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Development of tailored mesoporosity in carbonised cocoa bean husk

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ABSTRACT

Tailored mesoporous activated carbon has been prepared from a new lignocellulosic precursor, cocoa bean husk. The study has focussed on analysing the role the mineral matter of a lignocellusic precursor plays in the development of mesoporosity in activated carbon. Three new approaches have been developed to obtain tailored mesoporosity: i) controlled demineralisation; ii) activation of mixtures of the raw and demineralised cocoa precursor; iii) incorporation of iron via ionic interchange. The results prove that each of the above methods are suitable for developing activated carbon with different pore size distributions, including highly microporous, highly micro and mesoporous and highly macroporous activated carbons. In addition, the activation mechanism of these different carbonised samples has been analysed in order to explain the differences found in the development of porosity.

1. Introduction

Porous solids are materials of great interest for industry, both for their application as adsorbents and their use in heterogeneous catalysis [1,2]. In both cases, the most important characteristic of the porous solids is that they present a high degree of microporosity (pore size < 2 nm), which endows them with a high specific surface area, desirable for maximising the number of catalytic centres per unit of surface area, or a high volume of porosity, appropriate for offering a high capacity to adsorb molecules. For this reason, in most cases, the preparation of porous solids had been aimed at maximising the development of microporosity [1,2].

In the case of mesoporosity (pores of between 2 nm and 50 nm) its function has traditionally been to act as transitional porosity, facilitating the access of the reactives to the heart of the particles where the micropores are located [1–3]. However, in the last few decades, mesoporosity has acquired an important role in heterogeneous catalysis, providing a choice of the type of products which can be obtained in its core (steric effect), especially in reactions which involve species with high molecular sizes [4,5], where traditional catalysers, like aluminium oxide or zeolites, present limitations due to steric impediments. Thus, the discovery in 1992 (Mobil Oil Corporation) of a new type of silica with an ordered mesoporous structure (MCM-41) meant the beginning of a new field in materials engineering [6]. Since then, thousands of studies have been carried out on the synthesis of new mesoporous materials, focussed both on the type of precursor (silica, titania, zirconia, carbonaceous materials), and the development of new synthesis methods, like template synthesis (used in the synthesis of MCM-14), cooperative assemblage and nanomoulding.

From among all these materials, in the last few years there has been intense research on the development of carbons with ordered mesoporosity, which is linked to the excellent properties inherent in active carbons: high specific surface area, possibility of developing tailored porosity in their cores (both in size and in distribution of pore size), high chemical resistance, the possibility of chemically functionalising their surface, high mechanical resistance and good electrical conductivity. All these properties make them ideal materials for applications of adsorption and catalysis, and electrochemical uses (i.e. supercapacitors, sensors). Several methods have been used to prepare mesoporous carbons. In the case of activated carbon fibers, due are essentially microporous carbon, several approaches have been performed to enhance the mesopore region. These include catalytic gasification with a cobalt catalyst [7,8], steam–KOH reactivation [9], or by carbonization of a polymer blending [10]. One of the most common has been the

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technique of nanomoulding. This consists of using a mesoporous silica as a mould ("hard template"), the mesoporous walls of which are impregnated with an organic precursor, the whole is carbonised and then the silica skeleton is eliminated (i.e. HF) [11,12]. This process, as well as being expensive, takes quite a long time. Another shorter process is based on self-assembling reactions among different copolymers (polyethylene oxide and polypropylene oxides) and phenolic resin, with which a mesoporous structure is generated, which after carbonisation becomes a mesoporous carbon [13,14]. In this same line, we find carbon materials obtained from carbonising carbon aerogels and xerogels, which are obtained from hydrolysis-condensation reactions between hidroxybenzene and aldehydes [15–17].

In a recently study [18], active carbon monoliths were prepared employing a lignocellulosic precursor, cocoa bean husk, that has not been used for developing activated carbons, which have proved to be essentially microporous solids, with little development of mesoporosity. However, the development of mesoporosity in lignocellulosic precursors is a process which has been amply described in the literature [18–21]. This development is related to the presence of inorganic materials within the lignocellulosic composition of the precursor, which are well known catalysers of the gasification reaction of the carbon with CO_2, affecting not only the reactivity of the carbonised matter, but also the type of porosity developed [22–24]. Thus, for example, it has been proved that both alkaline earth metals, and Fe and Co, give rise to the formation of a high degree of meso and macroporosity in the activated carbon.

Considering the above, this study aimed at developing mesoporosity in carbonised matter obtained from cocoa beans husk, a precursor which has scarcely been investigated in the literature. Another additional aspect of the present study is that it provides a simple procedure for the controlled development of mesoporosity.

