

COMPREHENSIVE ANALYSIS OF CARBON MICROPORE STRUCTURE USING DFT MODEL APPLIED TO AR, N₂ AND H₂ ADSORPTION DATA

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Introduction

There is a growing interest in detailed and accurate methods for describing the pore structure of materials that are used or being developed for gas separation, gas chromatography and applications such as carbon double layer capacitors, hydrogen and natural gas storage as well as the removal of CO₂ from the atmosphere.

The pore structure of porous materials is usually described in terms of the pore size distribution (PSD), traditionally evaluated from the analysis of nitrogen or argon adsorption data measured at cryogenic temperatures (Gregg and Sing 1982). However, it was shown recently that it is useful to also use H₂ adsorption data (Jagiello and Thommes 2004). This is because H₂ can access some very small micropores that are not accessible to N₂ or Ar at cryogenic temperatures due to size restrictions, connectivity problems or slow diffusion. Analysis based on CO₂ adsorption was also recommended for similar reasons (Lozano Castelló et al. 2004).

A specific practical application of using H₂ for micropore analysis was recently reported in a study (Jagiello et al. 2006) where measurements of H₂ adsorption at 77 K below 1 atm were used for predicting high pressure H₂ adsorption on porous carbons at ambient temperatures.

It was shown recently (Jagiello et al. 2007) that using H₂ adsorption data measured at cryogenic temperatures in combination with standard N₂ isotherm at 77 K provides additional information about the adsorption system and extends the lower limit of pore size analysis below that of the standard nitrogen analysis. This approach also allows identifying portions of the N₂ experimental isotherm which are not fully equilibrated due to very slow diffusion to narrow micropores.

The purpose of this work is to discuss the advantages of the carbon micropore analysis based on adsorption measurements of standard adsorbates (N₂ at 77 K and Ar at 87 K) in conjunction with H₂ isotherms measured at 77 K. We support this discussion by the results obtained for activated carbons and carbon molecular sieves (CMS).

Experimental

Two sets of porous carbon samples were selected for this study. One consists of a series of microporous carbons with increasing porosity derived from poly(ethylene terephthalate), PET, precursor. The initial carbon sample, PC, is a char obtained by the pyrolysis of PET waste at 773 K in inert atmosphere. Activation of the PC sample with CO₂ at 1200 K for different time periods gave the following samples: PC12, PC35, and PC58, where the number indicates the percentage of burn-off. Details of experimental methods and adsorption data of N₂ and H₂ measured for these samples were reported elsewhere (Parra et al. 2004). Second sample set consists of three commercial CMSs from Supelco and it was analyzed using Ar and H₂ adsorption data (Jagiello and Betz 2007).

Results and Discussion

The PSDs of carbon samples were calculated by fitting of the model adsorption isotherms to the experimental data. Sets of theoretical model isotherms (kernels) for N₂ and H₂ at 77 K, and Ar at 87 K were calculated using the non local density functional theory (NLDFT). The calculations of kernels were performed following the implementation of Tarazona's NLDFT (Tarazona et al. 1987, Lastoskie et al. 1993). The slit pore model was assumed for carbon pores and the carbon-fluid interactions were described by the Steele potential (Steele 1974). Methods and parameters used in these calculations were reported elsewhere (Jagiello et al. 2007).

Usually, one isotherm of a single adsorbate is used for the calculation of a carbon PSD. Here, H₂ and Ar or H₂ and N₂ adsorption isotherms are fitted simultaneously by their corresponding model isotherms to obtain a single PSD as a solution for both experimental isotherms used in the analysis. When more than one isotherm is used, the PSD is obtained by solving the multi-kernel integral equation (Jagiello et al. 2004, 2007)

$$\min \sum_m^M \sum_i^{N_m} \left[V_m(p_i) - \int_{\alpha_m}^{\beta_m} K_m(p_i, w) f(w) dw \right]^2 \quad (1)$$

