

Silicalite-1 Hollow Spheres and Bodies with a Regular System of Macrocavities

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Silicalite-1 macrostructures in the form of hollow silicalite-1 spheres and bodies with a regular system of macrocavities were prepared using two types of polystyrene beads as shape-directing macrotemplates. The incompatibility between the organic support and the inorganic shell was circumscribed by using negatively charged substrates, reverse of their surface charge, and adsorption of zeolite nanoseeds. These pretreated microbeads were subsequently subjected to a continuous growth in a zeolite precursor mixture. The combustion of the polystyrene core leads to the transformation of the core/shell beads into hollow silicalite-1 spheres. The mechanical properties of the latter were found to be a function of the thickness of the silicalite-1 shell, the diameter-to-wall thickness (d:t) ratio, and the calcination conditions. Silicalite-1 bodies with a regular system of macrocavities were prepared by hydrothermal treatment with a silicalite-1 precursor mixture of a layer of pretreated polystyrene beads deposited in a confined space. The obtained body comprised the polystyrene macrotemplates, which after combustion left a regular system of macrocavities. The formation of silicalite-1 macrostructures and their specific properties was studied by XRD, SEM, and TG/DTA analyses and N₂ adsorption measurements.

Introduction

Materials with spherical geometry of nanometer to micrometer dimensions are widely used in different areas of process industries. In the past decade, extensive research was focused on the preparation of hollow microspheres. This is an important class of materials with applications ranging from the delivery of encapsulated products for cosmetic and medical purposes to their use as lightweight composite materials and as fillers with low dielectric constant in electronic components.¹ Applications for hollow microspheres also cover areas such as catalysis, acoustic insulation, piezoelectric transducers, and manufacture of advanced materials.² Various materials have been used for the preparation of hollow microspheres, for example, polymers, glasses, metals, and ceramics.¹ The methods currently used to fabricate a wide range of stable hollow spheres include nozzle reactor processes, emulsion/phase separation, sol–gel processing, and sacrificial core techniques.¹ The latter involves the use of cores that are coated with the material of interest. The core is subsequently dissolved or volatilized by heating, leaving the shell of the desired hollow microsphere.

The fabrication of hollow spheres has been greatly impacted by the layer-by-layer (LbL) self-assembly technique.³ This method allows the construction of

composite multilayer assemblies based on the electrostatic attraction between nanoparticles and oppositely charged polyions. The method is based on the pioneering work of Iler, who used oppositely charged colloidal particles to make films.⁴ Recent developments of the LbL approach extended the application of the method to construction of multilayer films of polyelectrolytes,³ proteins,⁵ nucleic acids,⁶ dyes,⁷ dendrimers,⁸ and inorganic particles.⁹ The majority of the LbL assemblies were built on flat substrates. An important extension of the method is the preparation of multilayers of colloids on three-dimensional substrates. For example, polystyrene beads were coated with homogeneous layers of colloidal silica particles.¹⁰ LbL-coated colloidal spheres of 640 nm, comprising layers of titania or silica, were used for the preparation of macroporous structures.¹¹

Microporous zeolite-type materials are widely used in areas such as catalysis, separation, ion exchange, and sensing. In recent years, there has been an intense interest surrounding the development of methods for the preparation of zeolites in a desired macroscopic shape

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or on a support with a predefined form. In general, a zeolite coating can be made via a classical hydrothermal synthesis. Such syntheses have shown that the formation of the zeolite coating is very sensitive to the chemical nature, the morphology, and the position of the substrate in the reactor as well as the reaction conditions.^{12,13} Very often, however, even substrates compatible with the zeolite precursor system require a pretreatment of the support or the use of seeds in order to grow a continuous film.^{14,15} For the preparation of continuous zeolite coatings on small three-dimensional inorganic objects, a more sophisticated approach such as seeding by pulsed laser deposition was applied.¹⁶

The incompatibility between the organic substrates and the aluminosilicate precursor species is a serious obstacle for the preparation of zeolite layers on such supports by direct hydrothermal synthesis. Recently, several groups reported on the preparation of shells of zeolite nanocrystals on polystyrene beads using the LbL self-assembly technique. Shells of silicalite-1 nanocrystals were deposited on monodisperse polystyrene beads with diameters of 530¹⁷ and 640 nm.¹⁸ The latter were used as building blocks for the preparation of ordered macroporous monoliths. The LbL approach was applied also for the preparation of zeolite coatings of LTA-, FAU-, BEA-, and MFI-type zeolites on larger (4–8 μm) polystyrene beads.¹⁹ Very recently, the LbL and hydrothermal synthesis techniques were combined for the preparation of core/shell polystyrene/zeolite A microbeads.²⁰ In contrast to the coatings prepared by the LbL technique, where the crystals are attached by electrostatic and hydrogen bonds, in this case the zeolite shell is built of well-intergrown crystals.

