Characterization of microporous carbons by using TGA curves measured under controlled conditions[1]

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Abstract

Microporous active carbons of differing structural and surface properties were studied by thermogravimetry (TGA) under controlled conditions. Weight loss curves were measured for various carbon samples wetted and saturated with water, *n*-butanol, benzene and *n*-heptane using a high-resolution thermogravimetric analyzer. This analyzer is capable of maintaining controlled conditions. Analysis of the TGA curves showed that molecules desorb from the surface via a multi-step process. For the samples wetted with liquids the initial step reflects evaporation of the excess liquid. The subsequent steps, observed for both types of samples (wetted in liquids and saturated in their vapors), reflect evaporation of adsorbate from pores and its thermodesorption from fine pores and from the carbon surface. These latter features of the TGA curves were used to obtain information about porosity and surface heterogeneity of the active carbons studied.

Keywords: TGA; Microporous carbon; Controlled conditions

1. Introduction

Active carbons are very popular adsorbents because of their widespread applications in industry, science and everyday life [1]. These materials possess a well-developed porous structure, which is a combination of micropores, mesopores and macropores [1–3]. An important feature of their structure is a large number of slit-like micropores of different sizes and shapes formed between twisted aromatic sheets of the matrix. Thus, the pore-size distributions for typical active carbons are complex and cover a wide range of

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pore widths. In addition to a great non-uniformity of the porous structure of active carbons, these materials exhibit a strong surface heterogeneity due to the presence of various functional groups, impurities and defects in aromatic sheets of the matrix.

Growing use of active carbons in science, technology and everyday life requires their many-faced characterization. Usually, the equilibrium sorption measurements are used to evaluate their surface and structural properties such as: specific surface area, adsorption capacity, total pore volume and microporosity [1–4]. Because of high microporosity of active carbons, accurate measurements of sorption on these solids are time consuming and often require a specially constructed apparatus. However, the use of commercially available equipment is often limited to simple gases and vapors. Thus, there is considerable interest in elaborating simple and quick methods to evaluate the sorption and surface properties of microporous active carbons. Among various methods, thermal analysis is a simple technique, which has been used commonly to study decomposition and thermal stability of various materials [5]. In contrast to sorption measurements, thermoanalytical techniques have no special limitations with respect to adsorbates used.

In the current work high resolution thermogravimetry (HR TGA), which utilizes the slow heating procedure under controlled conditions in order to increase the analytical resolution, has been used to study the sorption properties of microporous active carbons with respect to water and organic liquids such as: water, n-butanol, benzene and n-heptane. The long-term objective of this work, which supplements previous research [6–10], is the elaboration of optimal conditions for utilizing high resolution thermogravimetry to characterize porous solids.

2. Experimental

2.1. Thermogravimetric measurements

Thermodesorption of water, n-butanol, benzene and n-heptane from the surface of four active carbons was measured in a nitrogen atmosphere using a TA Instruments Inc. (New Castle, DE, USA) model TGA 2950 high-resolution thermogravimetric analyzer. The instrument was equipped with an open platinum pan and an automatically programmed temperature controller. The active carbons were obtained from Barnebey-Cheney (OH, USA). Prior to making the TGA measurements, each carbon was outgassed at 150°C in order to remove the physically adsorbed species. For each carbon/adsorbate system, two types of samples were prepared: (i) by immersing a given carbon in a pure liquid, and (ii) by exposing it to the vapor of the same liquid in a desiccator.

Immersion of each carbon sample was carried out in a quartz vessel by adding a given pure liquid in excess. Subsequently, the immersed sample was sonicated for 1 h in order to ensure complete wetting, and it was allowed to settle for an additional 8 h. The second type of sample was prepared by exposing about 100 mg of each carbon to a given vapor in a desiccator for 2 days.

The thermogravimetric (TGA) curves, which give the dependence of the weight loss of a sample as a function of temperature or time, were measured over a temperature range from 20 to 400°C. The heating rate was regulated automatically by the instrument

in order to maintain a constant temperature during a given thermal event. The maximum heating rate between thermal events was set at 5°C min⁻¹. The resolution and sensitivity parameters were 4 and 6, respectively.

