Different structures on the way to a stable periodic mesoporous organosilica material

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The introduction of the periodic mesoporous organosilicas in 1999 was the beginning of the exploitation of a wide field of highly ordered organically modified materials [1-4]. The application of different organosilica precursors of the formula \(3(R\text{O})_3R'-\text{Si(OR)}_3\) with \(R'\) being any organic unit (\(R = \text{methoxy, ethoxy}\)) gives the opportunity to form materials with chemically or biologically reactive sites uniformly incorporated into the pore wall matrix without blocking the pores. These materials have a high potential of being used for catalysis, separation and adsorption.

Due to the liquid crystal templating mechanism the size of the pores is limited to a narrow range between 2 and 10 nm. Larger pores could also be obtained but with increasing pore diameter the pore size distribution becomes broader, which reduces the selectivity of possible reactions inside the channels. In order to influence the size of the channels different structure directing agents, which form the liquid crystal in solution, has to be tested. In many cases, there is an evolution of the structure passing one or even more different structural states before reaching the final ordering [5, 6].

For our recent experiments we used the well established triblock copolymer Pluronic P123 and 1,4-bis(triethoxysilyl)benzene as organosilica precursor. The formation was followed with in situ small angle X-ray diffraction (SAXD) measurements at the soft condensed matter beamline A2 at DORIS III@DESY in order to obtain information about the behaviour if the liquid crystal formation and reformation during the synthesis. The same reaction was performed at different temperatures (40 °C, 50 °C, 60 °C, 70 °C and 80 °C) because the formation process of these materials is highly temperature dependent. The evolution of the SAXD patterns of the samples measured at 40 °C, 70 °C and 80 °C are shown in Figure 1.

Figure 1: Evolution of the SAXD patterns at different temperatures (from top: 40 °C, 70 °C, 80 °C).
The usual evolution of the structure is similar at temperatures between 40 and 70 °C. First, we can observe the evolution of a broad signal, starting with the addition of the organosilica precursor to the solution. This signal is increasing until several diffraction peaks are evolving from this signal. With increasing intensity of the sharp diffraction peaks the broad scattering signal disappears. In all cases we first observe the evolution of a cubic structure with the space group Pn3m. With ongoing reaction, that means, with ongoing condensation of the silica the structure changes from cubic to 2D hexagonal (space group: p6mm). At 40 °C the hexagonal structure is the final structure while temperatures above 50 °C induce a further phase transition to a lamellar phase. An interesting aspect of this experiment series is the instability of the lamellar structure after finishing the reaction. In all cases, the resulting solid was filtered off, washed with distilled water and dried in air over night. Only the sample measured at 80 °C showed a lamellar ordering in the powder X-ray diffraction pattern. All other samples seem to undergo a reorganisation back to the 2D hexagonal structure, which is the most common mesostructure for samples synthesised with the applied triblock copolymer. A lamellar ordered powder synthesised with P123 as structure directing agent is rather unusual regarding the phase diagram of this polymer that was published in 1994 by Wanka et al. [7]. We attribute this phase behaviour to the structure of the organosilica precursor and to the high reaction temperatures.

References