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Aromatic polyamides as new precursors of nitrogen and oxygen-doped ordered mesoporous carbons

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ABSTRACT

Polyamides are used for the first time as precursors in the synthesis of nitrogen- and oxygen-doped ordered mesoporous carbons (OMCs) by applying two synthetic methods, named here as: (i) organic phase synthesis (infiltration *in situ* by Yamazaki reaction-based method) and (ii) solid-state thermal polymerization (liquid infiltration and thermal polymerization of the monomer into the porosity of the template). In both cases, 3-aminobenzoic acid (MABA) and SBA-15 mesoporous silica are used as precursor and template, respectively, and the infiltration takes place in one single step. In the first method, the infiltration process is accomplished in situ through Yamazaki reaction of the MABA; in the second one, the MABA monomer is introduced into the channels of the silica template by incipient wetness dissolved in a common and low polluting organic solvent. After carbonization at 900 °C and removal of the template, OMCs with very narrow pore size distributions and nitrogen and oxygen contents as large as ~6 and 6.4–11.5 wt.%, respectively, are obtained. This work opens a new way to prepare advanced carbon materials, due to the wide variety of polyamides that can be synthesized by applying the two proposed methods to a large number of both aliphatic and aromatic precursors.

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1. Introduction

Porous carbon materials are solids constituted principally by carbon, having a well-developed porous texture (surface area, pore volume, etc.) and deserving a number of applications in different fields such as gas and liquid purification, mixture separation, catalysis, etc. [1–4]. Besides the classic uses, these materials are potentially useful for emerging applications of great interest such as storage of combustible gases (hydrogen, methane) or electrical energy storage (anodes in Li-ion batteries or electrodes in supercapacitors) [5–8]. These increasingly specific applications require that the involved materials have some specific properties concerning their porous texture, surface chemistry, crystalline order and morphology, in such a way that their behavior can be optimized for a given utilization. Porous texture is the main determining factor for most of the applications, and therefore many research efforts have been made to develop preparative methods leading to carbonaceous materials exhibiting an optimal porosity for a given application. In this sense, nanocasting is a powerful method for creating materials with a closely controlled porous nanostructure [8–12] that is being intensively applied for preparing ordered porous carbons. Within the nanocasting method, hard templating is one of the most used synthetic routes; based on the use of crystalline inorganic solids (such as zeolites, ordered mesoporous silica, etc.) as templates and the infiltration of the template porosity with a carbon precursor, a negative replica is obtained after the carboniza-

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tion of the resulting composite and the removal of the solid template. Thereby, depending on the template used, carbon materials with different structure and porosity can be obtained [8–11].

In order to optimize the behavior of a carbonaceous adsorbent in a given application, besides porosity, the surface chemistry can play a determining role. For instance, the incorporation of heteroatoms such as boron, nitrogen or oxygen in a carbon network can improve its electrical, mechanical, semiconductor and field emission properties [4,6,13–18]; this improvement of properties makes the synthesis of doped ordered porous carbons an interesting target, especially in the case of the mentioned heteroatoms. As concerns N-doped carbons, some works report their preparation by infiltration/polymerization and subsequent carbonization, using polyacrilonitrile [19,20], quinolone [17], diaminobenzene [21], aminoglucose [22] or ethylenediamine and carbon tetrachloride [23–25], as precursors. Other works accomplish the synthesis of N-doped carbons through chemical vapor deposition of acetonitrile [26,27] or by means of a post-treatment with NH_3 over an ordered mesoporous carbon (OMC) [25]. These works show that it is possible to obtain N-doped ordered porous carbon by selecting suitable synthesis conditions, but in some cases, multistep processes are required or a limited variety of precursors is available.

