POSTER

EVALUATION OF THE SPECIFIC SURFACE AREA AND TOTAL POROSITY OF ACTIVE CARBONS BY THERMOGRAVIMETRY

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Introduction

Active carbons are structurally and energetically heterogeneous adsorbents because they possess a complex porous structure and various surface groups [1]. Their porous structure contains micropores (widths below 2 nm), mesopores (widths between 2 and 50 nm) and macropores (widths greater than 50 nm). In many active carbons over 70% of the total pore volume arises from the micropores. Thus, determination of the microporous structure is one of the key problems in characterization of active carbons.

Adsorption-desorption isotherms are commonly used to determine the specific surface area, total porosity and pore-size distribution of active carbons. The micropore volume is usually determined by the t-plot or α_s-plot analysis, which bases on the comparison of the adsorption isotherm measured on a given active carbon with that on a non-porous reference carbon. However, a quantitative characterization of the structural heterogeneity of micropores requires accurate adsorption data measured at very low pressures. Although sorption methods are valuable, they are quite time-consuming. There is a great interest in developing simple and effective methods for characterization of novel nanoporous materials and optimization their preparation conditions.

Thermogravimetry is a simple technique to measure the weight-loss of a sample as function of temperature or time. It was suggested previously [2-4] that this technique can be employed to investigate porous structures of active carbons. In the current work a systematic study was carried out in order to make some recommendations concerning determination of the sorption properties of active carbons from high-resolution thermogravimetric measurements. Sorption and high-resolution thermogravimetric measurements were performed and correlated for 29 active carbons of different surface and structural properties.

Experimental

The weight-loss data were measured as a function of temperature for 29 active carbons immersed in n-butanol and n-heptane. Active carbons were obtained from various sources such as: Barnebey-Cheney (Columbus, OH), Calgon Carbon Co. (Pittsburgh, PA), Norit Co. (Amersfoort, The Netherlands) and ZSDD (Hajnowka, Poland). Some samples were prepared and modified in the Sorption Laboratory (Cracow, Poland).

Thermogravimetric (TGA) measurements were carried out by using a TA Instruments, Inc. (New Castle, DE) model TGA 2950 high-resolution thermogravimetric analyzer. The instrument was equipped with an open platinum pan and an automatically programmed temperature controller. The TGA curves were measured as follows: about 0.05 g of each active carbon was placed in the TGA pan and heated in a nitrogen atmosphere at a rate of 5 K/min in order to remove the physically adsorbed species. When the furnace reached 473 K, it was turned off and the sample allowed to slowly cool to ambient conditions with the furnace closed and nitrogen flowing. The furnace was opened, enough liquid added to the pan to immerse the sample, the furnace closed and the sample equilibrated for 1 hr. Subsequently, weight-loss curves were measured over a temperature range from 293 to 573 K. Between thermal events the maximum heating rate was set at 5 K/min. The resolution and sensitivity parameters were set at 4 and 6, respectively.

Equilibrium adsorption isotherms of argon were measured at 77.5 K on the active carbons studied using a custom-built sorption apparatus described in Ref. [5]. Before sorption measurements each carbon sample was outgassed at 473K. Argon isotherms were used to calculate the BET specific surface area (S_{BET}) and total pore volume (V_t), which was obtained from the amount adsorbed at $p/p_o = 0.98$. The S_{BET}- and V_t-values were correlated with the corresponding quantities evaluated

from the high-resolution thermogravimetric data.

