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MESOSTRUCTURED MATERIALS

Influence of chemical vapour infiltration conditions of acetylene on the structural and textural properties of EMT-type zeolite nanocasted carbon replica

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Abstract Ordered microporous carbons were synthesized by the nanocasting process using EMC-2 zeolite (EMT structure type) and acetylene as a mould and a carbon precursor, respectively. In this study, the conditions of the synthesis methods for preparing the ordered microporous carbons were examined. Temperature and duration parameters for the chemical vapour infiltration were optimized to yield an ordered carbon replica that displays up the three XRD diffraction peaks. This faithful replica exhibits also a high micropore volume (1.3–1.4 cm^3/g) with mainly supermicroporosity, a high specific surface area (>2900 m^2/g) and nearly no mesoporosity. The pore size distribution calculated with NLDFT method from nitrogen physisorption data shows three maxima at 0.6, 1.0 and 1.8 nm diameters. The second is due to the zeolite wall dissolution. The first and the third are attributed to different types of default. Compared to the classical two-step procedure, the direct infiltration with acetylene appears an interesting route for the preparation of ordered microporous carbon replicas with high micropore volume.

Introduction

Activated carbons are widely used for various applications such as catalysis and adsorption due to their high specific surface area and low cost. Nevertheless, these materials are not always adapted for emerging applications such as gas and energy storages, which require an accurate control of their pore size distribution (PSD) especially in the microporous range. For instance, atomistic simulation studies for gas storage [1] or experiments for supercapacitors [2] have shown that the carbon porosity has to be accurately controlled within the microporous range for optimized performances. Therefore, other synthesis routes have been developed such as nanocasting which consists of a carbon precursor infiltration into a porous template or mould (e.g. zeolite or ordered mesoporous silica) and its subsequent conversion to carbon. The removal of the template leads to a negative carbon replica with various porous characteristics deriving from template structures (e.g. size and shape of the porous network). New types of microporous materials, with peculiar pore morphologies, can be obtained if a zeolite (microporous) template is used. At the difference of mesoporous templates, infiltration of microporous moulds is a tedious problem since narrowness of their porosity precludes their high carbon loading by anticipating pore closure phenomena. Nevertheless, numerous samples have been successfully synthesised by this process and display interesting hydrogen storage capacities [3, 4], It is worth noting that these materials suffer usually from a lack of structural organisation. Adapted synthesis procedure [3, 5], could lead to well ordered replica but the choice of the zeolite template used is quite limited, mainly zeolite Y (FAU structure-type) and beta (*BEA structure-type). The resulting samples display in those cases only one single X-Ray Diffraction (XRD) peak. Both low resolution and single XRD peak preclude the extraction of structural data from the XRD pattern. Recently, Gaslain et al. [6] showed it was possible to obtain a zeolite carbon replica with a well-resolved pattern with more than three peaks by choosing the EMC-2 zeolite (EMT structure-type). Indeed, the latter displays also a three-dimensional pore structure but

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with hexagonal symmetry compared to the cubic one of zeolite Y. Its structure is characterised by a straight pore channel system running along the c direction at the difference of interconnected cages pore network of zeolite Y. Even if the large pore opening (up to 12-membered rings) is quite similar for both structures, the higher Si/Al framework ratio of zeolite EMC-2 compared with zeolite Y (3.8 instead of 2.5) implies a lower amount of counter cations (Na^+), and therefore more free space available for carbon infiltration in the porous network. Moreover, this mould allows getting additional structural information regarding the porosity of the carbon replica obtained (personal communication). The carbon replica was prepared using two steps as proposed by Kyotani et al. [7]: (i) impregnation of zeolite with furfuryl alcohol and polymerisation and (ii) propylene chemical vapour deposition (CVD) at 700 °C for 1 h. This two-step procedure is long and labourious, and so Hou et al. [8] showed that the first step could be omitted if acetylene gas was used for CVD. Hence, they prepared carbon replica of zeolite Y using acetylene at 600 °C. Hence, it appeared that infiltration conditions had been mainly explored for zeolite Y at the difference of zeolite EMC-2, which has a close structure. Since, zeolite Y carbon replicas have interesting adsorption potentiality, it was worth developing new preparation process with this EMC-2 zeolite mould. In order to speed up the process, we focussed on acetylene gas as a carbon precursor. Since the mould displays different pore topology and reactivity, influences of the synthesis parameters on the porous and structural characteristics of the carbon replica were investigated to define the optimal conditions for a faithful carbon replica.

