Formation of Ordered Mesoporous Carbon Material from a Silica Template by a One-Step Chemical Vapour Infiltration Process

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A well-ordered mesoporous carbon material has been prepared by a one-step chemical vapour infiltration process starting from a MCM-48 silica template.

Porous carbon materials are very attractive for widespread industrial applications especially for hydrogen storage, adsorbents, catalysts, electrode materials. The most common way to produce porous carbons is the carbonisation of precursors of natural or synthetic origin, followed by activation.[1,2] By this method, however, it is not possible to obtain carbon materials with a strictly controlled pore structure.[3] New approaches have been proposed based on a replication technique starting from a silica material used as porous solid template. A two-step preparation of an ordered microporous carbon has been proposed by different authors using Y zeolite as template.[4,5] In this case, the porous inorganic framework was first impregnated with furfuryl alcohol subsequently carbonised, followed by the chemical vapour infiltration of carbon using propylene at 1073 K. The recent discovery of ordered-mesoporous silica materials like the M41S-type molecular sieves[6,7] opens new possibilities to prepare ordered mesoporous carbons. In this frame, MCM-48, SBA-1 or SBA-15 silica materials were used as a porous solid template[8–10] and infiltrated with an appropriate carbon precursor as sucrose, furfuryl alcohol or phenolic resin followed by carbonisation. A carbon material with a controlled porosity and which retained the initial silica morphology was obtained after removal of the silica matrix by etching with hydrofluoric acid (HF). The use of a liquid impregnation method present some drawbacks; the following are mentioned by the authors: shrinkage of the silica network during synthesis, formation of an additional porosity during carbonisation, multi-stages process.

In the present work, another route has been proposed which is based on the chemical vapour deposition process using a gaseous carbon precursor. The lower viscosity of the gas is expected to be an advantage compared with the liquid impregnation. The preparation route and the properties of the carbon material obtained are described in this paper. Comparison with porous carbon prepared by liquid impregnation following the experimental procedure described in the literature[8] is also discussed.

The selected inorganic template is the MCM-48 silica material prepared by the procedure described by Schumacher.[11] The characteristics of the silica material are reported in Table 1. Considering its total pore volume[12] ($0.84\,cm^3/g$) and a carbon density equal to 2.0, the maximum amount of carbon which can be introduced inside the pores cannot exceed 60 wt%. The carbon was introduced into the silica channels via two methods: (i) chemical vapour infiltration process (CVI), (ii) liquid impregnation by a sucrose solution. In the first method, the MCM-48 solid placed in a horizontal reactor, was put into contact with propylene (2.5 vol% in an argon flow) at 1020 K during 12 h. At the end, the carbon represents about 50 wt% of the C/SiO_2 material (this value is close to the theoretical one). The second impregnation procedure was the one described by Ryoo:[8] the MCM-48 silica matrix was impregnated with a sucrose solution containing the maximum quantity of sucrose allowed by the pore volume of the inorganic template. After sucrose carbonisation, the carbon represents around 35 wt% in the SiO_2/C material which is consistent with the fact that around 1/3 of the initial weight of sucrose can be converted into carbon during carbonisation. Carbon materials were recovered after dissolution of the silica matrix in HF. EDX analysis indicates that no silica is remainded after HF treatment in the carbon material. SEM observations (not reported here) of the carbon materials C_p (issued from the CVI process) and C_s (originated from the liquid impregnation of sucrose) indicate that they retain the spherical morphologies of the silica template. Moreover, this technique evidenced that a second sucrose impregnation performed in order to increase the carbon content in the SiO_2/C material was not favourable and led to the formation of non-porous amorphous carbon at the outer surface of the silica matrix at the difference of the C_p sample obtained for similar carbon content in the SiO_2/C material. XRD patterns of silica template and carbon materials are reported in Figure 1.[13] As for the MCM-48 silica matrix, the carbon solid exhibits two structural characteristics: disorder at the atomic scale (no Bragg lines above $2\theta = 10°$) but distinct order at the mesoscopic level as indicated by the sharp low-angle correlation peaks characteristic of a cubic and highly-ordered periodic structure. The presence of a peak at $2\theta = 1.65$ corresponding to the (110) reflection indicates a symmetry change as already mentioned in the literature.[8,9] The periodic structure of carbon was also observed by HRTEM[14] (Figure 2). It can be satisfactorily observed in Figure 2A that material C_p exhibits a long-range structural ordering in agreement with the XRD data. This kind of feature can be only the results of a uniform pore filling during the CVI process. Figure 2B for material C_s is consistent with the literature data.[8] Therefore, the pore arrangement at a nanometric scale in material C_p suggests that the proposed CVI method is

Table 1. Characteristics of the MCM-48 silica matrix and the different carbon materials C_p and C_s: a_{XRD}, XRD unit cell parameter; a_{TEM}, TEM unit cell parameter, S_{BET}, specific surface area[16] and V_t, total pore volume[12]

Material	a_{XRD} (nm)	a_{TEM} (nm)	S_{BET} (m^2/g)	V_t (cm^3/g)
MCM-48	8.4	7.4	1100	0.84
C_p	8.2	7.3	970	0.63
C_s	7.6	6.8	1500	0.92

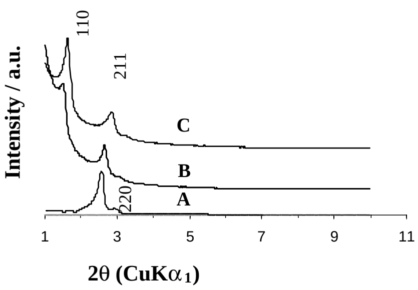

Figure 1. XRD patterns of: MCM-48 silica (A), carbons C_p (B) and C_s (C).

