JOURNAL OF MATERIALS SCIENCE **39** (2004) 1117–1119

Synthesis of ordered microporous silica by the solvent evaporation method

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Highly ordered mesoporous silicates with uniform cylindrical pores, such as MCM-41 [1], templated by the self-assembly of surfactant molecules have attracted much attention in last decade, because of their potential applicability as catalysts, adsorbents, large molecular sieves and so forth. The pore size can be controlled using templates with different chain lengths of carbon; however, the range of pore sizes is limited in the mesoporous region (larger than 2.0 nm) [2]. It is important to form porous materials with ordered pores between 1.3 and 2.0 nm (that is, smaller pores than MCM-41 type mesoporous materials and larger pores than conventional zeolites), from a scientific and practical perspective.

Some attempts have reported forming ordered pores smaller than 2 nm. One strategy is to use a short-chain surfactant as a templating agent. Although Ryoo *et al.* report [3] the synthesis of ordered silica with uniform pores on the border between the micropore and mesopore regions using short double-chain surfactants by hydrothermal reaction, the synthesis of ordered microporous silicates with pores of diameters smaller than 2 nm using *single* short-chain surfactants is difficult because of their low ability for self-assembly, which results in a poorly ordered or disordered structure [3, 4]. In another attempt, Sun *et al.* report synthesis of amorphous microporous silica using adamantamine as a template [5]. However, the pore structures were not ordered. Another possible method to form the small pores is thermal treatment at high temperature (1273 K), to shrink the silica framework. For example, Naono *et al.* report the synthesis and analysis of pore size distribution with pore diameters of 2–4 nm [6]. In this case, although X-ray diffraction peaks were detected in the calcined samples at 1273 K, the peaks were broadened and the higher diffraction peaks had disappeared due to the decrease of the structure order.

This paper presents the formation of ordered microporous silicates by the solvent evaporation method using *single* chain surfactant templates, which are the most popular templating agents in the synthesis of ordered mesoporous silicates. The solvent evaporation method was first demonstrated by Ogawa to form the silica/surfactant nanocomposite by dip-coating and then applied to form mesoporous silica thin films with hexagonal or cubic structure [7, 8]. From the reported data, the dip- or spin-coated films had a smaller unit-cell size than that of the MCM-41 type materials by hydrothermal synthesis when the same surfactant was used as a template, and were deduced to have ordered pores of sizes exclusively smaller than 2 nm. However, the pore structure was not investigated in detail because of the difficulty in measuring gas adsorption properties of the films due to their small total pore volume and surface area. Recently, we reported the formation of submillimeter-thick films of surfactant templated mesoporous silica by the solvent evaporation method [9], and almost the same method was applied to the preparation of ordered microporous silica described in this report.

In the synthesis of silicate/surfactant composites, 0.659 g (2.5×10^{-3} mol) dodecyltrimethylammonium chloride (C_{12}TAC) or 0.660 g (2.8×10^{-3} mol) decyltrimethylammonium chloride (C_{10}TAC) and 2.08 g of tetraethyl orthosilicate (TEOS) were dissolved into 4.61 g of ethanol, and then 1.80 g of 10^{-3} M hydrochloric acid was added to the mixed solution. The molar ratio of C_nTAC ($n = 10, 12$) to TEOS was optimized for each surfactant. The mixed solution was stirred for 5 h at room temperature and transferred onto a glass dish. The transparent solids were obtained after drying for several hours at 298 K, calcined at 873 K for 5 h to remove the template surfactants and then converted to a porous silicate material. The obtained porous silicas are called PS-12 and PS-10, the numbers of which refer to the chain length of carbon in the surfactants. The powder X-ray diffraction patterns were measured using a Rigaku Miniflex diffractometer (Cu/Ka radiation, operated at 40 kV and 30 mA). Fig. 1 shows the X-ray diffraction patterns for the samples PS-12 and PS-10. From the diffraction peaks of Fig. 1, it is concluded that PS-12 and PS-10 possess the same hexagonal symmetry

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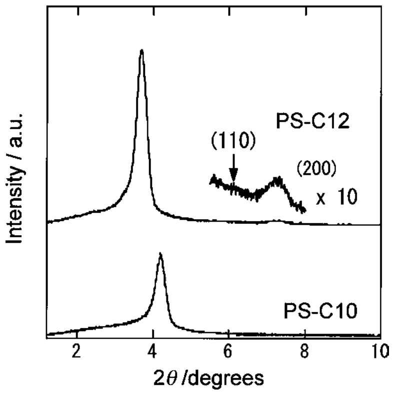

Figure 1 Powder X-ray patterns of the PS-12 and PS-10, after calcinations at 873 K for 5 h in air.