2.2. Adsorption measurements

Equilibrium adsorption isotherms of benzene vapor were measured on the active carbons studied using a vacuum-sealed apparatus custom-built according to McBain and Bakr's gravimetric method [11]. A detailed diagram with accompanying description of the equipment is given in Ref. [12]. The sample chamber was maintained at 20 ± 0.1°C by immersing it in a water bath. Before sorption measurements each carbon sample was outgassed at 150°C.

Adsorption isotherms of water vapor were measured at 25°C by using a conventional volumetric apparatus equipped with a mercury manometer. The establishment of the adsorption equilibrium was checked for each dose of water vapor separately.

3. Results and discussion

The equilibrium adsorption isotherms measured for benzene and water vapors were used to characterize the carbon samples studied and to correlate the adsorption data with those obtained by high-resolution thermogravimetry. Shown in Fig. 1 are the adsorbed amounts of benzene vapor, a (mmol g⁻¹), plotted as a function of the relative pressure p/p_0 for all carbons studied. These data are also plotted in Fig. 2 as a function of the adsorption potential $A = RT \ln(p_0/p)$ in order to show differences in the adsorption curves at low relative pressures. The benzene adsorption isotherms presented in Fig. 1 were util-
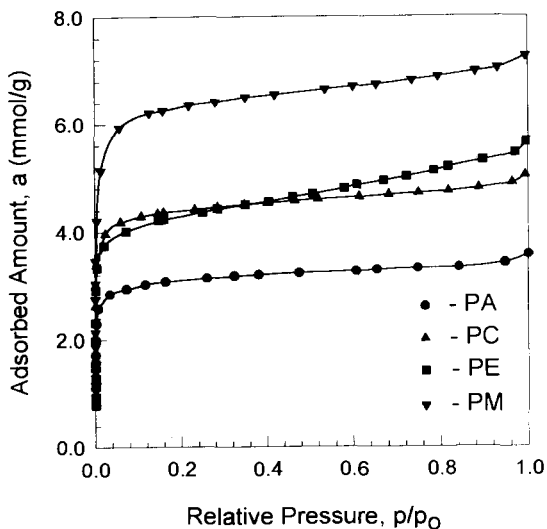

Fig. 1. Equilibrium adsorption isotherms of benzene vapor on the active carbons studied at 20°C.
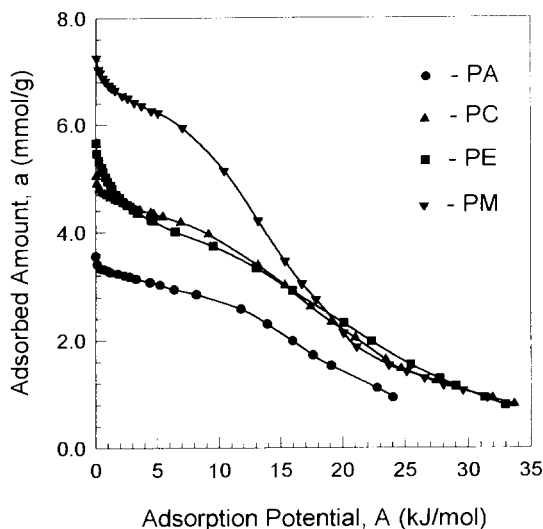
Fig. 2. Benzene adsorption data from Fig. 1 presented against the adsorption potential.

ized to calculate: (i) the total specific surface area of each carbon sample (S_t), (ii) its external surface area (S_e), (iii) the total amount of benzene adsorbed at $p/p_0 = 1$ (a_t), and (iv) the amount adsorbed in the micropores (a_{mi}). These quantities were evaluated by using the methods described in Refs. [3,13] and are summarized in Table 1. This table also gives the total amounts of adsorbed water vapor at the relative pressure $p/p_0 = 1$ and temperature equal to 25°C, which were evaluated on the basis of the experimental isotherms shown in Fig. 3.

