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Pore size distribution of ordered nanostructured carbon CMK-3 by means of experimental techniques and Monte Carlo simulations

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ABSTRACT

The design and study of new materials with specific properties is interesting in several scientific and technological fields. In the last years, nanostructured carbons (NC) have rapidly attracted the attention of some researchers due to their physicochemical properties useful for many applications among them in adsorption and catalysis.

In this work, the synthesis of a NC was carried out by a nanocasting method, using as a template a very ordered mesoporous material (SBA-15) and sucrose as carbon source. The final material consists of an ordered arrangement of parallel carbon nanorods bonded with some carbon nanowires (CMK-3 type), formed in the mesopores and micropores of the inorganic matrix. The inorganic matrix and the NC were structurally characterized by X-ray diffraction, texturally by N_2 sorption at 77 K, and morphologically by scanning electron microscopy. The Nitrogen experimental isotherms were simulated using Grand Canonical Monte Carlo (GCMC) method based on two kernels using slit and cylindrical pore models. From these models were obtained the pore size distributions (PSD) which were compared with those obtained by Quenched Solid Density Functional Theory (QSDFT) model. The GCMC simulation showed a good agreement with experimental adsorption isotherms and some differences with the corresponding pore size distribution obtained by Density Functional Theories Methods. These correlations validate the presented GCMC method as an alternative to study in detail the porosity of these materials.

1. Introduction

Energy and environmental problems have promoted the design of new materials to be used in more efficient processes. Nanostructured carbons (NC) have rapidly attracted the attention of researchers due to their physicochemical properties to be used in many applications as: separation processes (CH_4/CO_2 and N_2/O_2), gas storage (CH_4 and H_2), gas capture (CO_2) [1], energy storage as electrodes in lithium batteries [2,3] and electrochemical double-layer capacitors [4,5].

Unlike the traditional methods to synthesize carbon materials, a high control of porosity and ordered structure can be obtained using a nanocasting technique to produce novel materials. In this procedure, an inorganic porous material is chosen as a template and is impregnated with a carbon precursor (as sucrose, furfuryl alcohol, acetylene, etc.). Then, this composite is dried and pyrolyzed and the template is removed by hydrofluoric acid or sodium hydroxide leaching. Different templates like porous silica, zeolites, pillared clays, are used to obtain carbons with a variety of structures and pore sizes. Jun et al. [6] synthesized with this technique the first nanostructured carbon CMK-3 type. They used an ordered mesoporous material (SBA-15) as a template and sucrose as a carbon source. The resulting material was an exact negative replica of the SBA-15 porous structure formed by parallel interconnected carbon nanorods. This material became attractive due to its interesting textural, structural and morphological properties. In comparison with the corresponding template the synthesized carbon material exhibits a more hydrophobic nature, excellent mechanical strength and thermal stability, making it even more attractive for many applications [7–9].

The standard method used to characterize the texture of ordered mesoporous materials (OMM) is by the N_2 adsorption–desorption isotherms at 77 K [10–12]. In addition to these experimental analyses there are many theoretical and simulation studies that attempt to complete the characterization of these kinds of materials using the adsorption data. Particularly, the interest was focused on obtaining the Pore Size Distribution (PSD) of these materials.

In the last years, an important progress has been achieved using molecular theories to calculate the PSD of different materials where the most popular methods are supported by the Density Functional Theory, as the Non-Local Density Functional Theory (NLDFT) [13–15]. NLDFT method is a reliable and useful tool to study classical inhomogeneous fluids. This method describes the

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structure of simple confined fluids in simple confining geometries such as slits, spheres, cylinders (as is the case of SBA-15 materials) and hybrids [16,17]. NLDFT neglects the influence of connectivity in the pore model and assumes that the surface is smooth and rigid and that no surface functional groups are present, disregarding corrugation effects, swelling, and chemical heterogeneity. The fluid–fluid and solid–fluid parameters of the Lennard–Jones potentials are used to represent different adsorption systems [18,19]. This method produces some inaccuracies in carbons with heterogeneous surfaces and disordered pore structure. To overcome this problem, Gor et al. [20] presented an advanced NLDFT method named Quenched Solid Density Functional Theory (QSDFT), where the system is modeled using a distribution of solid atoms rather than a source of the external potential field. This fact, allows take into account the heterogeneity effects in carbons due to the surface roughness, improving the previous NLDFT that assumes flat, structureless and graphitic pore walls. This method was developed to obtain the pore size distribution taken into account the geometrical and chemical characteristics of micro-mesoporous carbons, in the range from 0.4 to 50 nm. The calculated theoretical isotherms (kernels) were developed for cylindrical, slit, and a mixture of these pore geometries. In the last one slit geometries are only considered for the micropores and cylindrical for the mesopores range [20]. These DFT methods (NLDFT and QSDFT) were developed and implemented in commercial sorption instruments.

Among the molecular methods, the Grand Canonical Monte Carlo (GCMC) simulation is also appropriate to be applied in the study of porous materials. GCMC was used for several authors [21,22] to model the adsorption process in CMK-3 type material obtaining reliable results. An interesting point to explore, which has not been developed by these authors, is the use of this methodology to obtain the PSD of these materials.

