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Facile synthesis of high quality mesoporous SBA-15 with enhanced control of the porous network connectivity and wall thickness†

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Convenient and commercially viable synthesis conditions are described, providing efficient and reproducible control of pore connectivity and pore wall thickness for the synthesis of high quality SBA-15 mesoporous silica.

SBA-15 is mesoporous silica composed of two-dimensional hexagonal arrays of channels that typically range from 5–9 nm in diameter.[1] It is commonly synthesized under strongly acidic conditions, using poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer as a structure-directing agent. Due to its appealing textural properties and high surface area, and appreciable thermal and hydrothermal stability, SBA-15 has recently attracted much research attention for potential applications in catalysis or separation processes (see ref. 2 for references). However, the precise character of the 1-dimensional channel or 3-dimensional interconnection of the pore systems has been a matter of debate for the past few years.[3–8] With respect to this, recent studies based on inverse platinum and carbon replication of the siliceous framework have demonstrated that the large uniform ordered pores of SBA-15 are actually accompanied by smaller disordered pores that provide connectivity between adjacent large pore channels.[4,5,9–13] However, direct control of the interconnecting porosity during synthesis still remains as a challenge in the study of SBA-15 type materials.[12,14] Such control is particularly desirable for applications involving host–guest interactions or adsorption and diffusion processes. In addition, there is at present a significant interest in synthetic methods that would suppress the network connectivity between the channels of SBA-15, for the production of ultra-large pore MCM-41 analogues.[12,14] Another important aspect of SBA-15 materials is linked to the commercial requirements for their synthesis. There is a strong demand for low cost processes, the possibility of scaling-up the batch size, high yields and synthesis efficiency. Here, we propose a simple synthetic approach allowing an easy and highly reproducible control of the network connectivity and wall thickness of SBA-15, by adjusting the SiO_2 : P123 ratio and decreasing substantially the HCl concentration compared with the original system.[1] In addition, the present synthesis conditions, with stirring at decreasing acid concentration, are suitable for the production of high-quality SBA-15 materials, irrespective of the synthesis batch size and the different natures of tetraethyl orthosilicate (TEOS) and sodium silicate.

All SBA-15 samples were prepared in aqueous solution using $EO_{20}PO_{70}EO_{20}$ (Pluronic P123, Aldrich) as a structure-directing agent. Either sodium silicate (DC Chemical, Korea, 25 wt% SiO_2 in aqueous solution, Si : Na = 1.5) or TEOS‡ (ACROS, 98%) was acceptable as the silica precursor. High-quality samples were obtained over a wide range of SiO_2 : P123 molar ratios (r) of 45–75. The HCl concentration could be decreased to as low as 0.1 M, although longer reaction times were required at low HCl concentrations, particularly when TEOS was used. In a typical synthesis batch (r = 60), 3.46 g of P123 was dissolved in 21.6 g of distilled water and 4.5 g of conc. HCl (35%). To this mixture, 42.9 g of sodium silicate (5 wt% SiO_2 diluted from 25 wt%) was quickly added under stirring at 35 °C. The mixture was stirred at 35 °C for 24 hours, and subsequently heated for 24 hours at 100 °C under static conditions. The solid product was then filtered and dried without washing at 100 °C. It should be noted that filtration proceeded very rapidly even with large synthesis batches, compared to that under previous synthesis conditions. To remove the template, the solid was slurried in an ethanol–HCl mixture, filtered, dried and then calcined in an air flow at 550 °C. Inverse platinum replication was used to identify the degree of pore connectivity according to the methods utilized previously.[5,10,11]

