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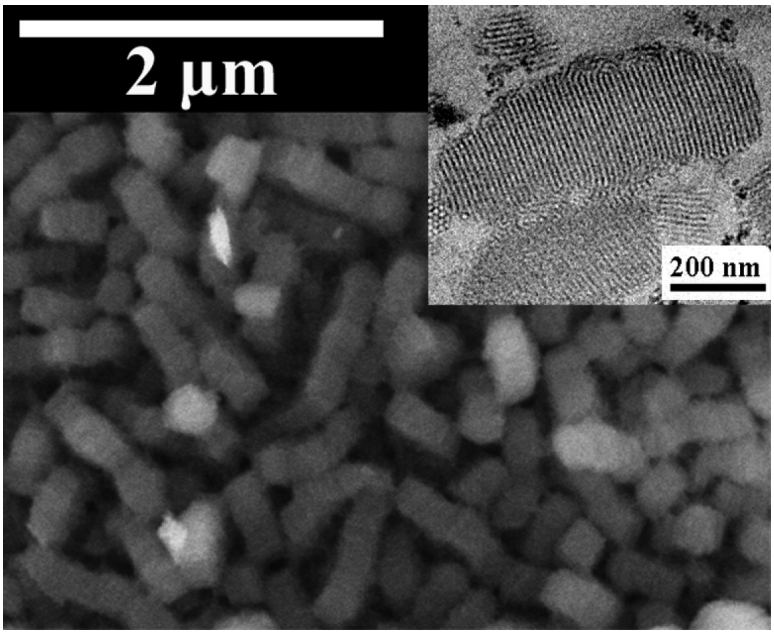

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Unusual Mesoporous SBA-15 with Parallel Channels Running along the Short Axis

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Submicrometer-sized mesoporous silica SBA-15 with cuboidlike morphology has been prepared by using excess amounts of decane as cosolvent in the presence of NH_4F. The channels of the resulting material run parallel to the short axis of the cuboidlike SBA-15, which had not been previously reported. It has also been found that the materials have a well-ordered channel structure with pore size ca. 12 nm.

Due to their uniform pore structure and high surface areas, mesoporous materials such as MCM-41 and SBA-15 have been studied extensively in the fields of catalysis, separation, adsorption, and even the fabrication of semiconductor or low dielectric devices.[1] Methods to tune the morphology,[2,3] pore size,[4−9] and particle size[10−15] of the mesoporous materials have long been the target of various groups. Organic cosolvents such as 1,3,5- trimethylbenzene (TMB), alkanes, and amines, etc. are often used to tailor the pore size of mesoporous materials, such as the cationic surfactant-templated MCM-41 materials. Among the alkanes used, decane has been proven to be a good swelling agent, though the obtained mesoporous silica materials are often disordered.[6]

Well-ordered mesoporous materials with short channels have attracted great attention because they are favorable for mass transfer. Control of the channel's length could be attained by decreasing the particle size or making the parallel orientation of channels running along the short axis. Nanoparticles of cationic surfactant-templated mesoporous materials such as MCM-41 have been obtained by changing the composition of starting materials,[11,12] by using a double surfactant system,[13] or by quenching the reaction by adding HCl.[14] The synthesis of nanosized SBA-15 is rarely reported. Typical SBA-15 materials have rope-like morphologies with a relatively uniform length of $\sim$1 μm and the channels running parallel to the long axis of the rope.[4] At the same time, SBA-15 with other morphologies such as fiberlike and doughnutlike, which have curving and even orbicular channel structures,[3] are also unfavorable for the mass transfer in separation and catalysis. Here, we present for the first time the synthesis of submicrometer-sized mesoporous silica SBA-15 with parallel channels running along the short axis. It has been attained by using large amounts of decane as the cosolvent in the presence of NH_4F during synthesis. Recently, this new type of material with short channels has been applied in the assembly of highly dispersed Ag nanoparticles in our laboratory. The obtained catalyst was evaluated in methane conversion, which exhibited good activity and stability at 773 K.