Results and Discussion

The TGA thermodesorption curves were measured for n-butanol and n-heptane on all active carbons studied. A typical weight-loss/temperature curve for a carbon sample immersed in n-butanol or n-heptane contains an initial distinct step, which is associated with evaporation of the excess liquid, and a decreasing segment, which reflects evaporation of adsorbate molecules from the meso- and micropores and their desorption from the carbon surface. Since in high-resolution TGA temperature is not a linear variable, the weight-loss/time curves should be used to estimate the total amounts adsorbed in the pores and on the surface. As can be seen in Figure 1, which presents typical time-dependent

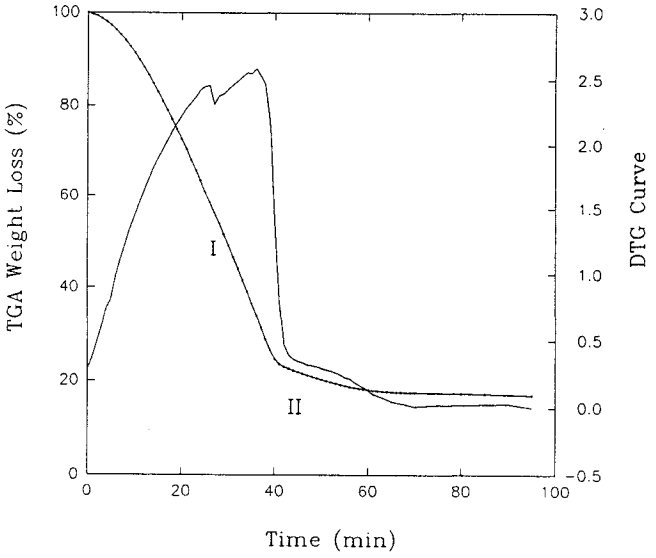

Figure 1 - The TGA weight-loss curve and its derivative (DTG) for thermodesorption of n-butanol from an active carbon. The points I and II refer respectively to the total adsorption capacity (total porosity) and the amount adsorbed in the pore walls.

TGA data for one immersed carbon sample, the DTG curve is helpful in localization of characteristic points on the TGA weight-loss curve. The point I on the TGA curve relates to the total adsorption capacity, whereas the point II provides information about the specific surface area and the micropore volume. The values of the weight-loss at the point I and II were evaluated for all samples and compared respectively with the total pore volumes and the BET specific surface areas, which were obtained from argon sorption data. A satisfactory correlation between the TGA characteristic values and the sorption parameters was obtained for all data sets. An illustration is shown in Figure 2, which shows a linear relationship between the BET specific surface area evaluated from argon sorption data and the TGA values obtained for n-butanol.

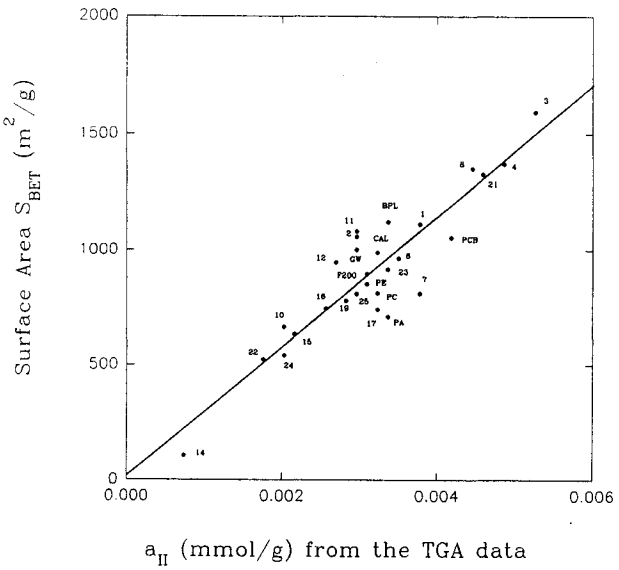

Figure 2 - Linear relationship between the BET specific surface area evaluated from argon adsorption data and the TGA weight-loss II (see Figure 1) obtained for n-butanol. Symbols at experimental points denote various active carbons.

Conclusion

A comparison of the sorption and TGA characteristic parameters for many active carbons showed that the high-resolution TGA data for n-butanol and n-heptane can be used to evaluate the specific surface area and total porosity of carbonaceous materials.

References

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