In the present study, a combination of LbL self-assembly and hydrothermal synthesis techniques was employed for the preparation of hollow zeolite macrostructures. The paper reports on the preparation of hollow spheres and bodies with large spherical cavities, both built of intergrown silicalite-1 crystals.

Experimental Section

Starting Materials. Two types of negatively charged cross-linked polystyrene beads were used as supports in this study: microbeads from gas permeation chromatography columns with an average diameter of 10 μm (Waters) and large beads (Rohm and Haas) with an average diameter of $\sim 260 \mu\text{m}$. A polycation (Rediflock 4150, Akzo Nobel) was employed as a charge-reversing agent. The colloidal silicalite-1 suspension was prepared according to the conditions given below.

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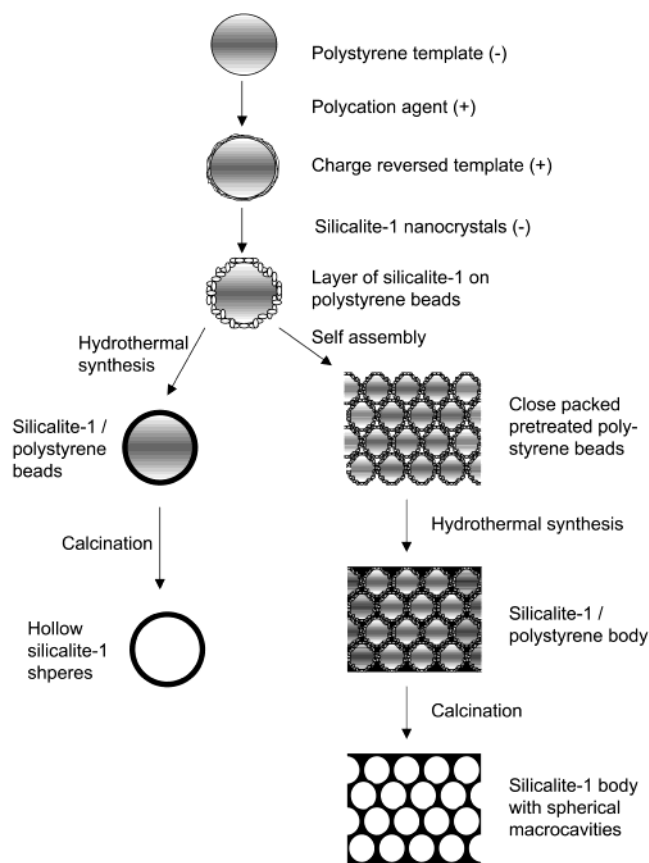
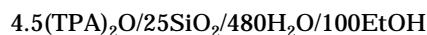


Figure 1. Schematic representation of the process for the preparation of hollow silicalite-1 spheres and bodies with a regular system of macrocavities.

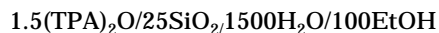
Synthesis of the Colloidal Silicalite-1 Suspension. The reactants used in the synthesis of the colloidal silicalite-1 suspension were tetraethyl orthosilicate (TEOS) (Merck), tetrapropylammonium (TPA) hydroxide (20% in water, Merck), and distilled water. After mixing of the reactants, the solution was allowed to hydrolyze for 14 h and was then treated hydrothermally at 60 $^{\circ}\text{C}$ for three weeks. The starting composition of the clear solution was as follows:



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 zeolite suspension was adjusted to ~ 9.5 by the addition of a 0.10 M NH_3 solution. A silicalite-1 suspension with a 3.1 wt % content was prepared.

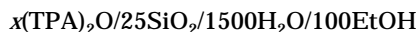
Preparation of Hollow Silicalite-1 Spheres. A schematic presentation of the preparation procedure is shown on Figure 1. The surface charge of the support under investigation was reversed by treatment with the polycation agent. The polystyrene beads were treated for 15 min with a 1 wt % aqueous Rediflock (Akzo Nobel) solution adjusted to pH 9.2 with NH_3 . Then, the beads were separated from the liquid and rinsed with a 0.1 M NH_3 solution in order to wash off excess polymer. The charge-reversed beads were then transferred into the colloidal zeolite suspension to electrostatically adsorb nanocrystals. After 30 min, the beads were separated from the colloidal suspension and rinsed several times with a 0.1 M NH_3 solution.

