Using DFT Analysis of Adsorption Data of Multiple Gases Including H_2 for the Comprehensive Characterization of Microporous Carbons

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Abstract

Hydrogen and Nitrogen adsorption isotherms at cryogenic temperatures (77 and 87 K) were used to characterize the microporosity of a series of gradually activated carbons, representing various pore size distributions (PSD). Carbon PSDs were calculated by simultaneous fitting of the DFT model isotherms to their experimental counterparts. Resulting PSDs represent robust characteristics of the carbon structures that are consistent with all the data used in the analysis. The range of pore size analysis in this method is extended to smaller pore sizes compared to the standard nitrogen adsorption analysis. In addition, it is shown that this approach allows to detect and exclude experimental points that are not fully equilibrated due to diffusion problems in narrow micropores. The results of the analysis of a series of carbons activated with systematically increasing burn-off show that the presented approach is a useful tool for a comprehensive characterization of microporous carbons, and for obtaining detailed and reliable carbon PSDs.

1. Introduction

Hydrogen storage by means of physical adsorption on various microporous materials is considered a safe and convenient method of handling hydrogen fuel for automotive applications [1, 2]. The most often studied candidates for such applications are activated carbons [3-5], synthetic carbons [6], single and multi-wall nanotubes [7,8], and metal organic framework materials [9,10]. Understanding the relationship between pore structure and hydrogen adsorption capacity under various temperature and pressure conditions is key in the development of materials that would be of practical significance for hydrogen storage. 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 isotherms measured at cryogenic temperatures [11]. However, for the PSD analysis of materials considered for hydrogen storage it is reasonable to also use H_2 adsorption data [12]. This is because a fraction of the pores accessible to H_2 may not be accessible to N_2 or Ar molecules especially at cryogenic temperatures. Practical advantage of using H_2 for micropore structure characterization was recently demonstrated in a study [13] where the H_2 adsorption data measured at 77 K below 1 atm were used for quantitative prediction of high pressure hydrogen adsorption on porous carbons at ambient temperatures. The H_2 adsorption was modeled by the Non-local density functional theory (NLDFT).

The purpose of this work is to show that H_2 adsorption data measured at 77 and 87 K may be used in conjunction with standard nitrogen adsorption isotherms, measured at 77 K, to derive carbon PSD consistent with both nitrogen and hydrogen adsorption isotherms. In this approach the lower limit of pore size analysis is extended below that of the standard nitrogen analysis. We show that, because of the fact that H_2 molecules can access smaller pores than N_2, our approach allows to characterize this part of carbon pore structure which is useful for hydrogen storage applications but is not “visible” by the N_2 analysis.

The usefulness of the simultaneous analysis of adsorption data of multiple gases to achieve a more complete characterization of carbon materials is demonstrated. An example of samples which cannot be explained by N_2 adsorption but can be well-described by using N_2 in conjunction with H_2 is presented. This is of significant importance for understanding and designing carbon micro structures for many applications of microporous carbons including hydrogen storage, energy storage, and gas separation.

2. Experimental

Adsorption isotherms of nitrogen at 77 K and hydrogen at 77 and 87 K analyzed in this study were measured on a series of microporous carbons with increasing porosity derived from poly(ethylene terephthalate), PET, precursor. The initial carbon sample, PC, is a ground char obtained by the pyrolysis of PET waste at 773 K under nitrogen atmosphere followed by an ulterior heat treatment at 1200 K for 1 h. The PC sample was then activated with CO_2 at 1200 K and, depending upon the degree of burn-off (12, 35, 58 and 76%), the following series of activated carbon samples was obtained: PC12, PC35, PC58, and PC76. Measured adsorption data and detailed experimental methods were reported and discussed elsewhere [14-16].

3. Results and Discussion

In this work, the calculations of all model isotherms were performed following the implementation of Tarazona's NLDFT [17] described by Lastoskie et al [18]. The slit pore model was assumed for carbon pores and the carbon-fluid interactions were described by the Steele potential [19]. Nitrogen NLDFT isotherms at 77 K were calculated using parameters reported elsewhere [20].

