Adsorption 3, 277–282 (1997)

Influence of Analysis Conditions on Low Pressure Adsorption Measurements and its Consequences in Characterization of Energetic and Structural Heterogeneity of Microporous Carbons

Y. BEREZNITSKI AND M. JARONIEC
Separation and Surface Science Center, Department of Chemistry, Kent State University, Kent, OH 44242, USA

K.P. GADKAREE
Corning Inc., Sullivan Park, Corning, NY 14831, USA

Received May 15, 1996; Revised October 22, 1996; Accepted October 28, 1996

Abstract. Nitrogen adsorption isotherms on nonporous and microporous carbons were thoroughly studied at low relative pressures. For nonporous carbons low pressure measurements seem to be unaffected by analysis conditions. However, these measurements on microporous solids may be affected by analysis conditions at relative pressures below 10^{-4}. It was shown that selection of proper equilibration time is crucial for correct measurements of equilibrium pressures during adsorption on microporous carbons. The isotherm shift induced by insufficient equilibration of the system may affect the surface heterogeneity and microporosity analysis. A comparison of the adsorption energy and pore volume distribution functions calculated from low pressure nitrogen adsorption isotherms measured at different equilibration times on a microporous carbon shows that this effect is smaller than it was expected.

Keywords: surface heterogeneity, nitrogen adsorption, micropore analysis, microporous carbon, low pressure adsorption

Introduction

Utilitarian importance of many adsorption processes depends on the physicochemical nature of adsorbents, i.e., their chemical, surface and structural properties. Therefore, many scientists concentrated their efforts on the development and characterization of novel porous materials, which can be useful as potential adsorbents, catalysts, and separation media. A quantitative evaluation of these properties is crucial for design and optimization of numerous sorption-based separation, purification, and catalytic processes (Bansal et al., 1988). In general, adsorbents are heterogeneous solids. Their heterogeneity may consist of the following components (Jaroniec, 1995): (i) *chemical heterogeneity*, which results from various functional groups and impurities present on the solid surface; (ii) *structural heterogeneity*, which arises from interconnected pores of different sizes and shapes, and; (iii) *surface heterogeneity*, which is due to the presence of various crystallographic and geometrical irregularities on the surface.

Adsorbent heterogeneity can be probed by adsorption of various adsorbate molecules differing in the size, shape and polarity. The equilibrium isotherm, which is a fundamental measurable quantity in adsorption, can be used to obtain the adsorption energy distribution that provides quantitative information about energetic heterogeneity of a given adsorbate-adsorbent system. In addition, structural heterogeneity of a porous solid can be estimated by calculating the pore volume distribution function, which provides information about contribution of pores of different sizes to the pore network.

Recent advances in adsorption instrumentation allow to obtain reliable measurements of equilibrium isotherms. New instruments provide a possibility to measure the amount adsorbed at very low relative pressures starting from 10^{-7}–10^{-6}, and consequently, to evaluate the energetic and structural heterogeneity of porous solids. Some aspects concerning high resolution adsorption measurements (HRADS) were discussed elsewhere (Maglara et al., 1994). It was shown that adsorption data measured on microporous solids at the relative pressures below 10^{-4} are sensitive to the sample pretreatment and analysis conditions, e.g., temperature and time of degassing, equilibration time, adsorptive dose and so on. The equilibration of microporous systems in the range of low pressures may be difficult to achieve because of slow micropore diffusion as well as significant thermal effects related to the high heat of adsorption. Consequently, if experimental conditions do not allow to achieve the equilibrium, the resulting adsorption isotherm does not represent the true equilibrium quantity.

The aim of the current work was to address the specificity of low pressure adsorption measurements, and to demonstrate how eventual changes in the adsorption isotherm may influence the evaluation of surface and structural heterogeneities of microporous solids.

Experimental

Carbon Samples. Two carbon samples studied in the current work were a synthetic carbon Ambersorb 572 produced by Rohm and Haas Company (Philadelphia, PA), and a nonporous carbon black Sterling FT-G distributed by the Laboratory of the Government Chemist, Queens Road, Teddington, UK. Ambersorb 572 is a commercial microporous carbon produced in the form of spherical particles by the controlled pyrolysis of highly sulfonated styrene/divinylbenzene ion-exchange resins. Its specific surface area is about 1000 m^2/g (Choma and Jaroniec, 1997). The specific surface area of Sterling FT-G is 11 m^2/g. Other details related to these carbons are reported elsewhere (Choma and Jaroniec, 1997; Olivier, 1995).

