



FAST KINETICS STUDY OF MESOPOROUS MATERIAL GROWTH BY SMALL-ANGLE X-RAY SCATTERING

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The combined use of a stopped-flow apparatus, the high flux available on beamline ID2A at the ESRF and of a fast CCD camera allows the determination of real-time nucleation and growth processes of an organic/inorganic liquid crystal within a time range from 20 ms to a few seconds.

These studies reveal microstructural mechanisms which are the key to synthesis of mesoporous materials.

Microporous materials such as zeolites are commonly used in industry as catalysts for chemical reactions and as molecular sieves for the separation of chemicals according to their molecular size. Zeolites, having pore sizes of less than 2 nm, are used to trap certain ions and very small molecules. Mesoporous materials, comparable to zeolites, have been of enormous interest since their discovery in 1992 [1] because their pore size is of the order of 2 to 50 nm in diameter, and thus they are able to accommodate larger molecules or complexed ions. Therefore, these materials have the potential for extending the fields of heterogeneous catalysis and separation. They could be used, for example, to increase the yield in the cracking process for asphaltenes, or as new molecular sieves for the separation of larger molecules [2].

Mesoporous materials are obtained by inorganic polymerization on the surface of direct micelles (often cationic surfactants). These micelles are destabilized by addition of a large quantity of inorganic multiply charged species, and in favorable cases, produce a well-organized hexagonal liquid crystal phase of closely packed charged apolar cylinders surrounded by polymerized inorganic oxide. In the final preparation step, the mixture is heated under hydrothermal conditions and the template is calcinated at high temperature. The final product shows a large specific area and exhibits a hexagonal order, as shown by small-angle x-ray scattering (SAXS) or by transmission electron microscopy (TEM) experiments.

The kinetic steps as well as the intermediate states are still unknown from the microstructural point of view in fast-growing organic-inorganic hybrid materials (formed “instantly” by precipitation). In the case of a slowly-growing (over a period of some hours) aluminosilicate zeolite, USAXS and WAXS, ultra small- and wide-angle x-ray scattering, experiments have been performed at the ESRF by T. Beelen [3], to provide evidence of the growth mechanism. In the case of mesoporous materials, some authors investigated the synthesis mechanism [2], but only a few of them concentrated on the very early stages of the formation of the material [4]. However, it seems to be in the very early stage that the final structure is determined, and therefore an understanding of the preorganization is relevant for control of the growth mechanism and hence also for control of the final structure and organization.

Our experiment has focused on the first preparation step of mesoporous zirconia. Two precursor solutions (in tanks S1 and S3) were mixed in a stopped-flow apparatus (Bio-Logic™), and pushed towards a 0.9 mm internal diameter quartz capillary located at the sample position on the high-brilliance SAXS beamline ID2A at the ESRF (Figure 1). The capillary was cleaned carefully between two mixing sequences by flushing with buffer (tank S2). 2-D scattering patterns were recorded by using the FRELON

CCD camera connected with a fast beam shutter (FBS). This setup allows very short exposure times of the order of 10 ms, following a minimum dead time of 6 ms (aperture of the FBS). The actual readout mechanism requires a minimum dead time of 0.4 s before the next acquisition. The dedicated stopped-flow software (Bio-Logic™) allows the definition of the desired acquisition start time for the mixing sequence. The flow rate is chosen for each motor to ensure a good mixing in the capillary before the acquisition starts.

Depending on the time-scale of the kinetics to be observed, we have adopted two experimental strategies:

a) “fast” kinetics measurements based on the following sequence: mixing, selecting as initial dead time

Fig. 1: Diagram of the stopped-flow apparatus. Stepping motors allow the choice of appropriate flow rates for mixing the components from the tanks S1, S2 and S3.

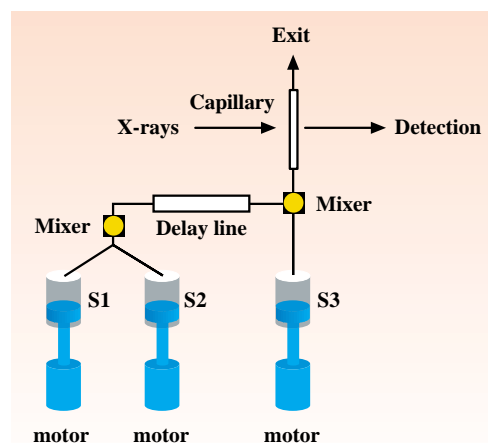




Fig. 2a: Typical intensity (I) obtained at the ESRF for a counting time of 10 seconds with a CTAB/zirconia mesoporous sample, after radial averaging and background subtraction. The Bragg peaks which provide evidence of the hexagonal structure have been indexed.