The TGA weight loss curves were measured for carbon samples immersed in pure liquids and for samples exposed to their vapors. For the purpose of illustration, the representative TGA curves are shown in Figs. 4–8. A comparison of the TGA curves for the loss of water, n-butanol, benzene and n-heptane from the PM carbon wetted in these liquids is shown in Fig. 4. The thermodesorption of n-butanol, benzene and n-heptane occurred over a wider temperature range than for water. Organic molecules interact more strongly with the carbon sample than water molecules and higher temperatures are re-

Table 1

The sorption parameters for active carbons studied evaluated from the benzene adsorption data

Carbon code	$S_t/(m^2\ g^{-1})$	$S_e/(m^2\ g^{-1})$	$a_t/(mmol\ g^{-1})^a$	$a_{mi}/(mmol\ g^{-1})^a$	$a_t/(mmol\ g^{-1})^b$
PA	650	40	3.56	2.92	15.5
PC	930	50	5.04	4.20	19.2
PE	910	170	5.66	3.49	20.5
PM	1130	90	7.26	5.98	

[a]The values of a_t and a_{mi} obtained from the benzene adsorption isotherms shown in Fig. 1 by using the Jaroniec-Choma equation [3].
[b]The values of a_t obtained from the adsorption isotherms of water vapor shown in Fig. 3.
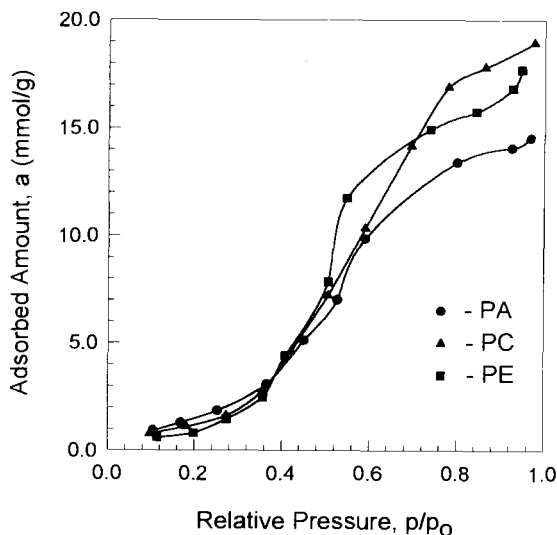
Fig. 3. Equilibrium adsorption isotherms of water vapor on the active carbons studied at 25°C.

quired to thermodesorb them from the carbon surface. Also, the heterogeneity effects of the carbon surface are manifested to a great extent on the TGA curves for organic molecules. A comparison of the TGA curves for n-butanol on the carbons studied is shown in Figs. 5 and 6. Analogous TGA curves for n-heptane on the carbons studied are shown in Figs. 7 and 8. Presented in Figs. 5 and 6, respectively, are the weight loss curves for the carbon samples immersed in n-butanol and for the samples exposed to n-butanol vapor. A comparative analysis of the TGA curves presented in Figs. 5 and 6 shows that they differ by one distinct step, which appears on the curves for the immersed carbon samples and is associated with evaporation of the excess liquid. The remaining part of the TGA curve for an immersed sample reflects evaporation of adsorbate molecules from the
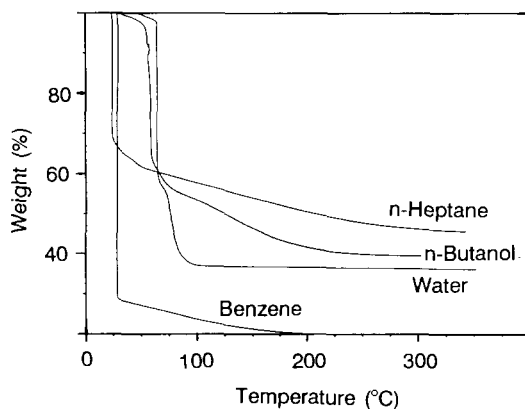

