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Influence of the nature of the metal hydroxide in the porosity development of carbon nanofibers

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ABSTRACT

In this study, highly porous carbon nanofibers (CNFs) were prepared by chemical activation in order to develop promising energy storage materials. The activation was performed at a temperature of 850 °C by using different metal hydroxides as the activating agents. Pore structures of the CNFs were analyzed using N_2/77 K adsorption isotherms. The presence of oxygen groups was analyzed by means of acid–base titration. The structural order (crystallinity) of the materials was studied by XRD and TGA analysis and the morphology and diameter distributions by means of TEM. The use of hydroxide of alkaline metals of low melting and boiling points (K, Rb, and Cs) led to the best results of porosity development. On the contrary, the pore opening was lower if the alkaline metal had a high boiling point (Na) or when alkali earth cations were used as activating agents. After the activation, the porous CNFs showed a decrease in diameter and scratches on their surfaces, as a consequence of the surface oxidation and opening of the graphitic layers, respectively. It was found that the specific surface area of the porous CNFs prepared using KOH and RbOH was more than 400 and 280 $m^2\ g^{-1}$, respectively, without loss of their fiber shape.

1. Introduction

Due to the particular structures and outstanding physical and chemical properties, carbon nanotubes (CNTs) and carbon nanofibers (CNFs) have been used in various applications, such as hydrogen [1], catalyst supports [2], and supercapacitors [3].

There are mainly three types of carbon nanofibers: the herringbone, in which the graphene layers are stacked obliquely with respect to the fiber axis; the platelet, in which the graphene layers are perpendicular to the fiber axis; and the ribbon, in which the graphene layers are parallel to the growth axis [4,5]. The morphology of CNFs depends on the temperature and C_2H_4/H_2 ratio used during the synthesis process and the catalytic metals and supports [6–8].

Comparing carbon nanotubes and nanofibers, the latter present a nanostructure made of graphite layers stacking which is more favorable for activation and adsorption phenomena [4]. In this regard, the specific surface area and porosity of carbons can be significantly modified by an activation process that removes the most reactive carbon atoms from the structure, increasing the surface area and porosity. Controlled pore size and pore size distribution are necessary for the application of those materials in a specific end use. The porous texture of the activated carbons depends strongly on both the activation process and the nature of the precursor. It has been shown [9–12] that some experimental variables have great influence on the porosity of the activated carbons prepared by chemical activation: the mass ratio activating agent/carbon material, the mixing method of the activating agent and parent carbon nanofiber, the temperature, the flow gas during the carbonization, and the activation time. Other parameters such the nature of the protector gas and the nature of the activation agent are also important and have not been considered extensively in the literature.

Most of the studies about activation of carbon material have considered KOH and NaOH as activation agents [9–13]. Chemical activation by hydroxides consists in solid–solid or solid–liquid reactions involving the hydroxide reduction and carbon oxidation to generate porosity [13–17]. 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 is independent of the hydroxide used and consists in the overlapping of redox processes [13,17]. The hydroxide reduction leads to H_2 and Na or K metals, whereas carbon is oxidized to carbonates (Na or K) according to the global reaction [18]:

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

In this work, we compare the effect of the metal present in different hydroxides during CNF activation: NaOH, KOH, RbOH, CsOH, $Mg(OH)_2$, $Ca(OH)_2$, $Ba(OH)_2$. Several characterization techniques, such as N_2 adsorption analysis, XRD, TGA, elemental composition, TPD-H_2, acid–base titration, and TEM, were used as a way to evaluate structural change in the activated CNFs.

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Structural changes in activated CNFs were related to the size of the metal parent in the hydroxide and its melting and boiling point used during the activation process.

2. Experimental

2.1. Preparation of CNFs

Carbon nanofibers were grown at atmospheric pressure in a fixed-bed reactor (quartz tube of 2.5 cm diameter and 75 cm length) located in a vertical oven at a temperature of 600 °C. In each synthesis run, 100 mg of the prepared catalyst (Ni/SiO_2) was placed in the center of the reactor and activated by heating (10 °C min^{-1}) in a flow dry 20% v/v H_2/He (100 cm^3 min^{-1}) at the desired reaction temperature (600 °C). The reduced activated catalyst was thoroughly flushed with dry He (100 cm^3 min^{-1}) for 1 h before introducing the C_2H_4/H_2 (4/1 v/v) feed. The growth time was 1 h. 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 [6–8].

