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Role of the Organic Linker in the Early Stages of the Templated Synthesis of Mesoporous Organosilicas†

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Classical MD simulations for surfactant/bromide/water solutions containing several organosilicate precursors show that the presence or the absence of molecular-scale periodicity in the pore walls of PMOs is dictated by the
10 **strength of the surfactant micelle-organosilica interaction and by the relative flexibility and orientation of the organic linker.**

Periodic mesoporous organosilicas (PMOs) are materials presenting unique structural properties due to their hybrid building blocks, based on organic and inorganic (silicate)
15 moieties, which self-assemble in aqueous solutions of surfactants under basic conditions to create ordered architectures with nanometer-thick walls and uniform pores between 2 nm and 30 nm wide.[1,2] The syntheses of the first examples of PMOs were reported in 1999 by three different groups,[3-5] upon using synthetic
20 strategies similar to those employed seven years before for obtaining the fully inorganic periodic mesoporous silicas (PMSs),[6] i.e., via the surfactant templated route, but using organosilicates instead of silicates as silica sources. In these works, the PMOs were synthesized from
25 bis(trialkoxysilyl)ethane[3,4] or bis(trialkoxysilyl)ethylene[4,5] precursors and solutions containing alkyltrimethylammonium bromide surfactants (alkyl = cetyl[4,5] or octadecyl[3]) and show surfaces with both hydrophilic and hydrophobic domains. Just a few years later, Inagaki et al.[7] reported the synthesis of an
30 ordered mesoporous organosilica hybrid material using benzene as the organic linker, having a hexagonal array of mesopores with a lattice constant of 52.5 Å and crystal-like pore walls that exhibit structural periodicity with a spacing of 7.6 Å along the channel direction, as confirmed by large angle XRD measurements. This
35 benzenesilica material displays both meso- and molecular-scale periodicity, with clearly alternating organic and inorganic layers on the pore surface. A similar molecular-scale periodicity was also observed for the mesoporous ethylenesilica (spacing of 5.6 Å) while it was absent when the materials were prepared from
40 ethanesilica or methanesilica, even though the latter showed highly mesostructured frameworks.[7] Inagaki et al. put forth a tentative explanation for the differences observed between the structures of benzene or ethylenesilicas and ethane or methanesilicas. They suggested that the size of the organic linker
45 and the strength of the organosilicate-organosilicate interaction are key factors for producing the materials with molecular-scale periodicity, which is promoted by the mesostructure resulting from the self-assembly of the surfactants. The latter species were suggested to have a decisive role in molecular-scale periodicity
50 but no explicit evidence was presented to support this argument.[7] A few years later, the same group reported the synthesis of benzene- and biphenyl-silica hybrid materials presenting ordered molecular scale periodicity without the use of surfactants.[8]

Even for the widely studied pure-silica PMS materials the
55 synthesis process is not well understood. Based on indirect experimental evidences, i.e., by analyzing the changes in the structures of the materials caused by different initial synthesis conditions, two alternative mechanisms were proposed for the synthesis of the PMS materials from solutions of cationic
60 surfactants and silicates,[6,9] i.e., the so-called liquid crystal templating (LCT) mechanism, in which silica condenses around a pre-formed stable surfactant liquid crystal phase, and the so-called cooperative templating (CT) mechanism, where the silicate species are promoting the formation of the liquid crystal template
65 from aggregates of surfactants (e.g. micelles or rods). Recently, our group has shed new light on the PMS synthesis process based on classical molecular dynamics (MD) simulations of aqueous silica/surfactant solutions under controlled conditions that closely resemble the experimental specifications in the early stages of the
70 synthesis of PMSs.[10,11] The simulations showed that silicate anions replace bromide at the micelle surface, occupying regions between the heads and the tails of the surfactants and promoting micelle growth.[10] The high silica concentration at the micelle surface promotes condensation, with larger silicate oligomers
75 leading to further micelle growth and possibly to micelle aggregation.[11] Based on these observations, a detailed molecular-level mechanism for the early stages of PMS synthesis was proposed, which supports the cooperative templating interpretation.[11] Recently, we have been extending these studies
80 using a coarse-grained model to examine the effect of silicates on the sphere-to-rod transition during PMS synthesis.[12]

Herewith, encouraged by the successful use of MD in the understanding of the synthesis of porous materials, three different computer experiments using atomistic models (additional details
85 in the ESI) were performed with the aim of unveiling the role of the organic linker in the structural differences observed between PMOs synthesized with different organosilicates. These experiments consider three different high-pH solutions where decyltrimethylammonium bromide is the surfactant and where the
90 organic linker is benzene, ethylene or ethane. These linkers were found to lead to a high degree, to a lower degree, and to no molecular-scale periodicity, respectively.[7]
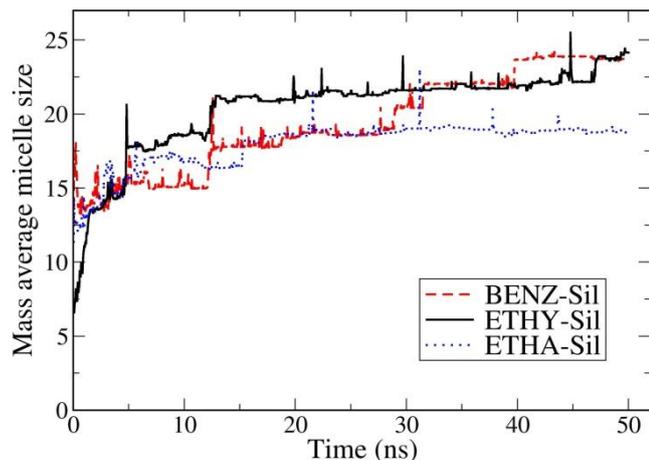
Fig. 1 Mass-average micelle size as a function of simulation time for the solutions with benzenesilica, ethylenesilica and ethanesilica.