After the adsorption of silicalite-1 nanocrystals the beads were subjected to a hydrothermal treatment. The molar composition of the solution used for the synthesis of the silicalite-1/polystyrene composites was as follows:



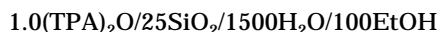
After 48 h at 95 °C, the silicalite-1/polystyrene particles were separated by suction filtration from the colloidal zeolite crystals, washed, and dried. The polystyrene beads and the TPA structure-directing agent were removed by a high-temperature calcination (600 °C for 5 h) under oxygen flow.

The effect of the TPA content in the synthesis mixture on the thickness of silicalite-1 shells was studied by using systems with the following molar compositions:



where x was 0.5, 1.0, 1.5, and 2.0. The syntheses were performed at 95 °C for 3 days. The obtained polystyrene/silicalite-1 beads were treated as described above.

Preparation of Hollow Silicalite-1 Bodies with a Regular System of Macrocavities. The pretreated beads were introduced into a cylindrical glass holder with a diameter of 10 mm, and the synthesis solution was added (Figure 1). A typical preparation includes mixing of 1 g of pretreated beads with 20 g of synthesis solution. The mixture was treated for 1 min under ultrasonic radiation and left to sediment for 30 min. The molar composition of the synthesis mixture used for the secondary growth was the following:



The glass holder was transferred in a stainless steel autoclave, which was heated at 95 °C for 3 days. After heating, the obtained body was separated from the crystals formed in the solution, washed, and dried. Combustion of the organic matter was performed at 600 °C for 5 h under oxygen flow.

Characterization. The particle size analysis of the zeolite nanocrystals was performed with a Brookhaven Instruments ZetaPlus. The powder X-ray diffraction (XRD) diagrams of the samples were recorded 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. Micrographs of the hollow silicalite-1 spheres and bodies were taken on a Philips XL 30 LaB₆ scanning electron microscope (SEM). The combined TG/DTA analysis of the samples was performed with a Setaram TG-ATD LABSYS thermal analyzer at a heating rate of $5^\circ\text{C}\cdot\text{min}^{-1}$ in an atmosphere containing 80% N₂ and 20% O₂. Nitrogen adsorption measurements were carried out on calcined samples with a Micromeritics ASAP 2010 surface area analyzer.

Results and Discussion

Hollow Silicalite-1 Spheres. The XRD diagrams of the silicalite-1/polystyrene beads prepared with the two types of polystyrene beads are shown on Figure 2a,b. Together with the characteristic peaks for the MFI-type material, a halo emanating from the polystyrene support can be seen. The halo is more pronounced in the composite prepared with the large polystyrene beads, where the silicalite-1/polystyrene ratio is lower. No differences were observed in the XRD patterns of the calcined materials; pure well-crystallized silicalite-1 was recorded in both cases (Figure 2c).

The amount of silicalite-1 deposited on the polystyrene beads was evaluated by TG analysis. The composites prepared with the 10- and 260- μm polystyrene templates contain about 28 and 12 wt % silicalite-1, respectively. The weight losses (Figure 3) include thermal degradation of the polystyrene beads, the TPA structure-directing agent, and the polycationic agent used for the adsorption of nanoseeds. The peaks corresponding to these weight losses are overlapping, and the evaluation of each of the components is difficult. Keep-

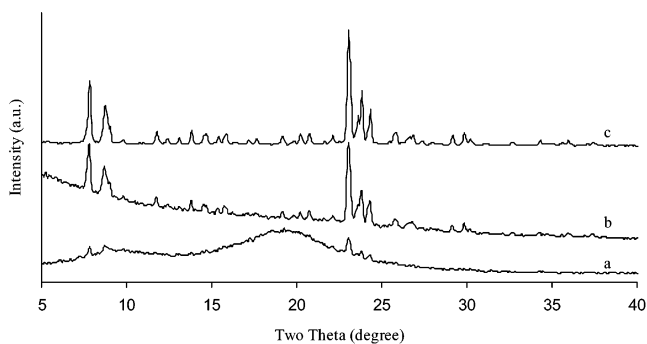


Figure 2. XRD patterns of silicalite-1/polystyrene beads prepared with (a) the 260- μm polystyrene beads, (b) the 10- μm polystyrene beads, and (c) the hollow silicalite-1 spheres obtained after calcination.

