ESRF	**Experiment title:** Multiscale structure of ordered porous oxide and carbon materials	**Experiment number**: 02 01 615
Beamline: BM02	**Date of experiment**: from: 19 April 2003 to: 22 April 2003	**Date of report**: **February 2004**
Shifts: 9	**Local contact(s)**: Dr. Erik GEISSLER	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Françoise EHRBURGER-DOLLE*, Isabelle MORFIN*, Erik GEISSLER*, Daniel CHARRIER*, spectro, CNRS-UJF, Saint-Martin d'Hères

Françoise BLEY*, Frédéric LIVET*, LTPCM, ENSEEG, Saint Martin d'Hères

Joseph DENTZER, Seifedine SAADHALLAH*, Cathie VIX-GUTERL, ICSI CNRS Mulhouse

Julien PARMENTIER, Mohammad REDA*, Valentin VALTCHEV, LMM, ENSCM, Mulhouse

Report:

Ordered nanoporous carbons can be prepared by a replica technique starting from an organised silica template. The silica template SBA-15, displays hexagonal arrangements of mesopores interconnected by micropores while MCM48 displays a cubic arrangement. Different routes are possible for introducing carbon into the pores of the silica: liquid impregnation by a solution of sucrose followed by carbonisation [1], chemical vapour infiltration (CVI) [2] or infiltration of pitch. After dissolution of the silica template by hydrofluoric acid treatment, a carbon material is obtained. Our aim was to investigate the role of several parameters (structure of the silica template, method of infiltration, amount of carbon infiltrated) on the multiscale structure of the carbon replica. To this end small-angle X-ray scattering (SAXS) measurements were performed over a broad range of wave vector q. Because of the close match in electron density between silica and carbon it is possible to investigate the silica mesopore filling.

Two different experimental set-ups were used. For measurements at ultra-small angles (USAXS), an incident energy of 7.9 keV (λ=0.157 nm) was selected in order to reach small q values, the distance between sample and detector being D=209 cm. The beamstop was a cross hair made from 300 µm platinum wire. With this set-up, the scattered intensity was determined between ca. 7×10^{-3} nm^{-1} and 10^{-1} nm^{-1}. In the second configuration, yielding data between ca. 8×10^{-2} nm^{-1} and 1.8 nm^{-1}, the energy was set to 16 keV (λ=0.077 nm) and the sample to detector distance was shorter (157 cm). The beamstop, a small pillar of 2 mm diameter lead wire, was fixed to a Kapton foil just upstream of the flight tube exit window. In all cases, an indirect illumination CCD detector (Princeton Instruments), cooled by a Peltier effect device, with pixel size d=50 µm was used.

In order to show an example of the type of information that is obtained from this series of experiments, we analyse here the SAXS curves obtained for samples derived from SBA-15.

The first figure shows the intensity curve obtained for SBA-15 containing 31 wt% of carbon, prepared by the liquid impregnation method (water solution of sucrose). This amount of carbon is nearly the maximum

