heterocondensation (Step b in Scheme 1). Finally, the etching of composite particles with solvents (Step c in Scheme 1) is performed. The yield of mesoporous particles was ≈20%. The organoalkoxysilanes form emulsion droplets in an aqueous medium owing to hydrophobicity and are then hydrolyzed in the presence of acid catalysts. The size of emulsion droplets can be controlled with the variation of the concentration of silanes, reaction temperature, and stirring rate.

Because of an unequal amount of organoalkoxysilanes in the mixture, some of PTMS in the mixture may form self-aggregated phases inside the emulsion droplets and be homocondensed while most of ATMS is heterocondensed with PTMS. The network made of homocondensed PTMS will be dissolved out after etching with an acetone wash[10] and will become porous, converting each spherical particle into a mesoporous structure. The porosity may be controlled by changing the ratio of the two monomers.

The effect of the PTMS and VTMS molar ratio on the formation of mesoporous particles was investigated. VTMS has three alkoxy groups which can be condensed with three different PTMSs. We assume that a molar ratio ([PTMS]/[VTMS]) of greater than 3 is needed to generate the mesoporous structure. When a molar ratio of less than 3 is used, the heterocondensation between VTMS and PTMS would mostly occur, producing nonmesoporous spheres. As expected, for a molar ratio of 2, no mesoporous structure was observed after the etching process with acetone. When the molar ratio was between 3 and 4,

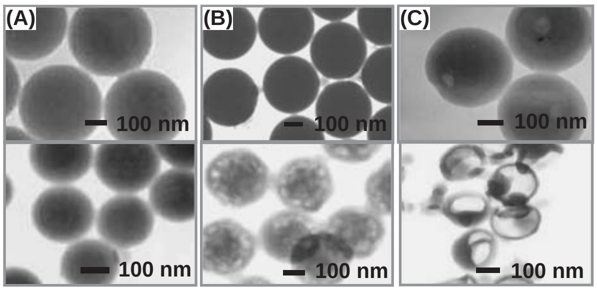


Figure 1. TEM images of organosilica particles with [PTMS]/[VTMS] ratio of (A) 2:1, (B) 4:1, and (C) 10:1 (Top views: ethanol washed. Bottom views: acetone washed).

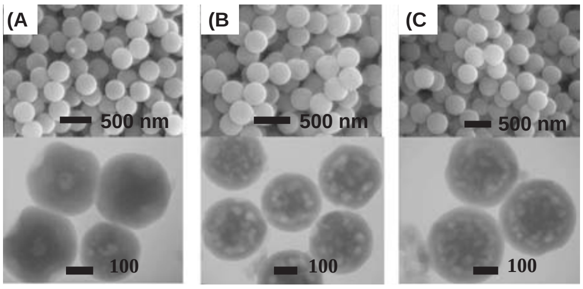


Figure 2. SEM and TEM images of monodisperse, mesoporous organosilica particles with various [PTMS]/[VTMS] ratios: (A) 3.0 (6.0/2.0), (B) 3.4 (6.2/1.8), and (C) 4.0 (6.4/1.6). Numbers in parenthesis indicate concentrations of silanes used (mmole).

mesoporous particles with controlled size and porosity were obtained (Figure 1). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) confirmed the formation of monodisperse mesoporous organosilica particles after etching with acetone (Figure 2). The SEM images of the organosilica particles show that the particles are monodisperse with diameters of about 370 nm regardless of the PTMS to VTMS ratio as long as the total concentration of alkoxysilanes is fixed. The porosity of the particles can be directly observed by TEM images. In the case of the particles prepared at [PTMS]/[VTMS] of 3, a small number of pores are observed with sizes larger than 50 nm. However, for the ratios of 3.4 and 4, mesoporous range-sized pores are entirely distributed in the particles. This indicates that the mesoporosity of the resultant particles increased with the molar ratio of [PTMS]/[VTMS].

The BET measurements showed the same trend. The surface area of the mesoporous silica particles increased with the PTMS/VTMS ratio. As the molar ratio increased from 3 to 3.4, and 4, the surface area increased from 555.7 to 595.5 m^2/g, and 665.9 m^2/g, respectively. This confirms the TEM observation that the mesoporosity of the resultant particles increased with the molar ratio. The N_2 adsorption–desorption isotherms of the three mesoporous silica particles with the PTMS/VTMS ratios of 3, 3.4, and 4 resulted in the same type IV isotherms according to IUPAC, each revealing a clear H_2-type hysteresis loop with a broad capillary condensation step at $P/P_0 = 0.45$–0.98.[11] This was in accordance with a BJH pore size distribution exhibiting a bimodal type of mesopores of ca. 50 nm and micropores of ca. 2 nm. This indicates that the resultant particles have a mesoporous structure with microchannels between the mesopores in the particles. When a molar ratio higher than 4 was used, particles started to lose the integrity of spherical morphology after etching with acetone resulting in distorted spheres. In addition, when a molar ratio higher than 10 was used, the particles were almost disintegrated to result in a hollow thin-shell structure after acetone washing. (Figure 1C)

Acetone was used primarily as the etching solvent but organic solvents such as dimethylformamide and tetrahydrofuran were also found to dissolve the homocondensed PTMS structure. ^{1}H NMR spectra for the filtrate of a redispersion of the PTMS/VTMS particles in acetone exhibited a signal peak around 7.4 ppm, which could be assigned to the phenyl group extracted from the composite mesoporous particles. In a mean while, the amount of vinyl group was relatively negligible.[11] This provides clear evidence that the PTMS moiety in the as-prepared organosilica particles was extracted with acetone, resulting in the formation of mesopores in the particles.

The thermal stability of the mesoporous particles was also investigated. Thermogravimetric analysis (TGA) results showed that the composite particles before etching exhibited high thermal stability up to a temperature of 600 °C and then a sharp decrease in the weight occurred to 900 °C.[11] The degree of weight loss for composite particles increased as the molar ratio of [PTMS]/[VTMS] increased. This is probably due to a higher portion of decomposable organic moieties in PTMS compared to those in VTMS. When the molar ratio reached 15, the TGA curve of the composite particles was almost the same as that of particles with only PTMS. SEM/TEM images of mesoporous particles with the molar ratio of 4, after calcination at 550 °C for 400 min under a N_2 atmosphere, revealed that the mesoporous particles are quite thermally stable maintaining their surface morphology and porosity after the heat treatment.[11]

In conclusion, large-pore mesoporous organosilica particles were synthesized by a self-template process using PTMS and VTMS. The mesopores in the organosilica particles were believed to be formed by extraction of the PTMS moieties from the homocondensed PTMS network within the particles using a simple treatment with acetone. The resultant particles have functionalities arising from the mixture of organosilane monomers for further applications. In addition, the sizes of the internal pores and resultant mesoporous particles could be easily controlled with reaction conditions such as etching solvent, the total concentration, and the concentration ratio of the two different silane monomers. In addition, the produced mesoporous particles showed a BET surface area of around 600 $m^2\,g^{-1}$ and BJH pore diameters of 40–50 nm with a narrow pore size distribution. With these novel properties of the mesoporous particles, this method is likely to find wide application in catalysis, nanoreactor, and drug delivery vehicle systems.

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