

First zeolite carbon replica with a well resolved X-ray diffraction pattern

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The present study demonstrates that for the nanocasting process with zeolites, a careful choice of the zeolite structure type (EMT) allows the formation of faithful carbon replica exhibiting up to three well resolved XRD peaks.

Porous carbon materials produced by traditional ways (*e.g.*, activated carbons) characterised by a highly developed internal surface area and porosity, have been widely used in catalysis and adsorption.¹ However, the complex internal structure of these carbons is not appropriate for new emerging applications such as gas storage (*e.g.*, methane or hydrogen²) or electric double-layer capacitors, which require carbon materials with predetermined porosity. Therefore, for these kinds of applications, porous carbons with finely tailored microporosity appear to be very promising materials due to their high surface area and specific pore size distribution. To meet these requirements, novel approaches have been developed and particular attention has been paid towards the feasibility of making porous carbons by the nanocasting process.^{3–5} Several groups have studied this process with templates including macroporous and mesoporous materials with different carbon precursors.^{4,6–8} Carbon replicas from microporous materials such as zeolites have also been synthesized.^{5,8–10} Among those, the more eye-catching results are certain carbon replicas prepared from zeolite Y^{11–13} (International Zeolite Association structure code: FAU) that showed impressively high surface area and micropore volume comparable to those obtained with activated carbons. Microporous zeolite-type materials represent an interesting and extreme test for replication strategies, because the dimensions of their channels and cages are quite similar to those of the infiltrated materials that constitute the replica. The question of paramount importance that remains to be met is: to what extent can the structural regularity of the zeolite pore network be transferred to carbon replica? Recent works achieved mainly by the Kyotani research group with various commercially available zeolites employed as templates have resulted in interesting carbon replicas.¹⁴ However, the powder X-ray diffraction (XRD) patterns of zeolite carbon replicas, unlike what can be observed for mesoporous carbon prepared by nanocasting from organized mesoporous silica, display none or in the better case, only one XRD peak. Starting from a medium size zeolite (*e.g.*, pore channels delimited by up to 10-membered rings such as the MFI structure), the carbon replica showed very

poor organization and only a broad weak peak was observed in the XRD pattern.¹⁴ This could be attributed to either the low carbon precursor loading and/or the spatial requirements for the precursor polymerization¹⁵ and limited subsequent carbon growth. Better replication was achieved by using large pore materials (*BEA, LTL and MOR structures, all including pore channels of up to 12-membered rings)^{10,14,15} but the obtained XRD patterns were too poor to extract some structural information. Different parameters can be advanced to explain such results. The disorder or the symmetry of the structure can be one of these parameters. This is the case for zeolite beta (*BEA structure code)^{7,10,14} that displays a disordered structure consisting of an intergrowth of at least two polytypes, or for zeolite Y (FAU structure code)^{5,10,14,15} which adopts a high symmetry cubic space group. On the other hand, zeolite L (LTL structure code) that possesses a one-dimensional channel system cannot produce a three-dimensional carbon replica.^{10,14} Moreover, the intersecting 12- and 8-membered ring pore channel systems of mordenite (MOR structure code) do not result in a carbon network because of poor carbon infiltration in the small 8-membered ring pores.^{14,15} Obviously, to answer the above question, a zeolitic material which combines a two- or three-dimensional large pore channel system with a non-cubic symmetry will have to be employed as a mold.

In the present study, zeolite EMC-2 (EMT structure code) was chosen from a large range of zeolite structures (more than 160 structure codes) as a model template to avoid the problems summarized above. This zeolite with large pore openings (up to 12-membered rings), which was first synthesized in our research group 15 years ago,¹⁶ is structurally related to the FAU structure type but displays a hexagonal framework (lower symmetry). This framework is formed by interconnected cages leading to a straight pore channel system running along the *c* direction, different to that of the already well-studied parent zeolite Y, which only displays interconnected cages. In addition, the Si/Al framework ratio of this zeolite is higher compared to zeolite Y (3.8 instead of 2.5), hence requiring fewer counter cations (Na cations) and leaving more space available in the porous network. Both these features should improve the infiltration of carbon precursors. Here, we present carbon replicas made by the nanocasting process using zeolite EMC-2 (Fig. 1), which under certain conditions (see experimental in the footnotes†), retains the regularity of the host channel system and thus the hexagonal symmetry.

