

HIGH-RESOLUTION MICROPORE ANALYSIS OF SYNTHETIC POROUS CARBONS

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Introduction

Active carbons play an important role in many areas of modern science and technology, such as purification of liquids and gases, separation of mixtures and catalysis (1, 2). The usefulness of active carbons results from their remarkable surface and structural properties, which manifest themselves in their high specific surface areas and sorption capacities (1-3). These in turn arise from the presence of a significant amount of micropores (according to IUPAC recommendations, pores are classified as micropores of width below 2 nm, mesopores of width between 2 and 50 nm and macropores of width above 50 nm). Active carbons are obtained by carbonization of various carbonaceous materials of natural or, more recently, synthetic origin. The carbonization is followed by chemical or physical activation (1, 2). The properties of active carbons can be tailored by a proper choice of carbonization and activation conditions, but the structure of carbonaceous precursors significantly influences the final product (3). The latter limitation can be overcome by using synthetic carbonaceous materials, such as phenolic (4) or styrene-divinylbenzene (5, 6) resins. The resulting synthetic active carbons were reported to have improved sorption (5) and mechanical (6) properties.

In the current study, several samples of synthetic active carbons obtained via controlled carbonization of phenolic resins were characterized using low temperature nitrogen adsorption over a wide range of pressures. The surface area of the samples was calculated using the standard BET method (7). The micropore volume and the external surface area were assessed from the high resolution α_s -plot method (7-10). In the latter method, a macroporous nongraphitized carbon black BP 280 (10) was used as a reference adsorbent. The pore size distribution (PSD) was calculated using the DFT software from Micromeritics (Norcross, GA) (11).

Experimental

Synthetic active carbons were obtained by controlled carbonization of phenolic resin precursors at the Corning Research Center (Corning, NY). The nongraphitized carbon black BP 280 was acquired from Cabot Co. (Special Blacks

Division, Billerica, MA, USA).

Adsorption measurements were performed using an ASAP 2010 volumetric adsorption apparatus from Micromeritics (Norcross, GA). Before measurements, the samples were degassed at 473 K for 2 hours in the degas port of the adsorption analyzer.

Results and Discussion

Shown in Figure 1 is an adsorption isotherm for the active carbon A. The adsorption isotherms measured for other samples (B, D, E) occurred to be quite similar in overall shape. One can notice a pronounced step related to the micropore filling at relative pressures close to 10^{-5} . Subsequently, the adsorbed amount rises gradually with the pressure increase. After the relative pressure of about 0.1 is reached, the further increase in gas uptake is relatively small, which indicates low mesopore volume of the sample. However, the pore structure of the active carbons under study seems to be quite readily accessible for nitrogen molecules, since the equilibration times during the measurements were not excessively long (3) and there was no evidence of low pressure hysteresis loops (7) on the adsorption-desorption isotherms.

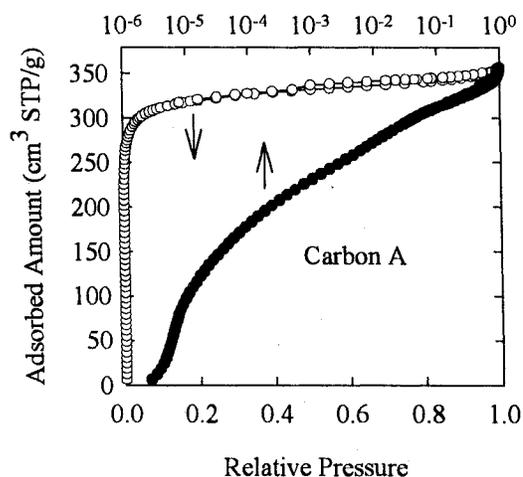


Figure 1. The adsorption isotherm for the active carbon A.

Surface and structural parameters for the active carbons are listed in Table 1. Adsorption data for a relative pressure range from 0.04 to 0.14 were used in the BET calculations. The total pore volume V_t was assessed converting the amount adsorbed at a relative pressure of 0.99 (expressed as a volume of the adsorbed gas) to the volume of the liquid adsorbate. The micropore volume and the external surface area were calculated using the high-resolution α_s -plot method. A macroporous nongraphitized carbon black Cabot BP 280 ($S_{\text{BET}} = 40.2 \text{ m}^2/\text{g}$) was used as a reference adsorbent. The adsorption properties of the BP 280 were compared (12) and found to be in a good agreement with previously reported adsorption data (9) for a nongraphitized carbon black.

Table 1. BET specific surface area S_{BET} , total pore volume V_t , micropore volume V_m and external surface area S_{ex} for the active carbon samples under study.

Sample	S_{BET} (m^2/g)	V_t (cm^3/g)	V_m (cm^3/g)	S_{ex} (m^2/g)
A	1170	0.55	0.49	40
B	700	0.33	0.29	20
D	890	0.39	0.38	< 10
E	870	0.40	0.37	20

The data listed in Table 1 show that the active carbons under study exhibit some differences in their surface areas and pore volumes. However, they have quite similar micropore size distributions (PSDs). Shown in Figure 2 is the PSD calculated using the DFT software (Micromeritics) for the active carbon A. In the case of all the samples, micropores of the size ca. 0.7 nm are the most abundant, but there are also noticeable amounts of larger micropores. Especially in the case of the carbon A, the latter micropores significantly contribute to its total microporosity. It was demonstrated that high resolution α_s -plot curves (not shown) provide some insight into microporous properties of the samples, allowing for a crude estimation of the micropore size.

Conclusions

Active carbons obtained from phenolic resin precursors were characterized using low temperature nitrogen adsorption measurements over a wide range of pressures. All the samples were shown to be essentially microporous. The most prominent feature of the active carbons under study is the presence of appreciable fractions of small micropores of width about 0.7 nm. Moreover, the samples exhibit variable amounts of wider micropores. It was shown that although the DFT software allows for a detailed characterization of microporous samples, alternative methods, such as the high

resolution α_s -plot are also useful for the micropore analysis.

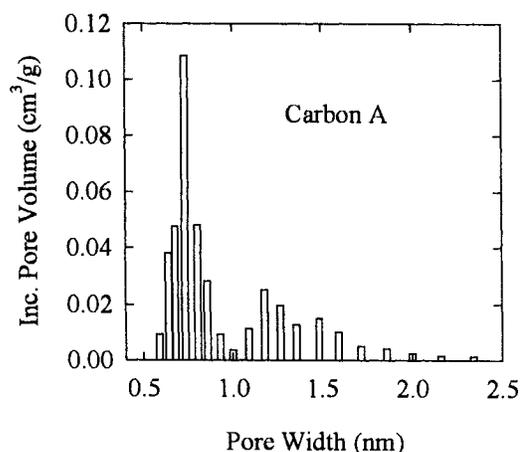


Figure 2. The micropore size distribution for the carbon A.

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