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Synthesis and characterization of large mesoporous silica SBA-15 sheets with ordered accessible 18 nm pores

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Abstract

Mesoporous silica SBA-15 in the form of 10-30 μm sized sheets with unusually large ordered pores has been synthesized using heptane as a cosolvent in the presence of NH_4F . The resulting morphology of 400 nm thick sheets that contain easily accessed, hexagonally arranged, 18 nm sized pores running parallel to sheet normal has not been previously reported. The material has a BET surface area of 541 m^2/g , large pore volume of 1.69 cm^3/g and ordered mesopore structure with a narrow pore size distribution around 18 nm. A mechanism for sheet formation based on heptane droplets acting as sites for self assembling of silica crystallites is suggested.

Keywords:

Mesoporous silica; SBA-15; Sheet; Large pore

1. Introduction

Since the first syntheses of SBA-15 [1], the pore size and morphology of the material has been extensively studied. One of the first papers showed that the pore size could be tuned between 5 and 30 nm using 1,3,5-trimethylbenzene (TMB) as a swelling agent [2]. This was later found not to be correct due to a phase transition from hexagonal to mesocellular foam structure [3] and the maximum pore size was instead 12 nm. Decane in combination with TMB has also been used as a cosolvent to enlarge the pores to 9 nm [4]. A study in which ethanol was used in combination with mixtures of sodium silicate and TEOS resulted in ordered SBA-15 with a d_{100} spacing of 12 nm [5]. Lately, other alkanes from hexane to dodecane have been used as swelling agents at low temperature syntheses [6-8]. The pore sizes for these materials vary between 9.7 and 15.7 nm depending on the alkane chain length.

Different alkanes in combination with NH_4F also yield different morphologies of SBA-15, from fibers to separate nanosized slices, depending on the type of alkane and the alkane to P123, and TEOS to P123 ratios [8]. However, the pore sizes remained constant for every alkane independent of the particle morphology. Other types of morphologies can be accomplished by adding different salts such as KCl [9] and NaSO_4 or MgSO_4 to the solution [10] or by changing the reaction conditions [11,12].

In the original synthesis of SBA-15 [2] the tubular pores are running through the long dimension of particles in the shape of fibers. When these fibers coalesce to form a film or sheet it has been difficult to avoid that the pores are running parallel to the film surface [13-15] which results in poor accessibility to the pores. Sheets, films or platelets with pores running perpendicular to the long dimension of the particle have though been synthesized by several groups e.g. by growing the film between bilayers[16], using substrates with conical holes [17] or using Zr(IV) ions in the synthesis[18]. Here we illustrate how heptane, used as a swelling agent, in combination with NH_4F can be used to produce several tenth of micrometer sized sheets with accessible 20 nm hexagonally organized and aligned pores running through the short dimension of the sheet.

2. Experimental

In a typical synthesis, 1.2 g of $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ (P123) and 0.014 g of NH_4F was dissolved in 42 ml HCl 1.3 M. The mixture was stirred at 20°C for 3 days. 27.9 ml heptane was mixed with 2.75 ml tetraethyl

orthosilicate (TEOS) and this mixture was added into the solution. The solution was then stirred with 1000 rpm for 20 h and then transferred to a teflon-flask for hydrothermal treatment at 100°C for 24 h. The product was filtered and washed with distilled water. To remove the template, the product was treated with 60 g H₂O₂ for 24 h at 100°C. The final product was then filtered, washed with distilled water, and dried overnight at 80°C.

Nitrogen sorption isotherms were obtained with a Micromeritics ASAP 2020 at 77 K with samples outgassed at 573 K for 9 h. Pore size distribution was calculated from the adsorption isotherm using the KJS- method [19] and the BET-surface area from the relative pressure of 0.06-0.17.

Scanning electron microscopy (SEM) was done with a Leo 1550 Gemini Scanning Electron Microscope with a working distance of 3-4 mm and an electron voltage of 3.0 kV. Sample material was placed on a carbon tape and coated with a thin layer of gold before being inserted into the microscope. Transmission electron microscopy (TEM) was performed with a FEI Tecnai G2 TF 20 UT microscope operated at 200 kV. Samples were prepared by dispersing sample in acetone and depositing it on a hollow carbon grid.

X-ray diffraction (XRD) was carried out with Cu K α radiation on a Kratky compact small angle system equipped with 1024 channel detector. The air scatter was reduced through evacuated flight tubes.