where p_i is the pressure of i -th adsorption point, V_m and K_m are the experimental adsorption isotherm and the kernel for m -th adsorbate, and $f(w)$ is the differential PSD to be calculated. The pore width, w , is considered here an “effective pore width” defined as $w = H - 3.4 \text{ \AA}$, where H is the distance between the centers of the surface carbon atoms in the opposite pore walls. We used the numerical algorithm SAIEUS (Jagiello 1994) to obtain a stable and physically feasible solutions for $f(w)$. Application of more than one adsorption isotherm for the PSD calculation using kernels generated by GCMC simulations was also recently reported (Konstantakou et al. 2007).

At 77 K hydrogen is a supercritical gas, its adsorption isotherms are of type 1 (Figure 1) and their shapes are only sensitive to pore sizes in the range of very small pores. For pores larger than $\sim 7 \text{ \AA}$ in width these isotherms become more and more similar to one another, and thus they do not differentiate between the sizes of these pores. It follows that in order to calculate carbon PSD in a full range of micro and mesopores it is necessary to use additional adsorbates such as N_2 or Ar at their boiling point temperatures (or below).

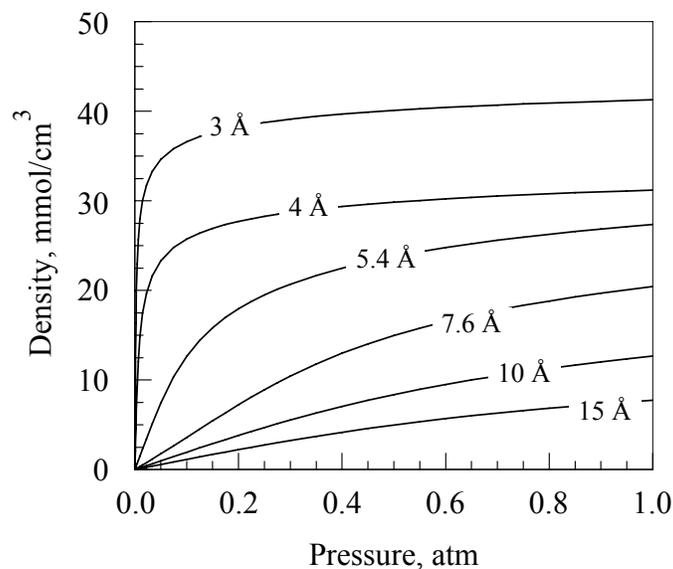


Figure 1. NLDFT model H_2 isotherms at 77.3 for selected effective pore widths. Densities are calculated as amount of H_2 molecules inside the pores per effective pore volumes.

In our study of pore structure of three CMS samples from Supelco we analysed the adsorption isotherms of Ar and H_2 measured at 87.4 and 77.3 K, respectively. Eq. (1) was used to calculate two variants of the PSD for each sample. One is based on the Ar isotherm alone and the other on both Ar and H_2 isotherms. The results of fitting Eq. (1) to the experimental data and the calculated pore size distributions are shown in Fig. 2. A good fit to both experimental isotherms was obtained for all samples. The fact that data for both Ar and H_2 can be fitted simultaneously using their respective kernels and a single PSD indicates that both models (kernels) are consistent. The value of lower pore size limit of PSDs calculated from Ar and H_2 data is slightly smaller ($\sim 3 \text{ \AA}$) than that for Ar data ($\sim 3.6 \text{ \AA}$). The most pronounced difference between the two variants of calculated differential PSD is in the range of smallest pores. This is due to the contribution of the smallest pores which are accounted for by the Ar/ H_2 variant but not by the Ar variant of calculations. It is important to note, however, that the overall magnitudes of the observed differences are relatively small.

