Formation mechanism studies on periodic mesoporous organosilicas (PMO)

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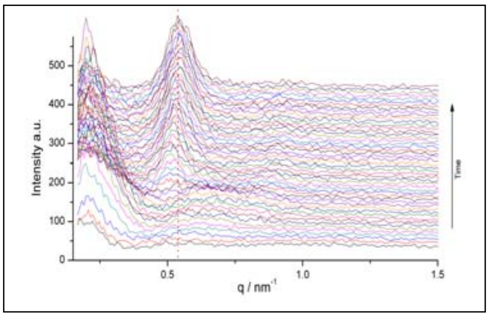
Despite some significant chemical knowledge about the synthesis of PMOs, not so much about their self-assembling process has been explained in the last decade. Little attention has been dedicated to the structural aspects of their formation[1-3]. Their kinetics and metastable structures occurring during their formation process have attracted attention only recently. Periodic mesoporous organosilica materials – PMOs have a wide range of applications, from chromatography to gas separation and storage.

For this beamtime, we looked at the dependence of the structure and lattice parameter from the size of the structure-directing agents, in addition to a variation of the acids providing the counter-ion in the reaction environment. With these studies we are aiming to lay on the lattice parameter size and thus, the pore diameters of the resulting materials.

We report on data collected at DUBBLE, project number CH3238, using a SAXS/WAXS simultaneous data collection, $\lambda = 0.154$ nm and sample-to-detector distance *ca*. 1.5 m. An *in situ* flow through setup consisting of a four neck reaction vessel, from which a sample is continuously pumped into a capillary in the beam, was installed. We measure the surfactant solution and after addition of the organosilica precursor, when we trigger the data acquisition to obtain the desired sequence of scattering patterns. The experiment ends when the flow in the capillary becomes irregular due to the growing particle size.

As an example, the temporal evolution of the SAXD patterns of a sample containing the triblock copolymer Pluronic P123 as structure directing agent and 1,4-bis(triethoxysilyl)benzene (BTEB) as organosilica precursor is shown below. In this case the pH was set to 1 by the addition of sulfuric acid.



The figure on the left shows that at the beginning no structure is present in the system, but one structure evolves with time, most likely lamellar (we can identify only one single diffraction peak unequivocally), however it does not change its lattice size

[1] Rebbin, V.; Rothkirch, A.; Fröba, M.; Funari, S.S.; In situ SAXD Studies on Phenylene- and Thiophene-Bridged Periodic Mesoporous Organosilicas (PMOs), *Chemistry Of Materials*, **2010**, 3746-3751.

[2] Rebbin, V.; Rothkirch, A.; Ohta, N.; Funari, S.S.; Formation mechanism Studies of Phenylene-Bridged Periodic Mesoporous Organosilicas (PMOs), *Langmuir*, **2010**, 9017-9022.

[3] M. Morell, C. V. Teixeira, M. Cornelius, V. Rebbin, M. Tiemann, H. Amenitsch, M. Fröba, M. Lindén, *Chem. Mater*. **2004**, *16*, 5564, and ref. therein.