Fig. 1 shows the evolution of the mass average micelle size with simulation time for the three different solutions considered in this work. The time evolution shows an initial stage of fast surfactant aggregation to form small clusters which eventually dissolve to form larger, more stable aggregates (Ostwald ripening process), similar to what was observed in previous simulations of surfactant self-assembly.[13] In later stages, micelles grow predominantly by fusion events, whereby two small micelles merge to form a larger one,[13] and these events appear as abrupt steps in the curves of Fig. 1. From time to time, the curves also present some spikes, which are due to short-lived contacts between two micelles that are for this short time considered to belong to the same aggregate by our cluster-counting algorithm. Fusion events occur several times during the course of the simulation until the system is mostly composed of isolated surfactants and nearly spherical micelles, similar to those already described for analogous solutions containing silicates instead of organosilicates.[10,11] From Fig. 1 it is clear that benzenesilica or ethylenesilica promote the formation of larger aggregates than those formed in the solution where the linker is ethane. In fact, the mass average micelle size in the case of ethane is ~17 surfactants (average value for the last 35 ns of simulation time), while in the other two solutions the average size is larger (~23 surfactants). Furthermore, by analyzing the aggregate size distributions obtained in the three solutions (see Fig. S1), it is clear that the solution with ethanesilica is characterized by an absence of large micelles (above ~22 surfactants), which are present in the other two solutions.

The larger size of the aggregates in the solutions containing benzenesilica or ethylenesilica when compared to the solution with ethanesilica most probably originates from the higher concentration of silica species in the regions close to the surfactant heads in the two former cases. This can be easily understood from the density profiles shown in Fig. 2, which were measured radially from the micelle center of mass (COM) for micelles of the same size, for the three different cases considered in this work. As expected, the micelles exhibit a hydrophobic core composed exclusively of surfactant tail atoms (green lines), followed by a well-defined peak for hydrophilic head atoms (purple lines) at the micelle surface. The densities of these groups are virtually the same for the three solutions. In the regions

between the surfactant tail and head atoms it is possible to find water (blue line) and organosilicates (black and red lines for the linker and for the silica moieties, respectively). Interestingly, not only the inorganic but also the organic parts of the organosilicas are found in the space between the surfactant heads, but the densities of the silicate moieties in the tail/head interface region are visibly larger when the linker is benzene or ethylene than when the linker is ethane. The interaction of the negatively charged silicate groups at the surface of the micelles with the positively charged regions of the surfactants leads to a more efficient screening of the head-group repulsion, which promotes the decrease of the surface curvature and hence the formation of larger micelles.[14] Thus, the presence of a larger local concentration of silicate groups at the micelle surface when the organic linker is benzene or ethylene is the main explanation for the larger size of the aggregates in these solutions. The differences in the molecular-scale periodicities of the PMOs synthesized with each of the different organosilicates considered in this work seem to have a different origin, which, as will be shown below, is already dictated in the very initial stages of the templating mechanism.
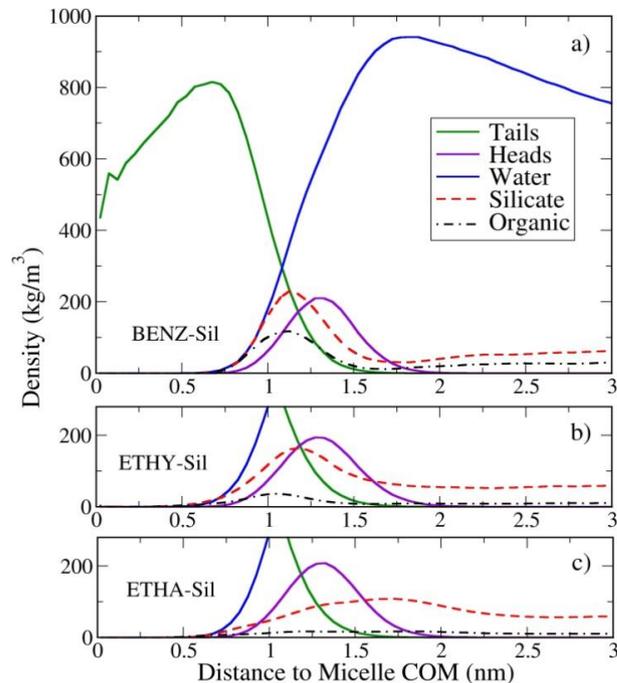

Fig. 2 Density profiles of micelles with ~20 surfactants formed in solutions with a) benzenesilica, b) ethylenesilica and c) ethanesilica.