The Lennard-Jones fluid-fluid interaction parameters ε_{ff} and σ_{ff} for H_2 were taken from Stan and Cole [21]. For the H_2 hard sphere diameter the value of σ_{ff} was used. For the solid-fluid interaction parameters the optimized values were used. These values were derived [13] by fitting the DFT isotherm calculated for the flat graphitic surface to the adsorption isotherm measured on a graphitized carbon black sample. The values of parameters used to calculate the H_2 model adsorption isotherms are summarized in Table 1. Due to the fact that at low temperatures hydrogen is a quantum fluid, the quantum corrections were applied in the calculations of H_2 isotherms by using Feynman's "effective potential" [21].

We calculated two sets (kernels) of model NLDFT isotherms of H_2 adsorption at 77.3 and 87.4 K in the pressure range of 0-1 atm. Fig. 1 shows selected model H_2 isotherms at both temperatures calculated for several pore widths. The pore width, w, is considered here an "effective pore width" [22] defined as w = H-3.4 Å, where H is the distance between the centers of the surface carbon atoms in the opposite pore walls. The isotherms in Fig. 1 are expressed in terms of the H_2 density calculated per effective pore volume. High values of the calculated H_2 density at 77 K in the 3 Å micropores, compared to the H_2 liquid density, were discussed in the earlier work [13].

Since hydrogen is a supercritical gas at 77 and 87 K its adsorption isotherms are of type 1. It is seen that their shapes for larger pores become increasingly more similar to one another, and thus less sensitive to pore sizes. This implies that in order to calculate carbon PSD in a range of mesopores it is necessary to use an additional adsorbate such as N_2 or Ar at their boiling point temperatures.

Mathematical procedure used to calculate the PSD can be described as fitting of the theoretical adsorption isotherms to the experimental data. Usually, one isotherm of a single adsorbate is used for such calculations. Here, a set of multiple adsorption isotherms is fitted simultaneously by their corresponding model isotherms to yield a single PSD as a common solution for all experimental data used in the analysis. Mathematically, the PSD is obtained by solving the multi-adsorbate and multi-kernel integral equation [23]

$$\min \sum_{m}^{M} \sum_{i}^{N_m} \left[V_m(p_i) - \int_{\alpha_m}^{\beta_m} K_m(p_i, w) f(w) dw \right]^2 \qquad (1)$$

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. To obtain a stable and physically feasible solution for f(w) we use the numerical algorithm SAIEUS [24] which utilizes the regularization procedure and imposes nonnegativity constraints on the solution [24, 25].

In our calculations using Eq. (1) we consider three sets of adsorption data measured for each carbon sample:

i. HH: two H_2 isotherms measured at 77 and 87 K

ii. HHN: the same two H_2 isotherms as in (i) plus the N_2 isotherm at 77 K

iii. N: single N_2 isotherm

To illustrate the problem of evaluating the PSD for larger pores (w>10 Å) using H_2 isotherms only, and the advantage of using N_2 in conjunction with H_2 adsorption data, we calculate two versions of the PSD for PC35 sample using HH and HHN data sets. The differential PSDs are shown in Fig. 2a and 2b for HH and HHN set, respectively. The error bars in this figure represent the statistical uncertainties calculated from the covariance matrix of the solution of Eq. (1) [24]. For pore widths smaller than ~7 Å the uncertainty in the calculated PSD values is relatively small in both cases, however in the case of the HH set (Fig. 2a) the uncertainty exceeds the calculated PSD for pores larger than ~10 Å. This is related to the fact that the H_2 isotherms for larger pores (>10 Å) are similar in shape (Fig. 1) which in mathematical terms means that they are linearly dependent. Such linearly dependent isotherms included in the kernel lead to the non-unique solutions of Eq. (1) even if regularization is applied. Fig. 2b shows that adding the N_2 isotherm to the fitting procedure significantly reduces the uncertainty of the calculated PSD. The result obtained from the combined data (HHN) represents the effective solution which is consistent with H_2 and N_2 isotherms. The cumulative PSDs (Fig. 2c) calculated for the two sets of data are in good agreement for w<10 Å and diverge for w>10 Å. This example demonstrates that H_2 isotherms (at 77 and 87 K) can be used for the PSD calculation only in the limited range of micropores smaller than 10 Å. However, for the characterization of larger pores an additional isotherm such as N_2 at 77 K is necessary.