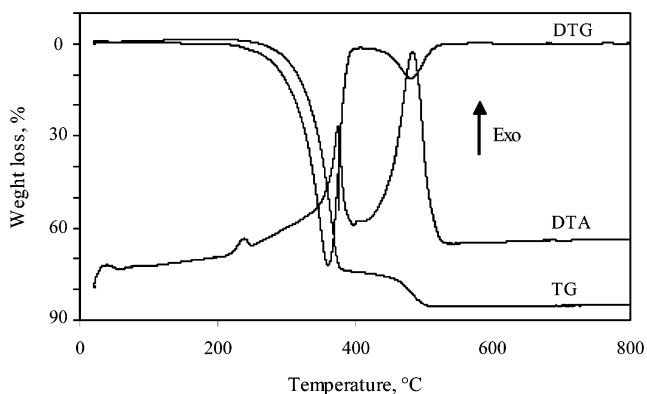


Figure 3. TG/DTA/DTG curves for the silicalite-1/polystyrene beads prepared with 10- μm polystyrene templates.

ing in mind that the silicalite-1 comprises ~ 11.5 wt % TPA and that the content of the polycation agent cannot exceed several percents,¹⁸ it was possible to estimate the content of polystyrene in the composite. These amounts are about 65 and 83 wt % for the 10- and 260- μm beads, respectively. The high-temperature weight losses between 500 and 800 °C are most probably due to the combustion of the residues of the cross-linked polystyrene. The accessibility of oxygen in the composite is limited, which may explain the relatively high temperature of combustion of the organic matter. The TG analysis of silicalite-1 crystals synthesized under the same conditions did not show a similar weight loss in the range 500–800 °C.

The specific surface area of the calcined silicalite-1 hollow spheres was determined by nitrogen adsorption. The values obtained for the two types of hollow spheres are similar, 418 and 411 m^2/g for the spheres templated by the 10- and 260- μm polystyrene beads, respectively. The specific surface area of silicalite-1 crystals synthesized under similar conditions was of the same order (~ 430 m^2/g). These values, coupled with the X-ray diffraction information, indicate a highly crystalline MFI-type material. For both materials, isotherms with identical, nearly horizontal adsorption and desorption branches, typical for microporous materials, were observed.

Micrographs corresponding to different stages of the formation of 10- μm silicalite-1 hollow spheres are shown on Figure 4. Figure 4a shows the homogeneous layer of silicalite-1 nanocrystals adsorbed on the surface of the polystyrene beads, which during the hydrothermal

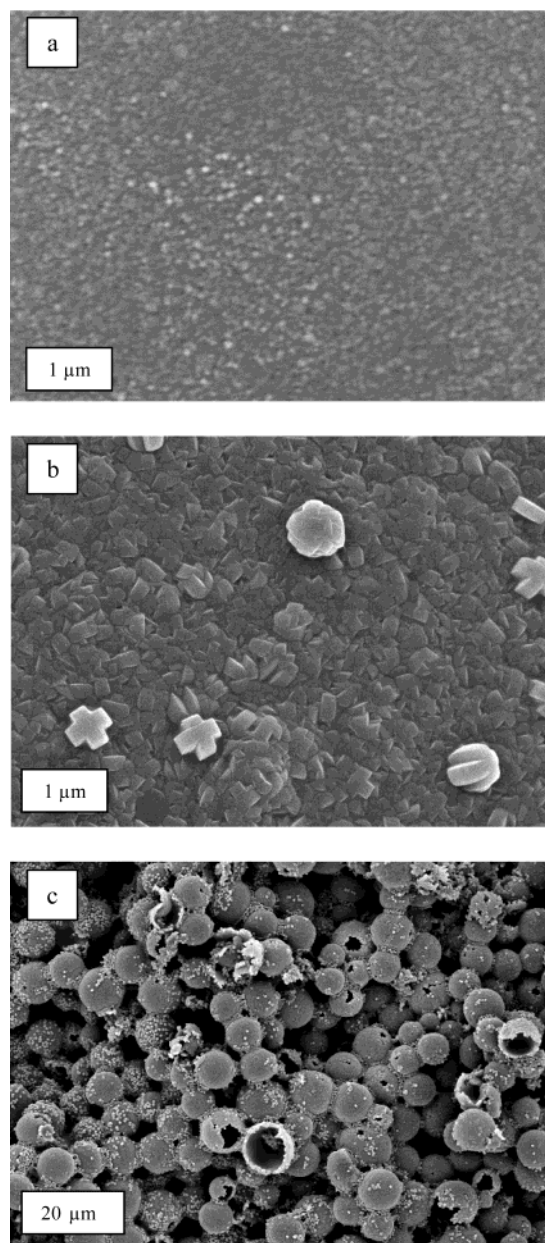


Figure 4. Close views of 10- μm polystyrene supports comprising (a) a layer of adsorbed silicalite-1 nanocrystals, (b) a film of intergrown silicalite-1 obtained after the hydrothermal treatment, and (c) the corresponding hollow silicalite-1 spheres obtained after calcination.

