Simple and Rapid Synthesis of Mesoporous Silica by Vacuum Solvent Evaporation

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Introduction

Mesoporous inorganic materials templated by surfactant molecular assemblies have attracted a great deal of attention because of their potential applications as catalysts, adsorbents, molecular sieves, and sensors, to cite but a few uses.[1] There are two major pathways by which these ordered mesoporous materials are synthesized: (1) a hydrothermal synthesis in which the products precipitate from inorganic surfactant aqueous solutions under alkaline or acidic conditions at temperatures as high as 373 K[2] and (2) a solvent evaporation method in which the source solution is concentrated with the evaporation of the solvent to form an ordered inorganic surfactant mesostructure.[3,4] This method is usually used in the form of spin- or dip-coating in the synthesis of supported or self-standing thin films less than several microns thick. In the formation of spin- or dip-coated films, the rapid evaporation of the solvent is essential in obtaining a highly ordered mesostructure.[5] The slow drying necessary for obtaining the large number of samples within a short time resulted in a less-ordered structure; this outcome makes it difficult to obtain thick films, monoliths, or a large amount of powders with high regularity because the polycondensation of silica species proceeds and the silica oligomers become too large to form the ordered mesoporous silica before the formation of the ordered surfactant mesostructure, which is induced by the solvent evaporation. We have recently developed a sol–gel synthesis method for the purposes of obtaining self-standing, submillimeter-thick, highly ordered mesoporous silica films and powders, in which an enhancement of both the solvent evaporation and the retardation of silicate condensation are simultaneously achieved by decreasing the amount of water in the precursor solution and by using a volatile solvent.[6-8]

The practical uses of these ordered mesoporous materials require a large quantity of materials for their production, even in the precommercial phase. In addition, the synthesis methods currently used, including ours mentioned above, are difficult to apply to mass production and/or continuous production situations because of their slow rate of synthesis. In the present study, a vacuum-assisted solvent evaporation method is developed as a simple and rapid synthesis technique for the preparation of highly ordered mesoporous silicas. This method allows for the large-scale and/or continuous formation of these kinds of materials.

Experimental

In this work, cationic surfactants [such as alkyltrimethyl ammonium chloride (C_nTAC)] and nonionic surfactants [such as $C_{16}H_{33}(OCH_2CH_2)_{10}OH$ (Brij56)] were used as structure-directing agents. The starting solution, a mixture of tetraethylorthosilicate (TEOS) as a silica source, surfactant as a structure-directing agent, hydrochloric acid, water, and ethanol (solvent), was stirred for 1 h at room temperature to hydrolyze the TEOS. The typical molar ratio of the starting solution was 1 TEOS:0.2 C_{16}TAC (or 0.142 Brij56):10 EtOH:1.8×10^{-4} HCl:10 H_2O. The solution was then transferred to a round-bottom flask and the solvent was evaporated using a vacuum rotary evaporator at 7×10^3 Pa for 1 h. This pressure was determined from a calculation of the saturated vapor pressure of the mixture of TEOS, H_2O, and ethanol using the Wilson equation to prevent the solution from boiling. If the solution is boiled by the strong reduction of the pressure, it is difficult to keep the solution homogeneous because of the white precipi-

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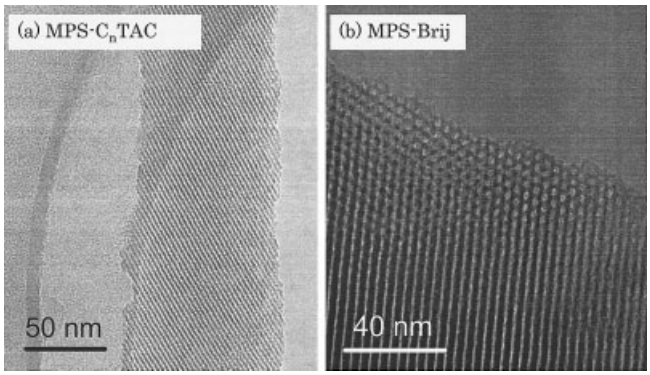

Figure 1. TEM image of (a) MPS-C$_n$TAC and (b) MPS-Brij.

