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**DUAL GAS ANALYSIS OF MICROPOROUS CARBONS USING 2D-NLDFT
HETEROGENEOUS PORE SURFACE MODEL AND COMBINED ADSORPTION
DATA OF N₂ AND CO₂**

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Abstract

Knowledge of the pore structure of carbon materials including micropores is crucial for applications such as double layer supercapacitors, gas separation and other applications requiring high specific surface area materials. High surface area is always associated with fine micropores. Standard pore size distribution (PSD) characterization methods of microporous carbons are based on nitrogen adsorption isotherms measured at 77 K in the relative pressure range of 10^{-7} - 1. Due to very slow gas diffusion into very fine pores at low relative pressures under such conditions the adsorption measurements may be extremely time consuming and sometimes inaccurate when the adsorption equilibrium is not achieved during the measurement. In this work we discuss an approach in which the carbon PSD is calculated from the combined N₂ and CO₂ data measured in the pressure range from 1 to 760 torr which corresponds to $(\sim 1.3 \times 10^{-3} - 1.0 \text{ p/p}_0)$ for N₂ at 77 K and to $(4 \times 10^{-5} - 3 \times 10^{-3} \text{ p/p}_0)$ for CO₂ at 273 K. Under such conditions the diffusion into micropores is usually fast and equilibration times are short for both measurements. In the PSD calculations we use 2D-NLDFT-HS models for carbons with heterogeneous surfaces. We discuss the range of sensitivity of the CO₂ isotherm to pore sizes and the relationship between N₂ and CO₂ data within this range. Finally we show that both isotherms can be fitted simultaneously with their corresponding models and as a result the unified PSD can be obtained. In this unified PSD the low end of the pore size range is mostly related to the CO₂ isotherm while the high end to the N₂ isotherm. We validated the unified PSD by showing its good agreement with the PSD derived from the full N₂ isotherm (in the range 10^{-7} -1 p/p₀) for several samples.

1. Introduction

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. It is well known, however, that carbon samples that contain very fine micropores are difficult to analyze at cryogenic temperatures due to size restrictions, connectivity problems or extremely slow diffusion at low relative pressures. As early as 1982, Rodriguez-Reinoso et al. [1] reported that measurements of N₂ adsorption isotherms at 77 K on some carbons with fine pores of molecular sizes required more than 100 hours for completion. Increasing measurement temperature to 90 K dramatically reduced equilibration time and improved accuracy of measured data.

To improve the analysis of carbon molecular sieves and microporous carbons, adsorption of CO₂ at 273 K was often applied [2, 3]. A qualitatively good agreement was reported [4] between the PSD results obtained from the isotherms of N₂, Ar, and CO₂ on the microporous activated carbon fiber in the pore size range below 15 Å. At 273 K, the diffusion and the equilibration processes of CO₂ molecules in small pores are significantly faster than those of N₂ or Ar at cryogenic temperatures, but the CO₂ adsorption data are only sensitive to small micropore sizes. The complementary information about the larger pores may be obtained from the N₂ or Ar adsorption isotherm measured at cryogenic temperatures at relative pressures above 0.001 where the diffusion and equilibration are faster than at low pressures.

To describe the PSD in the full pore size range it is necessary to combine the two parts of the PSD. One way of connecting the two parts referred to as the joined approach was recently described by Caguiat et al. [5] who proposed to make this junction at 10 or 20 Å. The authors showed by several examples that the two parts of the PSD calculated from N₂ and CO₂ intersect at one or more points around pore size of 10 Å. This is because due to its high uncertainty in this range the PSD calculated from CO₂ becomes oscillatory. Pore size near 10 Å is usually considered to be the upper limit of sensitivity for CO₂ analysis [6]. Similar oscillatory behavior of the CO₂ PSD in this range has also been shown elsewhere [7]

In this work we have fitted both experimental isotherms simultaneously with their corresponding theoretical models to yield a single PSD as a common solution for both experimental isotherms used in the analysis. Because a complete set of experimental points from

the N₂ and CO₂ isotherms is used in the fit, this method is statistically stronger and more robust than methods based on fitting the individual isotherms separately and overlaying calculated PSDs. A similar method was previously applied to the data of N₂ and H₂ at 77 K for the analysis of a series of activated carbons [8] and to the data of Ar and H₂ at 87 K for the analysis of molecular sieving carbons [9]

In our PSD calculations we use new 2D-NLDFT-HS model for carbons with heterogeneous surfaces [10, 11]. In the following text of this work we will use 2D-HS as abbreviated name of this model. This improved carbon slit pore model gives an excellent fit to the experimental data and is free from common artifacts usually obtained in the PSD analysis when the standard NLDFT model was used.