treatment induces the formation of the shell built of well-intergrown crystals (Figure 4b). The calcination of the silicalite-1/polystyrene beads provided all-silicalite-1 spheres, which are an exact but hollow replica of the polystyrene template (Figure 4c). A negligible part of the hollow spheres contains holes. A close view of these uncompleted spheres shows that the volume of the spheres is completely liberated from the polystyrene template. The SEM analysis also shows the presence of individual MFI-type crystals in these shells. Basically, the seeded synthesis provided well-intergrown layers where the individual crystals are difficult to be distinguished. The presence of large individual crystals in the silicalite-1 shell is an indication for a poor seed coverage of some areas of the support. Therefore, the observed uncompleted hollow spheres are rather a result of bare

areas in the adsorbed seed layer than of a mechanical destruction after the combustion of the polystyrene core.

After calcination of the 260-nm core/shell beads, a great part of the obtained hollow spheres were broken. A few spheres survived the calcination, but even these shells contained visible cracks. Cracks in the silicalite-1 layer were observed even after drying of the silicalite-1/polystyrene composite at 90 °C, which were provoked by the shrinking of the polystyrene core. Obviously the high diameter-to-wall thickness (d:t) ratio in this case is the main reason for the low mechanical strength of large silicalite-1 shells.

Although the calcination conditions are important, still the pretreatment procedure, namely, the homogeneous distribution of seed crystals, and the d:t ratio are the main factors controlling the strength of the hollow silicalite-1 spheres. Denser coverage of the support can be achieved by increase of the number of adsorption steps.^{19,20} Thus, besides the improved homogeneity of the zeolite film, the deposition of several layers of nanocrystals will have a positive effect on the thickness of the zeolite shell. Another way to decrease the d:t ratio for a specific system is to use a templating core with a smaller diameter. Finally, the thickness of the zeolite shells can also be changed by the composition of the starting system, the synthesis conditions, and the kinetics of film growth. These parameters can be varied broadly in order to obtain a film with the desired thickness.

The effect of the composition of the starting system, namely, the content of TPA, was studied in a series of experiments with the 10- μm polystyrene supports. All synthesis solutions used in this study were clear and free from particulate matter with a size exceeding 10 nm. The nucleation and crystal growth in such systems is uniform, and the formation of individual crystals prevails over the formation of aggregates. The utilization of such systems is important for the preparation of zeolite layers on three-dimensional objects: first, because the growth is homogeneous in the whole volume of the reaction vessel, and second, because the obtained composite is easily separated from the zeolite crystallized in bulk. All syntheses were performed under identical conditions. The changes of the content of the TPA structure-directing agent in the starting system has a pronounced effect on the thickness of the silicalite-1 shell. Thus, the variation of the $(\text{TPA})_2\text{O}$ content between 2.0 and 0.5 yielded silicalite-1 shells with a thickness between 400 and 3000 nm. The silicalite-1 films grown with starting mixtures containing 1.5 and 0.5 $(\text{TPA})_2\text{O}$ are shown in Figure 5a and Figure 5b, respectively. The thickness of the corresponding layers is 650 and 3000 nm, respectively.

A relatively high fraction of the hollow spheres prepared by the combination of LbL and hydrothermal synthesis techniques survives the combustion of the polystyrene support. This fraction is much higher than that of the hollow spheres prepared by LbL deposition,¹⁸ which is good proof of the stability of the synthesized material. The hollow zeolite spheres prepared by the LbL technique are stabilized only by weak interactions between the building nanocrystals, which explains their extremely low mechanical strength. The calcination of the material improves the mechanical properties due

