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Hierarchical micro-mesoporous carbons by direct replication of bimodal aluminosilicate templates

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ABSTRACT

The objective of this work was to produce carbons with controllable bimodal porosity in the micro-mesopore range. Hierarchical micro-mesoporous carbons were prepared by direct replication, using bimodal Y zeolite core/MCM-48 silica shell aluminosilicates as templates. Different variables of the chemical vapor deposition (CVD) process were studied in order to achieve a suitable infiltration of both meso and micropores of the templates. Thus, one-step infiltration with acetylene and also two-step infiltration with acetylene and propylene were performed to further investigate the effect of the precursor and CVD steps duration. One-step acetylene CVD gave the best results since the obtained carbons exhibited high specific surfaces areas of 1000–1323 m^2/g, and their X-ray diffraction and transmission electron microscopy analysis revealed that they faithfully replicated the hierarchical core–shell structure of the parent template. When propylene was used as carbon source a better replication of the mesoporous shell was achieved, but as a counterpoint, the replication of the microporous core failed.

1. Introduction

An intense research on the preparation of materials with controlled pore systems at different length scales is currently taking place. Accurate control of the pore size plays a crucial role in carbon material properties and performance [1,2]. Hierarchical materials represent a great breakthrough in materials science since they should favor the fast transport of molecules while keeping a good storage capacity. In order to obtain hierarchical micro-mesoporous carbons, the prevailing approach is post-synthesis activation of unimodal mesoporous nanocast carbons. Thus, activation with CO_2 or KOH generates microporosity in a quite controlled way in ordered mesoporous carbons [3–10]; meanwhile, the ordered structure is preserved to some extent. Another strategy for the preparation of hierarchical micro-mesoporous carbons is to assemble a block copolymer with a carbohydrate and TEOS in a soft-templating approach. In this method, the microporosity is produced after silica removal because TEOS and carbohydrates interact through hydrogen bonds and the silica is formed inside the carbon material [7,11–13]. These two approaches afford a close control of carbon mesoporosity, while the resulting microporosity is, to a large extent, uncontrolled and random. A method that could achieve a simultaneous control of both, micro and mesoporosity, is the replication of a suitable bimodal template. Thus, the obtained porous system would be completely controllable (pore size, shape, structure...) at different scale lengths.

Several works on the replication of hierarchical silica templates can be found in the literature. Thus, it has been possible to prepare bimodal carbons with intraparticle ordered mesopores (ca. 3–4 nm) and a complementary larger porosity arising from interparticle voids (ca. 30 nm–8 μm), [14–18] or carbons with uniform macropores (ca. 50–2 μm) connected with intraparticle mesopores (ca. 5–8 nm) [19,20]. Also, various bimodal carbons were prepared by combining nanocasting and molecular imprinting techniques. Thus, the simultaneous use of SBA-15 and colloidal silica as templates led to carbons with two pore systems in the mesopore range (one in the range of 2–3.5 nm and the other one in the range of 3.5–13 nm) [21,22]. Finally, hollow core/mesoporous shell silica structures were prepared and successfully used as templates for obtaining core/shell type carbon replicas. Both the diameter of the hollow core and the thickness of the mesoporous shell could be controlled in order to obtain different meso-macroporous carbons [23,24]. The common feature of all of these reports is that the control of the porosity is performed in the meso-macropore scales, but no in the micropore range. There are few works dealing with the replication of micro/mesoporous templates to obtain hierarchical carbons with a controlled micro and mesostructure. Yu et al. [24] prepared silicalite-1 core/mesoporous shell silica and tried to replicate it by liquid impregnation using phenol as carbon source. Despite they found a method to prepare nanocages with different core-shapes, they failed in the replication of the zeolite

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microstructure, which was their initial aim. Sakthivel et al. [25] synthesized MCM-48 silicas containing zeolite secondary building units in their walls. Further attempts to replicate these templates by liquid impregnation with sucrose were unsuccessful [26]. The aforementioned works tried to replicate the micropore structure by liquid impregnation using as a carbon source phenol [14,19], sucrose [16,26] or phenolic resins [24]. The molecular size of these carbon precursors is, especially considering their solvation sphere, too large to facilitate the penetration of molecules into the narrow (≈1 nm) zeolite channels. As a consequence, replication takes place mainly through mesopores and not through micropores. Chemical vapor deposition (CVD) could be a suitable method to replicate simultaneously the micro and mesoporosity of hierarchical templates. Not only the CVD method allows one to deposit large amounts of carbon, but it involves carbon precursors such as acetylene or propylene whose molecular sizes are small in comparison to the zeolite pores [27].

To the best of our knowledge, we report here the first preparation method for hierarchical carbons with highly-controllable porosity in the micro-mesopore range. Thus, we have prepared ordered micro-mesoporous carbons by simple CVD using acetylene or a combination of acetylene and propylene as carbon source, and a core/shell type aluminosilicate as template. Additionally, the direct replication of the hierarchical templates enables the obtaining of micro-mesoporous carbons in one step, eliminating the activation post-treatments that are necessary for preparing micro-mesoporous carbons from ordered mesoporous carbons. In the present work, the CVD variables and the characteristics of the template were varied and their effects on the porous and structural characteristics of the carbon materials were studied.