Experimental

Zeolite EMC-2 was prepared using a similar procedure to that described by Delprato et al. [9]. The final composition of the hydrogel was: 1.00 SiO_2: 0.10 Al_2O_3: 0.22 Na_2O: 0.087 18-crown-6: 14.00 H_2O. Sodium hydroxide was dissolved in distilled water. Sodium aluminate was added and the solution was stirred until total dissolution. After successive addition of the silica source (colloïdal silica; Ludox HS 40) and the templating agent (18-crown-6) under vigourous stirring for 24 h at room temperature, the hydrogel was placed in a Teflon-lined autoclave at 110 °C for 13 days. The resulting solid was washed with distilled water and dried overnight in an oven at 80 °C. The as-synthesised zeolite EMC-2 was calcined in air at 550 °C for 3 h in order to remove the organic template. For carbon infiltration, the calcined zeolite (1 g) was placed in a quartz reactor and heated at the temperature of the CVD (600–700 °C) under an argon flow. Then, acetylene gas (5% in argon by volume) was passed through the reactor at a constant total flow rate of 10 L h^{-1}. The CVD was performed for different times (1, 4, 5 or 25 h). Finally, a heat treatment at 900 °C for 4 h under argon flow was performed to improve the structural organisation as evidenced by Ma et al. [10]. The alumino-silica matrix was etched by using an excess of hydrofluoric acid (40%). The resulting carbon was filtered and washed with distilled water.

Hereafter, the samples are named Ac[temperature of CVD in °C] − [time of CVD in hours]. The complete dissolution of the parent zeolite was checked by X-ray fluorescence analysis (Philips Magix apparatus) and revealed a very low Al and Si content (<1%).

Carbon fractions in the carbon/zeolite composites were determined by thermogravimetric analysis (Seteram labsys in air) from the weight loss by oxidation of the carbonaceous part of the composite in the range 300–800 °C. The powder XRD patterns were recorded on a STOE STADI-P diffractometer using $CuK_{\alpha1}$ radiation ($\lambda = 1.5406$Å). The textural characteristics of carbon materials were determined from nitrogen adsorption–desorption isotherms at 77 K (ASAP 2010 or ASAP 2420, Micromeretics). Before the experiments, the samples were outgassed under vacuum at 90 °C for 1 h and 300 °C overnight. The isotherms were used to determine the total pore volumes at P/P_0 equal to 0.95, and the micropore volumes were calculated by applying the Dubinin–Radushkevich (DR) equation. The pore size distributions (PSD) were given with the non-local density functional theory (NLDFT) method for cylindrical pores using the software provided by Micromeritics (models N_2—Tarazona NLDFT, Esf = 30.0 K). The assessment of apparent surface area was done by the BET method for pressure range $P/P_0 = 0.01$–0.05 as recommended by Kaneko et al. [11] instead of the classical 0.1–0.3 range.

Results and discussion

Figure 1 shows the powder XRD patterns of carbon replicas and zeolite EMC-2. When the CVD was performed at 600 °C for 1, 4 or 5 h or at 700 °C for 1 h, the carbon replicas do not show diffraction peaks. The XRD patterns of the other carbons display three diffraction peaks at around 6° 2θ. These peaks are similar to those present in the XRD pattern of zeolite EMC-2: peaks (100), (002) and (101). These carbons display the same hexagonal symmetry as the host material. No peak in the 2θ angle domain around 20°, characteristics of graphitic layers stacking, is detected. This feature indicates the non-graphitic nature of the carbon replica.

