



Effect of drying on the mesoporous structure of sol–gel derived silica with PPO–PEO–PPO template block copolymer

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Abstract

The effects of drying method on the pore structure of mesoporous silica were studied from the viewpoint of enhancing closed porosity in mesoporous silica. The mesoporous silica was prepared via a sol–gel process using polyethyleneoxide–polypropyleneoxide–polyethyleneoxide (PEO–PPO–PEO) triblock copolymer (Pluronic P123) as the structure-directing template. The closed porosity was evaluated from the apparent mass density of the sample measured by a helium pycnometer. These mesoporous silicas were also characterized by transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and nitrogen adsorption. The drying method was shown to be responsible for the finally templated mesoporous structure of the silica. More rapid drying is more preferable for enhancing the closed porosity of the mesoporous silica. The closed pores were formed by immediate immobilization of copolymer molecular assemblies in the silica matrix due to the instant removal of the solvent and solidification at higher temperatures. The drying method, mainly affecting the drying rate, is highly influential on the finally replicated mesoporous structure in silica.

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1. Introduction

Since the first synthesis of mesoporous MCM-41 by the Mobil Research and Development Group in 1992 [1], the use of surfactants as templates or structure-directing agents has offered a new method in the synthesis of porous materials. Nonionic triblock polyethyleneoxide–polypropyleneoxide–polyethyleneoxide (PEO–PPO–PEO) copolymers have been successfully used as surfactant templates for synthesis of a series of periodic mesoporous silicas of hexagonal, lamellar, and cubic structures [2,3]. Considerable attention has been paid to controlling the pore size and enhancing the porosity by varying such synthetic parameters as the aging time and temperature. Obviously, these heat treatments

during the preparation are important in determining the final mesoporous structure of silica. The finally solidified silica structure is considered to be determined by a competitive process of two simultaneously occurring solidifications of the structure directing agent and silica, whose structural arrest is due to desiccation and condensation polymerization, respectively. This means that the finally replicated mesoporous structure of silica does not necessarily agree with the thermodynamically preferred phase structure of the structure-directing agent. Therefore, exploring the possibility of giving a variety in the final silica structure by the heat treatments can be an intriguing research subject from the viewpoint of materials nanostructure manipulation.

Mesoporous silica can be fabricated from molecular assemblies of PPO–PEO–PPO triblock copolymers as represented by SBA-15. Studies of SBA-15 mesoporous silica have recently reached various applications. Use of SBA-15

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as catalyst support is most widely examined because of the great capacity to increase catalytically active species [4–21]. The mesoporous structure of SBA-15 is advantageous to facilitate the full utilization of doped species. The abundant nanoporous structure is also promising in using SBA-15 as adsorbent [22–27]. The through-pore structure is also applicable for molecular sieves [28–31]. In particular, the adjustability of the nanopore size is expectedly fitting for selective molecular sieving. There have been works which report the use of SBA-15 as structure-directing templates for fabrication of other nanostructured species [32–38]. Nanowires have been reported to be formed by the nanoscale confinement effect by the nanoporous structure of SBA-15 [32–34]. The nanoscale porous framework is also effective for formation of nanoparticles [35–38]. These works examine the open-porosity structure of mesoporous silica where the functions of the nanopores are realized in the pore. On the other hand, the authors pay attention to fabricating mesoporous silica with a closed-porosity structure because it is more favorable for the materials stability in humid circumstances and mechanical properties. In an earlier work, the author have reported that the drying method could be highly influential on the resultant structure of mesoporous silica from the viewpoint of open-/closed-porosity [39]. Therefore, enhancing the closed porosity of mesoporous silica is an interesting research subject valuable for preparing low-dielectric-constant films with superior resistance to water uptake during long-term exposure to humid circumstances.

For these reasons, the authors have tried different drying methods in sol–gel process to synthesize the mesoporous silica with Pluronic P123 (PPO–PEO–PPO triblock copolymer commercialized by BASF) as the structure-directing agent of the mesoporous structure. The drying rate was focused on as the key factor affecting the competition between the solidification of the silica matrix and the formation of the liquid crystalline mesophase that determines the finally templated structure of the resultant silica. In the moderate drying process, the silica sol is gradually solidified as the solvent is evaporated, while the rapid drying occurs in a very limited time scale (\sim seconds). Therefore, different mesostructures of the silica can be obtained by different drying methods resulting in a considerable variation of the closed porosity [39]. In the present work, the formation process of the closed pores is also discussed based on the results of the TGA of the as-synthesized samples.

2. Experimental section

2.1. Synthesis

Tetraethoxysilane (TEOS) was used as silica source. The surfactant used was commercial triblock copolymer Pluronic P123 ($M_{av} = 5800$), EO₂₀PO₇₀EO₂₀, which was donated by BASF and used as provided. Sample preparation started from the initial solution with the molar ratio of TEOS 0.04,

water 1, ethanol 0.022, and HCl 0.001. These agents were mixed in a glass beaker and stirred at room temperature until a transparent solution was obtained. Then P123 was added and dissolved in this homogeneous solution. The weight fraction of P123 to water was fixed at 10%. The resulting solution was rapidly sprayed onto a temperature controlled Teflon-coated plate (rapid drying). To see the effect of the drying rate by comparison, other samples were prepared by transferring the solution into a glass dish and keeping it in a drying oven for a day (moderate drying). Finally, all the samples were calcined at 600 °C for 5 h in air to remove the copolymers.

The samples prepared by two different drying methods for the comparison were denoted as MD-X and RD-X, where X means the drying temperature, and MD and RD mean moderate drying and rapid drying, respectively.

2.2. Characterization

The mesostructure of the sample was observed by transmission electron microscopy (TEM, JEOL JEM-1010) operated at 100 kV. For the TEM observation, the samples were ground, dispersed in ethanol, and placed on copper grids covered with carbon micromesh coating. Nitrogen adsorption–desorption were performed at 77 K by a Coulter SA3100 after the sample was outgassed at 120 °C for 1 h. Thermogravimetric analysis (TGA) were carried out by Shimadzu TGA-50 with a heating rate of 10 °C min⁻¹ from 30 to 600 °C. The apparent density of the sample was measured by an Ultrapycnometer 1000 helium pycnometer (Quantachrome).

2.3. Calculation

The surface area was calculated by the Brunauer–Emmett–Teller (BET) method using adsorption data in the relative pressure range from 0.05 to 0.2. The pore size distribution was calculated from the adsorption curve of the isotherm by the Barrett–Joyner–Halenda (BJH) method. The open pore volume was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.9814. The porosity due to the closed pores (closed porosity) was estimated from the apparent mass density measured by helium pycnometer where the bulk density of silica matrix was assumed to be 2.23 g/cm³.

In the measurement of apparent density, the sample was weighed on an analytical balance and then saturated with helium in a test chamber whose inner volume is precisely known. The volume of the sample is estimated from the difference in the pressure of helium caused by the presence of the sample when the same known amount of helium is dosed into the test chamber. The apparent mass density is obtained by dividing the weight by the sample volume estimated as above. Only the closed pores are included in the volume because the dosed helium can penetrate only in the open pores [40]. Therefore, the closed porosity (P_c) due to

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