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Closed-porosity mesoporous silica produced by high temperature rapid drying

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In recent years, the demand for low inductivity (low-k) materials has led to extensive efforts to explore the applicability of porous materials. In particular, nanoporous materials are expected to contribute to the fabrication of usable inorganic low inductivity materials [1]. Using tri-block polylethyleneoxide—polypropyleneoxide—polyethyleneoxide (PEO-PPO-PEO) copolymers as surfactant templates, a series of highly ordered mesoporous silicas have been successfully synthesized as the well known SBA-series [2]. The hexagonally arrayed liquid crystalline silicas have various potential applications in separation or catalyst supports due to the properties of the open-porosity structures. However, such open structures are not necessarily suitable for low inductivity materials because the open-porosity structure could result in capillary condensation of water after a long exposure to humid circumstance [3]. In this regard, nanoporous materials with closed pores are more desirable for low inductivity materials because of such useful properties as mechanical strength and resistance to humidity. In the present work, mesoporous silicas with closed pores were synthesized by incorporating rapid drying with the sol-gel process. Here, triblock copolymer was used as the structure-directing agent. The effect of the drying temperature on the mesoscopic structure and closed porosity of the silica is discussed.

Closed mesoporous silicas were synthesized using PEO-PPO-PEO triblock copolymer (pluronic F127: EO_{106} $PO_{70}EO_{106}$ (Mav = 12600)) as the surfactant template. In typical experiments, starting agents with the molar ratio of 0.04 (TEOS:tetraethylortho silicate), 1 (water), 0.022 (ethanol) and 0.001 (HCl) were mixed in a glass beaker and stirred at room temperature until a transparent solution was obtained after the completion of hydrolysis of TEOS in the acidic condition. Then pluronic F127 was dissolved in this homogenous solution. The weight fraction of pluronic F127 to that of water was 0.1. Subsequently, the solution was rapidly dried by spraying onto a heated TEFRON-coated brass

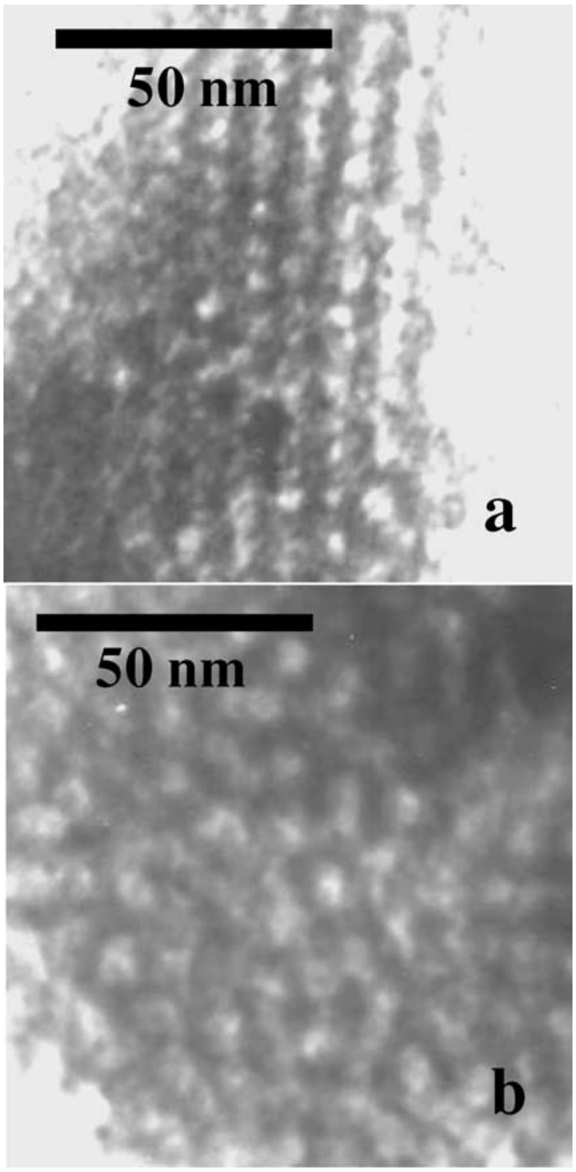

Figure 1 TEM images of calcined mesoporous silica using F127 tri-block copolymer as template prepared by rapid drying at (a) 90 °C and (b) 250 °C.