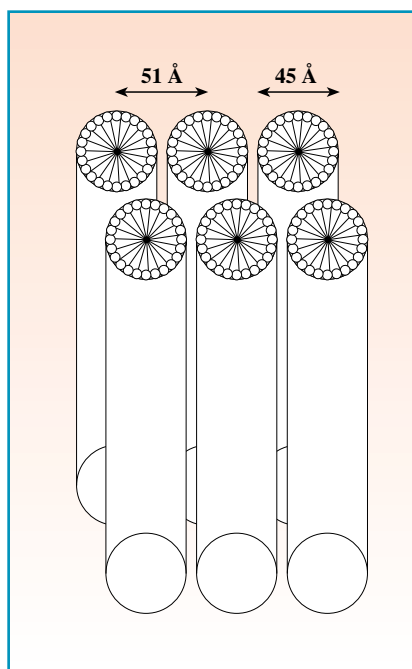
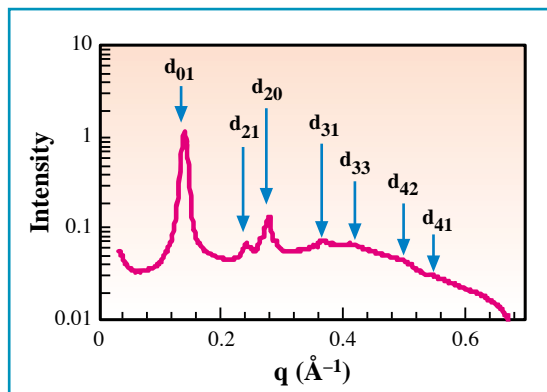


Fig. 2b: Schematic view of a hybrid liquid crystal. The surfactant cylinders are arranged in a hexagonal array; the polar volume within this hydrophobic template, covered by quaternary ammonium molecules, contains the zirconia network, which may lead to a mesoporous material after removal of the template.

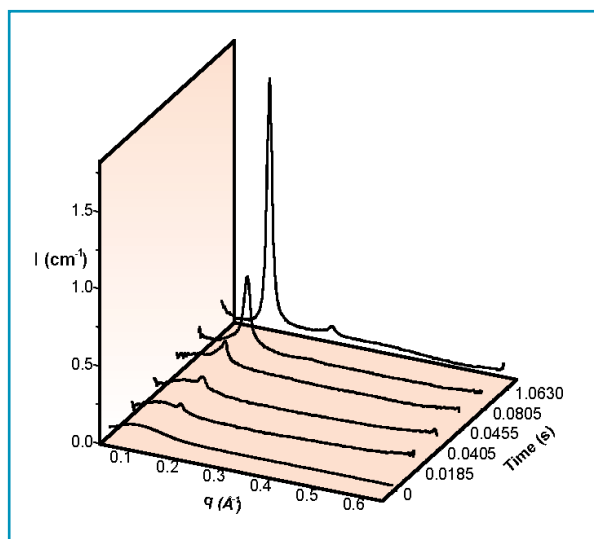


Fig. 3a: For fast kinetics experiments, SAXS patterns are recorded from 18 ms to 1 seconde, by changing the lowest initial dead-time. The first pattern (at 0 ms) corresponds to the one registered for the surfactant micellar solution as a reference.

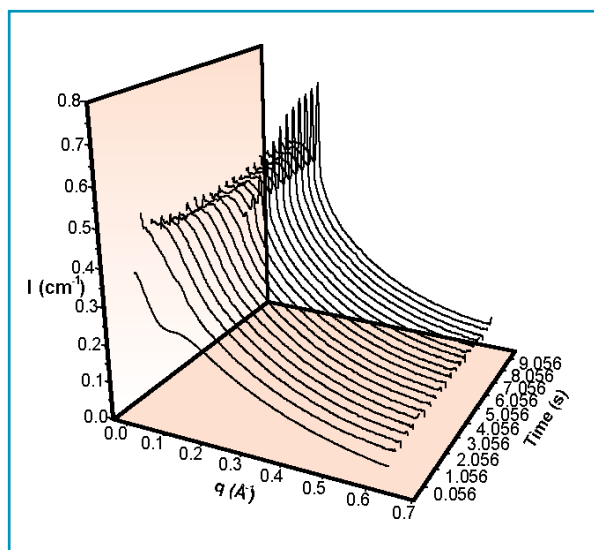


Fig. 3b: For the slow kinetics experiments, SAXS patterns were recorded from 56 ms to 10 seconds at 2 images per second. Here again, the first pattern corresponds to the initial solution of surfactant/ZrOCl₂ which was used as a reference.

the lowest one (6 ms), flushing and remixing with a longer dead time, again flushing, and so on.

b) “slow” kinetics measurements using a camera capable of recording two images per second, (lifetime of 0.1 s, separated by 0.4 s of dead time). The camera starts taking images just after the mixing.