A general trend could be deduced from the observation of Fig. 1 and Table 1. It appears that carbon replicas which do not show diffraction peaks around 6° are obtained from

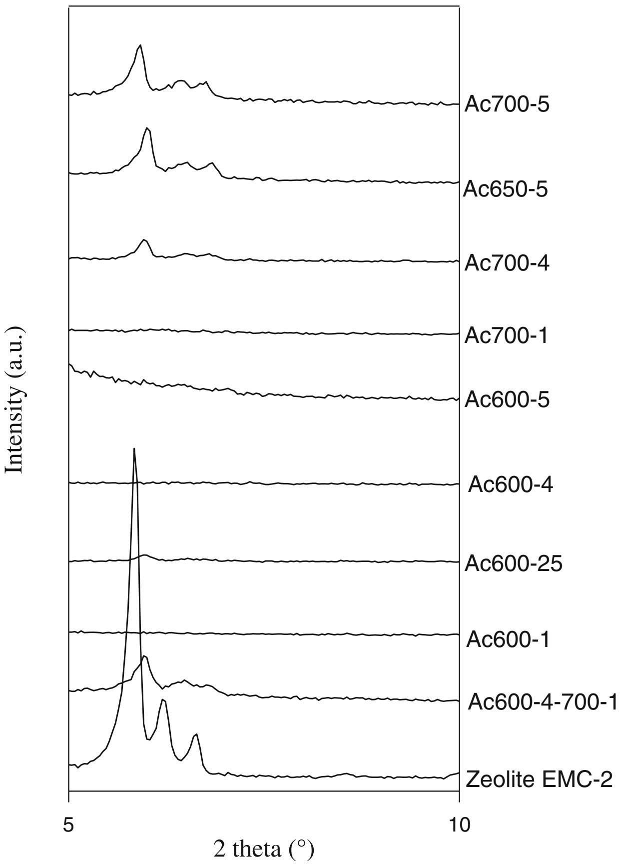

Fig. 1 XRD patterns (Cu $K_{\alpha 1}$ radiation) of the zeolite EMC-2 and the Ac600-4-700-1, Ac600-1, Ac600-4, Ac600-5, Ac600-25, Ac650-5, Ac700-1, Ac700-4, Ac700-5 carbon replicas

zeolite/carbon composites having small carbon fractions (4–9 wt%). It is believed that a low carbon filling content leads to an unsteady thin carbon network that cannot withstand the template removal which results in the collapse of the carbon replica structure. Nevertheless, the macroscopic shape observed by scanning electron microscopy (results not shown) is similar to the zeolite template due to the carbon coating on the surface of zeolite crystals as described by Kyotani for FAU replica [7].

The N_2 adsorption isotherms of carbon replicas are shown in Fig. 2. All the isotherms are of type I according to the IUPAC classification [12] with a high nitrogen uptake in the low relative pressure domain ($P/P_0 = 0–0.01$). This behaviour reveals the microporous character of these carbon materials. Observation of the total pore volumes reported in Table 1 evidences two different types of material; samples with high pore volume (1.27−1.44 cm^3/g) or low pore volume (0.5 cm^3/g). These features are correlated to the two types of XRD structural ordering and carbon content discussed previously: therefore, after a heat treatment, high pore volume is obtained only for materials that display both ordering and high carbon content. The other textural properties of the carbon materials such as BET surface area, micropore volume are also reported in Table 1. It appears that the ordered samples have a high micropore volume (1.29–1.41 cm^3/g) with nearly no mesoporosity (in the range of accuracy of ±0.02 cm^3/g). Comparison with EMT carbon replica obtained by a two-step infiltration procedure [6] shows that the one-step

Table 1 Carbon fractions in the carbon/zeolite composites, specific surface areas and pore volumes of the carbon replicas

