COMPARATIVE STRUCTURAL ANALYSIS OF MESOPOROUS CARBON FDU-16 WITH 3D-TEM , XRD REFINEMENT AND GAS SORPTION POROSIMETRY.

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Introduction

Ordered mesoporous materials with large and interconnected 3D pores are strongly studied because of their many potential applications, especially for uses involving selectively tuned diffusion or immobilization of molecules with large molecular weight. Among these materials, the compound denoted FDU-16 is formed by a cubic-centered packing of connected spherical cavities (space group Im-3m). For applications which require the diffusion of molecules, the diameter of the large cavities but also the pore entrance size connecting the cavities are important parameters to control [1]. It is worth to note that this type of cage-like structure is not appropriately analyzed by the conventional pore size determination methods based on gas adsorption and its complex structure is not fully elucidated. Therefore, structural investigations using recently developed techniques such as 3D transmission electron microscopy (3D-TEM) and X-ray Diffraction (XRD) structure modeling were carried out to solve accurately its characteristics.

Experimental

The synthesis of FDU-16 carbon phase was adapted from reference 2. The sample was calcined at 700°C. The rhombododecahedron macroscopic shape was observed by scanning electron microscopy.

3D-TEM, often referred as electron tomography, is a technique which allows to reconstruct the three dimensional structure of a sample, with nanometer scale resolution, from a series of 2D-TEM images recorded at different tilts angles [3]. The acquisition of the tilt series for 3D-TEM analysis was performed in bright-field mode on a JEOL 2100F microscope using the Gatan tomography software and a 2048 × 2048 pixels cooled CCD array detector. The 3D-reconstruction really provides direct information on the 3D-shape and connectivity of the cavities. For instance, its detailed analysis allows us to determine precisely the diameters of the cavities and the pore entrances.

The SAXRD pattern was modelled using the Rietveld [4] full-profile formalism. The structural parameters were refined by applying the continuous density function (CDF) technique [5] and the derivative difference minimization (DDM) method [6].

Nitrogen physisorption at 77K were recorded on a Micromeritics ASAP2010 apparatus.

Results and Discussion

3D-TEM revealed the cubic centred arrangement of the cavities with a lattice parameter of about 11 nm. Their individual analysis allowed to observe their roughly spherical shape with a mean diameter close to 3.6 nm (Fig. 1). The connexions between the spherical pores are hardly observable suggesting the presence of closed porosity that could explain partly the low pore volume measured by nitrogen physisorption at 77K (0.3 cm3/g). The defective nature of the cavities arrangement was also detected (Fig. 2).

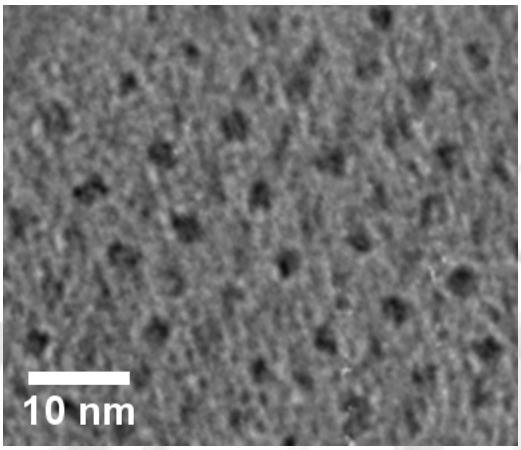

Fig. 1 Typical section through the reconstructed volume showing the arrangement and characteristics of the cavities; they have a roughly spherical shape with an average diameter of about 3.6 nm.

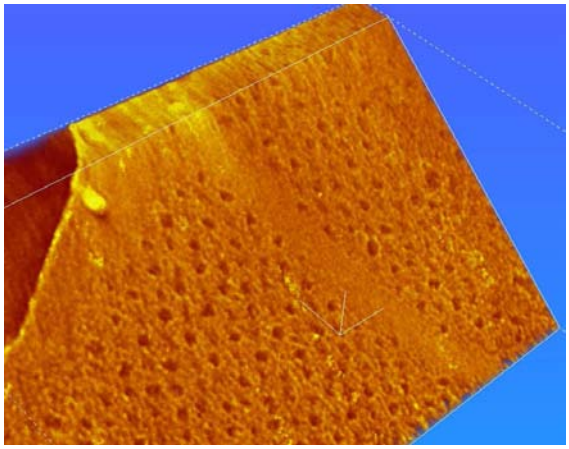

Fig. 2 3D image of the assembly allowing the direct observation of a typical stacking defect between two well organised areas.

The structural characterisations obtained by this technique were compared with the structural model determined by SAXRD form the diffraction pattern displays on Fig. 3.

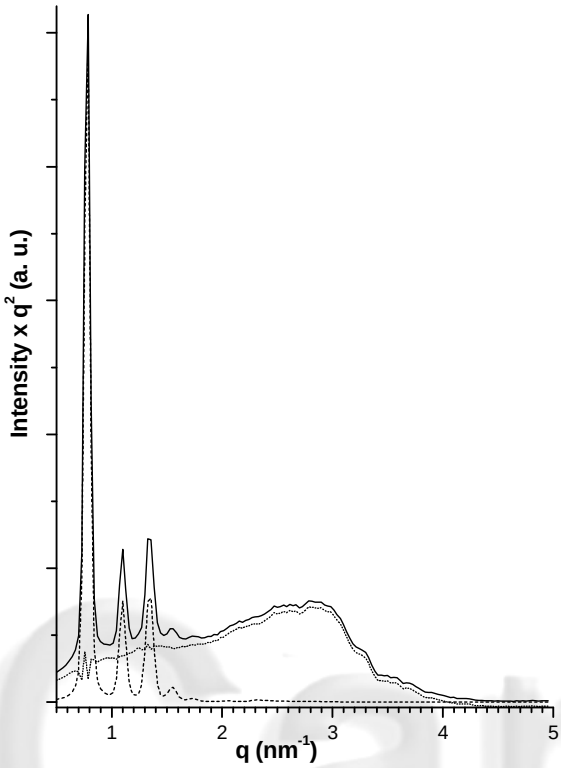

Fig. 3 Lorentz-factor corrected observed (solid line) calculated (dashed line) and difference (dots) SAXRD patterns of FDU-16 after the CDF-DDM refinement.

The refined cubic cell parameter is a = 11.5 nm and the spherical pore diameter D is around 4.7 nm. The slight discrepancy between 3D-TEM and SAXRD techniques is in the range of accuracy of the measurements.Nitrogen physisorption at 77K displays a type Ib isotherm with low BET surface area (673 m2/g) and pore volume (0.3 cm3/g). It suggests the existence of a high amount of closed-porosity.

Conclusions

The structure of this new type of ordered mesostructured carbon has been investigated by using three complementary characterization techniques. Details about pores, regarding their shape, diameter, stacking order, connectivity and accessibility to gas have been investigated.

References

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