In a systematic analysis of our samples we attempt to use Eq. (1) to fit a HHN adsorption data set as well as a single N_2 isotherm (set N) for all samples. The results of fitting the model to the experimental data are shown in Fig. 3 and 4, and the calculated differential and cumulative pore size distributions are shown in Fig. 5 and 6. A good fit to all three experimental isotherms (HHN) is obtained for all samples except for the PC carbon.

It should be kept in mind that PC sample was obtained after pyrolysis of the PET precursor and ulterior heat treatment of the char up to 1200 K, without further activation step. As a result, its porosity is poorly developed and mainly composed of narrow micropores (based on CO_2 adsorption data), as it has been described in earlier works [15,16]. It appears that due to slow diffusion and/or because of the pore connectivity problems [26] the N_2 adsorption isotherm measured for this carbon is not fully equilibrated. In comparison with other N_2 isotherms (Fig. 4) this isotherm (Fig. 4a) appears to be shifted to higher pressures, especially for low amounts adsorbed. The shift in the isotherm causes a corresponding shift in the PSD calculated from this isotherm (Fig. 5a). This erroneous shift in PSD is evident from the comparison with the PSD of PC12 (Fig. 5b). Even though the PSD calculated for PC sample from a single N_2 isotherm is incorrect, a fairly good fit was obtained in the analysis (Fig. 4a). On the other hand, when the whole HHN set of data is analyzed by Eq. (1) a dramatic deviation of the fitted N_2 curve (continuous line in Fig. 4a) from the experimental points is observed. Fitting a full HHN set of data for a given sample may be considered a test of consistency of the adsorption data for that sample. This test failed for the PC sample, which is in agreement with the results of Lozano-Castelló at al. [27,28] who concluded that due to diffusion problems the N_2 adsorption isotherms at 77 K cannot be used to characterize very narrow micropores (<7 Å) and suggested using CO_2 isotherms at 273 K instead.

In our analysis we decided to use the HH set to characterize the PC sample. The calculated narrow PSD, below ~10 Å is consistent with the sequence of PSDs (Fig. 5) showing gradual widening of pores sizes of carbons obtained by progressive activation with increasing burn-off [15].

Based on the above discussion of diffusion problems, and on inconsistencies in fitting of HHN sets some of the original low pressure N_2 adsorption points were excluded from the PSD analysis (full circles in Fig. 4). In such cases, in the range of very narrow pores, the PSDs were derived based on the information from H_2 data which for such pores is more accurate than that obtained from N_2 isotherm.

The PSDs of activated carbon samples presented Fig. 5 and 6 show the effect of activation of the initial PC sample whose narrow PSD is modified by activation process towards wider pores with increasing burn-off. It is clearly seen that with increasing degree of activation the difference between the results obtained from the HHN and N sets decreases. This is because the enlargement of pores is accompanied by the reduction the amount of small micropores including the narrowest ones which are not accessible to N_2 molecules.

These results are in good agreement with those reported in earlier works on the analysis of the PSD by CO_2 adsorption that is considered to be sensitive to sizes of narrow micropores [15,16].

4. Conclusions

We have demonstrated that simultaneous analysis of adsorption data of multiple gases, such as H_2 and N_2 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 to detect and disregard 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 adsorption analysis.

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

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Table 1. NLDFT parameters used in the calculations of H_2 theoretical isotherms.

