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Carbon materials with tailored porosity by self-assembly method: Influence of the synthesis conditions

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ABSTRACT

A series of different carbon materials have been obtained by self-assembly method under different conditions in order to study the effect of the nature of carbon precursor, pore forming agent and catalyst concentration on the textural, chemical and structural properties of carbon materials. Results show that using hexadecanol as pore forming agent produces mesoporous carbon materials with controlled mesopore size by varying the amount of pore forming agent. Specific surface areas up to 314 $m^2 g^{-1}$ can be reached. The microporosity of the samples decreases with the amount of the catalyst used during the synthesis from 0.12 to 0.01 $cm^3 g^{-1}$. On the other hand, the use of ethylene glycol as pore forming agent gives highly microporous carbon materials independently on the synthesis conditions (i.e. 0.19 $cm^3 g^{-1}$). The influence of pore forming agent nature and synthesis conditions on the chemical and structural properties of carbon materials is lower. The obtained samples present an amorphous structure with a slightly higher order degree than typical activated carbons. Results show that self-assembly is a promising method to obtain carbon materials for applications, in which a control of the textural properties is required, such as energy storage applications.

1. Introduction

Due to their large variety of physical, chemical and structural properties, carbon materials are very attractive for several applications: Li-ion batteries [1], double-layer capacitors or other electrochemical applications [2,3], catalyst [4,5], magnetic materials [6], for hydrogen and methane storage [7,8], etc. In most of these applications, porosity is a fundamental factor to take into account. An optimum pore size distribution can be determined according to material properties requirements [9–11]. This means, that in order to improve the properties of carbon materials, it is necessary to adapt and control their textural properties depending on the final application. Activated carbons are commonly the most used carbon materials due to their high porosity and easy preparation. However, the control and the adaptation of the pore size distribution is not always easy because porosity is commonly composed by wide pore size distributions, generally centred in microporous range and sometimes in the mesoporous range. These wide pore size distributions of activated carbons are derived form their preparation method (chemical and physical activation). In many cases it is not possible to control the final textural properties of the carbon materials. This is why, nowadays, there is an intense research in setting alternative methods for carbon materials development in which it is possible to tailor and control the final textural properties [12–14].

The template carbonization has been proven to be an excellent method for obtaining carbons with large surface area, high porosity and controlled pore size distribution in the mesopore range [15]. Many polymeric precursors including polyacrylonitrile, poly(furfuryl alcohol), poly(vinylidene chloride), and phenol resin have been applied as porous carbon precursors. The method includes filling of porous material (i.e. the template) with carbon precursor followed by carbonization and calcination steps. After the removal of the inorganic material, a carbon replica can be obtained. Therefore, textural and structural features of the template can be transferred to the final carbon material. Templates commonly used are zeolites, silicas, and ordered mesoporous materials like MCM-48 or SBA-15 [16]. This method offers great advantages to control the textural properties of carbon materials. However, it requires many synthesis steps and it is necessary to eliminate the inorganic template by non environmental friendly solutions, such as HF.

Another interesting templating method is self-assembly. The development of carbon materials via self-assembly method consist in mixing a carbon precursor and pore forming agents (also known as surfactants or porogeneous agents) which are amphiphilic molecules (i.e. composed by a hydrophilic and hydrophobic part). This characteristic of the pore forming agent induces the supramolecular organization or self-assembly of the molecules in micelles of different sizes which are the responsible of the pore

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development in carbon materials synthesized by this method. Once the organization of the different structures takes place, polymerization and curing occur to obtain a polymer which is finally carbonized under inert atmosphere. The polymerization of the carbon precursor occurs under an acid medium. Some works have already demonstrated that porous carbon materials can be obtained using this method [17,18] which offers a series of advantages such as the use of environmental friendly compounds during the synthesis and its easiness. However, in order to control the final properties of carbon materials by this method it is still necessary to study and understand the effect of different variables involved in the synthesis process. In this work, a series of different carbon materials have been obtained by the self-assembly method under different conditions. The effect of the nature of carbon precursor, pore forming agent and catalyst concentration on the textural, chemical and structural properties of carbon materials has been investigated.

2. Experimental

2.1. Synthesis of carbon materials

The synthesis of the carbon materials obtained in this work was carried out using the self-assembly method. In all cases furfuryl alcohol (F) was used as carbon precursor and p-toluensulphonic acid as catalyst (C). Two different pore forming agents (A) were used: hexadecanol and ethylene glycol.

Furfuryl alcohol (99%, Panreac) and p-toluensulphonic acid (98%, Panreac) were first mixed in a flask under magnetic stirring. After homogenization of the solution the pore forming agent was added (hexadecanol (95%, Aldrich) or ethylene glycol (99%, Panreac) and the mixture was stirred until a homogeneous solution was obtained. The flask containing the solution was sealed and placed in an oven for polymerization and ageing. The following heating program was used in this step: (i) start and 55 °C and hold for 2 h; (ii) ramp at 0.41 °C min^{-1} to 80 °C and hold for 5 h; (iii) ramp at 0.33 °C min^{-1} to 100 °C and hold for 4 h; (iv) ramp at 0.33 °C min^{-1} to 120 °C and hold for 4 h and (v) slow cooling to room temperature. As it is commented above, the influence of different synthesis conditions such as pore forming agent nature, and concentration, catalyst and carbon precursor was evaluated. Several samples were prepared and the different conditions used are schematised in Table 1.