To show that H_2 isotherm may provide complementary information to Ar data we analyzed Carboxen-1021 sample by using a set of data comprised of a full H_2 adsorption isotherm and a shortened Ar isotherm. The Ar isotherm was truncated at 0.0001 atm. Figure 3 shows the results obtained for the truncated data set compared to the results for both full Ar and H_2 isotherms. It is seen that the calculated PSDs are almost identical for both sets of data. Practical significance of this result is that it suggests that Ar adsorption isotherm measured above 0.0001 atm in conjunction with H_2 isotherm measured in the same range may provide almost the same quality of information about the carbon PSD as where Ar data were measured starting at 10^{-7} - 10^{-6} atm.

In the analysis of PC samples we used similar approach as in the case of CMS samples but instead of Ar and H_2 adsorption isotherms we used N_2 and H_2 . The calculated PSDs of activated carbon samples presented Fig. 4 show the effect of activation of the initial PC sample. The narrow PSD of PC sample is modified by activation process towards wider pores with increasing burn-off. We found a good fit of the model N_2 and H_2 isotherms to the experimental data for all samples except for the PC sample. This sample was obtained by the pyrolysis of the PET precursor without any further activation. As a result, its pores are poorly developed and have sized in the range of very narrow micropores, as it has been described earlier (Ania et al. 2006). It appears that due to slow diffusion and/or because of the pore connectivity problems the N_2 adsorption

isotherm measured for this carbon is not fully equilibrated. In comparison with other N_2 isotherms (Fig. 5) this isotherm appears to be shifted to higher pressures, especially for low amounts adsorbed. In our analysis we decided to use only H_2 data to calculate the PSD for this sample. The calculated narrow PSD, below $\sim 10 \text{ \AA}$ is consistent with the sequence of PSDs (Fig. 4) showing gradual widening of pores sizes of carbons obtained by progressive activation with increasing burn-off.