σ_{ff}, Å	ε_{ff}/k, K	σ_{sf}, Å	ε_{sf}/k, K
3.04	34.3	3.22	31.8

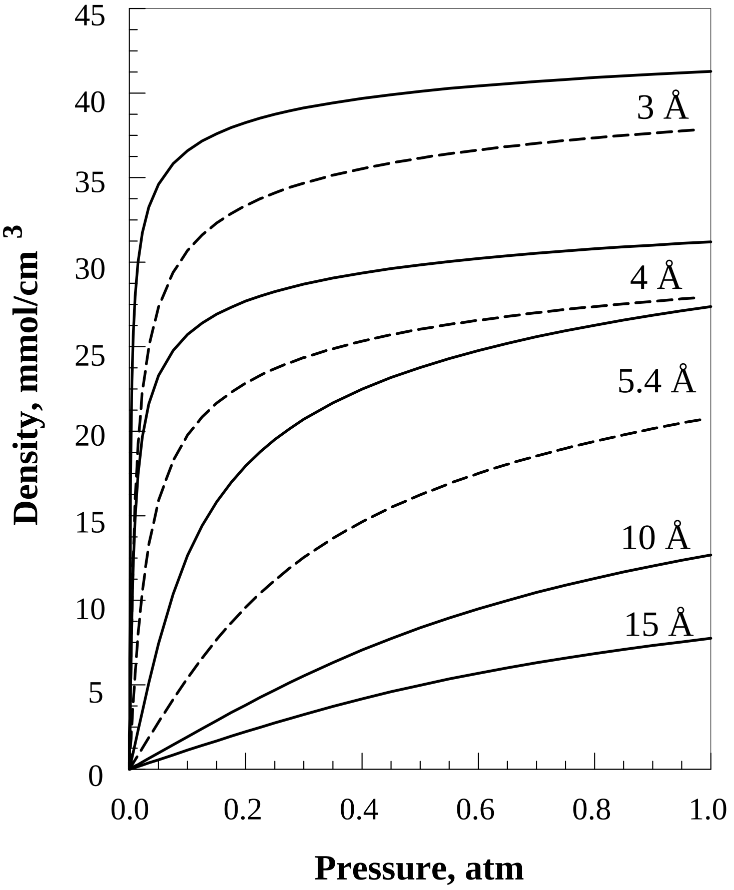

Fig. 1. Model H_2 isotherms at 77.3 (continuous line) and 87.4 K (dashed line) for selected pore widths expressed as densities inside the pores calculated per effective pore volumes.

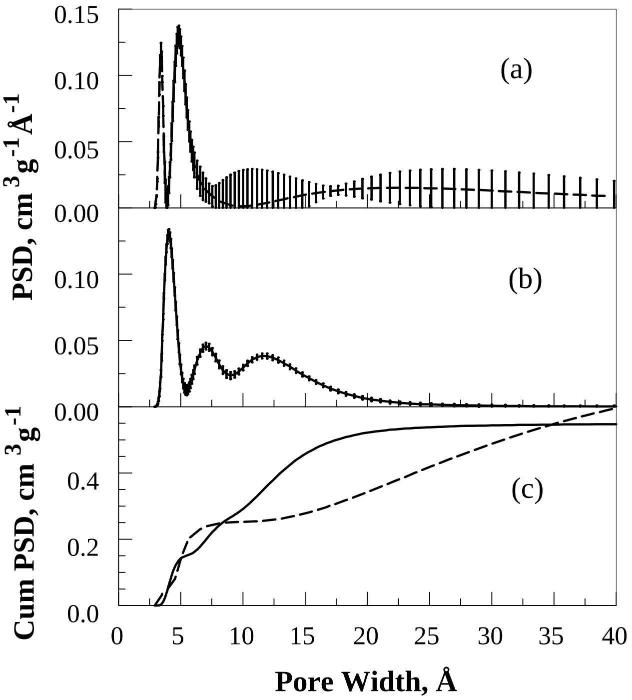

Fig. 2. Differential PSDs calculated for PC35 sample from (a) two H_2 adsorption isotherms, HH, and (b) from all three adsorption isotherms, HHN. Error bars represent uncertainties. (c) Cumulative PSDs calculated from the HH set (dashed line) and from the HHN set (continuous line).