2. Experimental

Carbon samples analyzed in this study were 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 a heat treatment at 1200 K for 1 h. The series of activated carbons was obtained from the PC sample by activation with CO₂ at 1200 K for variable periods of time. Preparation and properties of those samples were described in several papers [8, 12-13]. For the present study a new set of samples was derived from the original PC sample using the same activation procedure as previously. The following series of activated carbon samples was obtained: PC5, PC23, PC39, PC63 and PC85, where the number in the sample name represents the burn-off percent during activation of the PC precursor.

These samples constitute a representative set of activated carbons with progressively changing pore structures depending upon the degree of burn-off. We also analyzed a reference sample of non-graphitized carbon black BP 280 from Cabot Corporation a carbon molecular sieve C1021 from Supelco.

Adsorption isotherms of nitrogen at 77 K were measured for these samples using the high-resolution Micromeritics 3Flex instrument equipped with high-vacuum system, three micropore ports and three 0.1 Torr pressure transducers. The CO₂ isotherms at 273 K were measured using a Micromeritics ASAP 2050 extended pressure instrument in the pressure range up to 7600 Torr

that corresponds to $\sim 4 \times 10^{-5} - 0.26 p/p_0$ for CO_2 . The samples were degassed under vacuum at 600 K overnight prior to the adsorption measurements.

3. Results and discussion

In our PSD analysis of the new series of PC-derived samples, we apply a recently developed 2D-HS model for carbons with heterogeneous surfaces. This model incorporates energetical heterogeneity and geometrical corrugation of the carbon surface [10] and thus is more realistic than the standard NLDFT (1D) model that assumed carbon slit pores with flat and energetically uniform graphitic walls [14]. In our earlier characterization study [8] of the original carbon samples derived from the PC char we used that standard NLDFT model. It now seems appropriate to start by showing the differences between the results obtained from the two models. As an example we chose PC63 sample that contains micro and mesopores and we analyze its N_2 adsorption isotherm using both models. The results, presented in Figure 1 show two characteristic artifacts obtained with the standard NLDFT (1D) model, (i) the S-shaped deviation in the isotherm fit (Figure 1a); (ii) a sharp minimum or a “gap” near 10 Å in the calculated PSD (Figure 1b). In contrast, the results obtained with the 2D-HS model are free from these artifacts showing an excellent fit to the experimental data and a smooth regular PSD.

Figure 1. PSD analysis of N_2 isotherm for PC63 sample using the 2D-HS heterogeneous surface model and standard NLDFT slit pore model. Comparison of goodness of fit (a) and PSD plots (b) calculated by both models.

3.1. 2D-NLDFT-HS model for CO₂.

To our knowledge, artifacts similar to those of standard NLDFT model for N₂ were not reported for the CO₂ NLDFT model. Nevertheless, for consistency with our nitrogen model we developed an analogous model for CO₂ adsorption on carbon at 273 K. In the calculation of the theoretical isotherms (kernel) for this model we use the same implementation [14] of Tarazona's NLDFT [15,16] as in a recent paper [10]. Also, equations describing the carbon surface corrugation and energy heterogeneity have here the same form as they were introduced in that paper. Parameters used in our calculations are reported in Table 1.

Table 1. Parameters used to calculate the 2D-NLDFT-HS model (kernel) of CO₂ adsorption at 273 K in carbon pores with heterogeneous surface.

Intermolecular interaction parameters		Energy heterogeneity parameters, ref [10] eq 6		Surface corrugation parameters, ref [10] eq 7	
$\sigma_{ff} = d_{HS}(\text{\AA})$	3.49	β_1	0.0678	α	0.45
ε_{ff}/k (K)	227.9	β_2	0.756	λ	6.0
$\sigma_{sf}(\text{\AA})$	3.44	λ	6.0		
ε_{sf}/k (K)	79.9.0				

The fluid–fluid interaction parameters were obtained by fitting the mean-field DFT equation of state [17] to the bulk densities of the co-existing vapor and liquid phases taken from the NIST Database [18]. In the calculations, we assumed that the hard sphere and the LJ molecular diameters are equal, $d_{HS} = \sigma_{ff}$. The solid–fluid interaction parameters were obtained by applying the Lorentz-Berthelot combining rules using the values $\varepsilon_s/k=28$ K and $\sigma_s=3.4$ Å for carbon-carbon interactions in graphite [19]. The intermolecular interaction parameters used in this work

are consistent with those reported by Ravikovitch et al. [6]. In our calculations we use the same graphene carbon structure model with the same surface corrugation as it was established for the 2D-HS carbon model [10]. The surface energy heterogeneity, however, is expected to be rather adsorbate dependent and we evaluate the surface energy heterogeneity parameters β_1 and β_2 for CO₂ adsorption by fitting the theoretical model isotherm calculated for an open surface to the isotherm data measured on the non-graphitized carbon black BP 280 (Figure 2). The N₂ adsorption data on this carbon published by Kruk et al. [20] were considered a reference of heterogeneous carbon [21, 22] and used as such reference for the development of the nitrogen 2D-HS model [10].

