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Preparation of regular macroporous structures built of intergrown silicalite-1 nanocrystals

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Organized silicalite-1 bodies with a regular system of macropores were prepared. The procedure includes two stages. In the first, self-assembly of monodisperse polystyrene spheres and silicalite-1 nanocrystals is induced by the slow evaporation of the solvent. In the second stage a hydrothermal treatment of the self-assembled composite in a silicalite-1 precursor solution leads to intergrowth and closing of the mesopores between the nanocrystals building the walls of the macroporous structure. The mechanical properties of the macroporous zeolite structures obtained after removal of the polystyrene were substantially improved by this secondary growth of the zeolite crystals. The characteristic features of the self-assembled and hydrothermally treated macroporous structures were studied by XRD, FTIR, SEM, TG-DTA and nitrogen adsorption measurements.

1 Introduction

Recently, considerable efforts have been devoted to the preparation of different types of inorganic macroporous materials.[1] Such materials with uniform pore size in the range from 50 nm to 10 μm are expected to have advanced applications, including their use as photonic crystals,[2] optical devices[3] and as candidates for high speed computer device packaging.[4] Such structures can also be used as light-weight structural materials,[5] thermal and acoustic insulators,[6] catalytic supports and surfaces.[7] The most widely used approach for the preparation of such materials is the utilization of monodisperse polystyrene spheres for the creation of 3D template structures. These ordered structures offer a 3D scaffold for a variety of precursor materials which can be infiltrated in the voids between the colloidal spheres. After removal of the templating colloidal crystal, a 3D macroporous material with a well-defined periodic structure is obtained. Monodisperse silica spheres[8,9] and emulsion droplets[10] have also been used as templates for the preparation of ordered macroporous structures. Another approach for the preparation of ordered macroporous solids was developed by D. J. Pine and co-workers.[11] A regular network of macropores was obtained by self-assembly of monodisperse polystyrene spheres and TiO_2 nanoparticles. Thus, the template strategy, which is a commonly used approach in the synthesis of micro- and mesoporous materials, has been extended to the preparation of ordered macroporous monoliths.

In the area of catalysis and separation processes, ordered materials with well defined periodic structures and controlled sizes are highly desirable. This quest is especially urgent for zeolitic catalysts where the diffusion paths and the blocking of the channels could have a great effect on the performance of the material. Materials with bimodal micro-/macropore systems involving zeolites are of considerable interest, since they combine the benefits of each pore size regime. The extension of the template strategy to the preparation of macroporous materials opens up routes for the preparation of structures with bimodal-sized pore networks. Such a material was successfully prepared by a dual templating method.[12] Macroporous voids with a uniform diameter of about 250 nm were formed by using arrays of monodisperse polystyrene spheres and the microporous walls with tetrapropylammonium (TPA) as the structure-directing agent for silicalite-1. It seems, however, that the periodicity of the macropores prepared using this approach is limited. In addition the crystallinity of the zeolite walls is not very high. Another approach for the creation of organized macroporous zeolite structures is the infiltration of zeolite nanocrystals into the voids of a colloidal crystal built of monodisperse polystyrene spheres.[13–15] In this case the zeolite walls are fully crystalline but the mechanical properties of the material are limited since the connection between the building particles is based on weak electrostatic interactions. The mesopores which usually form between zeolite grains are not discussed in this article.

The present paper reports a novel combination of synthesis strategies which allows the preparation of highly crystalline zeolitic materials with a regular system of macropores. The control of the mechanical properties and textural mesoporosity of the material is also in the scope of the investigation.

2 Experimental

2.1 Starting materials

Monodisperse negatively charged polystyrene spheres (2.54 wt.% suspension) with a size of 535 nm were purchased from Polysciences, Inc. (USA). The colloidal silicalite-1 suspension was prepared according to the conditions given below.