Powder XRD patterns (K_{α} Cu radiation) of the carbon replicas, together with the pattern of zeolite EMC-2 are illustrated in Fig. 2. Both carbons (before and after heat treatment) show different degrees of structural ordering with diffraction peak(s) at around 6° 2θ . These carbons have a structural regularity with a periodicity

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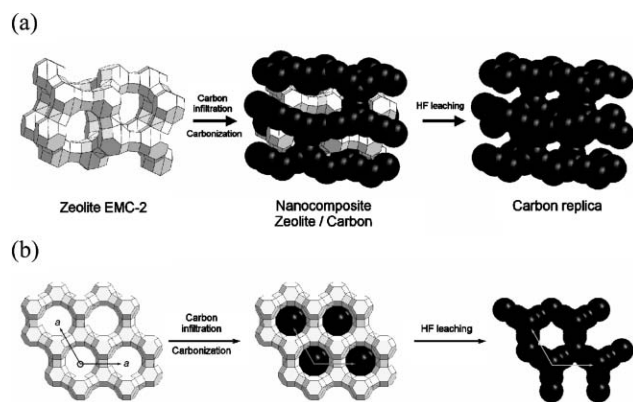


Fig. 1 (a) Schematic representation of the nanocasting process using zeolite EMC-2. (b) Representation of the same zeolite along the c axis showing that the zeolite hexagonal symmetry is kept in the final carbon replica.

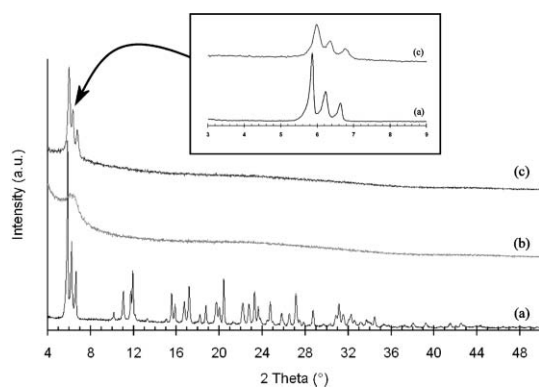


Fig. 2 XRD patterns (K_{α} Cu) of: (a) the zeolite EMC-2, (b) the carbon replicas prepared by furfuryl alcohol infiltration and propylene CVD and (c) the carbon replica prepared by furfuryl alcohol infiltration, propylene CVD and heat treatment at 900 °C under argon.

close to 1.4 nm. The best carbon replica (Fig. 2c) was obtained by the association of furfuryl alcohol (FA) impregnation and propylene (Pr) chemical vapor deposition (CVD) followed by a heat treatment (HT). To our knowledge, it is the first ordered porous carbon arising from a zeolite to exhibit three XRD peaks. These peaks are similar to those present in the XRD pattern (Fig. 2a) of the host zeolite EMC-2 (peaks (100), (002) and (101)). The presence of these three peaks was expected since after complete filling of the pores, the carbon replica should display the same hexagonal unit cell as that of the parent zeolite material as schematically represented in Fig. 1b. Such a result is sound proof that this new carbon has a long-range organization on the nanometric scale. On the other hand, in the absence of long-range order on the atomic scale (*i.e.*, distance between graphene stacks), no XRD peak can be expected at a higher 2θ angle domain.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses have been performed on the carbon replicas and the results (see Fig. 3 and 4, respectively) confirm that the carbon materials keep the macroscopic and nanometric organization of zeolite EMC-2. The carbon replicas retain all morphological features of the parent material including the crystal growth steps visible on the pinacoidal face $\{001\}$. No evident

