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SHORT COMMUNICATION

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ADSORPTION CHARACTERISTICS OF ACTIVATED CARBON HOLLOW FIBERS

Carbon hollow fibers were prepared with regenerated cellulose or polysulfone hollow fibers by chemical activation using sodium phosphate dibasic followed by the carbonization process. The activation process increases the adsorption properties of fibers which is more prominent for active carbone fibers obtained from the cellulose precursor. Chemical activation with sodium phosphate dibasic produces an active carbon material with both mesopores and micropores.

Key words: activated carbon hollow fibers; adsorption characteristics; regenerated cellulose; polysulfone.

Active carbon can be made with a wide range of structures, compositions and properties, depending on the nature of the organic precursor and process parameters. Accordingly, there are various kinds of porous carbon materials with different surface areas and a range of pore sizes [1]. Besides classical granular or powder active carbon forms there are new forms of active carbon: fibers and textiles, carbon molecular sieves, porous carbon membranes, carbon aerogels or cryogels, activated carbon hollow fibers (ACHF) [2,3]. These materials contain micropores (a pore size up to 2 nm) and mesopores (a pore size of 2-50 nm) which are the most useful pore sizes for adsorption, kinetic sieving and catalysis.

Hollow fibers are widely used as elements in modulus of hollow fibers membranes. The applications of this technology for the separation and purifycation in industry and medicine are numerous. These include the preparation of drinkable, high quality water, hemodialyzers in pharmaceutical industry, gas separation for industrial application, *etc*.

The adsorption characteristics of active carbons depend on the raw material and the methods and conditions used in carbonization and activation processes. Amongst the precursors applied for the preparation of carbon hollow fibers are polysulfone (PSF) [4,5], cellulose acetate [6], mesophase pitch [7], polyacrylonitrile (PAN) [3,8] and polyetherimides [9] and polyimides [10].

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The studies of activated carbon hollow fibers formation are, however, quite scarce. Some research was done with PAN as a precursor [3], and with filling or impregnating hollow fibers with activated carbon [5,6]. ACHF was obtained when the PAN hollow fibers were pretreated with ammonium dibasic phosphate and then further oxidized in the air, carbonized in nitrogen, and activated with carbon dioxide. The specific surface area of this ACHF varied from 269-1422 m^2/g as well as the surface area of mesopores from 34--1234 m^2/g, respectively, depending on the activation temperature [3].

In this study, the influence of the precursor, cellulose (HCF) and polysulfone (HSF) hollow fibers, on the adsorption properties of obtained ACHF after the chemical activation with a sodium dibasic phosphate aqueous solution is presented.

EXPERIMENTAL

HCF and HSF were used as a carbon and active carbon material precursors. Prior to the experiments these fibers were roughly cut. The carbon hollow fibers were prepared in one single step through the carbonization process. The carbonization process was performed in a nitrogen atmosphere up to 1273 K. The heating rate was 5 K/s. The samples were kept at the final temperature for 1 h.

The ACHFs were chemically activated before the carbonization process. For this process HCF or HSF were soaked in the aqueous solution of sodium phosphate dibasic for 1 h. The wet fibers were dried at 120 °C. The activation process was followed by the carbonization process, as previously described. Acti-

vated carbon samples were washed in distilled water to remove traces of soluble impurities.

The adsorption of nitrogen at 77 K, which presents a typical physical adsorption process, is the most current method for the porous solids characterization. The adsorption characteristics of ACHFs have been experimentally and numerically characterized according to their specific surface area, a micropore volume, a mean pore size distribution and the surface of mesopores and macrospores (external surface area).

The nitrogen adsorption/desorption isotherms at 77 K were determined using the gravimetric McBain balance method. Before obtaining sorption isotherms, the ACHF sample was degassed at the temperature of 523 K to remove any contaminants that may be present on the ACHF surface.