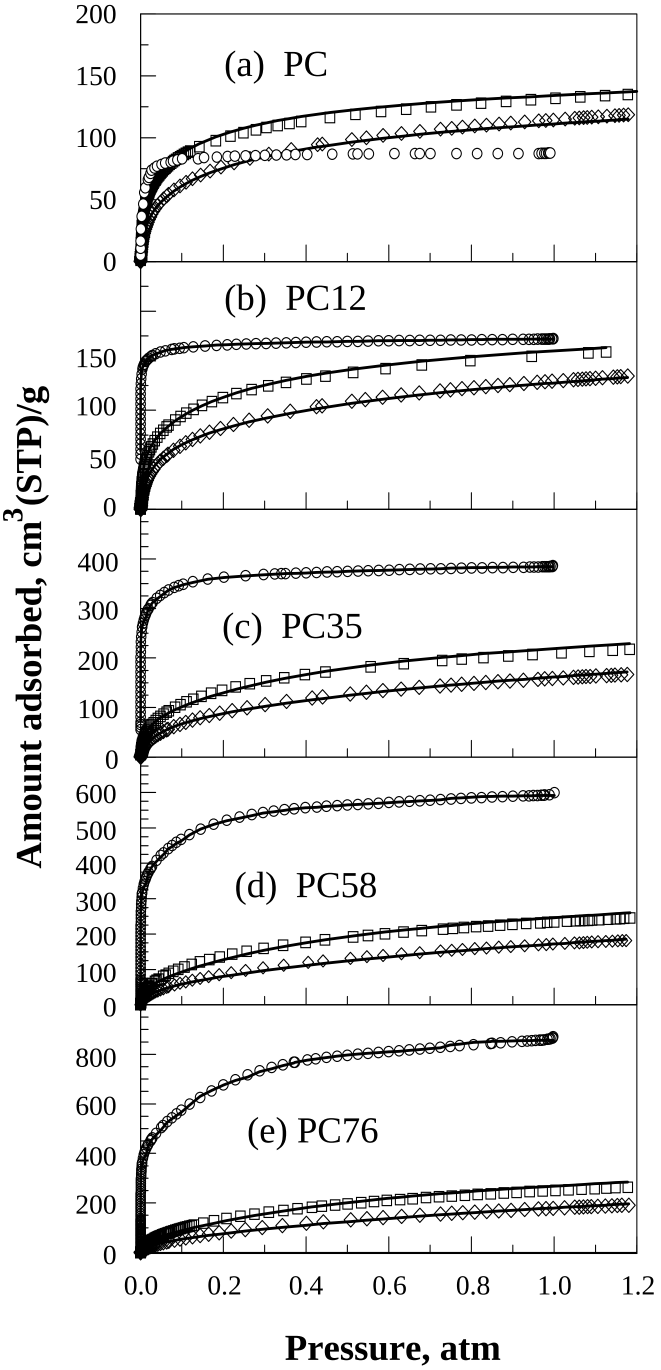

Fig. 3. Experimental adsorption isotherms of nitrogen at 77 K (circles), hydrogen at 77 K (squares), and hydrogen at 87 K (diamonds) for five samples. Fits by Eq. (1) are shown by continuous lines. In part (a) fitting was applied to H_2 adsorption isotherms (HH), in (b-e) to all three isotherms (HHN).

