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Influence of the activating agent and the inert gas (type and flow) used in an activation process for the porosity development of carbon nanofibers

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ABSTRACT

Carbon nanofibers (CNFs) were activated with different activating agents (KOH, $KHCO_3$ and K_2CO_3). The effects of different activations conditions, including type of protector gas (He, Ar and N_2) and helium flow rate on the properties of activated carbon nanofibers were studied. The structural changes in activated CNFs were investigated using the following characterization techniques: N_2 adsorption isotherms at 77 K, XRD, temperature-programmed desorption of hydrogen, TEM, TPO and elemental composition.

The results showed that the surface area increased by a factor of 3.3, 2.0 and 1.8 referred to the parent CNFs after the treatment with KOH, K_2CO_3 and $KHCO_3$, respectively. In addition, KOH generated a greater pore volume than the other activating agents; micropores were mainly generated during the process. Finally, different carrier gases were added during the activation in order to study their influence on the pore opening behavior of CNFs. It was found that the activation degree increased in the following order: Ar < N_2 < He. When He was used as the carrier gas, the microporosity was strongly developed.

1. Introduction

The generation of ordered carbonaceous structures such as fullerenes, nanotubes and nanofibers is a burgeoning area of research in catalysis [1–3]. The properties of carbon nanotubes (CNTs) and carbon nanofibers (CNFs) have attracted considerable interest from both scientific and technological point of view: catalyst supports [4], polymer reinforcement agents [5], fuel cell electrodes [6], adsorbents [7], energy storage [8], etc. In recent years, new carbonaceous materials with original structures such as CNTs and CNFs have been considered as potential candidates for adsorbents precursors [9,10]. One problem is that these materials have a low specific surface area and are essentially mesoporous, which represents a limitation for adsorption, since this properly is strongly dependent on the remarkable surface and structural properties of such materials. Thus, a good adsorbent usually has a high specific surface area, which arises from the presence of a reasonable number of micropores and high adsorption capacity [11,12].

In that regard, the specific surface area and porosity of carbons can be modified significantly by an activation process that removes the most reactive carbon atoms from the structure, thus increasing the surface area and porosity. Chemical activation has been shown to be a very efficient method to obtain carbons with high surface area and narrow micropore distribution. The most important advantage of chemical activation vs. 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 [13] and the corrosiveness of the chemical activation process [14].

On the other hand, comparison of carbon nanotubes and nanofibers show that the latter have a nanostructure that consists of stacked graphite layers, a structure that is more favorable in terms of activation and adsorption phenomena [9]. In a previous study [13,15,16], we investigated the influence of different parameters on the synthesis of CNFs using different catalytic metals and supports. It should be noted that the herringbone-type CNFs (used in this study) consist of graphene layers stack obliquely with respect to the fiber axis in which the curvature of the surface is determined by the presence of square or pentagonal carbon rings in the hexagonal network [9]. The pore structure of the CNFs provides a large number of shallow pores at the outer surface in which the edges of the graphene layers are directly accessible [9,10].

In order to optimize the activation process and thus further improve the performance of the activated carbon material, it is necessary to investigate the effects of different activation conditions on the final porous texture of the material. Many factors such as the raw material, the KOH/carbon material ratio, the activation temperature and the activation time play an important role in the activation process. These factors have been extensively studied [14,17,18]. Other parameters such the nature of the activating

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agent and the nature and flow of the protector gas are also important but investigations into these factors have been less extensive.

The work described here compares the behaviors of chemical activating agents different in nature (hydroxide vs. carbonate) during the activation of CNFs: KOH, $KHCO_3$ and K_2CO_3. Furthermore, differences in the porous structures of CNFs activated from a single precursor (KOH) but using different inert gases (N_2, Ar and He) was investigated. Finally, the influence of the inert gas flow rate was also evaluated. N_2 adsorption analysis, XRD, TGA, elemental composition, TPD-H_2 and TEM were used to study the structural changes that take place during activation.