	Carbon fraction (wt%)[a]	Apparent surface area (m^2/g) BET[b]	Pore volume (cm^3/g)		
			V_t^c	V_{micro}^d	V_{meso}^e
Ac600-4+700-1	21%	3024	1.42	1.34	0.08
Ac600-1	4%	n.d.	n.d.	n.d.	n.d.
Ac600-4	7%	1059	0.55	0.41	0.14
Ac600-5	8%	n.d.	n.d.	n.d.	n.d.
Ac600-25	25%	2903	1.27	1.29	0.0
Ac650-5	23%	3204	1.44	1.41	0.03
Ac700-1	9%	n.d.	n.d.	n.d.	n.d.
Ac700-4	24%	2999	1.30	1.32	0.0
Ac700-5	23%	2813	1.29	1.26	0.03

n.d. not determined

[a] Determined by TGA data from the weight loss of the carbonaceous part of the zeolite/carbon composite by oxidation in air in the range 300–800 °C

[b] Determined using the data range $P/Po = 0.01–0.05$

[c] Total pore volume determined at $P/Po = 0.95$ from N_2 isotherm

[d] From DR equation using N_2 isotherm

[e] Obtained from the total pore volume after subtraction of the microporous volume

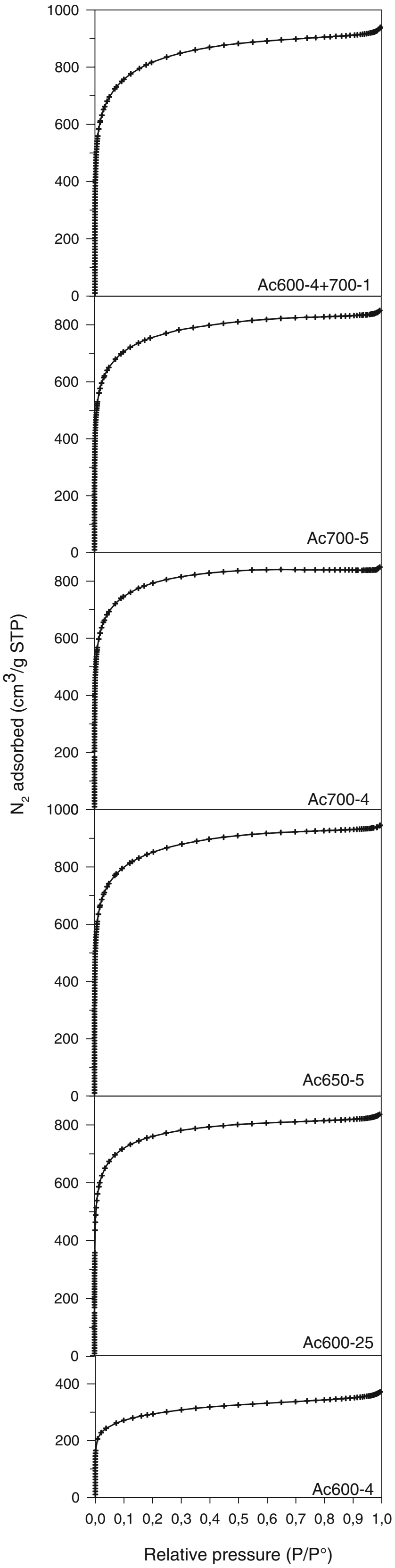

Fig. 2 N_2 adsorption isotherms (77 K) of Ac600-4, Ac600-25, Ac700-5, Ac700-4, Ac600-4+700-1, Ac650-5 carbon replicas

acetylene infiltration leads to carbon replicas having similar degree of organisation as regards XRD patterns and slightly lower textural characteristic as regards BET surface area (3204 instead of 4130 m^2/g) and micropore volume (1.4 instead 1.8 cm^3/g).