For “fast” kinetics measurements, zirconium sulfate is used as the zirconium source. Two solutions are prepared, one containing 2.5 g of cetyl trimethyl ammonium bromide (CTAB) dissolved in 85 g water and one containing 4.55 g of Zr(SO₄)₂ dissolved in 15 g water. This procedure has been described previously by Ciesla et al. [5].

For “slow” kinetics measurements, the overall composition, by weight, of one stock solution is: 2.5 g of CTAB, 4.2 g of ZrOCl₂, and 100 g of H₂O whereas the other solution contains 18% by weight of MgSO₄ in water.

After mixing at room temperature, a typical SAXS pattern of a zirconia network, which had grown around cylinders of CTAB organized in a hexagonal array, was obtained (Figure 2a) in the q -range from 0.03 to 0.6 Å⁻¹ (corresponding to Bragg spacings from 10 to 200 Å). This array of cylindrical templates are separated by a complementary volume containing all the polar components of the hybrid network of zirconia, surfactant counterions, water, and excess added salt. Since the distance between neighboring



cylinders is only 50 Å on average, the thickness of the zirconia walls, i.e. the distance of closest approach is only a few angstroms (Figure 2b). The second feature observable in the SAXS pattern is a broad form factor of zirconia species which are produced by the precursor particles.

Figure 3 shows the x-ray patterns obtained during both fast (a) and slow (b) synthesis. Growth of the Bragg peak intensity corresponded to the formation of the hybrid material. Since the Bragg peak was already at its final position in the first instants of detection and its width no longer continued to change, the growth mechanism should occur by a continuous process of inorganic oligomers feeding the growing microcrystal [6]. Moreover, at large angles, the patterns were superimposed, indicating that the size of the inorganic oligomers does not increase. Therefore, the solution behaves as a reservoir of micelles and of zirconia precursor nanoparticles.

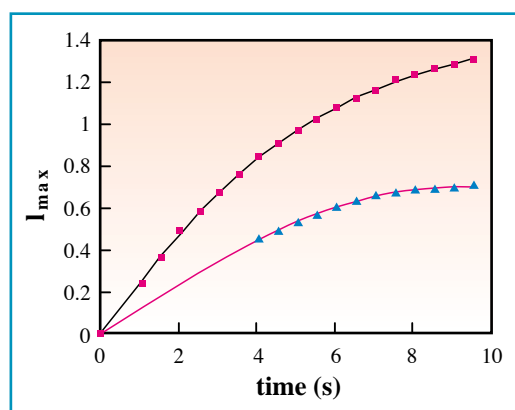
For the fast synthesis, the first order appeared just after 18 ms. This is the shortest time we were able to achieve with our experimental configuration. This time results from the addition of the minimum dead time (6 ms) and half of the minimum acquisition time that we had chosen to get good statistics (25 ms).

For the slow synthesis, the peak appeared after 0.85 s. By increasing the temperature from 21°C to 50°C, the growth kinetics became much faster (the first order peak occurrence varied from 0.85 s to 0.056 s).

To determine the relevant kinetic parameters, we tried different concentrations of the surfactant and different counter ions. In the fast kinetics experiments, magnesium sulfate was added directly to the zirconium sulfate solution to vary the ionic strength of the reaction media. Figure 4 shows the increase of the maximum intensity of the first order versus time for two different concentrations of surfactant / ZrOCl₂ solution, for the slow kinetics experiments.

These examples show that determining reaction kinetics in organized molecular solutions with a resolution of 20 ms is feasible on ID2A, once equipped with a stopped-flow apparatus. We believe that this methodology offers the opportunity of new fast SAXS kinetics studies, since sources of parasitic background

Fig. 4:
Evolution of the maximum intensity of the first order step (slow kinetics experiments) for two different concentrations. Triangles: 300 µl of CTAB/ZrOCl₂/water solution (S1) and 60 µl of MgSO₄ solution (S3). Squares: 300 µl of CTAB/ZrOCl₂/water solution (S1), 360 µl of water (S2) and 60 µl of MgSO₄ solution (S3).



scattering, flux through sample, and dead time in the detection systems are easily recoverable at the ESRF. ■

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ACKNOWLEDGEMENTS

Many thanks to T. Naranayan and O. Diat, of ID2A, for their helpful advice and assistance, and to J. Gorini, who helped us to ensure an accurate trigger between the stopped-flow apparatus and the CCD camera. Thanks also to P. Vachette for fruitful discussions and collaboration in the intermediate test of the stopped-flow setup. The very quick electronic device associated to the camera was developed by J.C. Labiche and the software control supported by the ESRF BLISS group.