As a typical synthesis procedure, 2.4 g of $EO_{20}PO_{70}EO_{20}$ (P123) was dissolved in 84 mL of HCl solution (1.07 M) and then stirred at room temperature until the solution became clear. Different amounts of decane ($C_{10}H_{22}$) (with weight ratios of decane to P123 ranging from 0:1 to 7.6:1) were then added into the solution. The mixture was stirred at room temperature for at least 1 h. Finally, 0.027 g of NH_4F was added under stirring as a hydrolysis catalyst, followed by 5.1 g of TEOS. The above mixture was stirred at 313 K for 20 h and then transferred into an autoclave for further reaction at 373 K for 48 h. The products were collected by filtration, dried in air, and calcined at 813 K for 5 h to remove the templates. Samples of different weight ratios of decane to P123 were thus obtained.

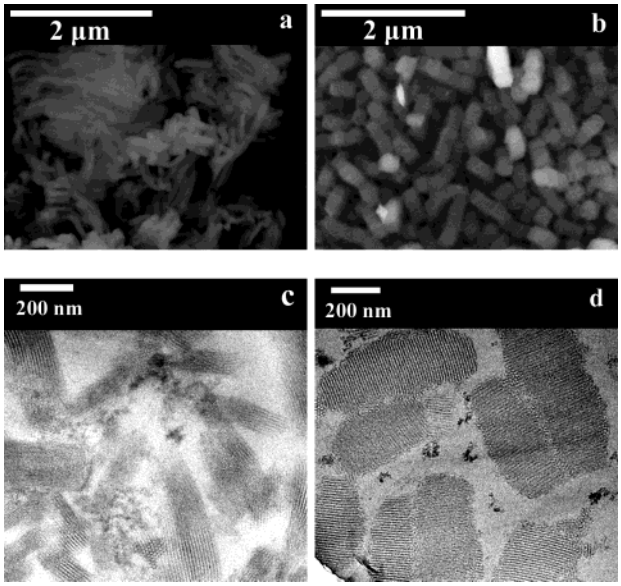

Figure 1. SEM images (a−b) and TEM images (c−d) of mesoporous silica SBA-15 synthesized at different weight ratios of decane to P123 in the presence of NH_4F: (a) and (c) 0.4:1; (b) and (d) 5.8:1. SEM images were taken on a Hitachi S8000 scanning electron microscope; TEM images were taken on a Philips CM 200 transmission electron microscope.

Without decane, particles with fiberlike morphology have been obtained in the presence of NH_4F.[16] When a small amount of decane is added (decane to P123 weight ratio 0.4:1), the morphology of the particles remains unchanged, but the fibers became thinner (Figure 1a). Figure 1c shows well-ordered channels running along the long axis of the fiberlike SBA-15. However when a large amount of decane is added (decane to P123 weight ratio 5.8:1), a dramatic change occurs, i.e., the morphology of the particles changes significantly from fiberlike into cuboidlike as shown in Figure 1b. The size of the cuboidlike particles is relatively uniform, about 500 nm long and 200 nm in width. Most importantly, Figure 1d clearly shows that the channels of cuboidlike SBA-15 run parallel to the short axis, which is around 200 nm in length. It is obviously different from all the SBA-15 materials previously obtained,[3,4] in

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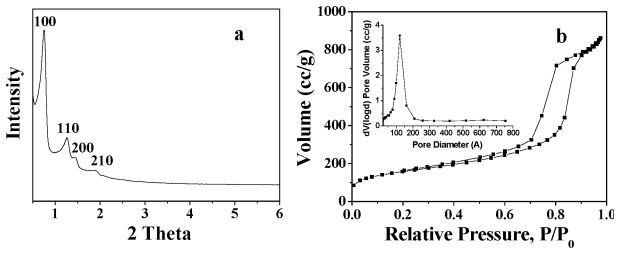
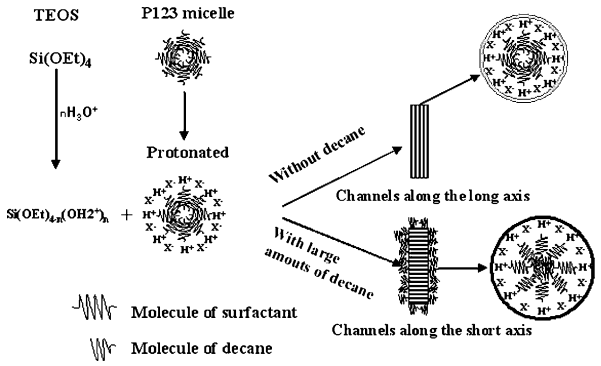