Fig. 4. Comparison of the weight loss curves for the PM carbon immersed in water, n-butanol, benzene and n-heptane.
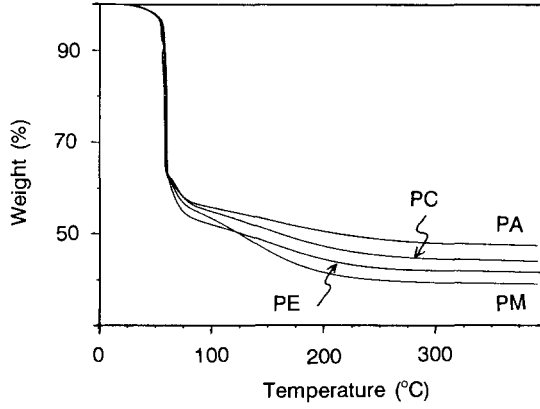
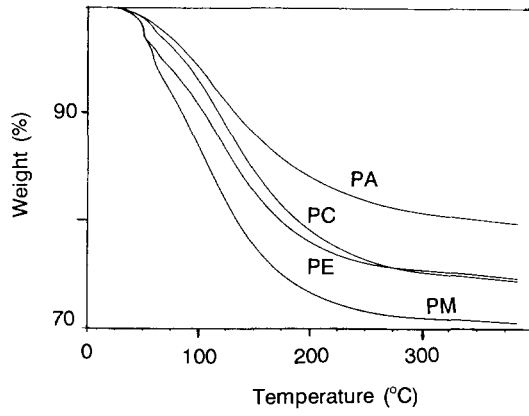Fig. 5. TGA weight loss curves for the carbon studied immersed in n-butanol.

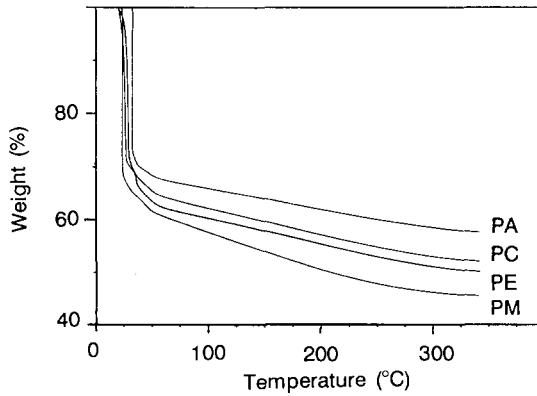Fig. 6. TGA weight loss curves for the carbon studied exposed to the saturated n-butanol vapor.

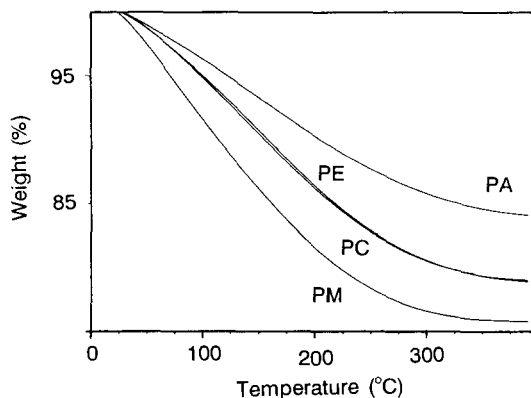Fig. 7. TGA weight loss curves for the carbon studied immersed in n-heptane.

Fig. 8. TGA weight loss curves for the carbon studied exposed to the saturated n-heptane vapor.

meso- and micropores and their desorption from the carbon surface. This part of the TGA curve is essentially the same with the weight loss curve measured at the same conditions for the same sample exposed to the vapor of a given liquid. As reported previously [9], the TGA curves for microporous active carbons are relatively smooth because these solids are strongly heterogenous. Therefore, evaluation of the specific surface area for these solids on the basis of the TGA data is difficult. However, the total amount adsorbed in the pores and on the surface can be estimated from the TGA data for an immersed sample and it agrees with that determined by exposing the sample to saturated vapor of a given liquid.