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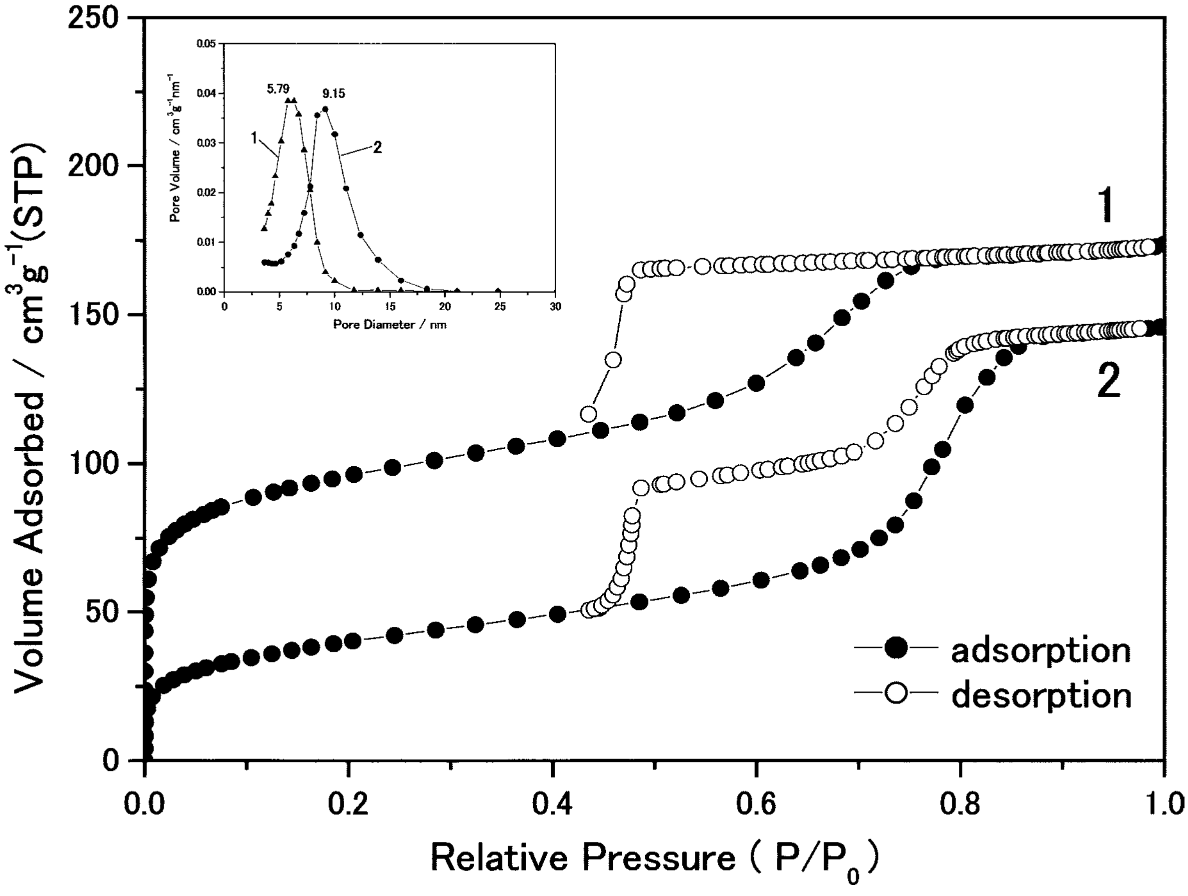

Figure 2 Nitrogen adsorption-desorption isotherms for the mesoporous silica prepared by rapidly drying at different temperatures: (1) 90 °C; (2) 250 °C. The inset shows the corresponding pore size distributions from the adsorption branch.

plate. A complete desiccation was carried out using a drying oven for a few hours. The final calcination was carried out at 600 °C for 5 h in air to completely remove the copolymer as the strucure-directing agent. All the samples were prepared by the same method except that the temperature of the rapid drying was varied from 90 °C to 250 °C.

Typical TEM (transmission electron microscopy) micrographs of the calcined mesoporous silica using pluronic F127 tri-block copolymer as the template are shown in Fig. 1. The images were observed by Jeol JEM-1010 (Nippon Denshi, Japan) operated at 100 kV. For the TEM observation, the samples were finely ground, dispersed in ethanol and placed on a copper grid with carbon micromesh coating. The sample dried at 90 °C has a liquid crystalline structure with a pore diameter of approximately 5 nm. However, in the case of drying at 250 °C, the liquid crystalline structure is absent and only isolated closed pores were observed with a larger pore diameter of 9 nm.

Fig. 2 shows typical examples of nitrogen adsorption-desorption isotherms and the corresponding pore size distributions calculated by the BJH method. The isotherms were measured at 77 K by Coulter SA3100 (Coulter, USA) after outgassing the sample at 120 °C for 1 h. Both the samples were described by the type IV isotherms attributed to typical mesoporous structures [4]. Similar to the isotherm of the earlier reported SBA-16, sample (1) showed a large type-H_2 hysteresis loop of a triangular shape indicating a narrow pore size distribution [5, 6]. The calcined silica has a pore volume of 0.27 cm^3 g^{-1} and BET surface area of 335 m^2 g^{-1}. The adsorption branch of sample (2) sharply rises from a relative pressure of about 0.7 showing that larger pores have been formed in the silica. The pore size distribution curves show the mean pore diameters of these two samples to be 5.79 nm and 9.15 nm, respectively, indicating that the pore size increases with the drying temperature. Compared to sample (1), sample (2) has a smaller pore volume of 0.22 cm^3 g^{-1} and BET surface area of 144 m^2 g^{-1}. This decrease is explained by the closed pores gradually becoming dominant with respect to the open pores, as the temperature of the rapid drying is increased.