Sorption Measurements. An ASAP-2010 volumetric multi-gas sorption analyzer (Micromeritics Inc., Norcross, GA) was used to measure nitrogen adsorption at 77.5 K. Additional adsorption measurements were done using OMNISORP-100 sorption analyzer (Hialeah, Florida). Prior to making adsorption measurements each carbon sample was outgassed under vacuum for two hours at 473 K. The adsorbed volume was measured as a function of the equilibrium pressure over a range of the relative pressures from 10^{-6} to the saturation pressure using high purity (99.998%) nitrogen.

Characterization Methods

Calculation of the Micropore Volume Distribution. An advanced numerical procedure based on the regularization method (Szombathely et al., 1992) was employed to evaluate the micropore volume distribution from nitrogen adsorption isotherms measured at 77.5 K. The starting point of this procedure is the following integral equation (Jaroniec and Madey, 1988):

$$\Theta_t(p) = \int_{H_{\min}}^{H_{\max}} J(H) \quad \Theta_l(H, p)\, dH \tag{1}$$

where $\Theta_t(p)$ denotes the total relative adsorption at the equilibrium pressure p, $\Theta_l(H, p)$ is the adsorption for uniform pores of size H, and $J(H)$ is the pore volume distribution in the pore size interval between $H_{\min}$ and $H_{\max}$.

The local adsorption isotherms $\Theta_l(H, p)$ for homogeneous pores of given sizes were calculated on the basis of the density functional theory (DFT) (Olivier, 1995). The integral Eq. (1) was inverted in order to obtain the pore volume distribution function $J(H)$. Calculations were performed using DFT-software (Olivier et al., 1994).

Calculation of the Adsorption Energy Distribution. The adsorption energy distribution (AED) functions were calculated from submonolayer adsorption data by inverting the following integral equation (Jaroniec and Madey, 1988):

$$\Theta_t(p) = \int_{\varepsilon \min}^{\varepsilon \max} H_l(p, \varepsilon) F(\varepsilon) d \tag{2}$$

where $\Theta_t(p)$ denotes the total relative adsorption, $H_l(p, \varepsilon)$ is the local adsorption isotherm for sites of the adsorption energy ε, and $F(\varepsilon)$ is the adsorption energy distribution in the energy interval from $\varepsilon_{\min}$ to $\varepsilon_{\max}$. The Fowler-Guggenheim (FG) adsorption isotherm was used to represent the local adsorption isotherm:

$$\Theta_l(p,\varepsilon) = \frac{K_L p \exp(zwH_l/kT)}{1\; K_L p \exp(zwH_l/kT)} \quad (3)$$

$$K_L = K_L^0(T)\exp(\varepsilon/kT) \quad (4)$$

where K_L is the Langmuir constant for adsorption sites of the energy ε. The pre-exponential factor $K_L^0(T)$ can be expressed in terms of the partition functions for an isolated molecule in the gas and surface phases (Jaroniec and Madey, 1988). This parameter was estimated according to Adamson's method (Adamson, 1990). The FG model represented by Eq. (3) describes the local adsorption with lateral interaction on the surfaces with a patchwise distribution of adsorption sites. Such model appears to be realistic for description of adsorption on microporous carbons (Jaroniec and Madey, 1988). In the current work two nearest neighbors ($z = 2$) were assumed, and the value of the interaction energy parameter $w/k = 95$ K was used to calculate the adsorption energy distribution by inverting the integral Eq. (2). This inversion was done by employing the regularization method discussed elsewhere (Szombathely et al., 1992).

Results and Discussion

The reproducibility of low pressure adsorption measurements can be influenced by initial pretreatment of the adsorbent sample. In order to avoid the effect of the pretreatment conditions each carbon sample was treated at identical conditions. The samples were outgassed for two hours at 473 K at the vacuum level of approximately 10^{-4} Torr. Other factors affecting adsorption measurements at low pressures are related to the specific instrumentation and analysis conditions. For instance, in case of volumetric measurements the dosage of gaseous adsorbate causes an increase in the pressure. As adsorption proceeds, the pressure decreases and the system is allowed to equilibrate. At equilibrium the pressure is measured, and again the next portion of adsorbate is dosed into the system. Hence, the experimental limitation of the equilibration time between two consecutive doses of the adsorbate may have a significant influence on the accuracy of determination of the equilibrium pressure.

For nonporous carbons such as Sterling FT-G the measurement conditions do not seem to have a significant impact on the reproducibility of adsorption measurements. Nitrogen adsorption isotherms measured on this sample using different equilibration times show an excellent reproducibility including the range of very low pressures (see Fig. 1). It indicates that the equilibration of the system is fast.

