Experimental report

02/04/2018

Proposal: **6-07-24** **Council:** 10/2016

Title: Forced water intrusion into deformable hydrophobic nanopores

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: SiO_2+ $CH_3(CH_2)_7Si(CH_3)_2Cl$ (10% organic fraction)

Instrument	Requested days	Allocated days	From	To
D16	6	5	15/02/2017	22/02/2017

Abstract:

Water in hydrophobic confinement is of general interest for industrial applications as well as the understanding of biological matter and more generally in the field of soft condensed matter. Ordered hydrophobic nanoporous materials provide well defined geometries to study water in hydrophobic confinement. While water confined in hydrophilic nanopores has been extensively studied, water confined in highly hydrophobic nanopores has been rarely considered especially because of the high pressure required to fill hydrophobic nanopores. The goal of this proposal is to quantify the deformation of hydrophobic grafted MCM41 nanoporous material upon water forced intrusion. These deformation measurements will provide information on the impact of confined water and interfacial energy on the mechanical properties of the confining material, a better understanding of the mechanics at pore scale and intrusion mecanism.

Forced water intrusion into deformable hydrophobic nanopores

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Experimental Report 9-12-444
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Ordered hydrophobic nanoporous materials provide well defined geometries to study water in hydrophobic confinement. MCM41 are mesoporous silica with controlled parallel monodisperse cylindrical channels arranged on a 2D hexagonal pore lattice. MCM41, that are natively hydrophilic, have been extensively used for the past 20 years to study confined water [4, 5, 8]. Their hydrophobic counterpart, such as silane grafted MCM41, have received much less attention. Hydrophobised MCM41 have mainly been studied with a macroscopic approach up to now. We propose to study the deformation of hydrophobic grafted MCM41 upon water intrusion at high pressure (450 bar). The water intrusion occurs in a narrow range of 50 bar at a typical pressure of 40 MPa depending on pore radius and hydrophobicity through Laplace pressure, while the spontaneous extrusion of water out of the pores, at aournd 20 MPa, is limited by a nucleation barrier [2].

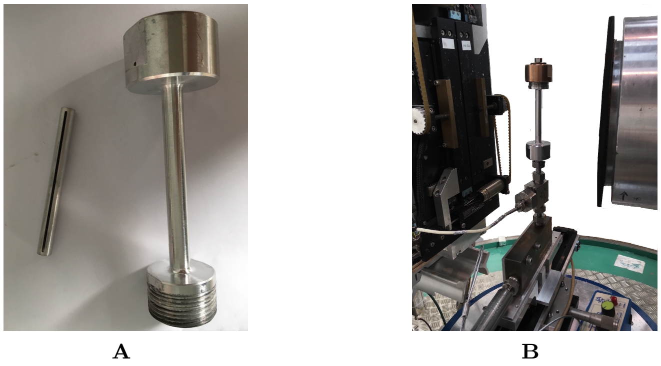


FIGURE 1. (A) High pressure cell and flat thin insert used for the experiment. (B) High pressure cell connected to a fluid separator, water pressure is directly measured at the base of cell.

EXPERIMENTAL APPROACH

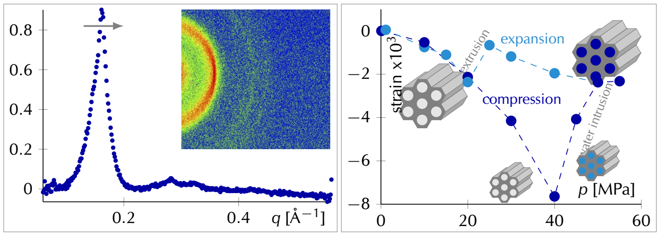
This study requires to control the pressure of the sample with an extreme precision of ±1 bar within a pressure range of 1000 bar. To this end a syringe pump has been used with a thermal regulation of the pressure sensor used for the pressure regulation in order to eliminate any shift of the pressure signal induced by the temperature variations. The pump that allows a fine pressure regulation uses a mineral oil as the pressurizing fluid. A separator visible in the figure 1B is used in order to transmit the pressure from the oil to the pure water of our sample. In order to measure precisely the water pressure a pressure sensor is mounted on the water side at the base of the high pressure cell that contains the sample.

To minimize neutron absorption by the cell, SANE prepared a thin aluminium cell 19PL10AL6 that can sustain 1 kbar with at total wall thickness of 2 mm and an internal diameter of 6 mm (see figure 1A). A flat insert with large access from the side wall has been used to be able to reach a high powder fraction ratio. The wetted powder at a high fraction ratio larger around 60% in volume is forced within the slit with a spatula The dry friction within the granular media is large enough to maintain the sample in place within the slit.