The sample powder was grinded and dispersed in isopropanol using a supersonic wave, then cast on the TEM grid.

tate, resulting in the less-ordered structure of the obtained sample. The base temperature was kept at 298 K during the solvent evaporation. After the solution reached a pastelike consistency, the pressure was reduced to 2×10^3 Pa and kept for 30 min. This resulted in the viscous, pastelike liquid changing to a white wet solid with slight bubbling. The temperature was then increased to 333 K, maintained for 30 min to evaporate the remaining solvent. The resulting solid, a C$_n$TAC or Brij/silicate nanocomposite, was easily taken from the round-bottom flask without adhering to the wall of the flask. The obtained silica–surfactant composite was calcined at 873 K for 5 h to remove the surfactant, resulting in a porous solid. The obtained mesoporous silicas (MPS) are referred to as MPS-C$_n$TAC and MPS-Brij in this paper, where C$_n$TAC and Brij designate the surfactants used in the synthesis, respectively.

For the characterization of the obtained mesoporous silicas, TEM, X-ray diffraction (XRD), and N_2 adsorption/desorption measurements were carried out. The TEM observations of the obtained samples were carried out using a Hitachi HF-2000 field emission transmission electron microscope at 200 kV of electron acceleration. The XRD measurements were performed using a Rigaku Miniflex diffractometer. The nitrogen absorption isotherm was measured using Belsorp-mini, fully automatic absorption isotherm measuring equipment (BEL Japan, Inc., Osaka, Japan).

Results and Discussion

The yield of SiO_2, defined here as the proportion of the obtained silica to the supplied TEOS, was >95% for all of the syntheses, indicating that only the ethanol and water were removed during the vacuum evaporation. A TEM image of the obtained samples [(a) MPS-C$_n$TAC and (b) MPS-Brij], prepared under the above-mentioned conditions, is shown in Figure 1. The stripes suggest the formation of a highly ordered mesoporous structure templated by surfactant molecular assemblies. Figure 2 shows the XRD patterns of (a) MPS-C$_n$TAC and (b) MPS-Brij after calcination. The XRD data indicated intense diffraction peaks at 2θ values between 2 and 3°, indicating the formation of the periodic mesostructure. From the TEM images and higher diffraction peaks in Figure 2, it is concluded that MPS-C$_n$TAC and MPS-Brij possess the same hexagonal symmetry as that of MCM-41. Figure 3 shows the

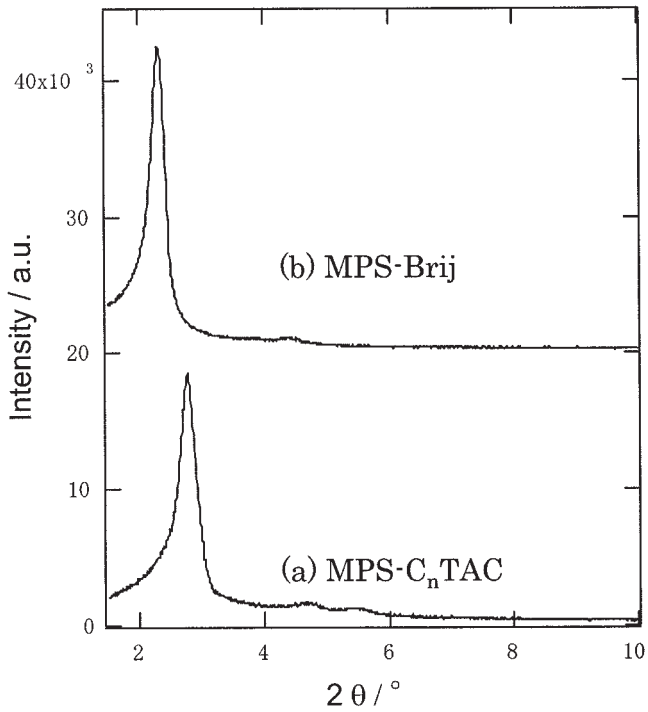

Figure 2. XRD patterns of (a) MPS-C$_n$TAC and (b) MPS-Brij.

The measurements were performed using Cu–K_α radiation, operated at 40 kV and 30 mA.