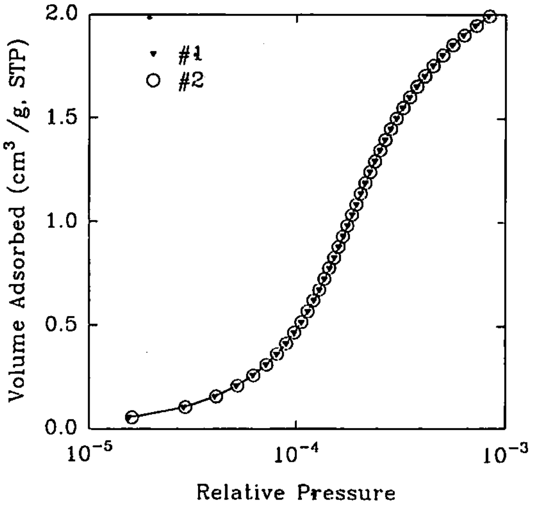

Figure 1. Comparison of 77.5 K nitrogen adsorption isotherms measured on the Sterling FT-G nonporous carbon by setting different maximum equilibration times: 0.2 hour for the isotherm 1, and 0.3 hour for the isotherm 2.

In case of microporous synthetic carbons such as Ambersorb 572 equilibration of the system is difficult due to the diffusion and thermal effects that affect adsorption in micropores. Figure 2 shows two

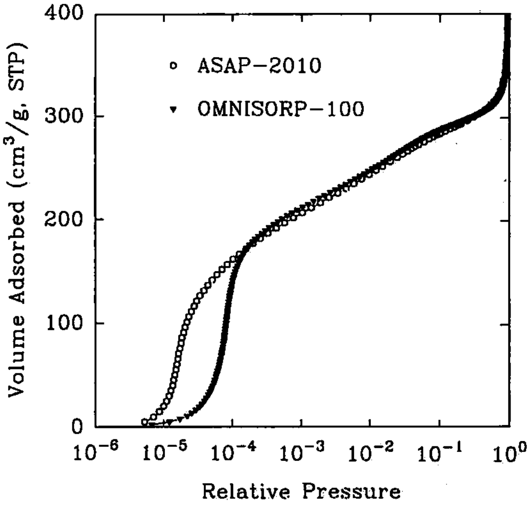

Figure 2. Comparison of 77.5 K nitrogen adsorption isotherms measured on the Ambersorb 572 microporous carbon using different adsorption instruments.

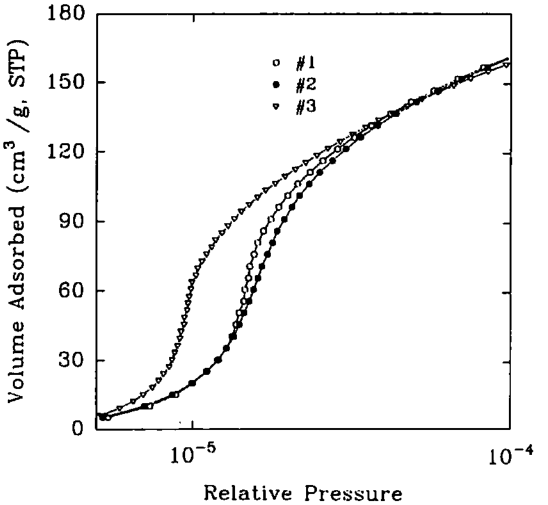

Figure 3. Comparison of 77.5 K nitrogen adsorption isotherms measured on the Ambersorb 572 microporous carbon by setting different maximum equilibration times: 0.5 hour for isotherms 1 and 2, 1 hour for the isotherm 3.

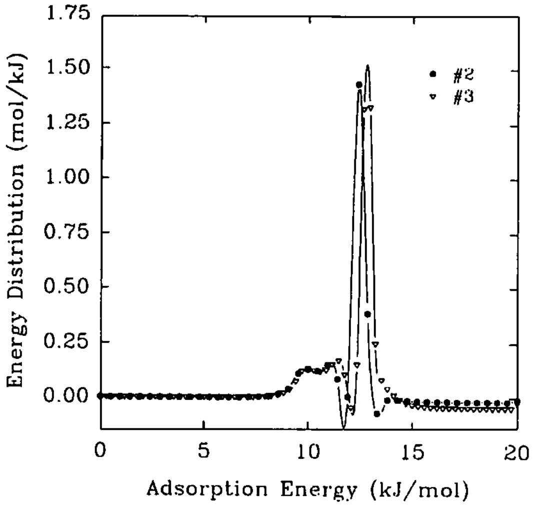

Figure 4. Comparison of the adsorption energy distribution functions calculated from the submonolayer range of isotherms 2 and 3.

