

Cage-like ordered silica with large mesopore volume synthesized by doubling amount of polymer, adding sodium chloride and lowering acid concentration†

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Cage-like ordered mesoporous silica, FDU-1, with about twice the pore volume and a narrower pore size distribution compared with those for previously reported samples was synthesized in a much shorter time by doubling the amount of block copolymer, adding sodium chloride and lowering the acid concentration.

Since the discovery of ordered mesoporous silicas (OMSs) in 1992 by the Mobil Company,¹ significant progress has been made in the synthesis, characterization, and application of ordered mesoporous materials (OMMs), which can be prepared using either ionic or nonionic surfactant templates. The latter show many advantages in comparison to ionic surfactants such as biodegradability, commercial availability, low cost and low toxicity. Polymer-templated OMMs became very popular due to the successful synthesis of highly ordered 2D hexagonal mesoporous silica, SBA-15, by Zhao *et al.*² using a poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) triblock copolymer having 20 and 70 blocks of PEO and PPO, respectively. Yu *et al.*³ synthesized another interesting OMS, FDU-1, with a 3D cubic structure having large cage-like mesopores. In this case, a poly(ethylene oxide)–poly(butylene oxide)–poly(ethylene oxide) triblock copolymer (PEO–PBO–PEO) with 39 and 47 PEO and PBO blocks, respectively, was used as a structure directing agent.

The polymer-templated cage-like OMSs have attracted a lot of worldwide attention because of their unique properties, *e.g.*, 3D structural ordering, large adsorption capacity, large and uniform pores with a tunable entrance size, extraordinary hydrothermal stability⁴ and low-cost silica source⁵ as well as their potential applications in catalysis,⁶ adsorption,⁷ immobilization of biomolecules⁸ and sensing devices.⁹ Despite significant progress in the synthesis of these OMSs, further advancement is required in improving their structural and adsorption properties as well as in the optimization of synthesis conditions. Kleitz *et al.*¹⁰ reported a new synthesis route to obtain high quality cubic OMSs by the addition of co-surfactant and by simply lowering the HCl concentration by a factor of four. Later, some improvement in the uniformity of pore entrance size and pore size distribution (PSD) upon salt addition was reported by Jaroniec and co-workers¹¹ for FDU-1 materials. So it was interesting to check how

the structural properties of cage-like mesoporous FDU-1 change with increasing the amount of polymer, decreasing the acid concentration and by adding sodium chloride as well as optimizing synthesis time.

Here we show a successful synthesis of highly ordered cage-like mesoporous FDU-1 by doubling the amount of the PEO–PBO–PEO triblock copolymer in the presence of sodium chloride at a low acid concentration. It was reported by Ryoo *et al.*¹⁰ that the condensation of siliceous species is slowed down at low acid concentrations, whereas sodium chloride favours interactions between those species and nonionic blocks of the polymeric template.^{12,13} This work demonstrates that by doubling the amount of block copolymer in comparison to the conventional recipe,³ decreasing the acid concentration by a factor of four and by adding sodium chloride, one can synthesize the FDU-1 material doubling the mesopore volume and getting a narrower pore size distribution compared with those obtained for samples synthesized according to previously reported recipes.^{3,5}

A slight modification of the original recipe³ by adding sodium chloride and lowering the acid concentration did not cause a significant improvement of the FDU-1 samples in terms of their pore volume. This can be seen in the ESI (Figs. 1S and 2S†) showing argon adsorption isotherms at $-196\text{ }^{\circ}\text{C}$ and the corresponding pore size distributions. Fig. 1 and the ESI (Fig. 1S†) show that it was necessary to double the amount of block copolymer, add sodium chloride and reduce the acid concentration to double the amount of argon adsorbed on the FDU-1 material. The samples studied in this work were synthesized by using the

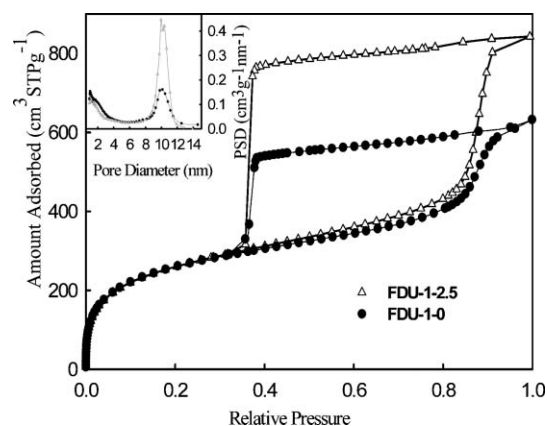


Fig. 1 Comparison of argon adsorption isotherms at $-196\text{ }^{\circ}\text{C}$ and the corresponding pore size distributions (PSD) for FDU-1-0 and FDU-1-2.5.