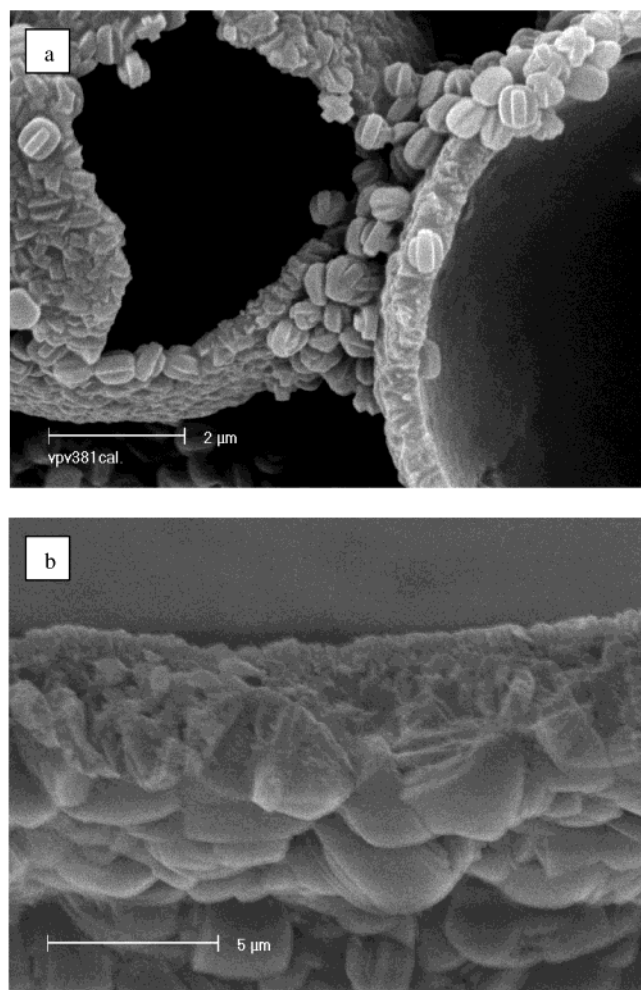


Figure 5. Thickness of the silicalite-1 shells grown with systems (a) $1.5(\text{TPA})_2\text{O}/25\text{SiO}_2/1500\text{H}_2\text{O}/100\text{EtOH}$ and (b) $0.5-(\text{TPA})_2\text{O}/25\text{SiO}_2/1500\text{H}_2\text{O}/100\text{EtOH}$.

to the interaction between the surface Si–OH groups resulting in the formation of Si–O–Si covalent bonds. However, the mechanical strength of the zeolite shell is still very low because of the limited contact surface between zeolite particles. In contrast, the secondary growth of adsorbed zeolite nanocrystals leads to intergrowth between the individual particles. Thus, the resulting silicalite-1 shell is built of intergrown crystals where the covalent bonding is dominant and the obtained shells are stronger than those obtained by the LbL technique.

As was discussed above, all stages of the preparation that have impact on the strength of the hollow material can be controlled; therefore, the preparation of hollow zeolite spheres with reasonable mechanical strength seems feasible.

Silicalite-1 Structures with a Regular System of Macrocavities. Further increase of the strength of the hollow zeolite materials can be achieved by formation of extended structures where the hollow part is included in a matrix of silicalite-1. The schematic presentation of the strategy used for the preparation of such materials is depicted in Figure 1 (right column). The procedure is exemplified by the preparation of bodies with large cavities. The 260- μm polystyrene supports were employed for this study. After reversal of the surface charge and adsorption of silicalite-1 nanocrystals, the polysty-

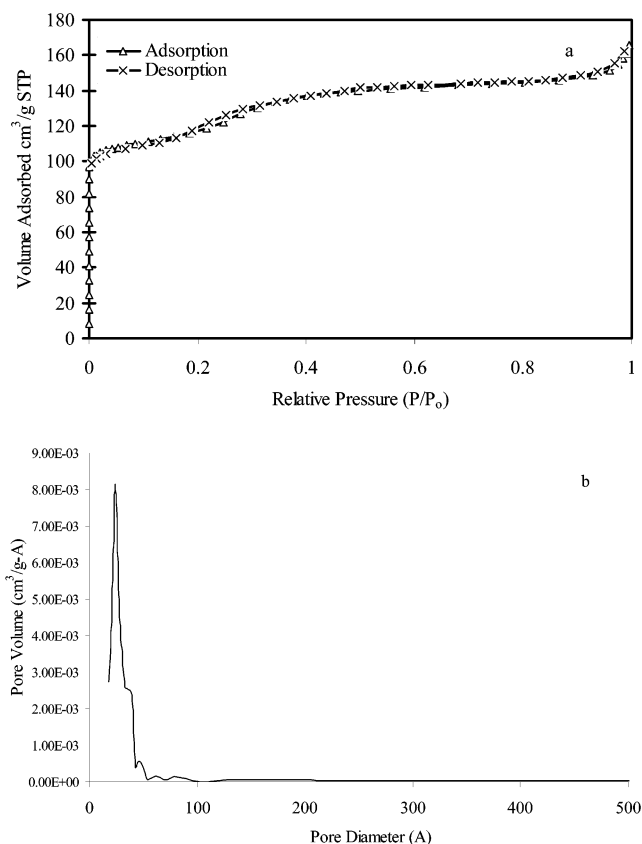


Figure 6. Nitrogen adsorption and desorption isotherms for a macroporous silicalite-1 body prepared with the 260- μm polystyrene beads (a). Distribution of the mesopores in the silicalite-1 bodies according to the BJH desorption (dV/dD) analysis (b).