After polymerization and curing, the polymers obtained were pyrolyzed at 800 °C under nitrogen flow in a tubular oven. The following heating program was used: ramp at 1.0 °C min^{-1} up to 800 °C and hold for 5 h under a flow rate of 100 $\text{cm}^3\,\text{min}^{-1}$ and slow cooling to room temperature.

2.2. Sample characterization

Textural characterization was carried out by CO_2 adsorption isotherms at 0 °C and N_2 adsorption–desorption isotherms at −196 °C in a pressure range of 0–1 bar, in a Quantachrome AUTOSORB-6. The Dubinin–Radushkevich (DR) method [19] was applied to the carbon dioxide and nitrogen adsorption isotherms in order to obtain the narrow micropore volume, W_{0-CO2}, and the wider micropore volume, W_{0-N2}, respectively. The BET apparent surface area was also evaluated from the nitrogen adsorption isotherms [20]. The pore volume at saturation, V_T, was also calculated.

The chemical properties of the carbon materials were also studied using elemental analysis and CO_2 and CO desorption temperature programmed (TPD) techniques.

X-ray diffraction and Raman spectroscopy were also used to characterize the structure carbon materials.

Table 1
Nomenclature and synthesis conditions of samples.

Sample	Pore forming agent	F/A ratio	F/C ratio
H1	Hexadecanol	1/5	33.3
H2	Hexadecanol	5/1	33.3
H3	Hexadecanol	1/5	16.6
H4	Hexadecanol	1/1	33.3
E1	Etilenglicol	1/1	33.3
E2	Etilenglicol	1/5	16.6

F, furfuryl alcohol; A, pore forming agent; C, catalyst.

3. Results

3.1. Textural properties of samples

Fig. 1 shows the N_2 adsorption–desorption and CO_2 adsorption isotherms of the carbon materials obtained using different amount of carbon precursor (furfuryl alcohol) and hexadecanol. When the same amount of furfuryl alcohol and hexadecanol (i.e. F/A 1/1, sample H4) or an excess of hexadecanol is used (i.e. F/A 1/5, sample H1) the samples obtained present a type I–IV isotherms according to BDDT classification [21] which corresponds to micro–mesoporous materials. However, when an excess of furfuryl alcohol is used (i.e. F/A 5/1, samples H2) the N_2 and CO_2 adsorption capacity of the

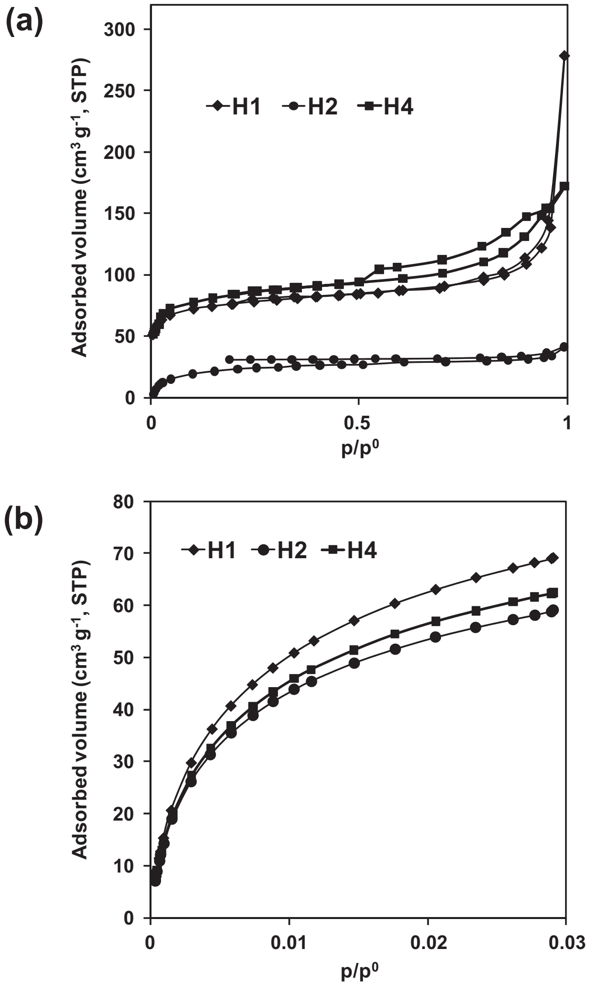

Fig. 1. (a) N_2 adsorption–desorption and (b) CO_2 adsorption isotherms of carbon materials obtained using different amount of furfuryl alcohol and hexadecanol during the synthesis.