The synthesis gives high yields of highly ordered mesoporous silica (close to 100% on the basis of silica recovery). Fig. 1 shows powder X-ray diffraction patterns for representative samples, synthesized with sodium silicate with r = 45, 60 and 75, respectively. A well-resolved 2-D hexagonal phase is obtained in all cases, with the diffraction peaks being characteristic of the hexagonal *p*6*mm* symmetry. A noticeable increase in *d*-spacing occurs with increasing SiO_2 : P123 ratio. In addition, the relative intensity ratio between the first low angle reflection (100) and the reflections at higher 2θ angles increases with increasing SiO_2 : P123 ratio while the high degree of order is retained, suggesting differences in the pore wall thickness to pore size ratios, and, most likely, an increase of the wall thickness.[15] The N_2 isotherms are of type IV with an H1 hysteresis loop and a pronounced capillary condensation step at high relative pressure, characteristic of high-quality large-pore

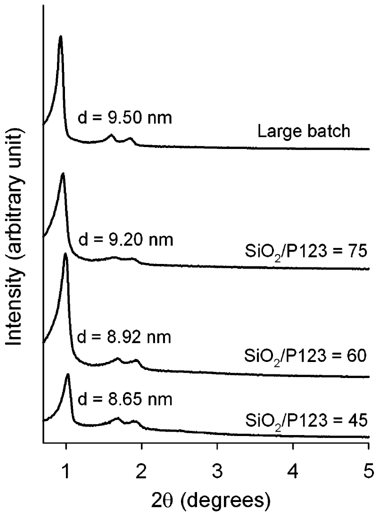

Fig. 1 Powder X-ray diffraction patterns obtained for calcined SBA-15 samples synthesized with sodium silicate (5% in water) and initial SiO_2 : P123 = 45, 60 and 75 (Rigaku Multiplex, operated at 2 kW, using Cu Kα radiation). The XRD pattern of calcined SBA-15 (SiO_2 : P123 = 60) synthesized in a large batch indicates no change in sample quality due to a batch size increase of 50 times.

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† Electronic supplementary information (ESI) available: structural parameters (Table 1) and N_2 adsorption–desorption isotherms at 77 K and pore size distributions for the SBA-15 samples with SiO_2 : P123 = 45, 60 and 75. The pore size was analysed with the adsorption branch using the BJH algorithm. See http://www.rsc.org/suppdata/cc/b3/b303696k/

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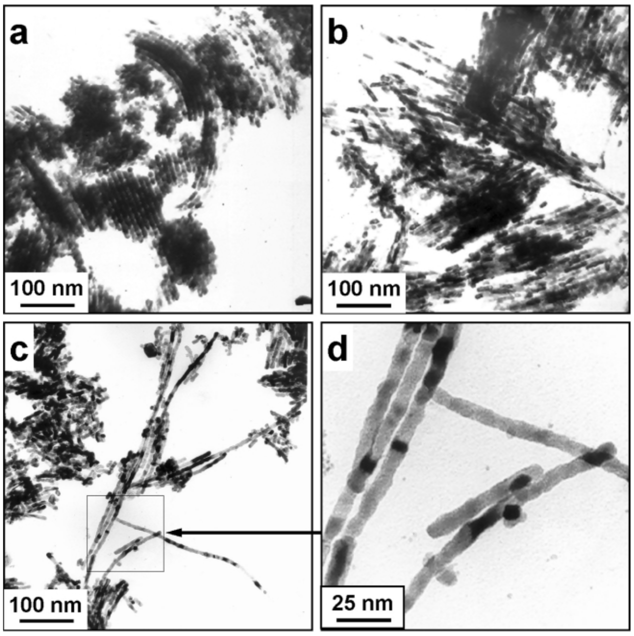

Fig. 2 TEM images of the platinum replicas of SBA-15 synthesized with different initial SiO_2 : P123 ratios: a) SiO_2 : P123 = 45, b) 60, c) 75, and d) magnification of the platinum replica for SBA-15 sample with SiO_2 : P123 = 75.

SBA-15 mesoporous silica (see Supplementary Information†). The pore size distribution is narrow in all cases. Lattice and textural parameters of the SBA-15 samples are listed in the Supplementary Information (Table 1)†. It can be seen that pore size, pore volume and BET specific surface areas decrease with increasing initial SiO_2 : P123 ratios. Direct observation of the isotherms confirms this evolution, with the capillary condensation step in the mesopores being shifted to lower relative pressures and a substantial decrease in adsorption capacity with the increase of SiO_2 : P123. It is therefore noteworthy that our synthesis method allows effective, systematic and simple control of the pore wall thickness of SBA-15.