2. Experimental

2.1. Preparation of CNFs

Carbon nanofibers were grown at atmospheric pressure in a fixed-bed reactor (consisting of a 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 form the carbon product by leaching the primary product in hydrofluoridic acid (48%) for 15 h with vigorous stirring followed by filtration and washing [13,15,16].

2.2. Activation CNFs

The experimental setup used for the preparation of activated CNFs consisted of a cylindrical quartz reactor inserted in a conventional horizontal furnace. As activating agents KOH, K_2CO_3 and $KHCO_3$ were considered. Parent CNFs mixed with the activating agent (1:4 g/g) and distilled water (10 ml water per 2 g activating agent) were kept at 85 °C for 4 h under stirring and then dried for 12 h at 110 °C. After that, the resulting material, was placed in a crucible at the center of the furnace. The heat treatment consisted of a first heating ramp from room temperature to 850 °C at a heating rate of 5 °C min^{-1}, followed by a 3 h plateau. Then, it was cooled back to the initial temperature [9]. He, Ar or N_2 were selected as inert gases and fed to the system at flow rates of 500 or 150 ml/min. The activated product was firstly washed with hydrochloric acid (5 M) to remove the activating agent and then with distilled water until neutral washings was obtained. Prior to characterization, the resulting material was dried at 110 °C for 12 h in air to remove water [14].

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 multi-point BET method, pore geometry and size distributions were evaluated using the standard BJH treatment and micropore 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. Mixtures of the parent CNFs with the activated agent were heated up to 850 °C under He, Ar or N_2 atmosphere at a heating rate of 15 °C min^{-1}, followed by a 3 h plateau. H_2 in the outlet gas composition was continuously 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 $5° \leqslant 2\theta \leqslant 90°$ (scan time = 2 s $step^{-1}$). This technique was used to determine the crystallinity of the carbon nanofibers.

Diameter distribution and 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 ultrasonics dispersion in acetone and. A drop of the resultant suspension was 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 thermogravimetric analyzer with a 20% v/v O_2/He mixture flow of 50 cm^3 min^{-1} and a heating rate of 5 °C min^{-1} from room temperature to 1000 °C.

Elemental composition 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.

3. Results and discussion

3.1. Influence of the activating agent

The corresponding nitrogen isotherms at 77 K were used to compare the different activated CNFs. Data for raw and activated CNFs are shown in Fig. 1. As can be seen, according to the IUPAC classification, all of the isotherms correspond to a mixture of 1–4 types associated with the presence of both micropores and mesopores. Once micropores are filled (Po < 0.03), the adsorption of the non-microporous surface begins. It seems clear that the adsorbed amount of N_2 for the activated samples both in the micropore and the mesopore zone increased if it is compared with that of the parent material. The presence of a hysteresis loop indicates that large quantities of non-micropores are present (due to capillary condensation in mesopores, macropores or on the external surface). On the other hand, $KHCO_3$ presents a slightly lower activation effect than K_2CO_3, but both proved to be less efficient than KOH. These results can also be appreciated in Table 1, in which

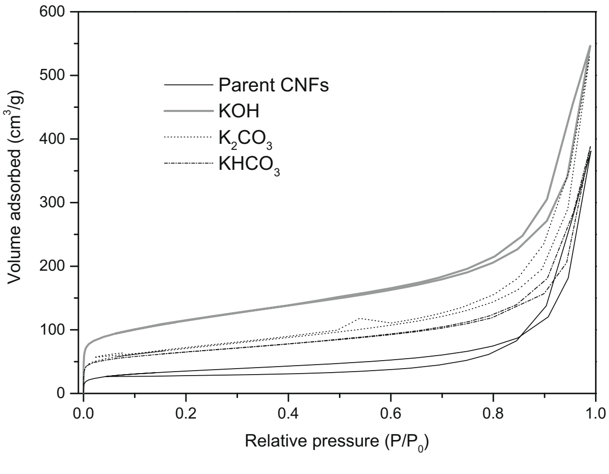

Fig. 1. Isotherms for the CNFs activated with different chemical agents.