2.2 Synthesis of the colloidal silicalite-1 suspension

The reactants used in the synthesis were tetraethyl orthosilicate (TEOS) (Merck), tetrapropylammonium (TPA) hydroxide (20% in water, Merck) and distilled water. After mixing of the reactants, the solution was allowed to hydrolyze for 14 hours and was then treated hydrothermally at 60 °C for three weeks. The starting composition of the clear solution used for the synthesis of the silicalite-1 suspension was as follows:

$$4.5(TPA)_2O : 25SiO_2 : 480H_2O : 100EtOH$$

The presence of ethanol (EtOH) in this composition is a consequence of the use of TEOS as a silica source. After the synthesis, the zeolite suspension was purified in a series of four steps consisting of high speed centrifugation, removal of the mother liquor and redispersion in water. The pH of the purified

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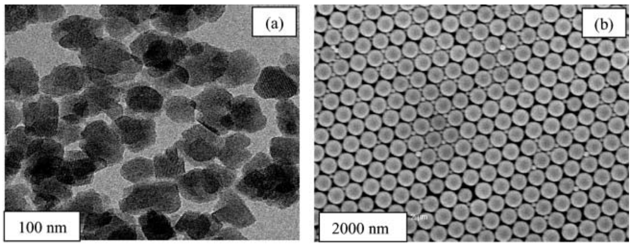

Fig. 1 TEM micrograph of the silicalite-1 nanoparticles (a) and SEM micrograph of the polystyrene spheres (b) used as starting materials.

zeolite suspension was adjusted to about 9.5 by the addition of a 0.10 M NH_3 solution. Silicalite-1 suspensions with a 1 wt.% and 3.0 wt.% content were prepared.

2.3 Preparation of ordered silicalite-1–polystyrene structures

A typical preparation includes mixing of 6 ml of a 1 wt.% suspension of silicalite-1 with 3 ml of a 1 wt.% polystyrene suspension in a polypropylene vessel. The proportions were chosen such that the zeolite particles could fully fill the voids between the close-packed polystyrene spheres when the water in the vessel was evaporated. The vessel was covered with a plastic paraffin film punched with a few holes and the drying was carried out in an oven at 60 °C. The paraffin film was used to slow down the evaporation since the rapid drying resulted in disordered macroporous materials. About two weeks were necessary to obtain a completely dry sample.

Some of the prepared composites were subjected to secondary growth. The hydrothermal treatment was performed with a precursor solution similar to the one used for the preparation of the colloidal silicalite-1 crystals. After 24 h at 95 °C the silicalite-1–polystyrene particles were separated by suction filtration from the colloidal zeolite crystals, washed and dried.

The polystyrene spheres from the self-assembled and hydrothermally treated composites were removed either by a chloroform extraction or by a high temperature calcination (500 °C for 5 h) together with the combustion of the TPA template.

2.4 Characterization

The particle size analysis of the zeolite nanocrystals was performed with a Brookhaven Instruments ZetaPlus. The powder X-ray diffraction (XRD) data of the samples were collected on a STOE STADI-P diffractometer in Debye–Scherrer geometry equipped with a linear position-sensitive detector (6° in 2θ) and employing Ge monochromated Cu $K\alpha_1$ radiation. The colloidal silicalite-1 particles were examined with a Philips EM 420 transmission electron microscope (TEM). Micrographs of the polystyrene spheres and silicalite-1 macroporous bodies were taken on a Philips XL 30 LaB_6 scanning electron microscope (SEM). The combined thermogravimetric-differential thermal analysis (TG-DTA) of the samples was performed with a Setaram TG-ATD *LABSYS* thermal analyzer at a heating rate of 5 °C min^{-1} in an atmosphere containing 80% N_2 and 20% O_2. FTIR analyses were performed on samples pressed in KBr with a Perkin Elmer PE-2000 FTIR spectrometer. Nitrogen adsorption measurements were carried out on calcined samples with a Micromeritics ASAP 2010 surface area analyzer.

3 Results and discussion

3.1 Preparation of silicalite-1–polystyrene ordered structures

The silicalite-1 nanocrystals used as primary building units for the preparation of the macroporous material are shown in Fig. 1a. The synthesized particles were relatively uniform in size with a mean diameter of about 50 nm according to the light scattering and TEM measurements. The ζ potential of the colloid was -41 mV. No other crystalline phase or indications of the presence of amorphous material were detected in the XRD pattern of the dried silicalite-1 sample. The monodisperse polystyrene spheres employed as macrotemplates are shown in Fig. 1b.