Figure 2. (a) Small-angle X-ray diffraction pattern and (b) N_2 adsorption−desorption isotherm of calcined mesoporous silica SBA-15 synthesized at decane to P123 weight ratio of 5.8:1 in the presence of NH_4F. Inset is adsorption pore size distribution by BJH method. XRD pattern was recorded on D/max-2500/PC diffractometer; N_2 adsorption−desorption isotherm was recorded on a NOVA 4200e surface area and pore size analyzer.

Scheme 1. Schematic Representation of the Bifunctional Roles of Large Amounts of Decane



which the channels are preferentially along the long axis. The change of channels orientation can be further confirmed by HRSEM images (Supporting Information: Figures S1, S2).

Figure 2a is a small-angle X-ray diffraction pattern of mesoporous silica SBA-15 materials synthesized with a 5.8:1 decane to P123 weight ratio in the presence of NH_4F. It shows four well-resolved peaks that can be well indexed as (100), (110), (200), (210) diffractions associated with a 2-D hexagonal symmetry (p6mm), indicating a well-ordered mesostructure. Figure 2b gives an N_2 adsorption−desorption isotherm of the same sample. It yields a type IV isotherm with H1-type hysteresis, which is a typical hexagonal cylindrical channel mesoporous material. This can also be confirmed by an HRTEM image (Supporting Information: Figure S3). The pore size reaches 12.1 nm and the BET surface area is 560 m^2/g. Therefore it can be concluded that the pore size of SBA-15 materials could be expanded by adding decane as a swelling agent. It should be mentioned that further increasing the amount of decane (e.g., at a decane to P123 weight ratio 7.6:1) leads to an unobvious change of pore size, but BET surface area increases to 610 m^2/g. The SEM/TEM results show a much smaller particle size (<200 nm) with an irregular morphology (not shown here).

Thus, decane used in the synthesis can be regarded as a swelling agent;[6] however it is not only a swelling agent. In the synthesis of large-pore SBA-15, when the weight ratio of the most used swelling agent, TMB,[7−9] to P123 was above 0.3, hexagonal to mesocellular foam phase (MCF) transition happened and disordered MCFs were obtained even in the presence of NH_4F,[8] which are templated by oil-in-water micromulsion.[9] However, in our experiments excess decane will not lead to the phase transition but instead may build discrete spaces within the synthesis mixture and thus confine the formation of silicate-doped micelles. As a result, the side-on condensations between short silicate-doped micelles are preferred; thus a new kind of SBA-15 with channels running parallel to the short axis was built (see Scheme 1).

Fluoride has been successfully used as a hydrolysis catalyst which can promote silica polymerization.[16] In our current study, the use of NH_4F is crucial for the formation of a highly organized porous structure, i.e., in the absence of NH_4F, disordered mesoporous silicas are obtained even with large amounts of decane. This indicates that NH_4F addition significantly improves the mesoscopic structure of silica, which serves as a key factor to synthesize the well-ordered SBA-15 with cuboidlike morphology.

In conclusion, unusual submicrometer-sized SBA-15 materials with highly ordered short-pore channels have been prepared by adding large amounts of decane, which plays a bifunctional role. As shown in Scheme 1, on one hand, decane functions as a swelling agent and can expand the pore size of the materials. At the same time, the decane can confine the formation of silica-doped micelles, resulting in a decrease of particle size and a change of the channels orientation. The resulting materials are expected to be favorable for mass transfer due to their short-pore channels.

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Supporting Information Available: HRSEM/HRTEM images of mesoporous silica SBA-15 synthesized at different weight ratios of decane to P123 in the presence of NH_4F. This material is available free of charge via the Internet at http://pubs.acs.org.

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