2. Experimental

2.1. Materials

Waste material from cocoa bean husk was supplied by Chocolates Valor S.A. (Villajoyosa, Alicante). It was ground to a fine powder in a helix grinder. Part of this powder was washed in an aqueous solution of H_2SO_4 (10% vol.) using agitation, which eliminated the mineral material in the bean husk. The effect of washing time on the degree of elimination of the mineral material was studied: 24 h, 1 h, 30, 15, 5 and 2.5 min. The washed solution was filtered, and the solid paste was washed with distilled water several times until the washing water had a neutral pH. It was then dried in a stove at a temperature of 100 °C. The nomenclature used was: **CS**, unwashed cocoa bean husk sample, **CA**, normal washed cocoa bean husk sample, CA84**L5**, cocoa bean husk sample washed for 5 min.

As well as different degrees of washing, two processes were applied to modify the cocoa bean husk precursor to achieve a controlled development of mesoporosity. In the first, "**hybrid**" samples were prepared, consisting of an intimate mixture of completely washed bean husk (1 day) and unwashed bean husk, using different weight ratios: 10/90, 20/80 and 30/70 (the nomenclature used was **1H**, in which the number 1 indicates a percentage of unwashed bean husk of 10%; **1CH** indicates that the unwashed cocoa bean husk were incorporated as carbonised matter in the hybrid mixture). The second consisted of incorporating Fe into the composition of the cocoa bean husk. This was done by adding a solution of $Fe(NO_3)_3 \cdot 9H_2O$ to the damp bean husk which had previously been washed for 1 h and after eliminating the water used for washing, and leaving the mixture for 15 min with agitation. The quantity of $Fe(NO_3)_3 \cdot 9H_2O$ in the solution ranged between 4 and 100% in relation to the initial weight of the cocoa bean husk, to cover a theoretical content of incorporated Fe of between 1 and 25% based on the final carbonised matter. The nomenclature of the samples obtained indicates the Fe content of the carbonised sample. For example, **C7Fe** indicates 7% of Fe.

2.2. Preparation of the carbonised activated cocoa bean husk

The different materials developed (unwashed bean husk, bean husk washed for different lengths of time and samples with incorporated Fe) were carbonised in a tube furnace (⌀ 6 cm, L 150 cm) in an inert atmosphere (N_2 100 cm^3/min) to 1000 °C, at a heating speed of 10°C/min, and maintained for 30 min at the maximum carbonisation temperature. The carbonisation yield was determined by weight difference.

The carbonised samples were activated in a tube furnace. Reactivity with CO_2 was studied previously using TG to perform the activation in the same conditions of reactivity for all the different materials treated. Once the temperature had been determined, all the samples were subjected to the following heating programme: heating in N_2 100 cm^3/min up to the activation temperature (between 725 and 880 °C), change to a current of CO_2 100 cm^3/min and maintaining for different time periods (1–10 h), at the end of which the furnace was switched off with a current of N_2 during cooling. The activation percentage (BO) was determined by mass balance. The nomenclature of the unwashed (**CS**), hybrid (**1CH**), washed (**CA**) and iron-containing (**C5Fe**) activated cocoa bean husk, includes two numbers at the end which indicate BO (i.e. CA44, BO of 44%); in the case of the samples with intermediate washing, the BO is indicated in the middle, CA84L5.

In order to eliminate the mineral material present in the activated samples they were washed with an acid solution (HCl or H_2SO_4 6 M), with agitation at boiling point for 12 h.

2.3. Characterisation

The elemental analysis of carbonized samples was determined by inductively coupled plasma mass spectrometry (Mark Agilent 7700x). For ICP-MS analysis, the solid samples (0.4 g) were ashed in a muffle furnace at 650 °C for 12 h, the produced ash was acid digested (50 cm^3 of 6 M HNO_3, 6 M HCl, and 0.5% HF) under reflux during 6 h. Aliquots of solution were diluted to 50 cm^3 using deionized water (Supplementary material, Table S1).

The reactivity of the different carbonised samples was obtained using thermogravimetric experiments in a TA Instruments, SDT 2960 analyser. Equally, the same equipment and similar heating conditions were used to determine the ash content of the different carbonised materials obtained as well as a series of selected active carbons. Thus 10 mg of treated cocoa bean husk were heated in an atmosphere of N_2 (60 cm^3/min) at 20°C/min up to 950 °C, and once this temperature was reached, there was a change to synthetic air and the temperature was maintained for 15 min.

The internal morphology of the materials was analysed by electron microscope (Transition Electron Microscope- TEM: JEOL; JEM-2010). Using the same microscope, a microanalysis was performed of certain regions using energy-dispersive X-ray spectroscopy (EDX). The crystalline structure of the materials obtained was determined by x-ray powder diffraction (PXRD; Seifiert diffractometer JSO Debye-Flex 2002, with Cu K_α radiation).

The skeletal density (ρ_{He}) of the carbonised samples was determined with a helium pycnometer (AccuPyc 1330 Pycnometer; Micrometrics). We used 0.2 g of previously degassed sample at 150 °C in a vacuum (1 Pa) during the whole night. The porous texture of the carbonised and of the activated materials was characterised using physical gas adsorption (N_2 at −196 °C and CO_2 at 0 °C) in two different analysers (Autosorb 6-B and Autosorb-6,