The samples are made of grafted MCM41 previously mixed through forced water intrusion in our lab setup. In order to prevent any contrast effects [9] blurring the evolution of the peak pattern upon intrusion, water will be a mixture of D_2O and H_2O to obtain an effective zero scattering length density. Neutrons are especially attractive for their ability to tune contrast and handle high pressure. The high flux of D16 is of paramount importance to shorten the acquisition duration for each measurement point. The D16 instrument at ILL is perfectly suited for high resolution diffraction study in intermediate Q range with the benefit of high flux. The D16 provides a Q range from 0.04 to 0.45 Å^{-1} that contains all of our three Bragg peaks at 0.15, 0.26 and 0.32 Å^{-1}. The percent resolution on wavelength and the small pixel size keeps peaks sharp and provide a fine Q spacing of 0.01Å^{-1}. The pressure cell and small incertitude required to measure peak shift lead to 3 h of acquisition for each detector. In addition to the side detector, the centered detector will record the full circle of the first peak with an large number of pixels that will considerably refine the peak sampling. As a result, 6 hours are required to measure each full spectra. We followed Bragg peaks from 1 to 600 bars upon water intrusion and extrusion. This corresponds to 15 spectra measurements.

RESULTS

The typical spectra obtained during the experiment is shown in the figure 2A after azimuthal integration of the 2D spectra and substractions of base lines. The deformation of the matrix is associated to the shift of the first Bragg peak that reflects precisely the shift of the lattice parameter. The relative deformation of the material is calculated as the relative shift of the Bragg peak. This shift is carefully determined from the shift of the area corresponding the local spectra integration around the maximum of the Bragg peak. Such a procedure enable the determination of the deformation with a precision of the order of 5.10^{-4}. Taking the empty hydrophobic pore at ambient pressure as the reference, the measured radial deformation of the pore according to the applied pressure is shown in figure 2A.



A **B**

Figure 2. (A) Typical diffraction pattern obtained from the azimuthal averaged profile shown in the inset. (BRelative variation of the pore lattice parameter according to the pressure and schematic of the associated nanopore state.

The figure 2B shows an hysteretic behavior associated to the intrusion/extrusion cycle of water within the pores. When the pressure increases (dark blue points in the figure 2B) one observes, for a pressure lower than 40 MPa, a compression of the matrix with a extremum deformation of the order of -8.10^{-3} reached at 40 MPa. From the 10 Gpa bulk modulus estimate on MCM41 [5] we expect a deformation at 10 MPa of the order of 0.1% which is in agreement with our measurement. Interestingly, this compression stage appears to be non linear with the applied pressure. Beyond 40 MPa, one observes a relaxation of the matrix on a pressure window less than 10 MPa. This stage is associated to the filling of the pores. At a pressure larger than 50 MPa no significant deformation seems to be observed. Additional points at pressure larger than 60 MPa would be needed to confirm this trend. The deformation level corresponding to the filled material is distinct form the null reference deformation. This difference is presumably related to the difference in surface tension at the inner pore interface. The filling of the pore corresponds indeed to a transition from a solid/vapor interface to a solid/liquid interface. The observed deformation a large pressure is consistent with a solid/liquid surface tension larger than the solid/vapor surface tension.

When the pressure is released (light blue points in the figure 2B) the strain is decreased with a non constant slope that is larger at lower pressure. The origin of this non linear behavior is currently unclear and probably related to the one observed during the compression stage. A potential explanation could be related to a dependence the surface tension either on the pressure or the deformation stage of the pores. This strain reduction continue up to 25 MPa approximately, pressure at which the water extrusion out of the pore occurs and leads back to a state identical to the state observed during the compression stage.

CONCLUSION

This experiment was successful in demonstrating the feasibility of measuring the pore lattice variation of ordered superhydrophobic nanopores. In particular, this experiment validate the high pressure instrumentation with efficient pressure stabilization required for such a measurement. Quantitative values of pore lattice parameter variation according to pressure have been obtained and present an unexpected non linear behavior with pressure.

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[1] M. Michelin-Jamois, C. Picard, G. Vigier, and E. Charlaix, Phys. Rev. Lett. **115**, 036101 (2015).
[2] L. Guillemot, T. Biben, A. Galarneau, G. Vigier, and E. Charlaix, Proc. Natl. Acad. Sci. **109**, 19557 (2012).
[3] B. Lefevre, A. Saugey, J. L. Barrat, L. Bocquet, E. Charlaix, P. F. Gobin, and G. Vigier, J. Chem. Phys. **120** (2004), 10.1063/1.1643728.
[4] M. Erko, D. Wallacher, A. Hoell, T. Hauß, I. Zizak, and O. Paris, Phys. Chem. Chem. Phys. **14**, 3852 (2012).
[5] J. Prass, D. Müter, P. Fratzl, and O. Paris, Appl. Phys. Lett. **95**, 1 (2009).
[6] G. Y. Gor, O. Paris, J. Prass, P. A. Russo, M. M. L. Ribeiro Carrott, and A. V. Neimark, Langmuir **29**, 8601 (2013).
[7] M. Schoen, O. Paris, G. Günther, D. Müter, J. Prass, and P. Fratzl, Phys. Chem. Chem. Phys. **12**, 11267 (2010).
[8] G. Y. Gor, L. Bertinetti, N. Bernstein, T. Hofmann, P. Fratzl, and P. Huber, Appl. Phys. Lett. **106**, 1 (2015).
[9] J. Prass, D. Müter, M. Erko, O. Paris, and IUCr, J. Appl. Crystallogr. **45**, 798 (2012).