The organized macroporous silicalite-1 structures were prepared by a two-step procedure. The first step of the preparation consists of the evaporation of the water from a mixture containing monodisperse polystyrene spheres and colloidal silicalite-1 crystals. A schematic representation of the self-assembly process of the polystyrene spheres and silicalite-1 nanocrystals is shown in Fig. 2. The monodisperse polystyrene particles used in this study bear a slight anionic charge from sulfate ester. The isoelectric point of different zeolite types is in the pH range 2–4,[16] and in alkaline media the zeolite particles are negatively charged. The fact that both the zeolite crystals and polystyrene spheres are negatively charged prevents uncontrolled agglomeration. The slow evaporation of the water in the system allows the polystyrene particles to organize themselves in an ordered lattice due to a gradual increase in their concentration. As water evaporates, the zeolite nanoparticles are driven by capillary forces to move close to each other and pack into the voids between the polystyrene spheres. After the complete evaporation of the water a homogeneous layer was observed on the bottom of the vessel. The layer was broken into pieces of several square millimeters in order to be taken out from the vessel.

The second step of the preparation consists of a hydrothermal treatment of the self-assembled silicalite-1–polystyrene composite (Fig. 2). During this treatment the silicalite-1 nanocrystals packed between the polystyrene spheres continue their growth. Together with the continuous growth of the silicalite-1 nanocrystals building the composite new crystals are formed. The growth of the silicalite-1 particles in the confined space between the polystyrene spheres leads to the formation of homogeneous walls of silicalite-1 built of well intergrown crystals.

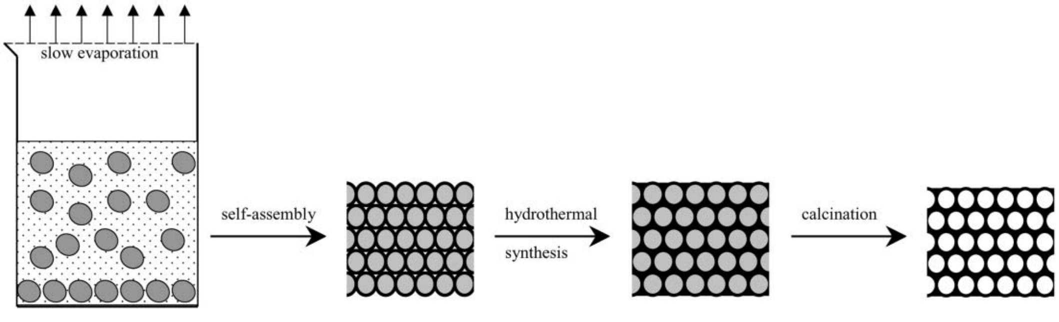

Fig. 2 Schematic representation of the process for the preparation of organized macroporous silicalite-1 structures.

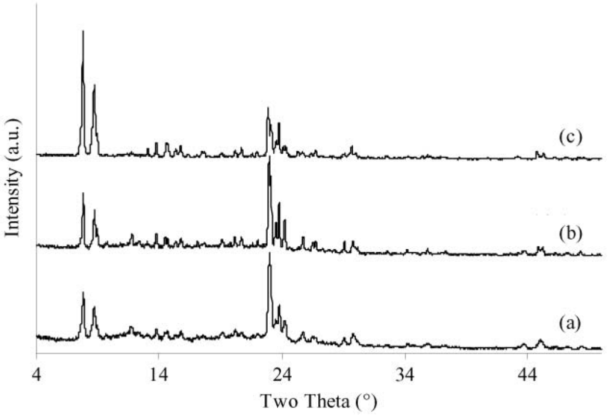

Fig. 3 XRD patterns of: (a) a polystyrene–silicalite-1 composite after the self-assembly procedure, (b) a polystyrene–silicalite-1 composite after the hydrothermal treatment, and (c) the micro-/macroporous silicalite-1 material obtained after calcination.