In the present work, the synthesis and characterization of an ordered mesoporous carbon type CMK-3 were carried out by different experimental techniques and Monte Carlo simulation. The CMK-3 was characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM) and nitrogen adsorption–desorption measurements, with the aim of evaluating their structural, textural and morphological properties. By Monte Carlo simulations two set of isotherms (kernel) were built based on slit and cylindrical pores in the Grand Canonical ensemble. From the experimental data, and the kernels obtained by GCMC, the PSDs were plotted and compared with those obtained by QSDFT method implemented into Quantachrome's data reduction software.

2. Experimental

2.1. Materials

Reagents used in these syntheses include the surfactant Pluronic P123 triblock copolymer (EO_{20}-PO_{70}-E_{20}) (Aldrich); tetraethyl orthosilicate (TEOS 98%) (Merck); hydrochloric acid (Merck); sulfuric acid (Merck); hydrofluoric acid (Merck); sucrose (Biopack) and deionized water.

2.1.1. Synthesis of template

An ordered mesoporous material, SBA-15, was synthesized under non-hydrothermal conditions [23] in order to use it as a template in the obtaining of the nanostructured carbon. The molar ratio used for the preparation of the SBA-15 was: $\mathbf{0{,}017}P123:\mathbf{1}TEOS:\mathbf{6}HCl:\mathbf{140}H_2O$. Pluronic P123 was dissolved in a 2 M aqueous solution of HCl and kept under stirring at 40 °C for 3 h. TEOS was drop-wise added to the solution, which was vigorously stirred at the same temperature for 4 h. This reaction mixture was aged at 40 °C for 20 h without stirring. Afterwards, the temperature was raised to 80 °C and maintained for 48 h. The resultant solid material was filtered and washed with deionized water until reaching a conductivity value smaller than 10 S/cm. Subsequently, the material was dried at 60 °C for 12 h and calcined at 550 °C for 6 h at 1 °C/min.

2.1.2. Synthesis of nanostructured carbon

The synthesis of the nanostructured carbon, type CMK-3, was performed based on different reported conditions [6,24,25]. The synthesis involves four main steps: (i) impregnation of the template with the organic precursor; (ii) polymerization; (iii) pyrolysis and, (iv) template removal. The synthesis was carried out using SBA-15 as a template and sucrose as carbon source. SBA-15 was impregnated with an aqueous solution of sucrose dissolved in sulfuric acid and water in a mass ratio of 1:1.3:0.14:5 (SBA-15:Sucrose:H_2S0_4:H_2O). The mixture was stirred at room temperature for 1 h and then it was dried at 100 °C for 6 h. Subsequently, the temperature was raised to 160 °C for 6 h. The resultant dark brown colored composite was impregnated a second time with a mixture of aqueous solution of sucrose, sulfuric acid and water with a mass ratio of 0.8:0.09:5. This composite was treated again at the same drying conditions to complete the polymerization step. The pyrolysis process was carried out by heating the mixture from room temperature (RT) up to 900 °C, in a N_2 flow of 180 ml/min with a heating rate of 3 °C/min. The final temperature was keeping for 6 h and then is cooling up to RT. The nanostructured carbon was recovered by leaching the mesoporous framework in a 5 wt.% hydrofluoric solution at RT for 24 h. The obtained carbon, without template, was filtered and washed several times with deionized water and ethanol (50:50% v/v) until the conductivity value was smaller than 10 S/cm. Finally, the nanostructured carbon was overnight dried at 80 °C. Fig. 1 shows a scheme of the geometrical structure and formation of the CMK-3 material.

2.2. Characterization

The structural characteristics of the template and the nanostructured carbon material were obtained from small angle X-ray diffraction (XRD) measurements in an X'Pert PRO MPD Philips diffractometer using Cu Kα radiation from 1 to 5° of 2θ. Scanning electron microscopy (SEM) images were taken on a LEO 1450VP, equipped with an Energy Dispersive Spectrometer (EDS) Analyzer, Genesis 2000. Measurements of N_2 (99.999%) adsorption–desorption isotherms at 77 K were carried out using a volumetric adsorption apparatus (AUTOSORB-1MP, Quantachrome Instruments). Samples were previously degassed at 150 °C for 12 h, up to residual pressure was smaller than 0.5 Pa.

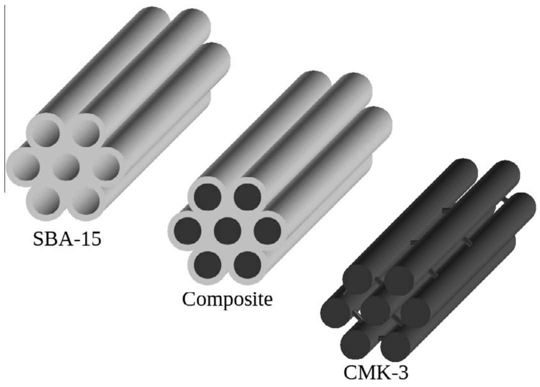

Fig. 1. Schematic structure of SBA-15 and CMK-3.