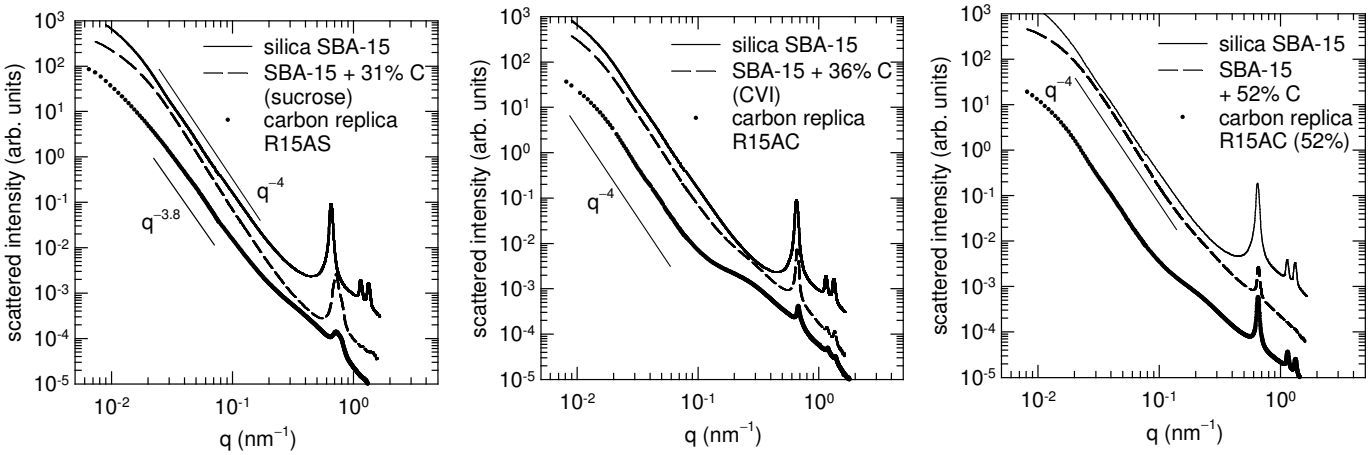
that can be infiltrated in a single step. It corresponds to about half that needed (63 wt%) to fill the silica pores completely. It appears that, as compared to the silica template SBA-15 (the curves have been shifted for the sake of clarity) the intensity of the main peak is smaller and the second and third peaks almost vanish, as a result of the decrease in contrast for filled pores. Furthermore, the peak is slightly shifted to larger *q*. This feature indicates a shrinkage of the sample due to evaporation of water coming from the sucrose solution. The corresponding carbon replica is poorly organised and its external surface is fractal (D=2.2).

When a similar amount of carbon is infiltrated by CVI (second figure), no shift of the peak is observed and the replica displays and the carbon replica seems slightly more organised. Scattering resulting from the external surface can fitted with a Porod law indicating that this surface is smooth.

The third figure shows the curves obtained for SBA-15 impregnated by CVI with 52% of carbon and the corresponding carbon replica. Because the values of the silica and carbon densities are very close but not known precisely enough, it is difficult to assign the small peak observed for the carbon filled silica to the presence of empty spaces still remaining within the silica pores or to a difference in the electronic contrast. The carbon material obtained after removal of silica displays the three peaks characteristic of SBA-15. The parameter of the two-dimensional hexagonal cell (a=11.09±0.05 nm) is the same as that determined for the silica template (11.01±0.05 nm) within the limits of experimental error and it agrees fairly well with the cell parameter obtained by HRTEM (11.2±0.6 nm) on the same sample. It follows that this material is a true replica of the silica template.

From this series of experiments it may be concluded:
- liquid impregnation by a solution of sucrose followed by carbonisation (liquid route) induces an affine shrinkage of the template and, hence, a shift of the whole replica structure towards smaller lengths
- by using propylene CVI (gas route), the original structure of the template is retained
- to obtain organised carbon, at least half of the template pore volume must be filled with carbon; complete filling of the silica pores by the liquid route therefore requires two steps.

Analysis of the data obtained for the other series of samples is currently in progress.



References

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(2) Vix-Guterl, C.; Boulard, S.; Parmentier, J.; Werckmann J.; Patarin J. *Chemistry Letters* 2002, *10*, 1062.

Publication

SAXS investigations of ordered porous carbon materials, F. Ehrburger-Dolle, F. Bley, E. Geissler, F. Livet, I. Morfin, J. Parmentier, J. Patarin, M. Reda, S. Saadallah, C. Vix-Guterl, Carbon'03, Oviedo (6-10 juillet 2003) *Extended Abstract* 184, A. Linares-Solano and D. Cazorla-Amoros Eds., Spanish Group of Carbon, CD-Rom, *ISBN 84-607-8305-7.*