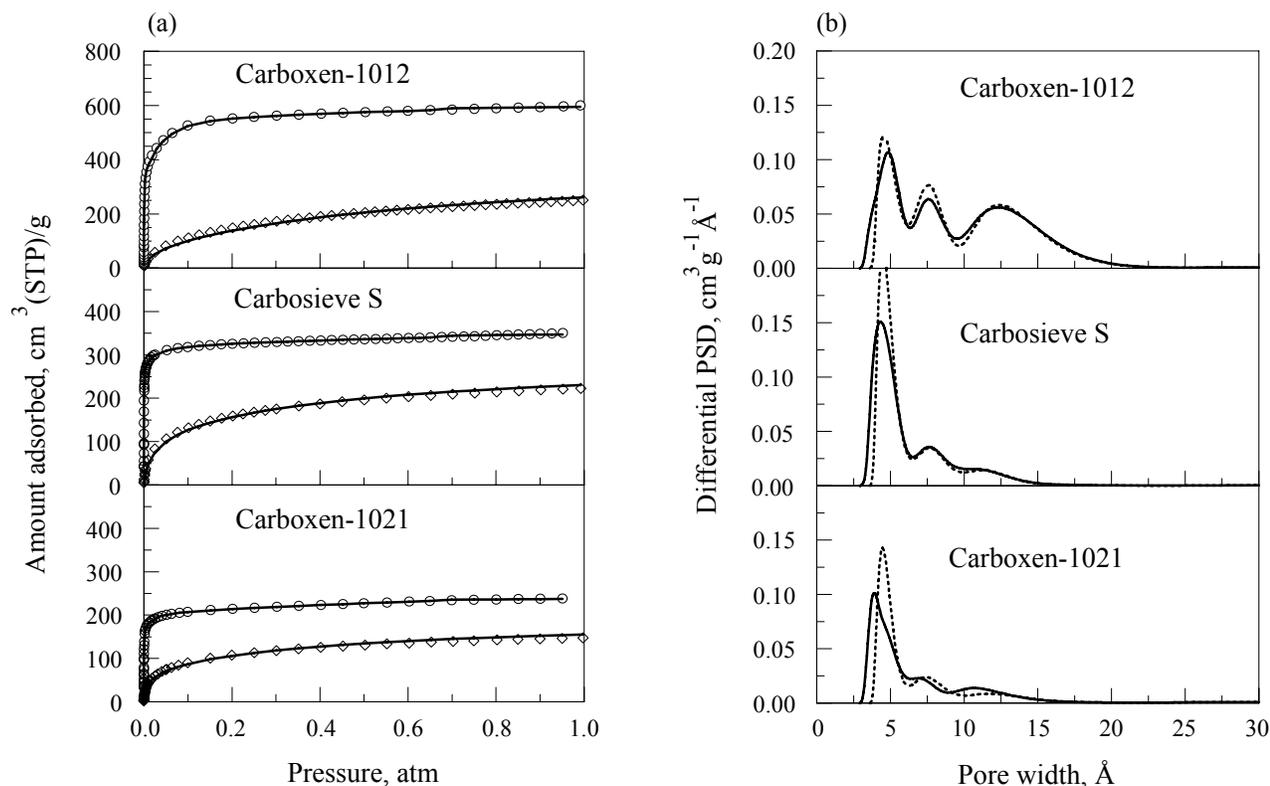


Figure 2. Adsorption data analysis of three CMS samples. (a) Experimental adsorption isotherms of argon at 87 K (circles), hydrogen at 77 K (diamonds). Continuous lines show fits by Eq. (1) applied simultaneously to both isotherms. (b) PSDs calculated by fitting Eq. (1) to both Ar and H_2 isotherms (continuous line), and to the Ar isotherm only (dotted line).

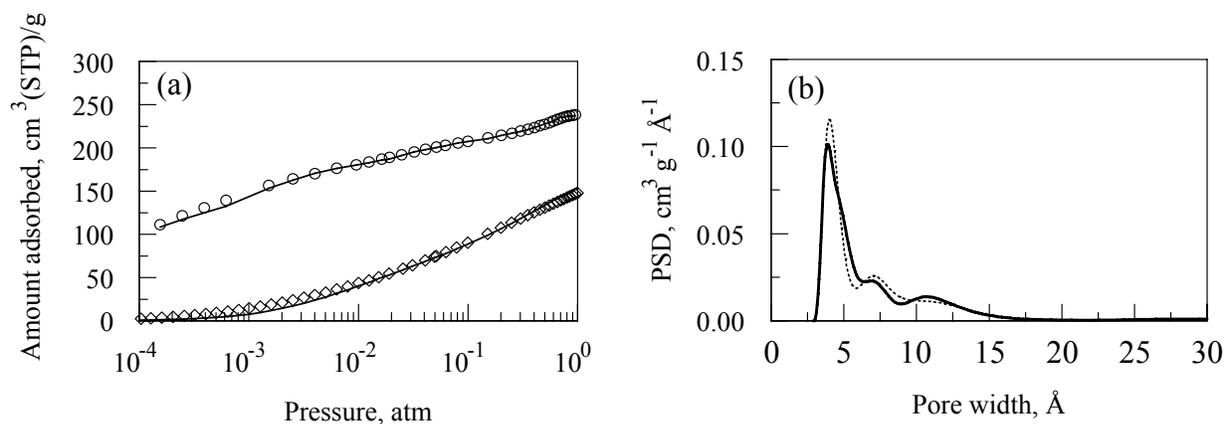


Figure 3. Analysis of truncated Ar data in conjunction with full H_2 isotherm for Carboxen-1021. (a) Experimental data used in the analysis and their fits by Eq. (1); notation is the same as in Fig. 2. (b) Calculated differential PSDs for data sets with full Ar isotherm (continuous lines) and with truncated Ar isotherm (dotted lines).