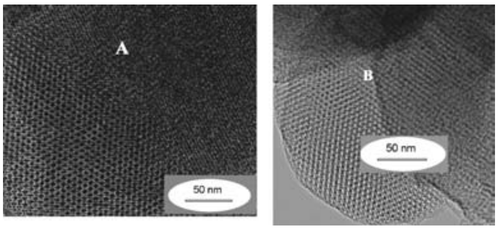

Figure 2. Typical HRTEM images of ordered mesoporous carbon molecular sieves: C_p (A) and C_s (B).

suitable to prepare carbon sieves as it will be confirmed by other structural and textural parameters. No drastic change of the unit cell parameter values (a_{XRD}) of the carbon materials is observed compared to the MCM-48 solid except the slight decrease which is attributed to the thermal treatment (see Table 1). However, it is noteworthy that this lowering is less important for C_p (2%) than for C_s (9%). This tendency is confirmed by the TEM analysis (a_{TEM} values[15] in Table 1). The difference between both *a* values (a_{XRD} and a_{TEM}) probably results from experimental errors during the calibration of the TEM images which is critical for the magnifications selected for the present observations. Therefore, it is suggested that the lattice contraction is markedly less pronounced during the CVI process than during the liquid impregnation one. This may be related to two parameters: (i) the processing temperature, (ii) the involving chemical process during the synthesis. The maximum temperatures which were reached during the preparation were equal to 973 K and 1173 K for CVI and sucrose methods, respectively. Such a temperature difference is sufficient to induce a lower thermal shrinkage of the silica matrix during the CVI process. In addition to this temperature effect, the chemical mechanism involved during the carbon formation has also to be taken into account. The CVI process consists of the deposition of a solid by a chemical reaction occurring within a gaseous phase (propylene in Ar in this work). Whereas in the second method, the impregnated sucrose is converted to carbon during a carbonisation step characterised by an important release of volatile matters (H_2O, CO_2, CO, H_2 and hydrocarbons) occurring from the bulk of the material. Undoubtedly, these chemical modifications in the confined environment of the filled MCM-48 pores induce strains in the silica network which is then more disturbed than during the CVI process. Moreover, the carbon samples exhibit high specific surface area (970 m^2/g and 1500 m^2/g for materials C_p and C_s, respectively (Table 1), values in the same range of order than the one of the MCM-48 material (1100 m^2/g). Whatever the type of carbon, it has been observed that the mesoporosity is broadly distributed with the presence of mesopores and large micropores (pore diameter ranging between 1.4 to 1.9 nm) (Figure 3).[16] The total pore volume (V_t) is higher for C_s as compared to C_p. This may be related to a more pronounced micro-and mesoporous character consequence of the incomplete filling of the MCM-48 silica matrix (as indicated by the carbon content) associated to the important gas release occurring during the carbonisation process. This is also consistent with the significant reduction of the unit cell parameter.

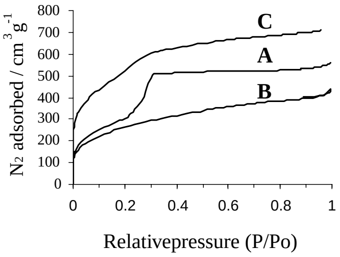

Figure 3. N_2 adsorption isotherms at 77 K for materials MCM-48 silica (A), carbons C_p, (B) and C_s (C).

In conclusion, this work shows the possibility to prepare an ordered mesoporous carbon sieves (as confirmed by HRTEM, XRD and N_2 adsorption isotherm) using a chemical vapour infiltration method. This process presents the following advantages compared to the liquid impregnation one: higher carbon content in just one step process; no further drying and heat-treatment steps (as it is the case for a liquid impregnation), milder experimental conditions inducing a lower thermal shrinkage of the silica matrix and consequently a lower lattice contraction. Moreover, chemical analysis of the carbon materials indicates that the C/O atomic ratio is much higher (by a factor of 3.5) for the carbon prepared by CVI as compared to the one obtained by liquid impregnation.

The simplicity of the preparation of this carbon material opens the opportunity of a large scale production for various applications as shape-selective catalyst and adsorbents, hydrogen containers and electrode materials. In particular, we have recently published the possibility to prepare silicon carbide with high specific surface area (>100 m^2/g) by heat treatment (T > 1470 K) of the SiO_2/C material.[17]

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14 The HRTEM images were performed on a TOPCON EM002B (200 keV, $C_s = 0.4$ mm) electron microscope.
15 a(TEM) is determined by HRTEM using the fringe spacings measured from the position of the Bragg peaks in the Fourier transformed images.
16 Determined by nitrogen gas adsorption measurements carried out on a Micromeritics ASAP 2010 apparatus.
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