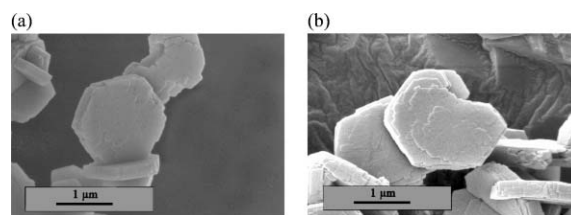


Fig. 3 SEM picture of: (a) the zeolite EMC-2 and (b) the carbon replica prepared by furfuryl alcohol infiltration, propylene CVD and heat treatment at 900 °C under argon.

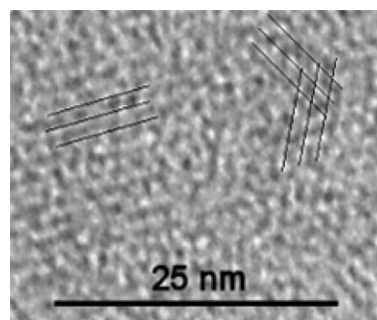


Fig. 4 TEM picture of the carbon replica prepared from zeolite EMC-2 by furfuryl alcohol infiltration, propylene CVD and heat treatment at 900 °C under argon.

shrinkage or hollow areas were observed in the obtained hexagonal carbon platelets, which confirm perfect replication of the zeolite structure. The carbon arrangement at the nanolevel scale was studied by high resolution TEM and revealed a local periodicity of carbon material. Although some defects could be seen in the carbon network, an inter-fringe distance of 1.4 nm was observed. This value can be directly correlated to that determined by XRD analysis. In addition, it was shown from EDX analysis that no traces of the zeolite matrix could be detected.

The carbon replicas were characterized by N_2 adsorption measurements at 77 K. Both isotherms are of type I, thus revealing the microporous character of these carbon materials (Fig. 5). This trend was confirmed by determination of the micropore volumes applying Dubinin–Radushkevich (DR) equations to these isotherms (Table 1). The mesopore volume was calculated by subtracting the micropore volume from the total pore volume determined at the relative pressure $P/P_0 = 0.95$. Only

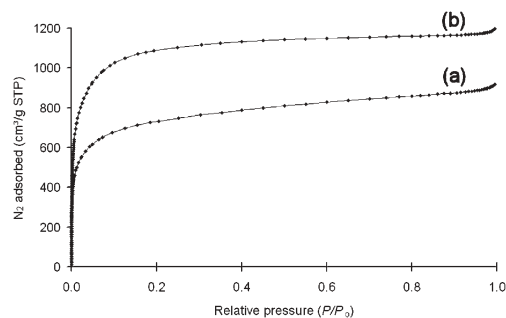


Fig. 5 N_2 adsorption isotherms of the carbon replicas prepared by: (a) furfuryl alcohol infiltration and propylene CVD and (b) both processes with heat treatment.

Table 1 Specific surface areas and pore volumes of the carbon replicas.

Sample	Specific surface area/m ² g ⁻¹		Pore volume/cm ³ g ⁻¹		
	BET ^a	BET ^b	V _t ^c	V _{micro} ^d	V _{meso} ^e
Carbon with HT	4130 ± 25	3225 ± 115	1.8	1.8	0.0
Carbon without HT	2700 ± 20	2185 ± 65	1.4	1.1	0.3

^a Determined using the data range $P/P_0 = 0.01-0.05$. ^b From the data range $P/P_0 = 0.1-0.3$. ^c Total pore volume taken at $P/P_0 = 0.95$ from the N₂ isotherm. ^d From DR equation using N₂ isotherm. ^e Obtained by subtracting the microporous volume from total pore volume.

