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Influence of the carbon precursors on the structural properties of EMT-type nanocasted-carbon replicas

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ABSTRACT

Nanocasted ordered microporous carbons are interesting candidates for studying specific properties related to applications where materials with tailored microporosity and controlled composition are required. In order to extend the choice of these model materials, a systematic study of the nanocasting process was performed using the original and non commercial zeolite EMC-2 (EMT-structure type) as a mould. The influence of the preparation routes on the structural properties of the carbon replicas was more specifically examined using acetylene, furfuryl alcohol and acetonitrile as carbon precursor with a single or double infiltration procedure. It appears, whatever the precursor, that optimized infiltration processes with a carbon filling content above 0.2 g/g of carbon composite yield to faithful carbon replicas with an ordered microporosity. These materials exhibit a high specific surface area (>2500 m^2/g) and a high micropore volume (1.3–1.6 cm^3/g) with nearly no mesoporosity. The pore size distribution, calculated with the NLDFT method from nitrogen physisorption data at −196 °C, shows maxima at 1.0 and 1.8 nm. The first maximum has been attributed to the porosity arising from the nanocasting of the zeolite framework and the second to the incomplete carbon filling of the mould. A strong adsorption capacity at low relative pressure has also been detected when acetonitrile was used as carbon precursor. The degree of the structural organization of the porosity was followed with the first three XRD diffraction peaks characteristic of the hexagonal symmetry of the EMT mould.

1. Introduction

Activated carbons are widely used for various applications such as catalysis support and adsorption materials 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 [1]. Therefore, other synthesis routes have been developed such as nanocasting which consists in 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 the templated structure (e.g. size and shape of the porous network) and the nature of the carbon precursor. The commercial Y zeolite (FAU-structure type) was often chosen as a mould and infiltrated with different carbon precursors in order to obtain carbon replicas. This zeolite displays a cubic symmetry (space group: Fd-3 m) with a three-dimensional pore framework formed by interconnected cages having around 0.7 nm of diameter. Therefore, it was a challenge to prepare the corresponding carbon replicas by infiltrating such a small porosity. Two preparation routes were developed. For the first one, precursors were used in liquid form, pure (furfuryl alcohol [2–5], vinyl acetate [2], acrylonitrile [2], phenol [6], pyrrole [7], styrene [7]) or dissolved in a solvent (pyrene [2]), and were impregnated within the porosity, subsequently polymerized and carbonized. The second route, based on the Chemical Vapor Deposition (CVD) process, was performed with gaseous precursors such as acetonitrile [8,9], propylene [3,4,8,10–13], formaldehyde [6], ethylene [7,9,14,15], butylene [13], acrylonitrile [3,16], acetylene [17–19]. The zeolite was placed in a furnace and heated to a temperature which corresponds to the pyrolitic decomposition of the gaseous precursor. Then, the carbon precursor was passed through the reactor and a carbon deposition took place onto the surface of the zeolite. Sucrose powder [20] was also used as carbon precursor and pressed with the zeolite and subsequently carbonized. Nevertheless no evidence of the microporosity infiltration and replication was shown.

For adapted preparation conditions, nano-ordered carbon replicas were produced, as evidenced by one sharp X-ray diffraction (XRD) peak at the same position (around $2\theta = 6°$) (Cu Kα) than the (1 1 1) peak of zeolite Y. The carbons which present this diffraction peak have high-surface area (>2000 m^2/g) and high micropore volume (>1.0 cm^3/g). Their exact porosity is still not well understood but recent investigations related to XRD refinement and

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molecular modelling [21,22] led to corroborating results with a three-dimensional regular carbon network and a porosity ranging from 1.0 to 1.7 nm. A peculiar value around 1.0 nm is expected in relation to the zeolite wall templating. It was proposed that its molecular structure could be described as a buckybowl-like nanographene assembly. Theses ordered nanostructures were obtained only when two successive infiltrations with two different precursors were used [4,23]: (i) impregnation of zeolite with furfuryl alcohol and polymerization, (ii) propylene chemical vapor deposition at 700 °C for 1 h. Nevertheless, this two-step procedure is long and laborious so Hou and co-workers [17] developed a one step synthesis by omitting the first step and by using acetylene gas for CVD. Hence, they prepared faithful carbon replicas of zeolite Y. In most of the cases, when the experimental conditions are not optimized, the replica displays a broad peak or no diffraction peak and a low pore volume.

Introduction of nitrogen in zeolite templated carbon materials has been studied for water adsorption [8] and hydrogen sorption capacities [9] by using nitrogen containing carbon precursors (acetonitrile). For carbons templated by zeolite Y, the X-ray diffraction line base displays only a weak shoulder around $2\theta = 6°$ when the chemical vapor deposition is performed at a temperature between 750 and 850 °C [9] indicating the low degree of organization of the material. Therefore, Hou and co-workers [8] used a double-step procedure: (i) impregnation of zeolite with furfuryl alcohol and polymerization and (ii) acetonitrile chemical vapor deposition (CVD) at 800 °C. In this case, they obtained also a microporous carbon but with a long-range ordering of zeolite Y, a high-surface area (2260–3310 m^2/g) and a high-pore volume (0.91–1.26 cm^3/g).

