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Effect of the nature the carbon precursor on the physico-chemical characteristics of the resulting activated carbon materials

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ABSTRACT

Carbon materials, including amorphous carbon, graphite, carbon nanospheres (CNSs) and different types of carbon nanofibers (CNFs) [platelet, herringbone and ribbon], were chemically activated using KOH. The pore structure of carbon materials was analyzed using N_2/77 K adsorption isotherms. The presence of oxygen groups was analyzed by temperature programmed desorption in He and acid–base titration. The structural order of the materials was studied by X-ray diffraction and temperature programmed oxidation. The morphology and diameter distribution of CNFs and CNSs were characterized by transmission electron microscopy. The materials were also characterized by temperature-desorption programmed of H_2 and elemental composition. The ways in which the different structures were activated are described, showing the type of pores generated. Relationships between carbon yield, removed carbon, activation degree and graphitic character were also examined. The oxygen content in the form of oxygen-containing surface groups increased after the activation giving qualitative information about them. The average diameter of both CNFs and CNSs was decreased after the activation process as consequence of the changes produced on the material surface.

1. Introduction

Carbon materials (amorphous carbon, carbon nanofibers, nanospheres and nanotubes, graphite, etc.) have been widely used in sewage water treatment, electrode base material for supercapacitors [1–3], catalytic support [4,5], fuel cells [6] or hydrogen storage because of its adsorption capabilities, higher safety features and energy storages [7,8].

However, controlled pore size and pore size distribution are necessary for the application of those materials in a specific end use. Thus, pore and distribution size can be controlled using activation process (physical or chemical). In that regard, the specific surface area and porosity of carbon materials can be modified significantly by an activation process that removes the most reactive carbon atoms from the structure and thus increasing the surface area and porosity. Chemical activation has been shown to be a very efficient method to obtain carbon materials with high surface area and narrow micropore distribution [9–11]. The most important advantage of chemical activation versus physical activation is that the sample is activated at a lower temperature. Other advantages are that higher yields and greater porosity are obtained and less time is required to activate the sample. Key disadvantages of chemical activation process are the need for a thorough washing step due to the incorporation of impurities arising from the activating agent, which may affect the chemical properties of the activated carbon [12] and the corrosiveness of the chemical activation process [13].

On the other hand, although the activation of carbon materials is a common and frequently used process, its mechanism is not well understood, and the various interpretations that can be found in literature underline the process complexity [14–16]. Most of the studies about activation of carbon materials have considered KOH and NaOH as activation agents [13–16]. Chemical activation by hydroxides consists in solid–solid or solid–liquid reactions involving the hydroxide reduction and carbon oxidation to generate porosity [13–16]. During the reactions CO, CO_2 and H_2 evolution is observed. A recent study suggests that the carbon/MOH (M = K or Na) reaction mechanism consists of the overlapping of redox processes [14,15]. The hydroxide reduction leads to H_2 and Na or K metals whereas carbon is oxidised to carbonates (Na or K) according to the global reaction [17]:

$$6MOH + 2C \leftrightarrow 2M + 3H_2 + 2M_2CO_3$$

Recent literature contains many examples of chemical activation processes of carbon using alkali hydroxide (KOH and NaOH, mainly) [14,18,19]. Nevertheless, few of them are focused on the influence of the carbon structure on the pore development. In this

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regard, the activation of materials with ordered graphitic structure (such as CNFs, CNS or graphite) could be performed in a different way if compared to that of amorphous carbon materials [20–22]. Also, the type of carbon nanofibers: herringbone, ribbon and platelet [4–23], could affect to the porous properties of the final activated material.

In this work, different carbon materials were chemically activating using KOH: amorphous carbon, graphite, CNSs and different types of CNFs (platelet, herringbone and ribbon) using several characterization techniques to evaluate the physico-chemical and structural changes produced in them.