2. Experimental

2.1. Synthesis of aluminosilica templates

Whilst the zeolite used in this study was a commercial Y zeolite (Molecular Sieve Type Y, ammonium, powder, Alfa Aesar), the MCM-48 was prepared in this work. The synthesis of the MCM-48 mesoporous silica was reported elsewhere [28]. We have slightly varied the initial molar relations (1:0.23:0.55:122 SiO_2/Na_2O/CTAB/H_2O) and we have fixed 100 °C and 12 h as parameters for the hydrothermal treatment (CTAB stands for cetyl trimethyl ammonium bromide).

Zeolite Y/MCM-48 composites were prepared by simply dispersing the commercial zeolite in the MCM-48 synthesis gel. The experimental details can be found elsewhere [29]. Thus, 10 mL NaOH 2 M was added to an aqueous solution of surfactant (78 mL H_2O and 8.8 g CTAB). After that, different amounts of commercial Y zeolite were added to the mixture and dispersed by vigorous stirring during 1 h at room temperature. Once the zeolite was correctly dispersed, 10 mL tetraethyl orthosilicate (TEOS) (98%, Aldrich) was added and the solution was vigorously stirred during 30 min. The resulting gel was treated at 100 °C for different times (12 or 24 h). The solid was recovered by filtration and CTAB was removed by calcination in air during 6 h at 550 °C. The weight percentage of Y zeolite in respect of the total SiO_2 was 5, 8, 10, or 20 wt.%. Samples were named as Bi-X-T, where X is the weight percentage of Y zeolite relative to the total composite weight (calculated by summing the amount of theoretical SiO_2 derived from TEOS hydrolysis and the amount of added zeolite). T is the time of thermal treatment in hours.

2.2. Synthesis of hierarchical carbons

The carbon materials were synthesized by CVD of acetylene and propylene as carbon sources. The selected temperature for acetylene deposition was 600 °C. Such a low temperature was fixed in order to deposit enough carbon inside the microporous channels of the template whilst the deposition of amorphous carbon in the external surface of the particles is minimized [27]. In the case of propylene, the selected deposition temperature was 750 °C.

2 g of template was placed in a vertical quartz reactor and subjected to one (acetylene) or two (acetylene/propylene) infiltration steps. The temperature was increased up to 600 °C in argon atmosphere (flow of 450 $cm^3\ min^{-1}$), and then a mixture of acetylene/argon (5.2% v/v) was passed through the reactor and maintained for different times. In some cases, a second infiltration step was performed by increasing the temperature up to 750 °C and switching the gas flow to a propylene/argon mixture (5.6% v/v) for different times. Finally, the samples were carbonized at 900 °C during 2 h under argon (flow of 450 $cm^3\ min^{-1}$) in order to increase their structural order [30]. The resulting composites were treated with HF (48%, Merck) for 7 h to remove the aluminosilica template, filtered and repeatedly washed with water. Finally, the resulting carbon was dried at 80 °C for 8 h. Carbons contained less than 1 wt.% of residue measured thermogravimetrically in air at 950 °C.

The aluminosilicate template, the carbon precursor nature and the duration of the CVD steps (which determines the amount of carbon deposited) were varied in order to study the effect of these variables on the porosity and structure of the resulting carbons. The carbon materials were denoted as C X T, where X and T have the same meanings as in template notation (Bi X T), followed by A (time of CVD in hours) P (time of CVD in hours), where A stands for acetylene and P for propylene. For example, C 10 12 A4 P4 is a carbon prepared by infiltration of Bi 10 12 aluminosilicate with acetylene during 4 h and propylene during 4 h.

2.3. Characterization methods

Nitrogen (99.999% pure) adsorption–desorption isotherms at −196 °C in the 10^{-6}–0.99 relative pressure range were measured in an Autosorb-1 (Quantachrome) volumetric adsorption analyzer. Prior to the measurements, all the samples were degassed overnight at 250 °C under vacuum. Porous texture parameters obtained from the N_2 isotherms were: the BET surface area, S_{BET}, calculated according to the BET equation [31]; the micropore volume, $V_{\mu p}$, calculated according to the Dubinin–Radushkevich (DR) equation [31]; the total pore volume, V_T, calculated from the nitrogen uptake at a relative pressure of 0.95, assuming it to be in the liquid state; and the mesopore volume, V_{mesop}, calculated as the difference between V_T and $V_{\mu p}$. The Quenching Solid Density Functional Theory (QSDFT) method [32] was used to obtain the pore size distributions (PSD) of the carbon materials.

X-ray diffraction (XRD) patterns were recorded in a Siemens D5000 diffractomer using Cu Kα radiation. The low-angle XRD patters were collected in the scanning range $2\theta = 1$–7°, with a step width of 0.01° and a time per step of 3 s. The high-angle XRD patters were collected in the scanning range $2\theta = 2$–30°, with a step width of 0.015° and a time per step of 1 s. Scanning electron microscopy (SEM) images were taken in a DSM-942 microscope (Carl Zeiss). Transmission electron microscopy (TEM) images were taken in a JEOL 2000 EX-II instrument operated at 160 kV.

3. Results and discussion

3.1. Materials used as templates

As indicated above, the synthesis and characterization of the aluminosilicates used in this work as templates has been discussed in detail in a previous work from our group [29]. Here, we only show the N_2 adsorption–desorption isotherms (Fig. 1) of the