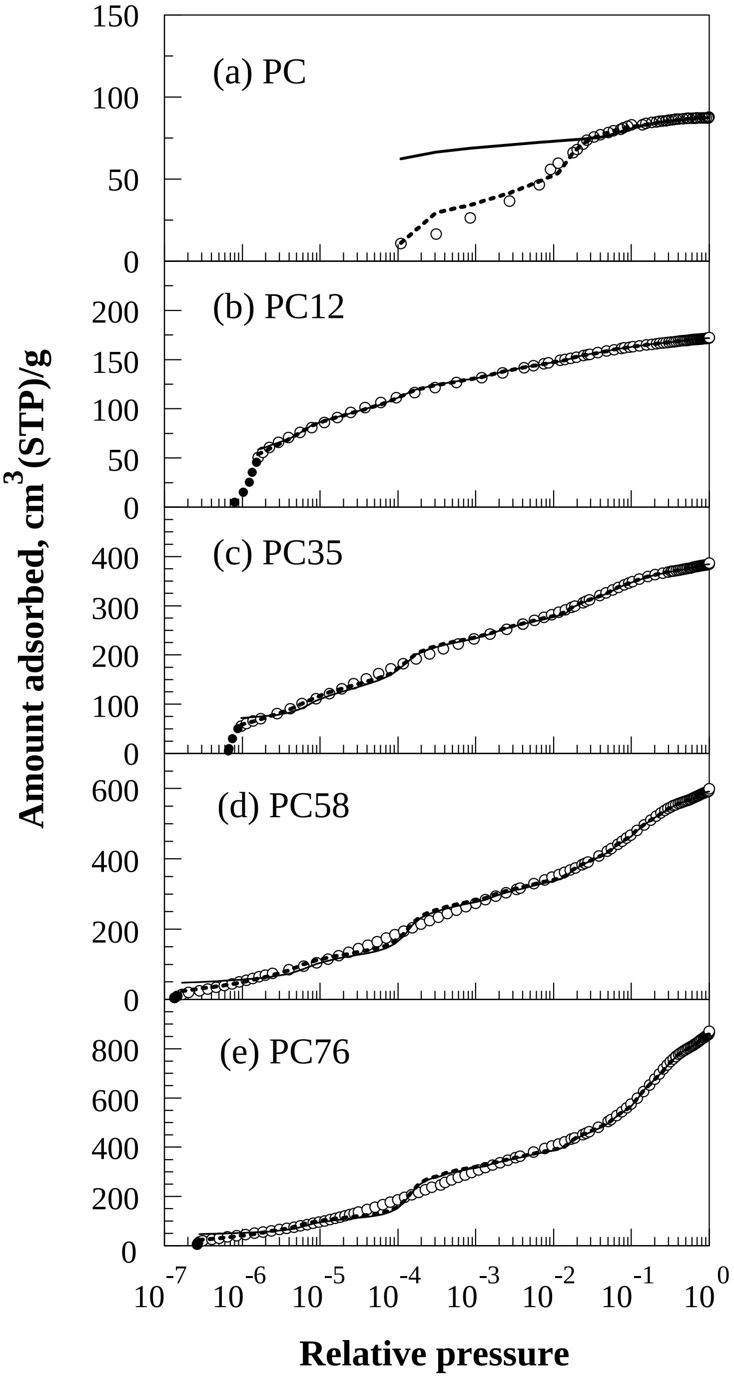

Fig. 4. Experimental adsorption isotherms of nitrogen at 77 K for five samples. Open and full circles represent points used and not used in the PSD calculations, respectively. Fits by Eq. (1) are shown by continuous lines for the case of fitting all adsorption isotherms, HHN, and by dotted lines for the fits of N_2 adsorption isotherms only.