3.2 Characterisation of the ordered silicalite-1 structures

The XRD pattern of the silicalite-1–polystyrene composites prepared by a self-assembly procedure shows the peaks characteristic of the MFI-type topology together with a halo emanating from the polystyrene template. The diffractogram of the sample subjected to the hydrothermal treatment differs slightly from that of the sample prepared by self-assembly (Fig. 3a). A halo is still visible in the as-prepared sample but the zeolite peaks are now more intense. Pure well crystallized silicalite-1 was obtained after the calcination of the composite (Fig. 3b).

The FTIR study confirmed the results from the XRD analysis. In the silicalite-1–polystyrene sample (Fig. 4a) the silicalite-1 absorption bands can be distinguished together with the most intense polystyrene absorption bands in the range 1450–1650 cm^{-1} and at about 650 cm^{-1} (Fig. 4b). After the chloroform treatment only the characteristic absorption bands for silicalite-1 together with C–H bands at about 1440 cm^{-1} can be seen in the spectrum (Fig. 4c). The weak band at about 1440 cm^{-1} is due to the tetrapropylammonium cation still occluded in the micropores of silicalite-1, which cannot be removed by a chemical extraction. Thus, the disappearance of the intense absorption bands of the polystyrene shows that the spheres used as macrotemplates can be removed by a chemical treatment. If some residual organic matter is still present in the material, it should be in a negligible amount since the IR analysis did not detect any traces. The calcination of the material leads to complete removal of both the polystyrene from the macropores and the TPA from the micropores of silicalite-1 (Fig. 4d).

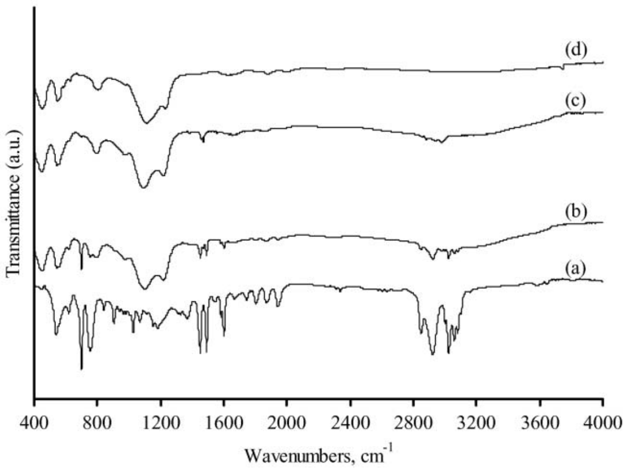

Fig. 4 IR spectra of: (a) the initial polystyrene beads, (b) a silicalite-1–polystyrene composite, and the composite after (c) chloroform treatment and (d) calcination.

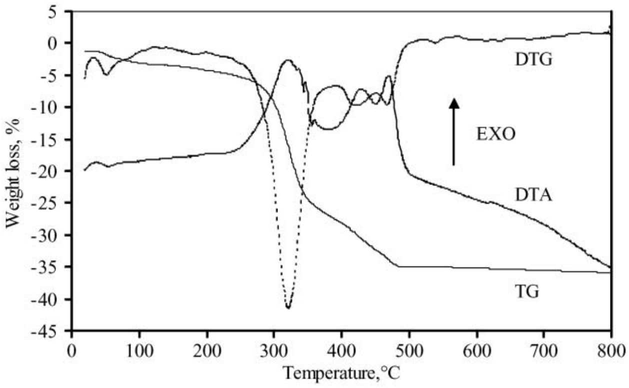

Fig. 5 TG-DTA-DTG curves for a silicalite-1–polystyrene composite prepared by the two-step procedure.

The combined TG-DTA-DTG analysis of a silicalite-1–polystyrene composite is presented in Fig. 5. The TG analysis shows that the composite comprises about 65 wt.% of calcined silicalite-1. The weight losses of the silicalite-1–polystyrene body are 4.1, 23.3 and 7.6 wt.% in the temperature ranges 20–190 °C, 190–390 °C and 390–510 °C, respectively. These weight losses include the combustion of the TPA structure-directing agent in the silicalite-1 crystals as well as of the polystyrene spheres. The silicalite-1 content of the self-assembled material before the hydrothermal treatment was lower (about 53 wt.%), which shows that the hydrothermal treatment leads to a substantial increase of the silicalite-1 content.