This type of synthesis was extended to other microporous zeolite templates with different pore morphologies, such as zeolite β [24–26], silicalite-I [24], and zeolite 13X [9].

Recently, Gaslain and co-workers [27] showed it was possible to obtain a zeolite carbon replica exhibiting more than three well resolved XRD peaks by choosing the EMC-2 zeolite (EMT-structure type) as mould and furfuryl alcohol and propylene gas as carbon precursors. Indeed, this mould displays a three-dimensional pore structure but with a hexagonal symmetry compare to the cubic one of zeolite Y. Its structure is characterized 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 compare to zeolite Y (3.8 instead of 2.5) implies a lower amount of counter cations (Na^+) and therefore more free space available for the carbon infiltration in the porous network.

As shown previously, infiltration conditions have been largely explored for zeolite Y whereas it appears nearly unexplored for zeolite EMT. Since the potentials of zeolite Y replica appears interesting owing to their high adsorption capacities, an extensive study on the preparation of EMT carbon replica using acetylene gas, furfuryl alcohol and acetonitrile as carbon precursors was performed and described in this present work. Specific influences of the carbon precursors on the porous and structural characteristics of the carbon replicas were particularly investigated.

2. Experimental

2.1. Synthesis of the mould

Zeolite EMC-2 was prepared using a similar procedure to the one described by Delprato and co-workers [28]. 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, followed by the silica source (colloidal silica; Ludox HS 40) and the structure-directing agent (18-crown-6). The solution was stirred under vigorously stirring for 24 h at room temperature and the hydrogel was placed in a Teflon-lined stainless-steel 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-synthesized zeolite EMC-2 was calcined in air at 550 °C for 3 h in order to remove the organic template.

For carbon infiltration, three precursors were used: furfuryl alcohol, acetylene and acetonitrile.

2.2. Carbon infiltration

2.2.1. Impregnation of furfuryl alcohol

This process was inspired from Ref. [4]. The calcined zeolite was dried overnight in a flask at 300 °C under vacuum. Liquid furfuryl alcohol was introduced into the cooled (25 °C) flask at reduced pressure, and then the zeolite and furfuryl alcohol mixture was left to stir for 24 h in a nitrogen atmosphere. The mixture was then washed with mesitylene to remove any excess of furfuryl alcohol. The polymerization (80 °C for 24 h followed by 150 °C for 8 h) and carbonization steps of poly (furfuryl alcohol) (700 °C for 4 h) successively took place in a quartz reactor under argon flow.

2.2.2. Chemical vapor deposition of acetylene

The CVD process used was derived from Ref. [17]. The calcined zeolite was placed in a quartz reactor and heated at the temperature of the CVD (600–700 °C range) under 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} for 4 h. Finally, a heat-treatment at 900 °C for 4 h under argon flow was performed to improve the structural organization as evidenced by Ma and co-workers [23].

2.2.3. Chemical vapor deposition of acetonitrile

The procedure followed here is described in Refs. [8] and [9]. Briefly the calcined zeolite was placed in a quartz reactor and heated at the temperature of the CVD (800–850 °C range) under a nitrogen flow. Then, a flow of nitrogen saturated with an acetonitrile solution at 0 °C was passed through the reactor for 2 or 3 h. Finally, a heat-treatment at 900 °C for 4 h under nitrogen flow was performed.

2.3. Common HF leaching procedure for carbon/zeolite replicas

The alumino-silica matrix was etched by using an excess of hydrofluoric acid (40%). The resulting carbon was filtered and washed with distilled water. The carbon material was refluxed

Table 1
Preparation of various carbon/zeolite composites.

Carbon precursors and treatments	Polymerization of furfuryl alcohol	Carbonization of poly (furfuryl alcohol)	CVD	Heat treatment
PFA700-4	80 °C 24 h + 150 °C 8 h	700 °C 4 h	No	No
PFA + Ac600-4-HT	80 °C 24 h + 150 °C 8 h	No	Ac 600 °C 4 h	900 °C 4 h
PFA700-4 + Ac700-4-HT	80 °C 24 h + 150 °C 8 h	700 °C 4 h	Ac 700 °C 4 h	900 °C 4 h
Ac600-4-HT	No	No	Ac 600 °C 4 h	900 °C 4 h
Ac700-4-HT	No	No	Ac 700 °C 4 h	900 °C 4 h
An850-3	No	No	Ac 850 °C 4 h	No
PFA + An800-2-HT	80 °C 24 h + 150 °C 8 h	No	Ac 800 °C 4 h	900 °C 4 h