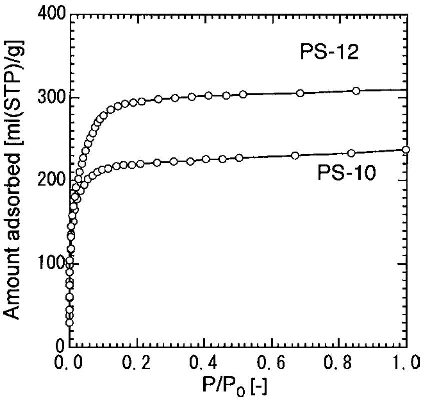

Figure 2 N_2 adsorption isotherms of PS-12 and PS-10 after removal of templating agents by calcination at 873 K for 5 h in air. The isotherms were measured using a BELSORP 28SA gas adsorption analyzer after outgassing the samples at 673 K for 8 h.

as MCM-41 or FSM-16 although the higher diffraction peaks were not observed for the sample PS-10. The center-to-center distance between two adjoining pores calculated from the (100) peak were 2.76 nm for PS-12 and 2.44 nm for PS-10.

Fig. 2 shows the adsorption isotherms of nitrogen on the samples at 77 K measured using an automatic adsorption analyzer (BELSORP 28SA, Nippon Bell Co. Ltd.). The samples were outgassed at 573 K for 8 h before the measurements. Each isotherm for PS-12 and PS-10 showed isotherms similar to type I in the IUPAC classification [10], clearly indicating microporous structure. The BET surface areas were 1184 and 894 m^2/g for PS-12 and PS-10, respectively. The pore size distribution (PSD) calculated using the Broekhoff and de Boer equation [11] with D-H algorithm [12] on the cylindrical pore model was ca. 1.65 nm for the sample PS-12. It was difficult to calculate the PSD for PS-10, because this method is not suitable for the calculation of pore sizes smaller than 1.5 nm. It should be noted that the nitrogen adsorption isotherms of the $C_{12}TAC$ or $C_{10}TAC$ templated ordered porous silica synthesized by hydrothermal reaction show typical type IV isotherm with a steep increase of adsorption amount at relative pressure 0.2, indicating that the pore is in the mesopore region and obviously larger than our sample PS-12 and PS-10, as reported by Kruk *et al.* [13]. The pore diameter of porous silica synthesized by the solvent evaporation method was smaller than that of porous silica synthesized by hydrothermal reaction when the same surfactant is used as a templating agent.

The cylindrical pore structure was examined using transmission electron microscopy (TEM). For each sample of PS-10 and PS-12, a regular array of cylindrical pores was clearly observed and the periodicity of pores showed good agreement with the results from the XRD measurements, as shown in Fig. 3a for PS-10 and b for PS-12.

Wang and Kabe pointed out in their paper [14], which reports the fine-tuning of pore size of MCM-41, the possibility of the existence of a water layer between the silica wall and the self-assembled micelle. In our synthesis, where ethanol was used as a solvent, the water/TEOS ratio was much smaller than that in the hydrothermal synthesis with the aqueous solution. This could be one reason for the formation of small pores in our method. There are other differences between these two synthesis methods other than the solvent, for example the temperature and catalyst. Therefore, further investigation is required to clarify the reason for the formation of smaller pores in the solvent evaporation synthesis.

In conclusion, the synthesis of microporous ordered silica was demonstrated using a common single-chain surfactant, alkyltrimethylammonium chloride ($C_{12}TAC$ and $C_{10}TAC$) as the templating agent. The pore diameter of porous silica synthesized by the solvent

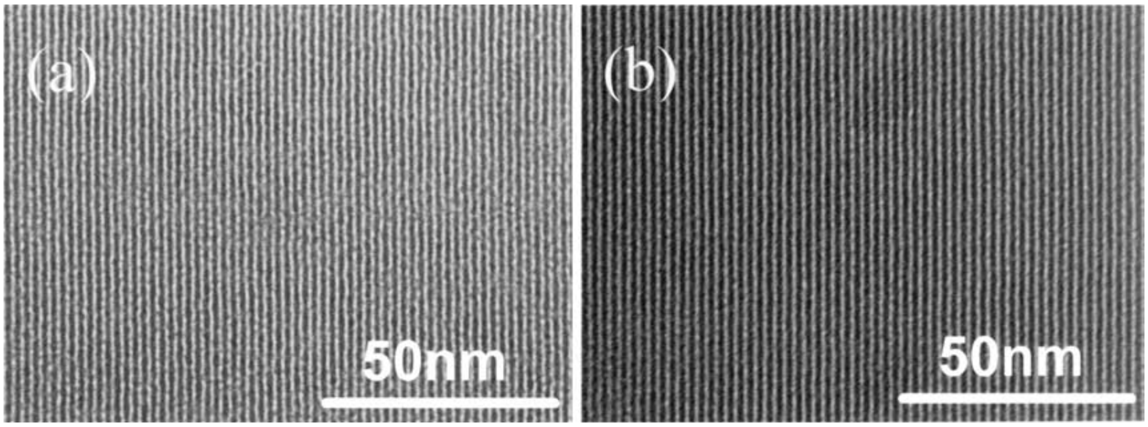

Figure 3 TEM images of calcined: (a) PS-10 and (b) PS-12. The microscopy was performed on a Hitachi HF-2000 operating at 200 kV.

evaporation method was smaller than that synthesized by hydrothermal reaction when the same surfactant was used as the templating agent. Additionally, therefore, this method is suitable for the preparation of ordered microporous silicas.

We thank Mr. Takashi Tanaka and Ms. Marie Shimomura for their kind help in the experiments and the New Energy and Industrial Technology Development Organization (NEDO) for its financial support.

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Received 19 May
and accepted 7 August 2003