In the present work, we report for the first time on two different methods for preparing carbons doped with both nitrogen and oxygen by using aromatic polyamides (polyaramides) as precursors. Polyamides are condensation polymers constituted by macromolecular chains where the amide functional group (–CONH–) is sequentially repeated. The wide variety of precursors and synthetic methods applicable leads to a great variety of polyamides, both aliphatic and aromatic. In previous works from our research group, we have used polyaramide fibers, poly (p-phenylene terepthalamide) (PPTA) and poly (m-phenylene isophthalamide) (PMIA), as precursors for preparing activated carbon fibers (ACFs) [28–34]. From these aromatic polyamides, ACFs with a considerably large amount of heteroatoms (N and O), high specific surface areas and pore volumes and uniform and narrow pore size distributions were obtained. In addition, their high carbonization yields pointed to the polyaramides as suitable precursors of ordered porous materials with interesting properties [33].

Here, nitrogen- and oxygen-doped ordered mesoporous carbons were synthesized through polymerization reactions of 3-aminobenzoic acid (MABA) within the porous network of a mesoporous silica template, SBA-15, and subsequent carbonization and removal of the latter. Two different methods of infiltration/polymerization were studied. In the first one, the infiltration was carried out in situ by adding SBA-15 to the reaction medium for polyamide synthesis, as described by Yamazaki et al. [35]. In the second method, the infiltration of the SBA-15 silica was carried out by incipient wetness impregnation of a certain amount of monomer dissolved in an organic solvent, followed by removal of the latter under vacuum. The porous texture, the structure and the surface chemistry of the resulting OMCs were studied in detail and they were related to the synthesis method used.

2. Experimental

2.1. Synthesis of the SBA-15 template

The mesoporous silica SBA-15 was used as template. This silica was prepared following the method described by Zhao et al. [36]. Pluronic P123 (Mw = 5800, Aldrich) (10.44 g) was dissolved in an aqueous solution containing 52.5 mL of 37% HCl (Merck). After complete polymer dissolution, tetraetoxysilane (TEOS, Aldrich) (22.64 g) was added dropwise and the mixture was kept under stirring (40 °C, 4 h). The molar composition of the starting reaction mixture was 0.017 P123/1 TEOS/145.8 H_2O/6.04 HCl. The resulting product was aged (125 °C, 72 h), filtered and calcined in air (550 °C, 6 h).

2.2. Synthesis of the ordered mesoporous carbons

The polymerization of the polyamide precursor in the SBA-15 porosity was carried out through two different routes, designated here as: (i) organic phase synthesis and (ii) solid-state thermal polymerization. In both cases, the monomer 3-aminobenzoic acid (MABA) (99%, Across) was used as polyaramide precursor. In the first case, the infiltration was done in situ by adding SBA-15 to the reaction medium, and following the Yamazaki reaction for polyamide synthesis [27,37]. In our case, the reaction was accomplished in a three-neck conical-shape flask equipped with a magnetic stirrer and a temperature controller. After placing SBA-15 mesoporous silica (1 g) in the reactor, this was connected to a vacuum line and heated (150 °C, 2 h); then, it was cooled down to room temperature and a nitrogen flow (100 mL/min) was continuously passed through the reactor in order to maintain an inert atmosphere during the process. N-methylpyrrolidone (99.99%, Sigma–Aldrich) (20 mL) was added to the reactor under vigorous stirring. Afterwards, MABA (2.76 g), calcium dichloride (93%, Sigma–Aldrich) (1.50 g) and pyridine (99%, Sigma–Aldrich) (14.5 mL) were added, and the final mixture was heated (100 °C) until complete dissolution of the solid reagents. Both the temperature (100 °C) and the vigorous stirring were kept constant until the completion of the reaction. Once the mixture became clear, triphenyl phosphite (97%, Sigma–Aldrich) (5.40 mL) was added to catalyze the monomer polymerization; when a time of 90 min had elapsed since catalyst addition, the final product was cooled to room temperature, filtered in order to remove the polymer excess, and then methanol (Rectapur, Prolabo) (100 mL) was added to precipitate it. The polymer/silica composite obtained in this way was washed in a Soxhlet apparatus with methanol for 4 h and dried (80 °C, 5 h). The dried polymer/silica composite was carbonized (heating rate of 10 °C/min to 900 °C, then kept for 30 min at this temperature) under argon (500 mL/min). The silica template was removed from the carbonized composite by treatment with hydrofluoric acid (48%, Fluka) and the final carbon was dried (100 °C, 12 h), being designated as PACor.

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