3. Results

Figure 1 shows TEM and SEM micrographs of 10-30 μ m sized SBA-15 sheets synthesized with heptane and NH₄F. Figure 1(a) shows that the sheets are fragments of spheres with a sheet thickness is \sim 400 nm (see insert). The sheets consist of agglomerated smaller crystallites with irregular shapes which are clearly seen in figure 1(a) and (b). The crystallites, which have been marked in figure 1(b), are approximately 400 nm long, 0.4 - 1.0 μ m wide and have their tubular pores arranged hexagonally. The long pore dimension is parallel to the surface normal of the sheet. By tilting the sample in the TEM it is possible to see how the different crystallites are oriented. From this it is obvious that all crystallites have the same pore orientation relative to the sheet. Since the sheets are curved the pore orientation of each crystallite will be slightly different in the micrograph. The pore size determined from TEM of 17.5 \pm 1 nm is larger compared to common synthesis methods of 6-12 nm [20-22].

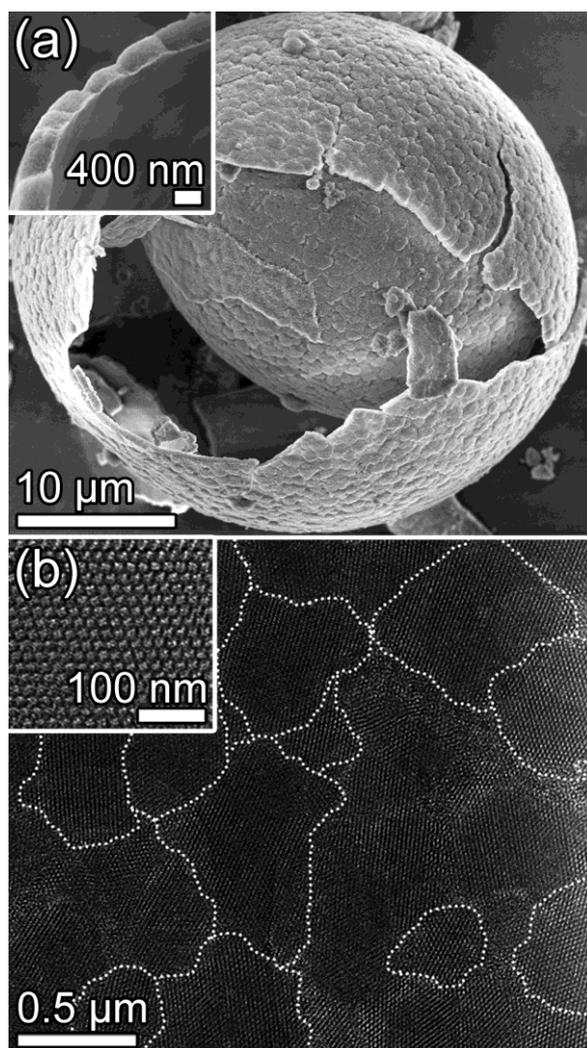


Figure 1. SEM micrographs (a) and TEM micrographs (b) of mesoporous SBA-15 with sheet morphology synthesized with heptane and NH_4F . The micrographs show (a) the size of the sheets, (a-b) crystallites attached to each other and (b) pores arranged in a hexagonal order.

Figure 2(a) displays a typical type IV nitrogen sorption isotherm with a type 1 hysteresis loop, characteristic of cylindrical channels hexagonally ordered from the SBA-15 sheets. The BET surface area is calculated to be $541 \text{ m}^2/\text{g}$ and the total pore volume at $P/P_0=0.97$ is $1.68 \text{ cm}^3/\text{g}$. The pore size was calculated to approximately 20 nm (see insert), which is a slight overestimation due to the method used [23]. The x-ray diffractogram in figure 2(b) shows two resolved peaks that indicate well ordered pores. The peaks are indexed as 100 and 110 lines in the hexagonal $p6mm$ structure with a unit cell parameter of 19.3 nm. Combining this data with TEM observations yields a wall thickness of 1.8 nm which is in accord with other SBA-15 materials synthesized with alkanes [24]. The peak at $2\theta = 1.23$ in the diffractogram may originate from the less ordered tissue phase at the crystallite boundaries.

