A 3D-TEM study of the shape of mesopores in SBA-15 and modified SBA-15 materials†

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The mesopores in SBA-15 are curved on a mesoscopic length scale and even more so in the case of modified SBA-15, which implies that using the particle size of these types of materials in diffusion studies may strongly underestimate the path length relevant for intraparticle diffusion.

In the last decade there has been a huge increase in research on ordered mesoporous materials. With their unique textural properties (uniform pores with diameters of roughly 3–30 nm) these materials bridge the gap between (microporous) zeolites on the one hand and amorphous meso- and macroporous oxides on the other. Information about the diameters of the pores and the thickness of the walls is often obtained with XRD, N_2-physisorption and TEM. More recently, the porous crystal structures of several SBA materials, a representative class of ordered mesoporous materials, have been characterised in three dimensions on a microscopic level using electron crystallography, a form of 3D-TEM.[1] Most of the characterisation of mesoporous materials focuses on the shape and size of individual pores, that is at the microscopic length scale (< 10 nm). This type of information most often has been obtained from TEM images taken at high magnifications. This may easily lead to the general idea that SBA-15[2] (and other mesoporous materials) consists of hexagonally packed straight pores, also at the mesoscopic length scale (10–1000 nm). Also the often published scheme for the mechanism of MCM-41 formation can be due to this idea (see Fig. S1†). Despite the high ordering of the mesopores on a microscopic scale, these materials appear to have irregularly curved pores on a mesoscopic scale. Here we show how a series of TEM images of the same particle taken at different tilt angles (tilt series) gives valuable information on the three-dimensional ordering of the mesopores on a mesoscopic scale.[3]

Materials were prepared by dissolving 4 g of Pluronic P123 (non-ionic triblock copolymer, $EO_{20}PO_{70}EO_{20}$) in 150 ml of a 2 M HCl solution. Subsequently, different amounts of TEOS (tetraethylorthosilicate) were added. The molar ratios of TEOS/surfactant were 59 (SBA-15) and 125 (modified SBA-15). The solution was stirred for 8 h at room temperature and then aged for 16 h at 353 K. The white solid was filtered off, washed and calcined at 823 K.[4,5] Using a Technai-20 (200 kV) microscope we have acquired tilt series of the two samples of *ca.* 141 images over an angular range of ±70°.†

The amount of TEOS used during the synthesis of SBA-15 appears to influence the shape of the particles and the curvature of the pores. The higher the TEOS to template ratio, the more curved the pores. Fig. 1 shows two TEM images taken at different tilt angles, of the same SBA-15 particle. This sample had the lower TEOS to template ratio.

From the left image in Fig. 1 it seems that the pores, with a diameter of 8 nm, are indeed straight. However, in combination with the right image of Fig. 1, it is clear that in the largest particle the pores are U-shaped, whereas the pores in the smallest particle are indeed almost straight. Fig. 2 shows an enlargement of part of Fig. 1(b) to illustrate the U-shape of the mesopores at larger length scale. Nonetheless, the pores are still hexagonally arranged as is expected for SBA-15 materials. Fig. 3 shows a TEM image of the modified SBA-15 sample prepared with the higher TEOS to template ratio. It is clear that the pores of this material are very curved. While the mesopores in SBA-15 run smoothly over say 0.5 μm of length, the modified SBA-15 displays smaller domain sizes (*ca.* 0.1 μm) for the ordered mesopores. See ref. 4 for details and relevant TEM images. From the movie of the aligned images of the entire tilt series this curvature is even more visible, since the three-dimensional shape of the pores becomes clear.† It is then apparent that the particle shown in Fig. 3 is really one big particle (with a few small fragments on the top right) and that the mesopores are continuous throughout the whole particle.

Thus, although these materials have a high ordering of the mesopores on a microscopic scale, they have irregularly curved
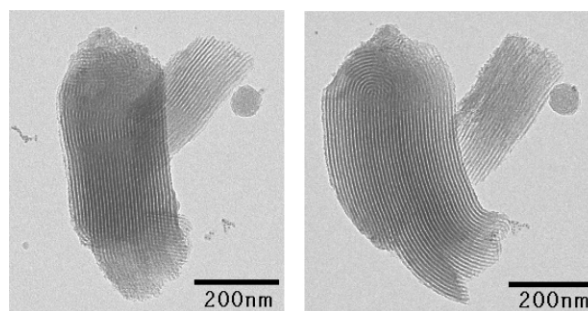

Fig. 1 TEM images of the same SBA-15 particle at different tilt angle.

Fig. 2 Enlargement of part of Fig. 1(b) showing the U-shape of the mesopores (image size 200 × 200 nm).

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† Electronic supplementary information (ESI) available: Fig. S1: schematic view of the MCM-41 formation mechanism. Movie S2: Aligned TEM tilt series of the SBA-15 particle from Fig. 1 (sample with the lower TEOS to template ratio). Movie S3: Aligned TEM tilt series of the SBA-15 particle from Fig. 3 (sample with the higher TEOS to template ratio). See http://www.rsc.org/suppdata/cc/b2/b204943k/

pores on a mesoscopic scale. This results in a length of the pores which can be over twice the size of the particle. Therefore, the diffusion path length through the mesopores cannot be estimated in a straightforward way from the particle size of these
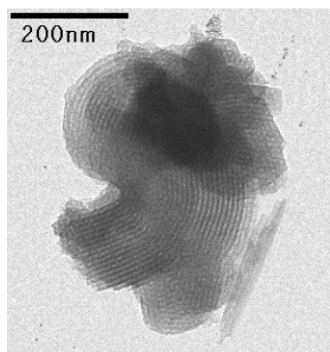
materials. In many diffusion studies, the particle size is taken as an estimate for the diffusion path length. Since the diffusion length is present as a quadratic term in the equation for the characteristic time of diffusion, a factor of two (or even higher) in difference between the particle size and the real diffusion path length can have serious implications for the outcome of the diffusion model.

Fig. 3 TEM image of a modified SBA-15 particle synthesised with a higher TEOS to template ratio.

Notes and references

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