† Electronic supplementary information (ESI) available: Figs. 1S–4S: argon adsorption isotherms, pore size distributions, small-angle X-ray scattering patterns and thermogravimetric weight change curves for a series of FDU-1 samples. See <http://www.rsc.org/suppdata/cc/b4/b416683c/>

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following molar composition: 1 TEOS : 0.0147 polymer : 1.4074 HCl : 2.57–6.09 NaCl : 165.68 H₂O. In a typical synthesis, 4 g of EO₃₉BO₄₇EO₃₉ (B50-6600 from Dow Chemicals) were dissolved in 90 ml of distilled water and 30 ml of 2M HCl followed by the addition of different amounts of sodium chloride (NaCl from Fischer) under vigorous stirring at 45 °C to obtain the NaCl : polymer mass ratio = 0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0, where zero refers to the synthesis without salt addition. The synthesized FDU-1 samples are denoted as FDU-1-*x*, where *x* indicates the salt-polymer weight ratio. After one hour of mixing, the synthesis gel was cooled down to room temperature and 8.30 g of tetraethylorthosilicate (TEOS) were added dropwise under vigorous stirring, which was continued for 6 hours. The resulting gel was subsequently aged at 100 °C for 6 hours under static conditions instead of the usual 24 h. The white solid was washed with deionized water, filtered and dried at 80 °C. The template was removed by calcination in air at 540 °C for 4 h.

Fig. 1 shows argon adsorption-desorption isotherms for two calcined FDU-1 samples (with and without an optimal amount of sodium chloride), denoted as FDU-1-2.5 and FDU-1-0, respectively, which are type IV with a pronounced H1 hysteresis loop starting at a relative pressure of about 0.80–0.85 and abruptly ending at ~0.35, which is typical for good quality, large pore, cage-like structures.⁵ As can be seen from this figure, the step for the capillary condensation for FDU-1-2.5 is about twice the height of that for FDU-1 obtained without salt addition, which reflects better uniformity of the mesoporous structure and about twice the volume of ordered mesopores. A comparison of the pore size distributions (see inset in Fig. 1) shows that the distribution peak for FDU-1-2.5 is not only narrower but also about three times higher than that for the sample without salt addition.¹⁴ The sample FDU-1-2.5 exhibited a BET specific surface area of 830 m² g⁻¹, a total pore volume of 1.1 cm³ g⁻¹, and a pore diameter of about 10 nm, estimated according to the KJS method elaborated for the cylindrical pore geometry¹⁴ (see Table 1). Note that the pore diameters estimated by using an equation derived for *Fm3m* symmetry,⁵ which utilizes the unit cell from small angle X-ray scattering data and adsorption pore volumes (see ESI, Fig. 3S and Table 1S†) are about 4 nm larger than those estimated by the KJS method.

Fig. 2(a) shows a comparison of argon adsorption isotherms for a series of FDU1-*x* samples synthesized for different salt-polymer mass ratios. As can be seen from this figure, the optimal salt-polymer ratio lies between 2 and 3. There is almost no difference among isotherms for the samples synthesized at this salt-polymer ratio range except for a less steep desorption branch for FDU-1-2,

Table 1 Structural properties of the FDU-1 samples studied^a

Sample	$S_{\text{BET}}/\text{m}^2 \text{g}^{-1}$	$V_t/\text{cm}^3 \text{g}^{-1}$	$V_{\text{mi}}/\text{cm}^3 \text{g}^{-1}$	w/nm
FDU-1-0	801	0.80	0.16	10.1
FDU-1-1.5	650	0.61	0.09	8.0
FDU-1-2	830	1.10	0.11	10.1
FDU-1-2.5	811	1.10	0.12	10.0
FDU-1-3	708	1.06	0.10	10.0
FDU-1-3.5	558	0.66	0.08	8.4
FDU-1-4	455	0.62	0.05	9.0

^a S_{BET} = BET specific surface area; V_t = total pore volume; V_{mi} = micropore volume (including the volume of interconnecting pores); w = diameter of primary mesopores.

