A molecular-level view of the synthesis of the MCM-41 mesoporous material

Germán Pérez-Sánchez[1], José Richard B. Gomes[1], Natália D.S. Cordeiro[2], Szu-Chia Chien[3], Scott M. Auerbach[3], Peter A. Monson[3], Miguel Jorge[4]

1 — Department of Chemistry & CICECO, University of Aveiro
2 — University of Porto
3 — University of Massachusetts, USA
4 — University of Strathclyde, UK

Periodic mesoporous silica (PMS) materials are tailor made ordered nanomaterials. Their synthesis follows a surfactant template approach, involving multiple silica reactions in aqueous surfactant solutions and a delicate interplay between hydrophobic forces, electrostatic interactions and phase equilibrium, which makes the study of PMS synthesis a difficult task. Indeed, intense research was performed for the most representative archetypal example of a PMS material, the hexagonal-ordered MCM-41, but the mechanism leading to its formation yielded seemingly conflicting information.

Our group adopted a multiscale computational approach, starting with quantum mechanical calculations to parameterize a classical all-atom model to finally calibrate a mesoscale coarse-grained model for silica/surfactant water solutions [1]. This approach allowed to access progressively larger time and length scales without compromising accuracy, while maintaining a level of realism that enables direct comparison with experimental data (Fig. 1). This is a major advance over previous modeling studies, which were either restricted to short simulation times or to less realistic structural models.

From long classical molecular dynamics simulations with large molecular systems, it was found that the addition of silica monomers to a surfactant solution induces the fusion of small spherical micelles to form elongated rod-like aggregates, Fig. 2a. However, the presence of monomers alone is not sufficient to promote the formation of the hexagonal phase. Instead, the formation of this phase requires some degree of silica oligomerization, Fig. 2b. The silica oligomers act as multidentate binding sites, bridging the surfactant headgroups in different micelles, which promotes the formation of larger surfactant aggregates. The model was able to attain the relevant time and length scales to study PMS synthesis in detail, capturing the effects of pH, temperature and concentration, opening the door for realistic computer material design.

FIGURE 1
Multiscale strategy from quantum mechanics atomistic (left) to classical coarse-grained (right) simulations

FIGURE 2
Effect of silica monomers (a) and oligomers (b) in the formation of larger aggregates