POROSITY OF CARBON NANOTUBES

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Progress in the large-scale production of carbon nanotubes has opened up possibilities for new applications in some areas of adsorption and catalysis. In this paper we will discuss the characterization of single and multiwalled nanotubes by nitrogen, butane and methane adsorption. Nitrogen adsorption data will be used to calculate pore size distributions of the nanotubes. The incorporation of carbon nanotubes into pitch to change the porosity of the resultant activated carbon will also be discussed. By altering the pore structure of the pitch-based carbon fibers from highly microporous to a wider size distribution of micro and mesopores, new applications of the fibers can be envisaged in areas of environmental science and catalysis.

INTRODUCTION

Recently, methods have been developed at the University of Kentucky to synthesize high purity multiwalled carbon nanotubes (MWNT) in quantities that allow the study of the bulk properties of the material. Continuing work is aimed at improving both the rate of production, by operating on a larger scale, and a simplified process to reduce costs. The suitability of use of nanotubes in applications of gas adsorption, separation and catalysis has been investigated. Currently there is little reliable information available in the literature concerning the pore structure and surface properties of pure carbon MWNTs. Most work have been conducted on samples of low or uncertain purity that may contain high concentrations of amorphous and/or graphitic carbon as a contaminant. In contrast, materials produced at the Center for Applied Energy Research (CAER) are typically better than 95% pure MWNT.

The core diameter of single wall nanotubes (SWNT) is close to 1 nm, with little variation between samples, a value which falls in the range normally defined by micropores (pore entrance diameter < 2nm). MWNT, in contrast, show a small variation in core diameter, typically ranging from 3.5 to 7nm, and hence fall in the mesopore range (diameters 2 to 50nm). The uniformity of the nanotubes and thus the narrow distribution of pore sizes present in the sample, should make them excellent materials for gas separation applications. As an example, the diffusion rate of methane into MWNT bundles has been found to be up to ten times faster than that for butane, offering the prospect for the development of systems providing efficient molecular sieves.

Another objective of the current work is to use carbon nanotubes to modify the porosity of pitch-based activated carbon fibers (ACFs). These are normally derived from isotropic petroleum pitch precursors through a sequence of well-defined process stages, culminating in activation of the isotropic carbon fibers in steam or nitrogen, generating the high surface area and pore structure that is typified by a narrow distribution of micropores. The objective of dispersing mesoporous carbon nanotubes in the isotropic pitch before processing into activated carbon fibers is to produce fibers that are not only significantly more mesoporous, but also show significant improvements in other properties, e.g. strength and electrical conductivity. This could enable the procurement of activated carbon fibers with pore structures tailored to specific environmental applications. This paper will focus on the porosity characterization of multiwalled nanotubes and comparison with single walled tubes, and the introduction of these tubes into pitches to alter the pore structure of the product activated carbon.

EXPERIMENTAL

Single wall nanotubes (SWNTs) manufactured by Carbolex Inc. using a carbon arc process with Ni/Y catalyst, were purified by refluxing in 2M nitric acid for 24 hours, filtered and then sonicated in dimethyl sulphoxide (DMSO) for 12 hours before drying. Multiwalled carbon nanotubes were produced at CAER by the catalytic decomposition of a ferrocene-xylene mixture at a temperature of about 700°C and at atmospheric pressure (1). Scanning electron microscopy (SEM) was used to estimate the purity of the MWNT samples. One of the MWNT samples was leached in hydrochloric acid to reduce the amount of iron catalyst from an as-produced concentration of about 5%, in order to determine its affect upon pore structure and accessibility. In a parallel series of experiments, the effect of the inclusion of carbon nanotubes in a pitch matrix precursor on the porosity of the active carbon derived from it was determined. A sample of SWNT suspended in DMSO was dispersed in the pitch by intimately mixing the suspension with a solution of the pitch in a suitable solvent. A high power ultrasonic probe was used to ensure that the nanotubes were completely dispersed before the solvents were recovered by distillation. The pitch samples were then activated by heating in a steam atmosphere at 877°C to generate an active carbon. Characterization of the pore structures was carried out using an OMNISORB 610 instrument to obtain nitrogen adsorption isotherms at 77 K. The mesopore volume, surface area and pore size distribution were calculated using the BJH method (2).

RESULTS

Porosity of Nanotubes

Adsorption isotherms of SWNT and MWNT are compared in Fig. 1. The MWNT sample is ~100% purity as determined by SEM. The adsorption isotherms for both samples are typical of mesoporous carbons, with the MWNT giving considerably higher nitrogen adsorption. The mesopore size distribution of the two samples is shown in Figure 2. The multiwalled sample clearly has a higher mesopore volume with an average pore size of ~3.5 nm. This corresponds approximately to the diameter of the central core of the MWNTs as determined by transmission electron microscopy to be in the range of 3-7 nm, Figure 3. Elsewhere, it has been shown that the average pore diameter of MWNTs is 4-6 nm (3). The calculated mesopore volumes of MWNTs and SWNTs are shown in Table 1. The SWNT have a mesopore volume of 0.05 cc/g while that of the pure MWNT sample is about 0.45 cc/g.

Table 1. Mesopore volume of different nanotube samples.