rene beads were introduced in the synthesis solution and left to sediment. The synthesis procedure transformed the layer of polystyrene beads in an entire composite body, which was easily separated from the zeolite crystals formed in the bulk and calcined. The calcination did not provoke disintegration of the material.

TG analysis of the obtained silicalite-1/polystyrene body showed that the content of silicalite-1 is ~ 39 wt %. The amount of polystyrene was evaluated to be ~ 54 wt %, keeping in mind that the composite contains 3–4 wt % polycation agent and the content of the structure-directing agent in the MFI-type material is ~ 11.5 wt %. The calcined material possesses the XRD pattern typical for MFI-type materials. No halo indicating the presence of an amorphous phase was detected.

The total specific surface area of the sample was 409 m^2/g , which corresponds to a well-crystallized MFI-type material. The type I adsorption/desorption isotherm of the calcined material (Figure 6a) shows the microporous character of the material. A steep rise in the uptake, followed by a flat curve at low relative pressures, corresponds to filling of micropores with N_2 . The upward turn of the isotherm at relative pressures 0.2–0.4 followed by an almost flat part is indicative of the presence of small mesopores present in the body, which was confirmed by the BJH pore size analysis. According to the BJH calculation, the major part of the mesopores are in the range 17–100 Å with a sharp maximum at ~ 25 Å (Figure 6b). At high relative pressures, another

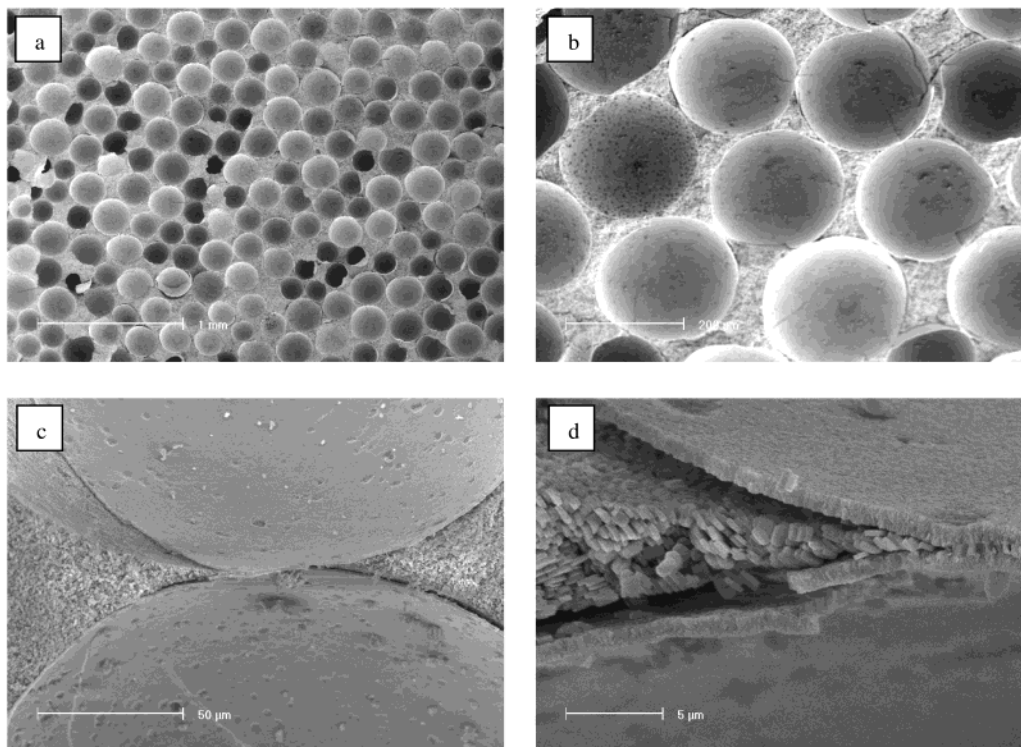


Figure 7. SEM micrographs of a cross section of a calcined silicalite-1 body: (a) and (b) general view of the regular system of macrocavities left after combustion of the polystyrene macrotemplates; (c) and (d) close views of the silicalite-1 crystals deposited between macrocavities and the film grown on the surface of the polystyrene beads.