2. Experimental

2.1. Preparation of carbon nanofibers (CNFs)

Carbon nanofibers were grown at atmospheric pressure in a fixed-bed reactor, consisting on a quartz tube of 9 cm diameter and 100 cm length located in a horizontal electric furnace (JH Hornos) with an effective heating zone of 80 cm. Supported catalyst was placed in a quartz boat, which was kept inside the heating zone during the carbon nanofibers synthesis. In each synthesis run, 2 g of the prepared catalyst (10% Ni/SiO_2) was placed in the centre of the reactor and activated by heating (10 °C min^{-1}) in a flow dry 20% (v/v) H_2/He at the desired reaction temperature (450, 600 and 850 °C). The reduced activated catalyst was thoroughly flushed with dry He for 1 h before introducing the C_2H_4/H_2 (4/1, v/v) feed. The growth time was 1 h and space velocity of 25,000 h^{-1}. Silica supports were subsequently separated from the carbon product by leaching the primary product in hydrofluoridic acid (48%) for 15 h with vigorous stirring followed by filtration and washing with distilled water until neutral washing obtained. The resulting materials were dried at 110 °C for 12 h in air to removal water prior to activation [24].

2.2. Preparation of carbon nanospheres (CNSs)

Carbon nanospheres growth was carried out by direct pyrolisis of benzene at atmospheric pressure and 950 °C in a continuous plug flow reactor, consisting on a quartz tube of 3 cm diameter and 60 cm length placed in a temperature programmable oven. Benzene was led to the reactor by using a Bronkhorst CEM (Controller Evaporator Mixer), using He as the inert carrier gas. The ratio between benzene and He was maintained at 1:4 (v/v), with a total inlet flow of 150 ml min^{-1}. Carbon nanospheres growth was monitored for up to 2 h on stream. After the reaction, the reactor was cooled at room temperature in a flow of He prior to off-line analyses [25]. For comparison purposes, CNS received the same HF treatment as CNFs.

2.3. Amorphous carbon (C) and graphite (G)

Amorphous carbon and graphite was supplied by PANREAC and SIGMA–ALDRICH, respectively. For comparison purposes, both materials also received the same HF treatment as CNFs and CNSs.

2.4. Chemical KOH activation of the carbon materials

The experimental set up used for the preparation of activated carbon materials consisted of a horizontal quartz reactor tube located inside a conventional horizontal furnace. Carbon precursors were chemically activated with KOH. Carbon precursors were mixed with the activating agent (1:4, g/g) and distilled water (5 ml water per 1 g activating agent) [20–22]. The mixture was heated at 85 °C for 4 h under stirring and then dried at 110 °C for 12 h. The mixture was placed on a ceramic crucible located inside the horizontal quartz reactor. The heat treatment consisted of a heating ramp from ambient temperature to the final heat treatment temperature (850 °C) at a heating rate of 5 °C min^{-1}, followed by a 3 h plateau. Then, the system was cooling back to the initial temperature. He was selected as the inert gas with a flow rate of 700 ml min^{-1} [20–22]. The activated products were firstly washed with hydrochloric acid (5 M) to remove the KOH and then, with distilled water until neutral washings were obtained. The resulting materials were dried in air at 110 °C for 12 h to remove water prior to characterization [13,17,26].

2.5. Characterization of carbon materials

Surface area/porosity measurements were carried out using a Micromeritics ASAP 2010 sorptometer apparatus with N_2 at 77 K as the sorbate. The samples were outgassed at 453 K under vacuum (6.6×10^{-9} bar) for 16 h prior to analysis; specific surface areas were determined by the multi-point BET method, mesopore volume and size distributions were evaluated using the standard BJH treatment and micropore volume and size distribution were evaluated using the Horvath–Kawazoe (H–K) equation.

Temperature-programmed desorption of hydrogen (TPD-H_2) profiles were recorded on a Micromeritics AutoChem 2950 HP apparatus. Samples were heated up to 850 °C under He atmosphere at a heating rate of 15 °C min^{-1}, followed by a 3 h plateau, during which the H_2 in the outlet gas composition was monitored.