Pore size distribution curves are shown in Fig. 3. The presence of a small portion of mesopores is also evidenced. Surprisingly, all the curves have a similar shape, except for the Ac600-4 sample that presents a collapsed structure with a low pore volume. They show three pore diameter maxima located at 0.6, 1.0 and 1.8 nm. The latter peak has a position far above the porosity expected for a zeolite-carbon replica (which should be that of a zeolite wall around 1 nm) and extends in the mesoporous range up to 4–5 nm. It is suggested that an incomplete filling of the template leads to such a broadly distributed porosity with a size higher than the zeolite wall. This behaviour has already been encountered for mesoporous silica replication as shown by Fuertes et al. [13]. The highest micropore volume and specific surface area are obtained for the Ac650-5 carbon. It is worth noting that this sample also displays one of the best ordered structures by XRD. In the case of Ac600-4 carbon, the sample appears to have mainly a strong contribution of ultramicropores with a PSD maximum at 0.6 nm and a minor contribution of pores with size higher than 1 nm. This sample has a low micropore volume due to the collapse of its structure. This ultramicroporosity may be attributed to the intrinsic porosity of the carbon matrix. Disappearance of the pore diameter maxima at 1.0 and 1.8 nm for such a sample suggests that the latter types of porosity are correlated to the ordered structure. Since porosity around 1.8 nm could be related to voids in-between nano-ordered domains, porosity at 1.0 nm could be ascribed to the replication of the faithful part of the zeolite as suggested by several studies with the related zeolite template of FAU- structure type [14, 15].

Conclusions

It was possible to obtain carbon replica of zeolite EMC-2 with only acetylene as carbon precursor. The time and the temperature parameters of CVD have been optimised to synthesise a faithful carbon replica. Such an ordered structure, obtained after a high temperature treatment, is only observed for a high carbon loading and leads to a carbon material having mainly a microporous feature. PSD determined by NLDFT method suggests that the porosity is broadly distributed with three pore diameter maxima at 0.6, 1.0 and 1.8 nm. The first is attributed to intrinsic porosity of the CVD carbon, the second is due to the zeolite wall dissolution (ordered pore network of the carbon replica). The third maximum arises from the incomplete filling of the zeolite template. Compare to the classical two-step procedure, the direct infiltration with acetylene appears an interesting route for the preparation of ordered microporous carbon replicas with high micropore volume.

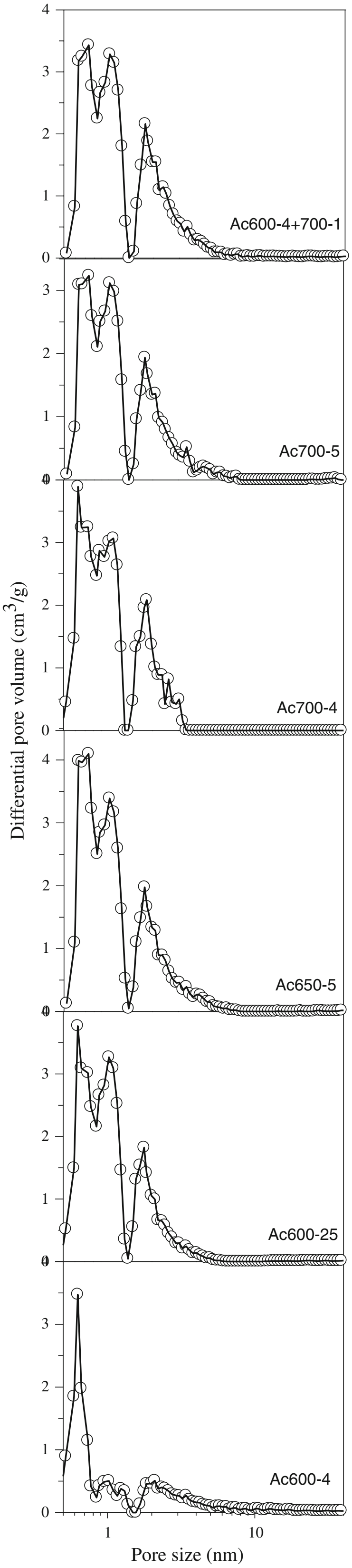

Fig. 3 Pore size distribution curves determined by applying DFT method to the N_2 adsorption isotherms of Ac600-4+700-1, Ac600-4, Ac600-25, Ac650-5, Ac700-4, Ac700-5 carbon replicas

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