It is possible to ascertain the nature of the network connectivity by imaging isolated platinum replicas prepared inside the pores of the SBA-15 sample.[5,10,11,13] In the TEM images (Fig. 2), connections between the main channels of SBA-15 can be visualized as bridges between platinum nanowires. Bridged self-standing platinum networks are obtained at SiO_2 : P123 = 45, shown in Fig. 2a, implying full network connectivity of the mesoporous silica. Fig. 2b is representative of an intermediate situation with some connectivity remaining. In contrast, no network of Pt nanowires is seen for the SBA-15 sample synthesized with SiO_2 : P123 = 75, as exemplified in Fig. 2c. Only isolated long nanowires or self-agglomerated separate platinum nanowires are observed (Fig. 2d). This result is similar to the one reported for MCM-41, which consists of separated continuous walls,[10,16] or to SBA-15 materials synthesized at low ageing temperatures ($\leq$ 60 °C).[13] Such isolated nanowires were also synthesized in SBA-15 by Han *et al.*, but the exact SBA-15 synthesis temperature was not specified.[17] On the basis of the replication method, we can thus conclude that high quality SBA-15 with connected pore channels is produced at low SiO_2 : P123 ratios, whereas SBA-15 exhibiting isolated pores can be generated at higher SiO_2 : P123 ratios. Furthermore, under our synthesis conditions, it is likely that the walls of SBA-15 synthesized at high SiO_2 : P123 ratio still contain a complementary microporosity (based on high amounts of N_2 adsorbed at low P/P_0, Supplementary Information†). The micropores are, however, not so large as to form Pt replicas interconnecting adjacent channels.

Previous reaction conditions[1–4,11] usually employed high concentrations of the HCl catalyst, which led to very rapid precipitation of silica. Detailed structures of the mesophase were somewhat difficult to control under these conditions due to fast reaction, because the mesostructured materials were obtained by the kinetically controlled competitive assembly of organic and inorganic species into nanostructured domains. In addition, under high HCl concentrations, only a narrower range of SiO_2 : P123 is acceptable for the synthesis, with a marked decrease in ordering. The synthesis reactions were generally carried out under static conditions, in order to slow down the kinetics. In the present synthesis study, the acid concentration has been sufficiently lowered, and the reaction mixture was well stirred. We believe that the formation of mesophases can therefore be governed more thermodynamically as the HCl concentration decreases. It is then likely that sudden intermicellar condensation of silica can be prevented. Higher amounts of silicate species can be allowed to combine with the hydrated PEO chains of P123 at high SiO_2 : P123 ratios, leading to a significant decrease in the pore-connecting PEO–PEO interactions between adjacent micelles, and to pore-wall thickening. Thus, the SiO_2 : P123 ratio seems to be the main factor affecting the degree of pore connectivity under the present low HCl concentration. Moreover, slowing down the overall kinetics allows facile synthesis of the highly ordered and tunable materials even in an ultra-large batch (Fig. 1, top).

In conclusion, synthesis conditions for SBA-15 could be optimised through our insights into the kinetically controlled competitive assembly of organic and inorganic species. The present synthesis conditions (low concentrations of the toxic HCl, low-cost sodium silicate, and thorough mixing of reactants) are suitable for SBA-15 with an excellent degree of mesoscopic order, tunable pore wall thickness and pore connectivity. The cost-effective conditions with the possibility of facile scaling-up are readily adoptable for large-scale commercialisation of SBA-15 with tailored structures and textural properties.

Notes and references

‡ The synthesis with TEOS uses 3.46 g of P123 dissolved in 62.8 g of distilled water and 2.0 g of conc. HCl (35%), to which 7.44 g of TEOS is subsequently quickly added under stirring at 35 °C.

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