nitrogen adsorption isotherms measured on Ambersorb 572 using different instruments, ASAP-2010 and OMNISORP-100. As seen from this figure a reasonable agreement between two isotherms is observed for the relative pressures above 10^{-4}. A discrepancy between adsorption isotherms in the low pressure range can be caused by the lack of 1 Torr transducer in the Omnisorp unit used. In order to have good recognition of experimental factors that influence sorption equilibria in micropores further adsorption measurements were carried for Ambersorb 572 on the ASAP-2010 instrument.

Figure 3 shows low pressure parts of nitrogen adsorption isotherms on Ambersorb 572 at 77.5 K. These isotherms were measured using incremental dose 3 or 5 cm^3/g, and setting different maximum equilibration times, i.e., 0.5 hour (curves 1 and 2), and 1 hour (curve 3). As can be seen from Fig. 3 isotherms 1 and 2 show a fair agreement, while the isotherm 3 is shifted to the left in comparison to curves 1 and 2. This shift between curves 1 and 3 may be attributed to insufficient equilibration in case of isotherms 1 and 2. This illustration shows that a special care is recommended when low pressure adsorption isotherms are measured on microporous solids. Due to sensitivity of low pressure adsorption measurements a change in experimental conditions can alter the isotherm data. It is interesting to know how these changes affect the evaluation of the surface and structural properties of microporous solids.

Adsorption energy distribution functions, which are commonly used to characterize surface heterogeneities of solids, were calculated from submonolayer isotherm data using INTEG program (Szombathely et al., 1992) described in the experimental section. The numerically stable AED functions were obtained with the regularization parameter 0.01 (see Fig. 4). As can be seen from this figure AEDs calculated from isotherms 2 and 3 are similar. They both exhibit two peaks: a broad low-energy peak in the range of 9–11 kJ/mol, and a sharp high-energy peak in the range of 12–13 kJ/mol. As expected, the longer equilibration time allows for a better assessment of high energy sites. The AED function corresponding to the isotherm 3 (measured using 1 hour equilibration time) is shifted in the direction of high adsorption energies by about 0.5 kJ/mol.

Even though the AED functions are acceptable they are not fully adequate because of small negative oscillations visible at high adsorption energies, which are related to the small relative pressures (see Fig. 4). Since the equilibration time most likely affects the low pressure part of the adsorption isotherm, the initial part of this isotherm was truncated in order to eliminate negative oscillations of the energy distribution. This truncation was done approximately at the point where the shape of the adsorption isotherm changes from concave to convex. Namely, first 15 points of the isotherm 2, and first 20 points of the isotherm 3 were not used to calculate AEDs, i.e., the relative pressures from 0.0000099 to 0.0024298 for the isotherm 2, and from 0.0000178

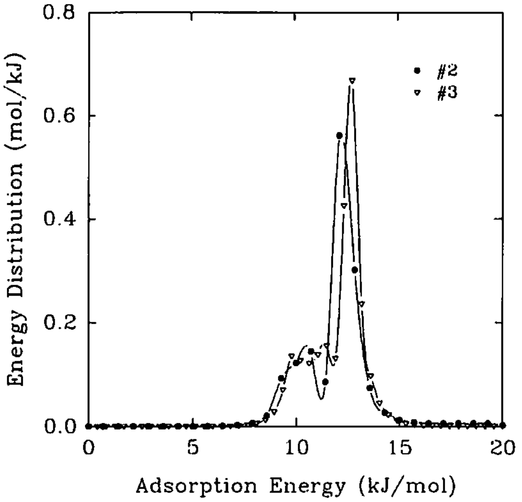

Figure 5. Comparison of the adsorption energy distribution functions calculated from the truncated submonolayer range of isotherms 2 and 3.