The values of the specific surface area (S_{BET}) were obtained by a multi-point analysis of adsorption isotherms applying Brunauer-Emmet-Teller (BET) equation [11].

Pore volume (V_p) and pore size (r_p) distribution were determined from the nitrogen desorption isotherms using Barrett, Joyner, and Halenda (BJH) method [11].

The α_s-plot [11] was used to calculate the external surface area (S_{ext}), as well as the total surface area (S_{tot}), and the micropore volume (V_{mic}). Non-graphitized carbon black BP 280 (S_{BET} = 40.2 m^2/g) was used as a reference adsorbent.

A scanning electron microscope (SEM; JEOL Model) was used to examine the cross section of activated carbon hollow fibers.

RESULTS AND DISCUSSION

In the process of obtaining carbon hollow fibers from a cellulose precursor, the individual fibers are found to have adhered to their neighbors making a unique mass of isotropic glassy carbon after the carbonization process. The reason for that could be an intramolecular rearrangement of cellulosic units to levoglucosan (1,6-anhydro-β-*d*-glucopyranose). The carbonization process of the polysulfone hollow fibers produced fine carbon hollow fibers with a small surface area (S_{BET} = 3.2 m^2/g).

The adsorption characteristics of chemically activated hollow fibers, both cellulose and polysulfone, increased after carbonization. It is well-known that nitrogen adsorption at 77 K is a convenient and powerful method to evaluate specific surface areas, pore volumes, and pore size distributions of porous solids. Isotherms of nitrogen adsorption and desorption at 77 K by ACHF are shown in Figure 1.

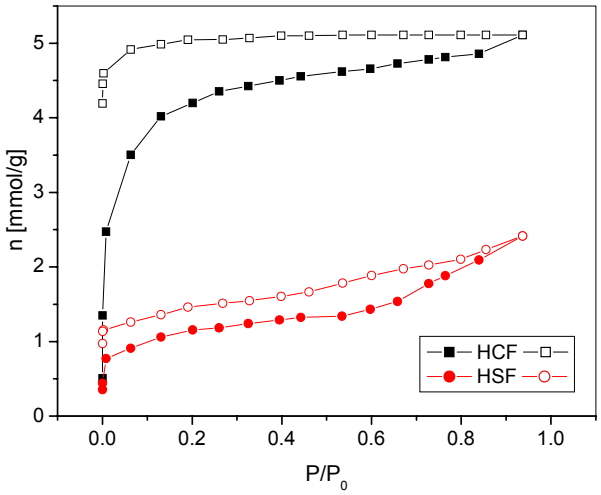

Figure 1. Nitrogen adsorption-desorption isotherms for ACHF: solid symbols - adsorption, open symbols - desorption.

These sorption isotherms exhibit hysteresis type H4, according to IUPAC classification and indicate the presence of mesopores and slit shaped micropores [12]. Also, it is obvious that ACHF obtained from hollow cellulose fibers has better adsorption characteristics which are confirmed by calculation. The values of the specific surface area (S_{BET}) calculated using the BET equation as well as the micropore volume (V_{mic}), the external (S_{ext}) and the total surface area (S_{tot}), derived from the α_s-plots, are shown in Table 1. The α_s-plots are shown in Figure 2.

Table1. Adsorption characteristics for ACHF determined from BET and α_s-plots

Sample	S_{BET} / m^2 g^{-1}	V_{mic}/ cm^2 g^{-1} STP	S_{ext}/ m^2 g^{-1}	S_{tot}/ m^2 g^{-1}
HCF	341	0.038	97	157
HSF	88	0.008	14	20