The density profiles for the organic linkers follow closely the behavior observed for the inorganic parts of the organosilicates (c.f. compare black and red curves in Fig. 2), i.e., for the solution containing benzenesilica there is a well-defined peak for the organic part and the peak becomes visibly broader in the case of ethylenesilica and virtually disappears in the case of ethanesilica. Please note that for the former two situations, the highest density for the organic linker is found for distances from the micelle COM that are within the density maxima calculated for the surfactant tail and head atoms, which was also observed in simulations with monomeric silicate precursors.[10] Thus, in the solutions with these species, most of the organosilicates are

interacting with the micelle surface and are located in between the head groups.[15] A contrasting behavior is found for the solution with ethanesilica, for which the maximum of the silica density is outside the highest density region for the surfactant head groups. In this case, the organic linkers seem to be much more mobile and a well-defined peak is absent. In fact, a detailed analysis of characteristic radial distribution functions for these solutions (see Fig. S2) shows that while benzenesilicates and ethylenesilicates are predominantly lying with their silicate-organic-silicate axis parallel to the micelle surface (i.e., with both silicate moieties adsorbing within the head-group layer), ethanesilicates prefer to orient their Si-Org-Si axis perpendicularly to the surface, but with much less order.
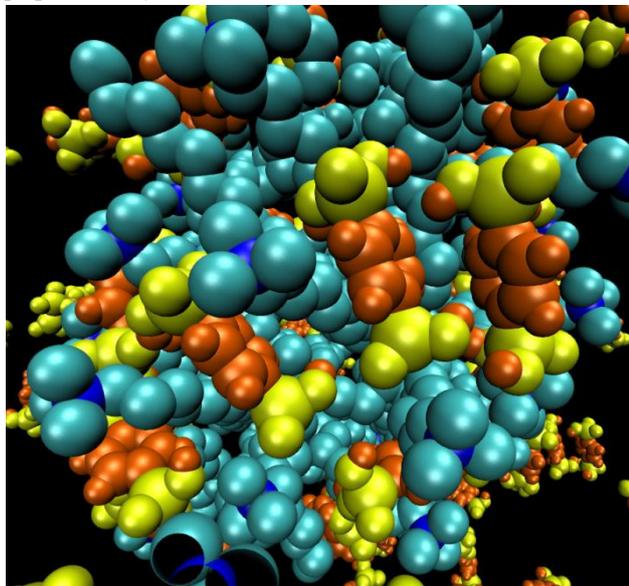

Fig. 3 Snapshot of a micelle formed in the solution containing benzenesilicates (orange and yellow spheres) and surfactants (light and dark blue spheres). Water molecules were removed for clarity.

The larger mobility of the organic linker suggested for the solutions with ethanesilica, whereby rotation around the single C-C bond is energetically accessible, is in contrast with the much more rigid structures of benzene (planar ring) and ethylene (double C=C bond). Furthermore, the organic moieties of benzenesilica and ethylenesilica (cis or trans configurations) are planar, which differs from the non-planar configurations of ethanesilica.[16] This suggests that the former organosilicates can more easily fit into the space available between the surfactant heads, which will lead to a high degree of organization and, eventually, to the molecular-scale periodicity reported by Inagaki et al.[7] Indeed, visual inspection of the micelles formed during the simulations for the solution containing benzenesilica already show some evidence for the origin of the molecular-scale periodicity observed experimentally for the PMO synthesized with that precursor. In Fig. 3, it is possible to see that some benzenesilicates are adopting a configuration where the molecular plane of the aromatic rings is normal to the surface and following the curvature of the micelle, suggesting a high degree of organization that will facilitate the π–π stacking of the bridging functional groups, which was suggested as the main reason for having structures with pore walls with crystal-like domains and exhibiting structural periodicity.[17] This reasoning is compatible with the observation of molecular periodicity for PMO materials synthesized from other organosilicas with rigid linkers such as biphenylene.[1,18] In ethanesilica, where precursor molecules are flexible and oriented mostly perpendicularly to the micelle surface, this kind of ordering is suppressed and materials with molecular-level periodicity are not formed.

In summary, our results confirm that the early stages of PMO synthesis, like for their parent PMS materials, are controlled by the interaction between silicates and the surface of surfactant micelles. Furthermore, the presence or absence of molecular-scale periodicity in the pore walls of the PMO materials obtained from these solutions is due to different mechanisms of interaction between surfactant micelles and organosilicates at the very early stages of the templated synthesis process. Precursors that adsorb strongly and orient their Si-Org-Si axis parallel to the micelle surface may lead to materials with molecular-scale periodicity, while with more flexible precursors that are less ordered this periodicity is not observed. These results shed new light on the synthesis mechanism of this class of materials, and constitute a further step leading to the computational design of PMOs with desired properties for specific applications.

Notes and references

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