A general view and a close view of the macroporous material prepared by self assembly of polystyrene spheres and silicalite-1 nanocrystals, the latter after the material had been subjected to a chloroform treatment, are shown in Fig. 6. Particles with sizes up to several mm^2 were found in the product (Fig. 6a). The individual nanocrystals building the regular network are easily distinguishable (Fig. 6b). The hydrothermal treatment of the self-assembled polystyrene–silicalite-1 composite does not influence the regular system of macropores as can be seen in Fig. 7a, where a general view of a calcined macroporous silicalite-1 structure prepared by the two-step procedure is shown. However, the subsequent hydrothermal treatment of the self-assembled composite in a zeolite precursor solution had a pronounced effect on the appearance of the macroporous material. SEM analysis of the calcined sample shows that during the secondary growth denser and thicker zeolite walls were formed (Fig. 7b). In contrast with the self-assembled macroporous material (Fig. 6b) the individual silicalite-1 crystals building the macroporous walls are no longer distinguishable since they form a well intergrown layer. Although the walls of the material are much thicker a connection between the macropores *via* apertures of about 50 nm can be observed (Fig. 7c).

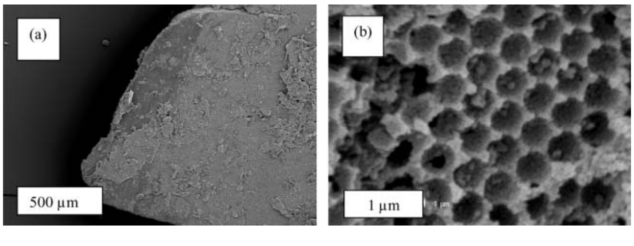

Fig. 6 Silicalite-1–polystyrene composite body prepared by self-assembly of monodisperse polystyrene spheres and silicalite-1 nanocrystals (a). Close view of a cross section of the material after chloroform extraction of the polystyrene (b).

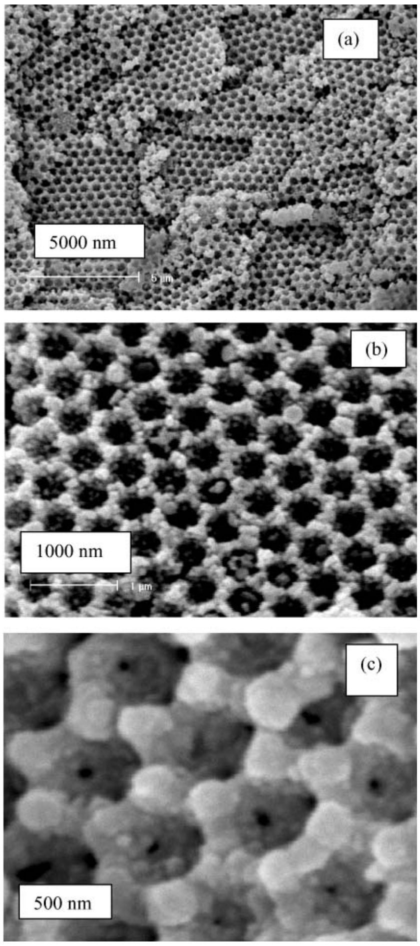

Fig. 7 SEM micrographs of a calcined macroporous silicalite-1 structure prepared by the self-assembly procedure followed by hydrothermal treatment: (a) general view of the regular system of macropores, (b) a closer look at the macropores where the walls built of intergrown nanocrystals are visible, and (c) the openings between the regular system of macropores.