upward turn can be seen, which is indicative for the filling of the interparticle spaces. The large cavities left after combustion of the polystyrene beads cannot be detected by N_2 adsorption. A total single-point pore volume of $0.28 \text{ cm}^3/\text{g}$ was measured. Since the pore volume of a highly crystalline MFI-type material is $\sim 0.20 \text{ cm}^3/\text{g}$,²¹ the observed difference also confirms the presence of mesopores in the material.

A silicalite-1 body with a volume of $\sim 1 \text{ cm}^3$ was broken into pieces and studied by SEM. The surface shown on Figure 7a is 8.4 mm^2 , where the system of macrocavities left after the combustion of the polystyrene beads can be seen. Although in some areas their distribution is rather regular (Figure 7b), the difference in the size of the polystyrene beads does not allow their perfect packing. A closer view of the material shows that there is no connection between the cavities (Figure 7c). A thin well-intergrown film of silicalite-1 of $\sim 1\text{-}\mu\text{m}$ thickness covers the surface of each polystyrene bead (Figure 7d). The growth of this film is induced by the silicalite-1 nanocrystals adsorbed on the beads before the synthesis. Even in the areas where the polystyrene beads touch each other, the film has grown between them (Figure 7d). The presence of this film is the reason for the dark and bright spots observed in Figure 7a. The difference in the contrast depends on the way the thin silicalite-1 film covering the beads was broken. Most probably the small mesopores detected by N_2 sorption measurements are situated in the film; i.e., they form pinholes in the intergrown layer. The space between the polystyrene beads is filled with well-shaped nonintergrown silicalite-1 crystals, which are very homogeneous

in size ($\sim 1 \mu\text{m}$) and whose orientation seems to be parallel in some areas (Figure 7c). Better intergrowth of these crystals might be achieved by a second hydrothermal treatment, which would further improve the mechanical properties of the material. A second synthesis could also induce an additional growth in the silicalite-1 film and close the pinholes. Besides the formation of pinhole-free material, the intergrowth between crystals will improve the mechanical properties of the zeolite body. The problem of the mechanical properties of zeolite shells prepared by self-assembly of nanoparticles was discussed above. The zeolite macrostructures possessing large macrocavities or macropores face the same problem. However, the macroporous zeolite structures built of intergrown crystals, e.g., prepared by a combination of LbL and hydrothermal synthesis techniques, seem to be much more stable and thus more suited for practical applications.

Conclusions

Hollow silicalite-1 macrostructures were prepared by using two types of polystyrene beads as macrotemplates. The incompatibility between the organic support and the inorganic shell was circumscribed by using negatively charged substrates, reverse of their surface charge, and adsorption of nanoseeds followed by a hydrothermal treatment with a silicalite-1 precursor mixture.

Silicalite-1 shells were prepared on 10- and $260\text{-}\mu\text{m}$ polystyrene supports. The pretreated microbeads, covered by a layer of adsorbed silicalite-1 nanocrystals, were subsequently subjected to continuous growth in a precursor mixture. The secondary growth leads to the formation of an intergrown silicalite-1 film. After com-

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bustion of the sacrificial core, hollow silicalite-1 shells were obtained. Film growth, film homogeneity, and film thickness as well as the mechanical properties of the silicalite-1 shells obtained are dependent on the homogeneity of the adsorbed layer of silicalite-1 seeds and the synthesis conditions. Besides the characteristics of the silicalite-1 film grown on the polystyrene macrotemplate, the stability of the hollow spheres also depends on the diameter-to-wall thickness ratio and the calcination conditions.

Silicalite-1 bodies with a regular system of cavities were prepared by sedimentation of a layer of pretreated polystyrene beads followed by a hydrothermal treatment. After combustion of the polystyrene beads, the body kept the morphological features of the silicalite-

1/polystyrene composite. There is no connection between the cavities because of the well-intergrown film crystallized on the surface of the individual polystyrene beads. The space between the polystyrene beads is filled with loosely attached monodisperse silicalite-1 crystals. A further strengthening of the silicalite-1 matrix might be achieved by a second hydrothermal synthesis.

The approach described here can most likely be used for the synthesis of other hollow zeolite materials with different properties and of potential applied interest.

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