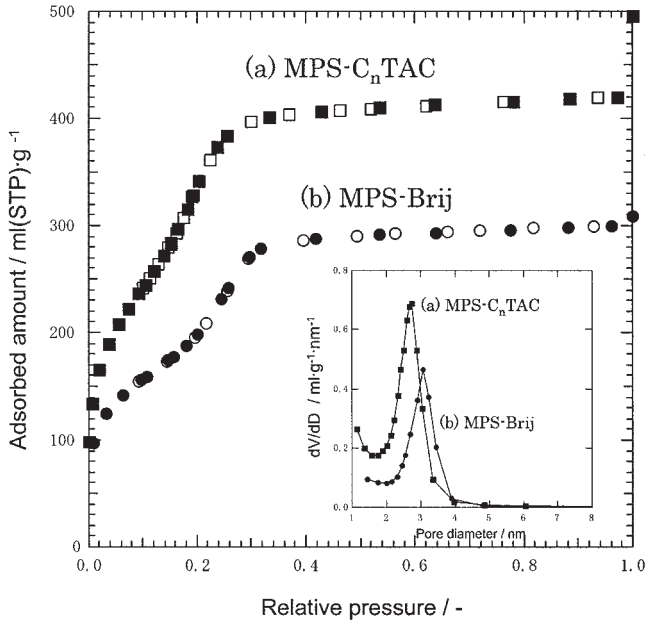

Figure 3. N_2 adsorption/desorption isotherms and pore size distribution curves of (a) MPS-C$_n$TAC and (b) MPS-Brij.

The measurements were made at 77 K after an 8-h degassing treatment of the samples at 573 K under nitrogen. The filled symbols represent adsorption and the unfilled symbols represent desorption.

adsorption/desorption isotherms of nitrogen for the samples at 77 K. The isotherms were similar to type IV in the IUPAC classification, clearly indicating a mesoporous structure. The BET surface areas were 1150 and 707 m^2/g for MPS-C_nTAC and MPS-Brij, respectively. The pore size distribution (PSD) curves were calculated using the Broekhoff–de Boer equation[9] with the D-H algorithm[10] using the cylindrical pore model, as shown in the inset of Figure 3. The most common pore size for the samples in this study was about 2.65 nm for MPS-C_nTAC and about 3.07 nm for MPS-Brij. These pore diameters are smaller than those of MCM-41 synthesized by hydrothermal reaction, where the pore diameters are around 3.8 nm,[11,12] although the surfactant with the same alkyl chain length (C_{16}) is used as a templating agent.[5,8] The main reason for this difference in the pore diameter is, in our opinion, the difference of the synthesis conditions such as temperature, the amount of water in the starting solution, and the use of ethanol as a solvent, although further investigation is necessary to elucidate this phenomenon.

There are two rate processes in our synthesis method: (1) the rate of solvent evaporation, which induces the self-assembly of the surfactant micelles and (2) the rate of polycondensation of the silicate species. It is considered that the well-ordered mesostructure can be obtained only when these two rate processes are well balanced. To produce the large amount of the products within a short time, it is necessary to evaporate the solvent rapidly without changing the "balance " of the above-mentioned rate processes. One strategy to accelerate the solvent evaporation is to increase the temperature, although this resulted in the less-ordered structure because the polycondensation of silica species was also accelerated. Thus, we used reduced pressure for the acceleration of the solvent evaporation, which induced only the solvent evaporation. From the structural characterization of the obtained samples described above, it is confirmed that this approach was successful and the ordered structures of the MPSs obtained by this method possess the same qualities as those from the previous method,[6,8] although the total synthesis time was substantially reduced using the method reported here regarding the synthesis of a large amount of sample compared with conventional methods.

It should be noted that it was not necessary to filter and wash the sample using this method, whereas thorough washing after filtration is needed to prevent any change or collapse of the ordered structure from the conventional hydrothermal synthesis. In addition, the particle size of the obtained mesoporous silica powders was >100 μm. This is an advantage when the MPSs are used as adsorbents because the size-enlargement processes often cause a decrease in the adsorption properties arising from the addition of binder.

It is also possible to prepare many kinds of metallosilicates in which the metal is incorporated into the silica network. This can be done simply by adding metal salts, such as $Al(NO_3)_3$, $ZrO(NO_3)_2$, and the like, into the starting solution. Although there are many reports on the synthesis of ordered mesoporous silicas or metallosilicates under milder conditions and/or simpler procedures[13-15] compared to the conventional hydrothermal synthesis, the novel method described herein has many advantages such as a fast reaction rate, no filtration or washing, and large particle size.

Conclusion

In the present investigation, a rapid vacuum solvent evaporation approach to the synthesis of highly ordered mesoporous silicas under weakly acidic conditions is illustrated. In this synthesis method, both cationic and nonionic surfactants can be used as structure-directing agents. In comparison with the conventional hydrothermal synthesis or sol–gel synthesis, the present method is believed to be more preferable in terms of the rapid and large-scale synthesis of ordered mesoporous silicas because of the short synthesis time and the fact that no filtration or washing is required after the formation of the mesoporous silica/surfactant nanocomposite. It is evident that this simple and rapid synthesis method is capable of remarkable productivity and allows for large-scale manufacturing of highly ordered mesoporous silicas.

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