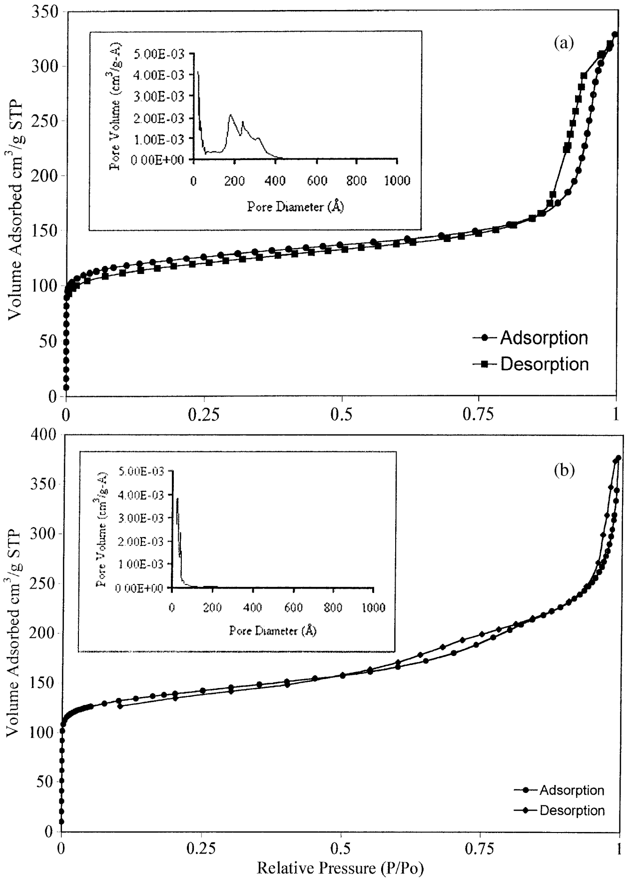

Fig. 8 Nitrogen adsorption and desorption isotherms for the macroporous silicalite-1 structures prepared by the self-assembly procedure (a) and the self-assembly procedure followed by a hydrothermal treatment (b). The inserts represent the corresponding BJH desorption d*V*/d*D* plots.

The surface area of a calcined macroporous silicalite-1 structure prepared by self-assembly was determined by nitrogen adsorption to be 407 $m^2 g^{-1}$. A similar value was obtained for the material subjected to a secondary growth (428 $m^2 g^{-1}$). These values indicate a well crystallized product. For both structures, isotherms with identical, nearly horizontal adsorption and desorption branches, typical for microporous materials, were observed (Fig. 8a and b). In addition, the upward turn of the isotherms at high relative pressures indicates filling of interparticle spaces. For the self-assembled sample a distinct hysteresis loop indicative of mesopores can be seen on the isotherm. The shape of this hysteresis is of the H1 type which is often obtained from agglomerates of spheroidal particles of fairly uniform size.[17] The detected hysteresis loop shows that the monodisperse silicalite-1 crystals form textural mesopores in the self-assembly process. According to BJH calculations the majority of the mesopores are in the size range 100–450 Å (Fig. 8a). This relatively broad distribution is obviously due to the random orientation of silicalite-1 particles, which results in the formation of mesopores of different sizes. The adsorption–desorption isotherms of the sample subjected to secondary growth are nearly the same as those of the material prepared by self assembly. However, a negligible hysteresis loop at high relative pressures was observed in this case, which shows that during the secondary growth a substantial number of the mesopores are closed. This result was confirmed by BJH pore size analysis, by which only very small mesopores with two peaks in the range 20–80 Å were found (Fig. 8b). Obviously these small mesopores are due to pin-holes in the intergrown zeolite layer. The N_2 adsorption does not allow evaluation of the pore volume of the macropores left after the removal of the polystyrene macrotemplate. The analysis of the adsorption data showed that the contribution of the mesopores closed during the hydrothermal treatment is not substantial. The total pore volumes of the macroporous silicalite-1 structures prepared by self-assembly was 0.51 $cm^3 g^{-1}$, while for the hydrothermally treated material, where the mesopores in the range 100–450 Å are closed, it was 0.49 $cm^3 g^{-1}$. The calculated pore volumes for pores below 20 Å for these two materials were 0.14 and 0.15 $cm^3 g^{-1}$, respectively. These values are close to the ones reported for a well crystallized silicalite-1.