For the experimental conditions described in the preceding section the total weight loss for a carbon sample exposed to the saturated vapor is equal to the total adsorption capacity. The values of the total adsorption capacity determined by measuring the total weight losses for the carbon samples exposed to the saturated vapors (as illustrated in Figs. 6 and 8) are summarized in Table 2. These values can be also evaluated on the basis

Table 2

Comparison of the values of the adsorption capacity evaluated on the basis of the TGA data for the immersed and saturated carbon samples

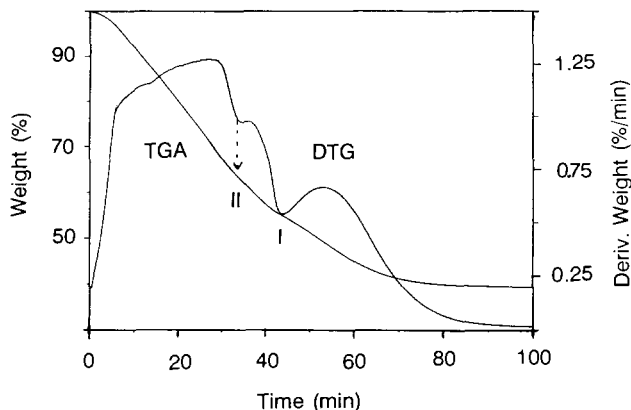| Adsorbate	Sample	Total adsorption capacity in mmol g^{-1}			
		PA	PC	PE	PM
Water	Immersed	16.8	20.4	20.6	34.3
	Saturated	16.5	17.9	17.9	30.6
Butanol	Immersed	3.8	5.5	5.7	7.5
	Saturated	3.6	5.3	5.2	7.2
Benzene	Immersed	3.6	5.1	5.6	7.3
	Saturated	3.5	5.0	5.2	7.1
Heptane	Immersed	2.7	3.6	3.7	5.6
	Saturated	2.5	3.3	3.3	5.3

Fig. 9. The time-dependent TGA and DTG curves for the PM active carbon immersed in n-butanol.

of the weight loss measurements for the immersed samples (note that these measurements do not require a time consuming procedure to saturate each solid sample with a given vapor under controlled conditions). As can be seen in Figs. 4, 5 and 7 each weight loss curve for the immersed sample has a characteristic point, which is the intersection of the sharp step (reflecting evaporation of the liquid excess) with the slowly decreasing portion of the TGA curve. This point provides information about total adsorption capacity of a porous solid. As can be seen in Fig. 4, its evaluation from benzene thermodesorption data is easy. For other adsorbates the transition between evaporation of the liquid excess and thermodesorption of adsorbate from the porous structure is less distinct. In such cases the derivative of the time-dependent TGA curve can be used to localize the characteristic point on the weight loss curve. This is illustrated on Fig. 9, which shows a comparison of the time-dependent cumulative (TGA) curve and the corresponding differential (DTG) curve for the PM carbon immersed in n-butanol. Point II on the TGA curve relates to the total adsorption capacity, whereas point I provides information about the volume of micropores. The TGA curves for other immersed samples are analogous. The values of the weight loss at point II were evaluated for all samples and are analogous with those determined for the samples exposed to the saturated vapors (see Table 2). As can be seen in Table 2 the values of the total adsorption capacity evaluated from the TGA curves for the samples immersed in liquids are slightly higher than those obtained on the basis of the TGA curves for the samples exposed to the saturated vapors. This can be due to incomplete saturation of the carbon samples.

Presented in Table 1 are the values of the adsorbed amount of benzene and water at a pressure close to the saturation pressure. These values, evaluated by independent sorption measurements, are in good agreement with those obtained from the TGA data (see Table 2). A comparison of these data shows that the values of a_t calculated from the TGA curves for the immersed samples are slightly smaller than those evaluated by adsorption from the vapor phase. This difference may be due to the overlapping of the evaporation and thermodesorption processes. The difference between the energies required to evaporate molecules from the bulk liquid phase and to thermodesorb them from the large

mesopores is small and a partial overlapping of these two processes makes evaluation of the characteristic point on the TGA curve difficult.

4. Conclusions

It appears that the values of the adsorption capacity evaluated from the TGA curves measured for the immersed carbon samples agree with those obtained by saturation of the samples in the vapor phase. Also, these values match those obtained by independent sorption measurements (compare the values for benzene given in Tables 1 and 2). The current work demonstrates that the HR TGA weight loss curves measured for the immersed carbon samples are useful for the characterization of microporous active carbons.

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