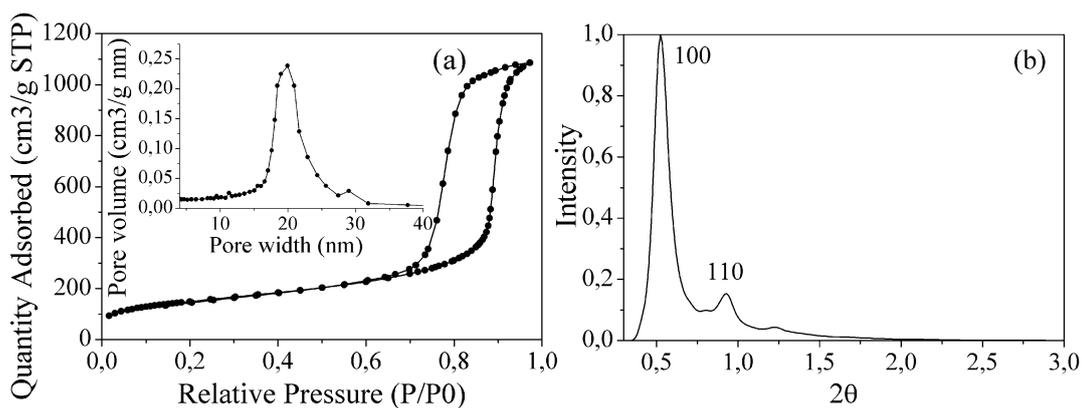


Figure 2: (a) N_2 isotherms with the pore size distribution calculated with the KJS method inserted and (b) X-ray diffractogram of mesoporous silica SBA-15 synthesized with heptane and NH_4F with the P123 removed with H_2O_2 .

4. Discussion

Heptane is working as a swelling agent during the synthesis of SBA-15 resulting in unusually large pores arranged in sheet morphology with all the pores running along the sheet normal. When other swelling agents such as TMB are used, a phase transition from hexagonal to mesocellular foam occurs when the TMB to P123 ratio exceed 0.3[3]. The maximum theoretical value, which also has been shown experimentally, of the pore size before the phase transition is 12 nm [25]. This value has though been exceeded when other swelling agents such as nonane or hexane in the presence of NH_4F have been used [24], where NH_4F increases the hydrophilic volume of P123 and the packing factor stays less than 0.5 for large amounts of oil. Heptane appears to efficiently expand the hydrophobic volume of the micelle, resulting in large pores.

Our results suggest that the sheets are formed from small crystallites, building blocks, which also form the rods seen in previous studies with NH_4F [21]. These rods are built up by several hundred nm-long crystallites, i.e. similar to how the crystallites are acting as building blocks for the sheets presented here but with a different assembling structure. The crystallite surfaces have different hydrophobicity, where the micelle ends are more hydrophobic than the mantel surface due to the hydrophobic core of the micelles [26]. It has earlier been shown that alkanes in the synthesis shorten the lengths of the crystallites (fibers), which can give different morphologies [8]. In our case, heptane both shortens and swells the pores and act as a template for aligning the crystallites in to a sheet morphology. With only small heptane additions to the synthesis the micelles are enlarged but no heptane droplets are formed, i.e. the heptane preferred site is the micelle core until those sites are saturated. Earlier studies have

shown that, the hydrophobic parts of the crystallites attach to each other e.g. [8,21,26]. This is done to reduce the energy of the system resulting in a low degree of pore alignment between crystallites. However, when there are heptane droplets present in the reaction bath (heptane to P123 molar ratio \geq 470) the hydrophobic ends of the crystallites in the formed microemulsion prefer to attach to the outside of the droplets instead. The crystallites are not firmly bonded to the oil and can move along the oil-water interfaced until several crystallite mantles attach to each other. Hydrolyzed TEOS binds the crystallites together to form the sheets, see figure 3.

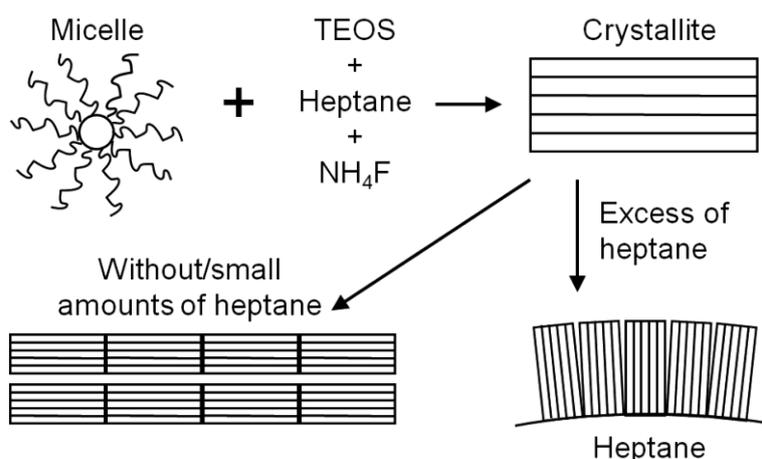


Figure 3: Schematic representation of the role of heptane in the formation of different morphologies of SBA-15 due to the hydrophobic ends of the crystallites.

5. Conclusion

This study shows that it is possible to synthesize mesoporous silica SBA-15 with pores as large as 20 nm when NH_4F and excess of heptane is used. The 400 nm thick sheet morphology with easily accessible pores either as free standing membranes or films attached to supports open for applications in macromolecular catalysis and storage.

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