XRD analyses were carried out on a Philips X'Pert instrument using nickel filtered Cu Kα radiation; the samples were scanned at a rate of 0.02° $step^{-1}$ over the range $5^\circ \leq 2\theta \leq 90^\circ$ (scan time = 2 s $step^{-1}$). This technique was used to evaluate the graphitic nature of the carbon materials.

Average diameter and morphology of the different CNFs and CNSs were probed by transmission electron microscopy (TEM) using a Philips Tecnai 20T, operated at an acceleration voltage of 200 keV. Suitable specimens were prepared by ultrasonics dispersion in acetone with a drop of the resultant suspension evaporated onto a holey carbon supported grid. The average diameter was measured by counting ~200 CNFs and CNSs on the TEM images.

Temperature-programmed oxidation (TPO) was used to the qualitatively determination of the carbon materials crystallinity. The analyses were performed on 50 mg samples using a Micromeritics AutoChem 2950 HP apparatus with a flow of 50 ml min^{-1} of 20% (v/v) O_2/He mixture and a heating rate of 5 °C min^{-1} up to 1000 °C.

The elemental composition of the carbon materials were determined using a LECO elemental analyzer (model CHNS-932), which had an IR analyzer for carbon, hydrogen and sulfur and a TCD analyzer for nitrogen. Oxygen was assessed by difference up to 100%.

Temperature-programmed decomposition in helium was used to do a qualitative analysis of oxygenated groups formed in the surface of the carbon materials. Analyses were performed on 50 mg samples using a Micromeritics AutoChem 2950 HP apparatus with a flow of 100 ml min^{-1} helium and then heated (5 °C min^{-1}) up to 1000 °C.

Acid/base titrations were performed by immersing 25 mg of sample in 50 cm^3 solution of 0.1 M NaCl (blank) and 0.1 mM oxalic acid, acidified to pH 3 with HCl (0.1 M) and continuously stirred under He atmosphere. A 0.1 M NaOH solution was used as titrant, added dropwise (3 cm^3 h^{-1}) using a 100 Kd Scientific microprocessor-controlled infusion pump. The pH was monitored using a Dow-Corning pencil electrode coupled to a data logging and collection system (Pico Technology Ltd.) [27]. Surface acidity was presented in this paper as millimoles of NaOH needed to neutralize any surface groups of $pK_i \leq 7\,g^{-1}$ of carbon material, as successfully employed in related literature [28].

3. Results and discussion

Representative images of the parent (non-activated) samples are shown in Fig. 1. Amorphous carbon is an allotrope of carbon that does not have any crystalline structure and, thus, some short-range order can be observed. Graphite is a layered compound in which each layer, the carbon atoms are arranged in a hexagonal lattice with separation of 0.142 nm, and the distance between planes being 0.335 nm. CNSs are characterized by an agglomeration of spherical bodies with diameters in the range 200–500 nm. The presence of CNSs as conglomerates has been attributed to an accretion via the carbon atoms at the edge of the "curling" graphitic flakes, which contain dangling bonds with unpaired sp^2 orbitals at the open sites, in contrast to the chemically inert C_{60} [29]. Different types of CNFs can be obtained depending on their synthesis temperature. Platelet type structures (hexagonal planes perpendicular to the fiber axis) were produced at a synthesis temperature of 450 °C; *fishbone type* structures (graphene layers terminate on the surface with a determinate inclination angle) were predominant at a synthesis temperatures of around 600 °C, whereas, ribbon (hexagonal planes staked parallel to the fiber axis) type structures started to be produced at high temperatures (i.e., 850 °C).

Porous texture characterization measurements for the parent and activated carbon materials are listed in Table 1. It can be observed that the BET surface area of activated samples was, in all cases, significantly larger than that of the non-activated ones due principally to an increase of the micropore volume, thus showing the important effect that the treatment had on the porosity development of different carbon structures [20,22].

Nitrogen adsorption/desorption isotherms are presented in Fig. 2. Isotherms associated with different carbon materials (activated or not) can be attributed to a combination of types I and IV (according to the IUPAC classification). Thus, isotherms corresponding to amorphous carbon showed a high N_2 adsorption