3.3 Discussion

The macroporous silicalite-1 structures prepared by the self-assembly procedure are built of individual silicalite-1 nanocrystals. The closest distances between the nanoparticles in the walls of the macropores depend on their morphological features and repulsive/attractive forces between crystals. In the course of self-assembly, formation of bonds stronger than hydrogen bonds cannot be expected. The weak interactions between the building particles make the ordered structure fragile and explain the extremely low mechanical strength. On the other hand during the hydrothermal treatment the secondary growth of silicalite-1 particles leads to intergrowth between the individual particles. Thus, the resulting silicalite-1 macroporous structures are built of intergrown crystals where the covalent bonding is dominant. Although no special tests were performed, the difference in the strength of the self-assembled and hydrothermally treated samples is easily distinguishable. After the hydrothermal treatment and calcination procedure the macroporous zeolite bodies, usually with a size of several square millimeters, do not show any tendency to disintegrate and break into smaller pieces, which is typical for calcined self-assembled materials. A certain pressure is necessary to break the material prepared by a combination of self-assembly and hydrothermal treatment procedures. Thus, different laboratory manipulations can be performed with the hydrothermally treated silicalite-1 structures without risk of breaking the particles.

4 Conclusions

Macroporous organized silicalite-1 structures were prepared by a combination of self-assembly and subsequent hydrothermal synthesis procedures. During the self-assembly procedure the monodisperse polystyrene spheres form liquid crystals with voids filled with silicalite-1 nanocrystals. The hydrothermal treatment of this composite leads to formation of dense well intergrown walls. As a result a material with substantially improved mechanical properties comprising only small mesopores was obtained. The calcination of the composite provides an organized micro-/macroporous structure.

The micro- and macroporosity of the material can be tailored by the type of zeolite employed and the size of the polystyrene macrotemplate, while the textural mesoporosity can be partially controlled by the secondary growth process.

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References

1 O. D. Velev and E. W. Kaler, *Adv. Mater.*, 2000, **12**, 531.
2 E. G. Judith, J. Wijnhoven and L. V. Willem, *Science*, 1998, **281**, 802.
3 Y. Xia, B. Gates, Y. Yin and Y. Liu, *Adv. Mater*, 2000, **12**, 693.
4 R. D. Miller, *Science*, 1999, **286**, 421.
5 M. Wu, T. Fuji and G. L. Messing, *J. Non-Cryst. Solids*, 1990, **121**, 407.
6 E. Litovski, M. Shapiro and A. Shavi, *J. Am. Ceram. Soc.*, 1996, **79**, 1366.
7 M. P. Harold, C. Lee, A. J. Burrgraaf, K. Kaizer, V. T. Zaspilas and R. S. A. de Lange, *MRS. Bull*, 1994, **19**, 34.
8 A. A. Zakhidov, R. H. Baughman, Z. Iqbal, C. X. Cui, I. Khayrullin, S. O. Dantas, I. Parti and V. G. Ralchenko, *Science*, 1998, **282**, 2244.
9 Y. A. Vlasov, N. Yao and D. J. Norris, *Adv. Mater.*, 1999, **11**, 165.
10 A. Imhof and D. J. Pine, *Nature*, 1997, **389**, 948.
11 G. Subramaniam, V. N. Manoharam, J. D. Thorne and D. J. Pine, *Adv. Mater.*, 1999, **11**, 1261.
12 B. T. Holland, C. F. Blandford and A. Stein, *J. Am. Chem. Soc.*, 1999, **121**, 4308.
13 L. Huang, Zh. Wang, J. Sun, L. Miao, Q. Li, Y. Yan and D. Zhao, *J. Am. Chem. Soc.*, 2000, **122**, 3530.
14 Y. J. Wang, Y. Tang, Z. Ni, W. M. Hua, W. L. Yang, X. D. Wang, W. C. Tao and Z. Gao, *Chem. Lett.*, 2000, 510.
15 G. Zhu, S. Qiu, F. Gao, D. Li, Y. Li, R. Wang, B. Gao, B. Li, Y. Guo, R. Xu, Zh. Liu and O. Terasaki, *J. Mater. Chem.*, 2001, **11**, 1687–1693.
16 J. P. Brunelle, *Pure Appl. Chem.*, 1978, **50**, 1211.
17 S. J. Gregg and K. S. W. Sing, in *Adsorption, Surface Area and Porosity*, 2nd Edition, Academic Press, London, 1982, 287.