2.2. Activation CNFs

The experimental setup used for the preparation of activated CNFs consisted of a horizontal quartz reactor tube with a conventional horizontal furnace. CNFs mixed with the activating agent were placed in a boat at the center of the reactor tube. CNFs were chemically activated with different agents (NaOH, KOH, RbOH, CsOH, $Mg(OH)_2$, $Ca(OH)_2$, $Ba(OH)_2$). CNFs were mixed with the activating agent (1:4 g/g or 1:1.15, 1:0.80, 1:0.46, 1:0.34, 1:0.80, 1:0.57, and 1:0.23 molar ratio for each activating agent, respectively) and distilled water (10 ml water for 2 g activating agent). The mixture was heated at 85 °C for 4 h under stirring and then dried for 12 h at 110 °C. The activating agent/CNFs mixture was placed on a ceramic crucible located inside a horizontal quartz reactor tube with a conventional horizontal furnace. 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, followed by a 3 h plateau. Then the system was cooling back to the initial temperature [4,10,11]. He was selected as inert gas with a flow rate of 500 ml/min. The activated product was first washed with hydrochloric acid (5 M) to remove the activating agent and then with distilled water until neutral washings was obtained. The resulting material was dried for 12 h at 110 °C in air to remove water prior to characterization [9,10].

2.3. Characterization of CNFs

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 multipoint BET method, pore geometry and size distributions were evaluated using the standard BJH treatment, and micropore size distributions were evaluated using the Horvath–Kawazoe (H–K) equation.

Temperature-programmed desorption of hydrogen (TPD-H_2) profiles was recorded on a Micromeritics AutoChem 2950 HP apparatus. The samples with NaOH, KOH, RbOH, CsOH, $Mg(OH)_2$, $Ca(OH)_2$, $Ba(OH)_2$were heated up to 850 °C under He atmosphere at a heating rate of 15 °C/min, 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 CuKα radiation; the samples were scanned at a rate of 0.02° $step^{-1}$ over the range $5° \leqslant 2\theta \leqslant 90°$ (scan time = 2 s $step^{-1}$). This technique was used to evaluate the crystallinity of the carbon nanofibers.

Diameter distribution and the morphology of the carbon nanofibers 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 ultrasonic dispersion in acetone with a drop of the resultant suspension evaporated onto a holey carbon supported grid. The diameter distribution was measured by counting ~200 CNFs on the TEM images.

Temperature-programmed oxidation (TPO) was used to determine the crystallinity of the carbon nanofibers. The analyses were performed on 10-mg samples using a Perkin-Elmer TGA7 termogravimetric analyzer with a flow of 50 ml min^{-1} of 20% v/v O_2/He mixture and with a heating rate of 5 °C min^{-1} up to 1000 °C.

The elemental compositions of the carbon nanofibers 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.

The carboxylic, phenolic, and lactonic groups were determined according to Boehm titration. These acid groups differ in their acidities and can be differentiated by neutralization with 0.05 N solutions of NaOH, Na_2CO_3, and $NaHCO_3$. The basic groups can be neutralized with 0.05 N solution of HCl. Therefore, 0.1 g of CNFs was placed in 10 ml of the commented solutions. The vials were sealed and shaken for 24 h and then filtered. The filtrate solution was pipetted and the excess of base or acid was titrated with HCl or NaOH 0.05 N, respectively. These solutions were added dropwise (3 cm^3 h^{-1}) using a 100 Kd Scientific microprocessor-controlled infusion pump and the pH was monitored using a Dow-Corning pencil electrode coupled to a data logging and

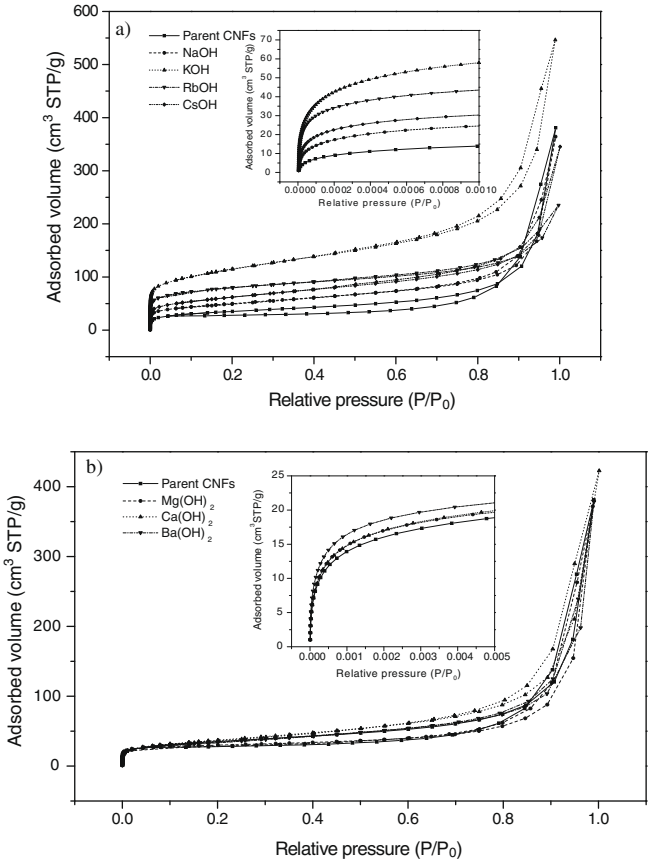

Fig. 1. N_2 adsorption–desorption isotherms of CNFs activated using: (a) alkali hydroxides, and (b) alkali earth hydroxides.