Sample ID	Purity (% MWNTs)	Mesopore volume(cc/g)
SWNT	~100%	0.05
MWNT-A	~95%	0.47
MWNT-B	~100%, leached	0.48

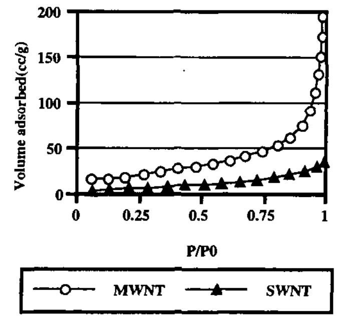

Figure 1. N_2 Adsorption isotherm of MWNT and SWNT

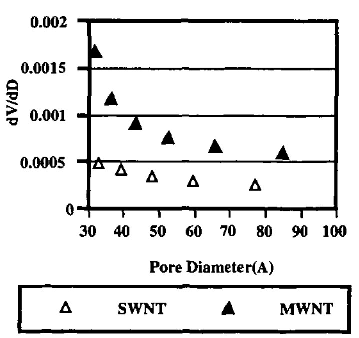

Figure 2. Pore size distribution of SWNT and MWNT

Observations by TEM have shown that small iron particles are present at the ends of the tubes, a consequence of their catalyzing nanotube growth. They are also found intermittently along the core of the innermost tube and in this location may not be accessible by the hydrochloric leaching agent. The acid treatment removes approximately 50% of the iron catalyst and probably improves access to the core of the MWNTs by removing iron from the ends. Even though the total mesopore volume is not significantly enhanced, Table 1, it does seem to broaden the mesopore size distribution slightly.

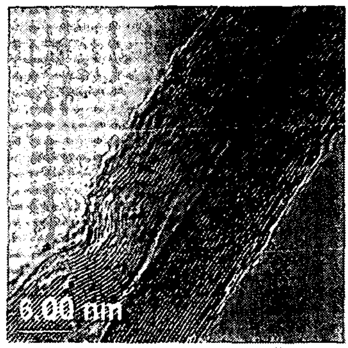

Figure 3. TEM micrograph of MWNT

Addition of SWNTs to pitch to modify the pore structure of activated carbons

A nitrogen adsorption isotherm of activated carbon derived from pitch powder is shown in Figure 4 together with that of the pitch with 5% SWNT incorporated. The pure petroleum pitch based carbon has a very microporous structure, illustrated by the flat isotherm, whereas the pitch with SWNT incorporated has a mesoporous structure, shown by the higher adsorption of nitrogen at high partial pressure. This isotherm is typical of a mesoporous activated carbon. The inclusion of SWNT in the precursor pitch has generated a high mesopore volume in the product active carbon without impairing the retained microporosity. The pore size distribution of the pitch with and without nanotubes is shown in Figure 5. It is evident that the activated carbon has a very narrow pore structure while the carbon with SWNT has a broader pore structure with more porosity in the mesopore range (20-500A).

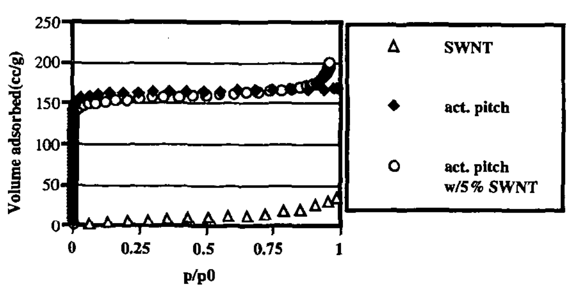

Figure 4. N_2 adsorption isotherms of activated pitch and activated pitch with SWNT

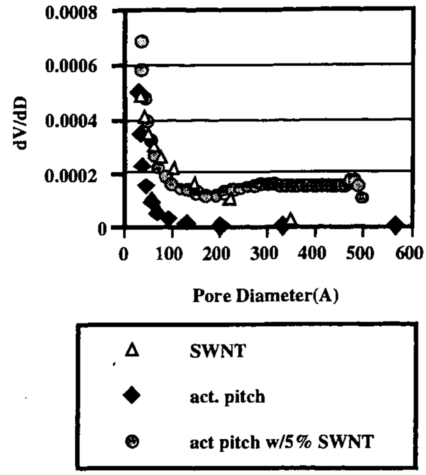

Figure 5. Pore size distribution of activated pitch and activated pitch with SWNT

ACKNOWLEDGEMENTS

The authors wish to acknowledge Rodney Andrews, David Jacques and Apparao Rao at the CAER for supplying samples of MWNTs and Carbolex Inc. for supplying SWNTs. We also acknowledge the financial support from the NSF MRSEC grant DMR - 9809686. The TEM micrograph was taken by X. Fan, Department of Chemical and Materials Engineering, University of Kentucky.

REFERENCES

1. Andrews, R., Jacques, D., Rao, A. M., Derbyshire, F., Qian, D., Fan, X., Dickey, E.C., Chen, J., Chem Phys Lets, 1999, April 16.
2. Gregg, S.J, Sing, K.S.W, in "*Adsorption,Surface Area and Porosity*", 2nd ed., Academic, London , 1982, 94-100.
3. Bonnamy, S., Gaucher, H., Metenier K., Pellenq, R., Nalimova V., Frackowiack, E.. and Beguin, F., Abstract presented at the British Carbon Group, Leeds, 1998.