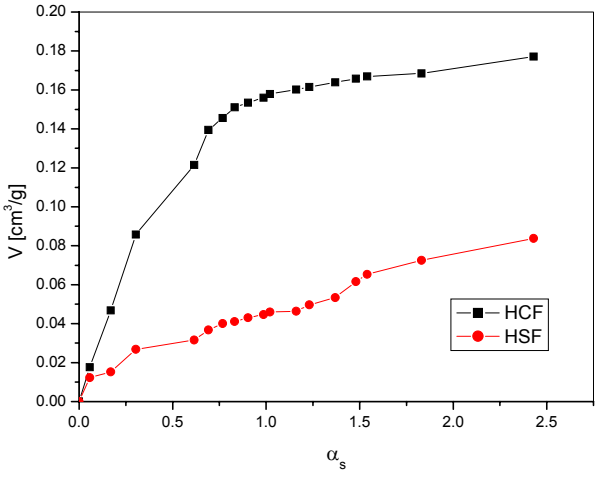

Figure 2. α_s-plots for activated carbon hollow fibers obtained from different precursors.

The values of the surface area (S_{tot}) calculated using α_s-plots are lower than those evaluated from the BET plot. The reason for that could be that the reference adsorbent does not have a structure similar to ACHF. Moreover, calculated adsorption characteristics for ACHF samples obtained from HCF are multiplied higher than those for the HSF precursor. Both samples posses a very pronounced external surface area that confirms developed mesoporous structure. The size of mesopores is in the range of 2-12 nm (see Figure 3).

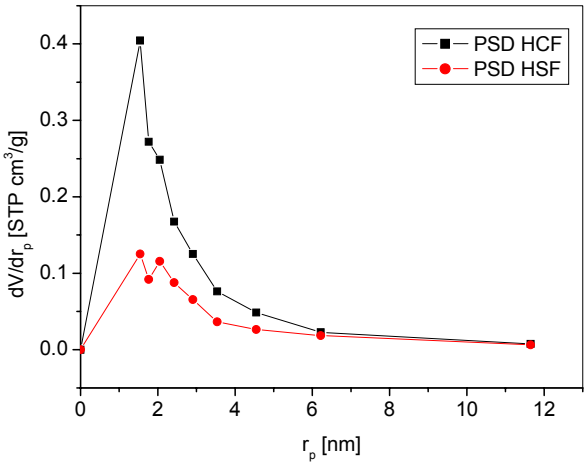

Figure 3. Pore size distributions (PSD) for ACHF.

Activated carbon hollow fibers obtained from polysulfone precursor are presented by SEM micrograph in Figure 4.

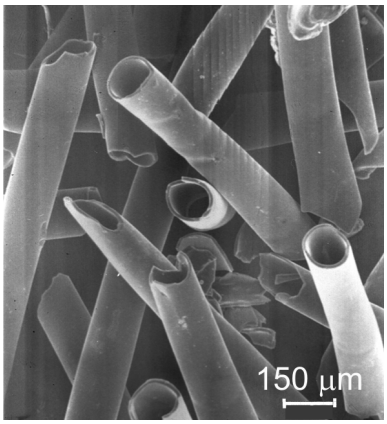

Figure 4. SEM micrograph of activated carbon hollow fibers obtained from polysulfone precursor.

CONCLUSIONS

Activated carbon hollow fibers were prepared through the chemical activation of cellulose and polysulfone hollow fibers followed by the carbonization process. The sodium phosphate dibasic as an activator, in addition to micropores formation, influences the formation of a mesoporous structure in activated hollow carbon fibers.

Hollow cellulose fibers are more convenient for the preparation of the active carbon hollow fibers than the hollow polysulfone fibers because after the activation and carbonization processes they have a larger specific and external surface area. Also, hollow cellulose fibers are cheaper.

Various kinds of porous carbon materials are widely used as adsorbents, catalytic supports, *etc*. Active carbon hollow fibers compared to classic active carbon possess higher ratio of geometric area to volume which improves the heat and a mass transport. In the future work, it would be interesting to investtigate the effects of other activation methods on the adsorption characteristics of these materials, as well as their possible application for the adsorption of various contaminants in fluids, or for catalytic supports.

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