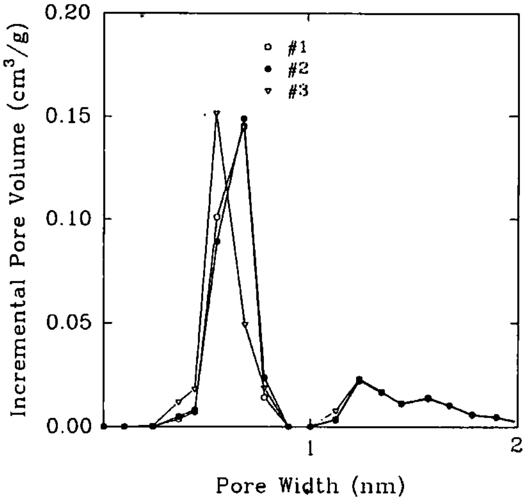

Figure 6. Comparison of the incremental micropore volume distribution functions calculated from the whole range of isotherms 1, 2 and 3.

to 0.0018967 for the isotherm 3 were used. All other parameters of the model were kept the same.

The resulting AEDs calculated from the truncated isotherms 2 and 3 are shown on Fig. 5. The general shape of the energy distribution functions and their relative position appear to be almost unchanged. The distributions exhibit two peaks. The broad low energy peak is seemingly unaffected by truncation, while the sharp high energy peak appears to be broader and almost twice smaller than its original counterpart. That may be viewed as a direct result of truncation, which eliminates points corresponding to high energy adsorption sites. Nevertheless, a general shape of the energy distributions have not been changed substantially. The AED function calculated from the isotherm 3 is shifted to the right due to longer equilibration time that allows for a better characterization of high-energy adsorption sites.

Figure 6 shows incremental micropore volume distributions calculated from the whole isotherms 1, 2 and 3 using the DFT-software (Olivier et al., 1994). As expected the micropore volume distribution calculated from isotherm 3 is shifted to the lower pore range due to larger equilibration time. It seems that the isotherm shift induced by change in the equilibration time has a more pronounced effect on the micropore analysis than on the AED function.

However, it should be noted that from numerical viewpoint the evaluations of the adsorption energy and micropore volume distributions are based on the inversion of the integral equation of the same type. Therefore, the observed difference in the sensitivity of both distributions towards the change in the experimental conditions can be attributed mostly to inadequateness of the assumed local isotherms. The micropore volume analysis is based on the inversion of the integral Eq. (1) using the set of simulated adsorption isotherms for homogeneous pores. However, in the AED analysis the integral Eq. (2) is solved assuming the FG model for the local isotherm. In the later case, in order to obtain physically meaningful solutions of the integral Eq. (2), i.e., to avoid negative oscillations of the AED function, points below relative pressure of 10^{-5} were not used. Due to this procedure the resulting energy distributions show somewhat smaller sensitivity towards the change in equilibration conditions.

Conclusions

Low pressure nitrogen adsorption isotherms measured on the nonporous carbon Sterling FT-G and microporous carbon Ambersorb 572 were thoroughly analyzed in order to estimate the effects of experimental conditions on the evaluation of the surface and structural heterogeneity of solid adsorbents. For nonporous carbons low pressure measurements seem to be unaffected by experimental conditions as illustrated by comparing adsorption isotherms measured on Sterling FT-G at different equilibration times. In contrast, the equilibration time seems to play a key role in measuring adsorption isotherm data on microporous carbons at the relative pressures below 10^{-4}.

It was shown that the sensitivity of low pressure adsorption measurements to a change in analysis conditions has a certain impact on the calculation of the adsorption energy and pore volume distribution functions. Assumption of longer equilibration time allows for a better characterization of the structural and energetic heterogeneities of microporous solids because of more accurate measurements of the equilibrium relative pressures below 10^{-4}, and, consequently, improves the resolution of the high energy range of AEDs. However, due to theoretical limitations of currently available methods the initial points of the isotherm measured at the relative pressures below 10^{-5} seem to have an insignificant impact on the resulting AED function. The AED calculated from the isotherm measured by allowing one hour equilibration time is shifted only by 0.5 kJ/mol towards higher adsorption energies in comparison to AED calculated from the isotherm measured with 0.5 hour equilibration time.

In addition, the current method of calculation of the AED functions based on the regularization procedure seemingly has a problem with description of isotherm data at the relative pressures about 10^{-6} as evidenced by small negative oscillations on the distribution curve. Thus, this method can be effectively applied for submonolayer adsorption data measured for the relative pressures above 10^{-5}.

The micropore volume distribution function also appears to be affected by analysis conditions. The longer equilibration time results in a shift of the distribution towards smaller pores. Surprisingly, the observed differences in the low pressure segments of the adsorption isotherms seem to have a smaller impact on the shape of the resulting adsorption energy and micropore size distributions than it was expected. Nevertheless, the measurement of low pressure equilibrium adsorption isotherms on microporous solids need further systematic study, which are currently carried in our lab.

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