The closed porosity of the mesoporous silica was evaluated from the apparent mass density of the sample measured by helium pycnometery where the bulk density of silica matrix was assumed to be 2.23 g/cm^3 (Quanta Chrome, Germany). In the measurement of the apparent density, the sample was weighed on an analytical balance and subsequently saturated with helium in a test chamber for which the inner volume is known precisely. 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. Only the closed pores are included in the overall captured volume of the sample because the helium can penetrate the open pores [7]. The apparent mass density is obtained by dividing the weight of the sample by its volume estimated as

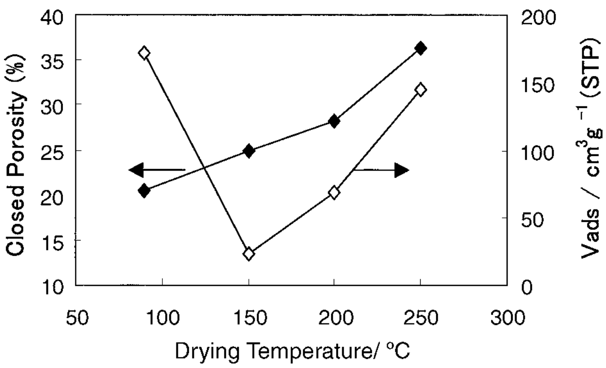

Figure 3 Dependence of closed porosity and nitrogen adsorption volume at 77 K on the drying temperature.

described above. As shown in Fig. 3, the closed porosity increases with the drying temperature. As stated previously [8], more rapid drying is preferable for replicating the mutually isolated pluronic micelles which result in the closed pores in the mesoporous silica. The higher drying temperatures, which cause more rapid drying, are expected to promote the formation of the closed pores. For the open-porosity volume, indicated by the total amount of adsorbed nitrogen, the drying temperature dependence is opposite that for the closed pores. Below 150 °C, the open pores decrease with drying temperature suggesting that the closed-porosity type geometry is more preferably formed at the higher drying temperature. However, above 150 °C, the higher temperature is considered to promote the formation of the open pores, too. More detailed discussion will be given in our following works.

In general, the copolymer in an aqueous solution undergoes the fast process of the micellization and the slower process of the formation of the liquid crystalline phase [9–11]. Therefore, the rapid drying at the higher temperature that facilitates the solidification of the silica matrix creates the closed porosity structure. When the silica/copolymer solution was rapidly dried at the higher temperature, the micellar structure was immediately immobilized prior to the phase alteration toward the liquid crystalline array. When the temperature is lower, e.g., at 90 °C, the micelle will have more time to be rearranged in the liquid-crystalline structure during the drying process resulting in the open pores of hexagonal or cubic arrays. This speculation is consistent with the TEM images and measurements of the closed porosity.

In conclusion, mesoporous silica with a closed-porosity structure was prepared by the rapid drying of silica sol. The drying temperature was shown to be important in determining the final mesoscopic structure and closed porosity of the silica because the rate of drying is directly responsible for the finally templated structure of the pluronic F127 molecular assemblies. The new method of high temperature rapid drying in sol-gel process is expected to be valuable for producing the low inductivity materials with closed nanopores which are desirable due to such properties as mechanical strength and resistance to humidity.

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References

1. R. D. MILLER, *Science* **286** (1999) 421.
2. D. ZHAO, J. FENG, Q. HUO, N. MELOSH, G. H. FREDRICKSON, B. F. CHMELKA and G. D. STUCKY, *ibid.* **279** (1998) 548.
3. G. WIRNSBERGER, P. YANG, B. J. SCOTT, B. F. CHMELKA and G. D. STUCKY, *Spectrochimica Acta Part A* **57** (2001) 2049.
4. B. LEE, D. LU, J. N. KONDO and K. DOMEN, *Chem. Commun.* (2001) 118.
5. W. LUCKENS, JR., P. SCHMIDT-WINKEL, D. ZHAO, J. FENG and G. D. STUCKY, *Langmuir* **15** (1999) 575.
6. C. YU, Y. YU and D. ZHAO, *Chem. Commun.* (2000) 575.
7. K. MURATA, K. KANEKO, F. KOKAI, K. TAKAHASHI, M. YUDASAKA and S. IIJIMA, *Chem. Phys. Lett.* **331** (2000) 14.
8. L. PEI, K. KURUMADA, M. TANIGAKI, M. HIRO and K. SUSA, submitted to *Chem. Commun.*
9. I. GOLDMINTS, J. F. HOLZWARTH, K. A. SMITH and T. A. HATTON, *Langmuir* **13** (1997) 6130.
10. M. J. KOSITZA, C. BOHNE, P. ALEXANDRIDIS, T. A. HATTON and J. F. HOLTZWARTH, *ibid.* **15** (1999) 322.
11. P. ALEXANDRIDIS and T. A. HATTON, *Coll. Surf.* A **96** (1995) 1.

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