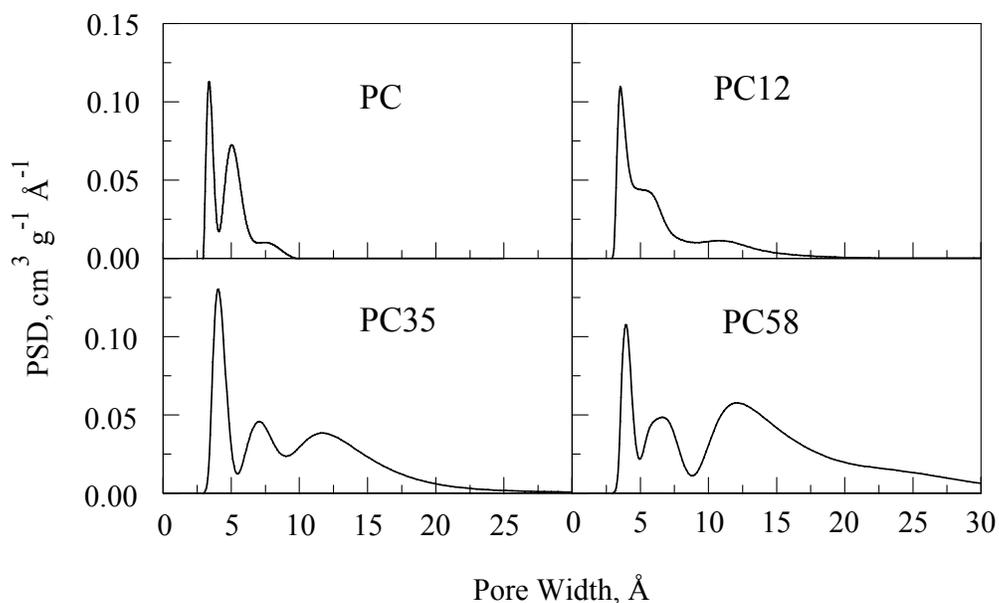


Figure 4. Calculated PSDs showing the development of porosity for four PC samples. In all cases except for PC sample calculations were performed by fitting Eq. (1) to N₂ and H₂ adsorption isotherms. For PC sample only H₂ isotherm was used.

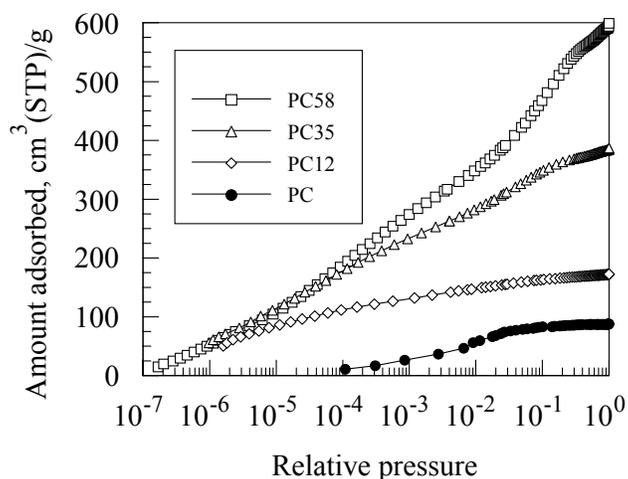


Figure 5. Experimental N₂ isotherms for four PC samples.

Conclusions

We have shown that our approach based on the simultaneous analysis of adsorption data of multiple gases, such as H₂ and N₂ or H₂ and Ar measured at cryogenic temperatures, by using the multi-kernel adsorption integral equation has several advantages for the accurate characterization of microporous carbon materials:

- The calculated PSDs are robust and consistent with more than one adsorption isotherms.
- This approach allows detecting experimental points that are not fully equilibrated due to very slow diffusion to narrow micropores.
- The range of pore size analysis is extended to smaller pore sizes compared to the standard nitrogen or argon adsorption analysis.
- Data of the two isotherms provide complementary information about the carbon porosity in the range of micro and mesopores.

Proposed approach can be considered a useful tool for a comprehensive characterization of activated carbons, and for obtaining detailed and reliable carbon PSDs.

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