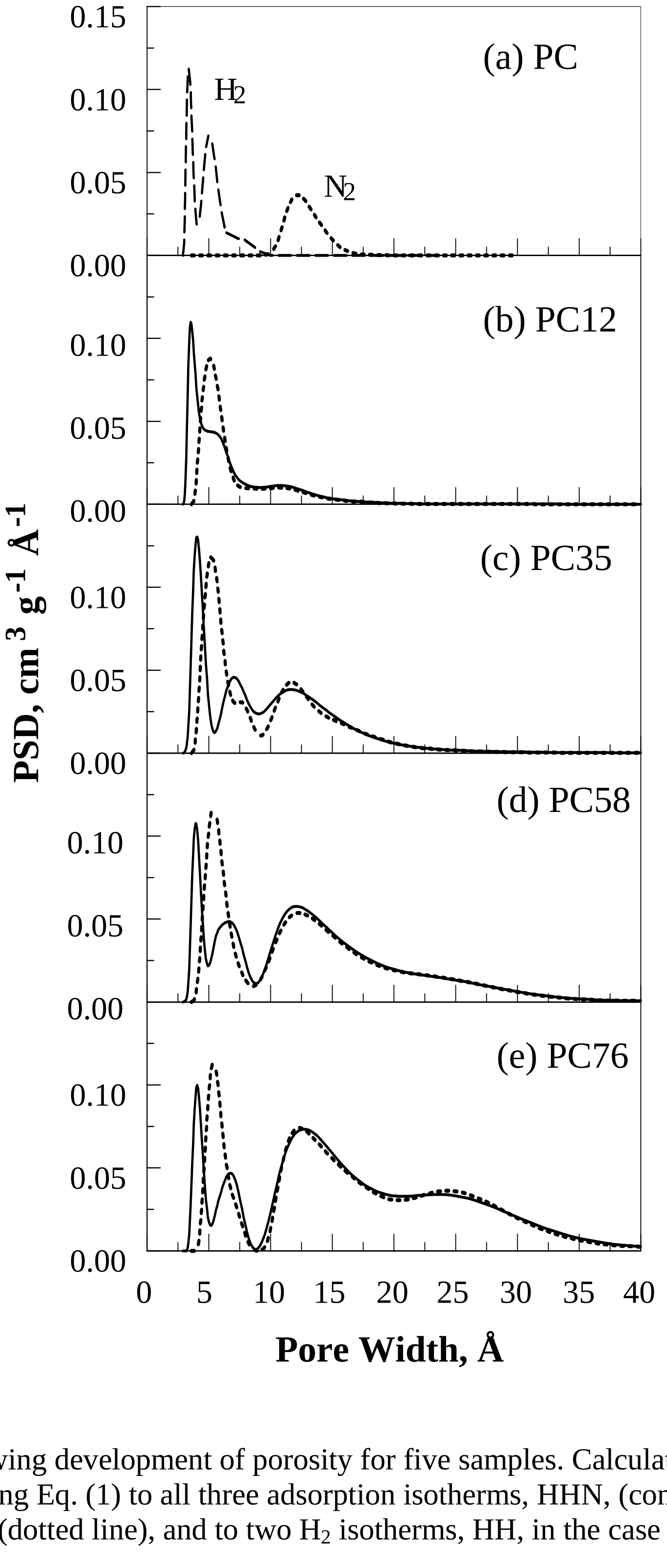

Fig. 5. PSDs showing development of porosity for five samples. Calculations were performed by fitting Eq. (1) to all three adsorption isotherms, HHN, (continuous line), to N_2 isotherm only (dotted line), and to two H_2 isotherms, HH, in the case of PC sample (dashed line).

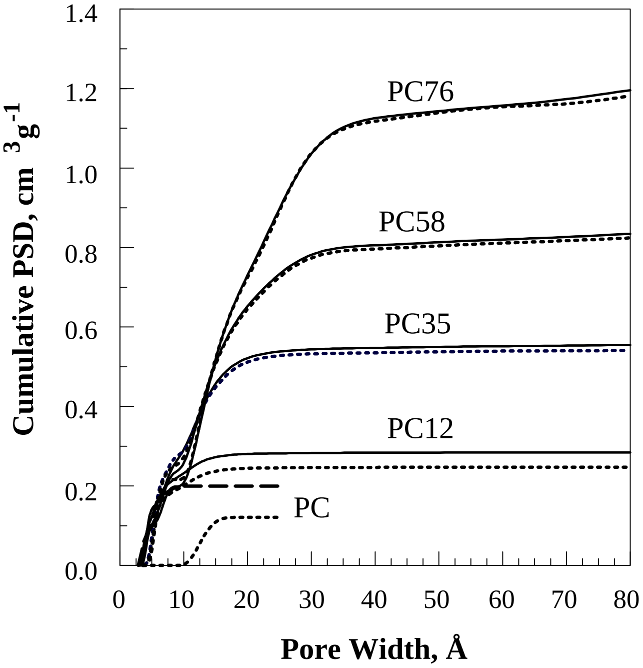

Fig. 6. Cumulative PSDs for five samples. Notation as in Fig. 5.