the carbon replica that did not receive the extra heat treatment exhibits some mesoporosity. The specific surface areas determined by the BET method are also reported in Table 1 for two relative pressure ranges: $P/P_0 = 0.01-0.05$ and $P/P_0 = 0.1-0.3$. The first relative pressure domain has been recommended by Kaneko *et al.*¹⁷ for microporous carbons, but in that case, the surface areas seem to be over-estimated as recently showed by Matsuoka *et al.*¹³ On the other hand, using the latter domain, the values can be underestimated.¹³ Although these BET surface areas do not represent “true” surface areas for such microporous materials, the values obtained give a good order of magnitude. It is worth noticing that the best carbon displays a high micropore volume and no mesoporosity, in difference to the carbon materials prepared from zeolite Y.¹² The presence of a straight pore channel system in zeolite EMC-2, together with a limited amount of Na cations can explain this difference, since the diffusion of the carbon precursors is facilitated. Therefore, this can lead to a better filling of the pores and a more organized carbon.

In the present study, it has been shown, for the first time, that the appropriate choice of the zeolite mold is a requirement for the preparation of a faithful carbon replica that exhibits more than one XRD peak. The use of EMC-2 (EMT structure type with a three-dimensional channel system of large pores, a hexagonal symmetry and a Si/Al ratio close to 4) leads to a carbon replica that displays up to three well-resolved XRD peaks. The latter correspond to the (100), (002) and (101) reflections of the parent EMT-type zeolite and proved that the hexagonal long-range ordering has been retained. Further improvement of zeolite replication by carbon might be achieved by carefully choosing the zeolite structure type among the 165 assigned to date and its composition. In this context, zeolite materials with two- or three-dimensional large pore channel systems and a limited amount of charge balancing alkaline cations are expected to be very promising molds for carbon replication. For instance, the UTL,¹⁸ BEC,¹⁹ and -CLO²⁰ structure types present all the aforementioned requirements and merit consideration for future studies.

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Notes and references

† Experimental: zeolite EMC-2 was prepared hydrothermally using a similar procedure to that described by Delprato *et al.*¹⁶ A hydrogel with the overall composition: 1.00SiO₂:0.10Al₂O₃:0.22Na₂O:0.087 18-crown-6:14.00H₂O was aged for 24 h at room temperature and placed in a Teflon-lined autoclave at 110 °C for 13 days. The solid was washed with distilled water and dried overnight in an oven at 80 °C. This raw zeolite EMC-2 was calcined in air at 550 °C for 5 h. Carbon replicas derived from zeolite EMC-2 were prepared following largely the nanocasting method proposed for zeolite Y by the Kyotani research group.¹² Zeolite EMC-2 was dried overnight in a flask at 300 °C under vacuum. Liquid furfuryl alcohol (FA) was introduced into the cooled flask at reduced pressure, then the zeolite and FA mixture was left to stir for 10 min and further left to stir for 24 h in a N₂ atmosphere. The mixture was then washed with mesitylene to remove any excess of FA. The polymerization and carbonization steps of PFA successively took place in a quartz reactor under a flow of Ar. The infiltrated zeolite was heated up at 80 °C for 24 h, then at 150 °C for 8 h and finally at 700 °C for 4 h before being returned to room temperature. Next, this composite zeolite-carbon was placed in a quartz reactor and raised to 700 °C under an Ar flow. When the temperature reached 700 °C, propylene gas (2.5 % in Ar by volume) was passed through the reactor at a constant total flow rate of 10.2 L h⁻¹ for 24 h. A second batch of material received a heat treatment (HT) and was further raised and kept at 900 °C for 4 h under a flow of Ar. Both mixed materials were leached with an excess of HF (40 %) for 24 h and subsequently refluxed with an excess of HCl (36 %) for 4 h to ensure complete dissolution of the inorganic template and subsequent byproducts. The resulting carbons were filtered and washed with copious amounts of distilled water and air-dried for 12 h at 80 °C.

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