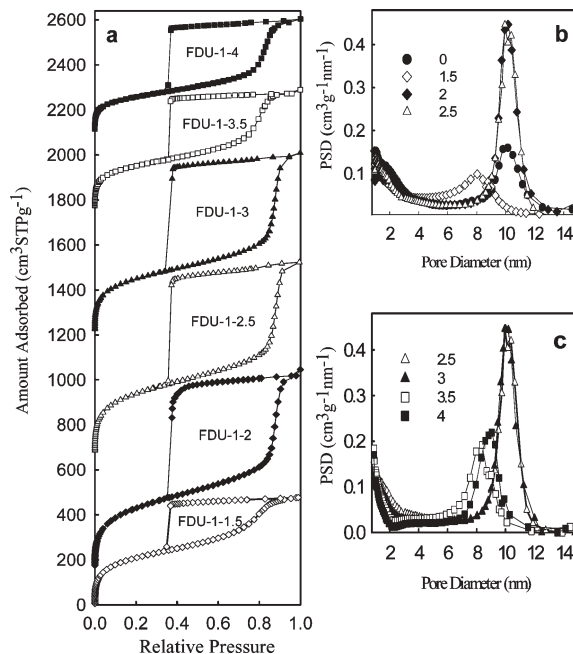


Fig. 2 (a) Comparison of argon adsorption-desorption isotherms at -196 °C for a series of FDU1-*x* samples synthesized at different salt-polymer mass ratios. The isotherms for FDU-1-2, FDU-1-2.5, FDU-1-3, FDU-1-3.5 and FDU-1-4 were offset vertically by 170, 680, 1220, 1770 and 2110 cm³ STP g⁻¹, respectively; (b), (c) the corresponding pore size distributions calculated according to the KJS method.¹⁴

which suggests some nonuniformity in the size of the cage entrances. Fig. 3 shows the pore volume plotted against the salt-polymer ratio for the samples studied, which clearly indicates the best range of this ratio between 2 and 3.

The samples synthesized below and above the optimal salt-polymer mass ratio range exhibit a less steep capillary condensation step and consequently a broader PSD. Moreover, the micropore and primary mesopore volumes for the aforementioned samples are lower than those for the FDU-1-*x* samples with *x* between 2 and 3. In addition, the mesopore diameter for those samples was about 1–2 nm smaller in comparison to the samples synthesized at optimal conditions (see Table 1). Also, the PSD peak for the samples synthesized beyond the optimal range of the

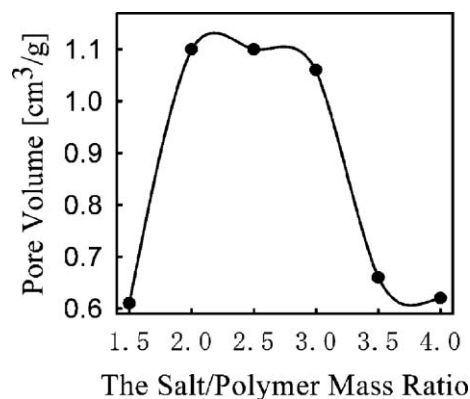


Fig. 3 Dependence of the total pore volume on the salt-polymer mass ratio for the samples studied.

salt-polymer ratio is about 2–3 times smaller than that for the FDU-1-*x* samples (*x* = 2, 2.5, 3) and shifted in the direction of smaller pores.

Thermogravimetric data shown in the ESI in Fig. 4S† indicate that the samples synthesized in the presence of sodium chloride show weight change curves analogous to those reported for SBA-15 prepared with salt addition too.¹⁵

In conclusion, doubling the amount of PEO-PBO-PEO block copolymer, adding sodium chloride and reducing the acidity of the synthesis gel afforded FDU-1 samples with improved uniformity of mesopores and pore entrances. Moreover it led to a significant narrowing of PSD. Furthermore, the proposed recipe reduces the time of the first synthesis step from 24 to 6 hours.

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