Figure 2. Adsorption isotherm of CO₂ measured at 273 K on the reference sample BP280 in the pressure range up to ~ 10 atm and its fit with the 2D-HS model using parameters from Table 1.

The kernel for 2D-HS model was calculated with parameters from Table 1 in the relative pressure range from 10^{-7} to $0.3 p/p_0$ which for CO₂ corresponds to the interval of 0.003 torr - 10 atm. Selected isotherms from this kernel are shown in Fig. 3. Labels attached to several isotherms show pore sizes in Å for which they were calculated. Pore size in our approach is defined as the effective pore width $w = H - 3.4$ Å where H is the physical width measured between

the centers of the surface carbon atoms of the opposite walls. The isotherms shown in part (a) of Fig. 3 are expressed in terms of the excess CO₂ density calculated per effective pore volume, while in part (b) the isotherms are expressed as amount adsorbed per unit surface area of the pore. Part (b) of this figure is particularly explanatory in showing the ranges of overlapping between the isotherms of different pores sizes and the isotherm of the open surface. In mathematical terms the overlapping isotherms are linearly dependent and thus not sensitive to the pore sizes. To establish the upper limit of the pore size sensitivity for the CO₂ isotherms measured up to 0.3 p/p_0 we notice that the isotherm of the 18 Å pore overlaps the open surface isotherm almost up to 0.3 p/p_0 , while the isotherms of the 16 Å pore and smaller depart from this isotherm at some point of $p/p_0 < 0.3$. It follows that the limit of the CO₂ sensitivity to pore sizes is between 16 and 18 Å. Obviously, this limit will be lower for adsorption isotherms measured in the lower pressure range; and for typical measurement up to 1 atm it was established to be less than 10 Å [6].

Figure 3. Selected excess adsorption isotherms for CO₂ at 273 K calculated using the 2D-HS pore model. Isotherms expressed in terms of the fluid density (a) and amount adsorbed per unit surface area (b).

3.2. Dual gas carbon PSD analysis using 2D-NLDFT models applied to N₂ and CO₂ data.

The usual mathematical procedure used to calculate the PSD of a porous material from gas adsorption data can be described as fitting the theoretical kernel to the experimental adsorption isotherm. Here, a set of two adsorption isotherms is fitted simultaneously with their corresponding kernels to yield a single PSD as a common solution for all experimental data used in the analysis. Mathematically, the PSD is obtained by minimizing the following expression [8-9].

$$\min \sum_m^2 \sum_i^{N_m} \left[V_m(p_i) - \int_{\alpha}^{\beta} K_m(p_i, w) f(w) dw \right]^2 + \lambda \int_{\alpha}^{\beta} [f''(w)]^2 dw \quad (1)$$

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, λ is the regularization (smoothing) parameter and $f(w)$ is the differential PSD to be calculated. A numerical method for obtaining stable and physically feasible solution for $f(w)$ is implemented in the SAIEUS program [23] and this program is used for data analysis in this work. To test the consistency between PSDs calculated from N₂ and CO₂ data we analyse a series of six PC samples introduced in the experimental section. These samples constitute a representative set of activated carbons with progressively changing pore structures depending upon the degree of activation burn-off. Figure 4 shows a quantitatively good simultaneous fit of N₂ and CO₂ isotherms with the corresponding 2D-HS models obtained for the following four of six samples: PC-23, PC-39, PC-63 and PC-85. Their calculated PSDs are shown in Figure 5. The isotherm data used in the analysis of these samples cover the relative pressure range from 4×10^{-5} to 0.26 for CO₂ and from 10^{-8} to 1.0 for N₂. We will refer to these pressure conditions as to full pressure ranges. The results of the simultaneous analysis of N₂ and CO₂ isotherms indicate that these isotherms of a given carbon are partially correlated via corresponding models and a common PSD. The range of this correlation corresponds to the range of the CO₂ sensitivity to pore sizes.

Figure 4. Simultaneous fit of the 2D-HS models to the N_2 and CO_2 isotherms (full pressure range) measured on four carbons PC-23, PC-39, PC-63 and PC-85 presented in linear (a) and logarithmic (b) scales.

Figure 5. Differential PSDs based on simultaneous fitting the 2D-HS models to both N_2 and CO_2 isotherms (full pressure range) measured for the PC-Char and its activated derivatives: PC-5, PC-23, PC-39, PC-63 and PC-85.

For the less activated PC-5 and not activated PC-Char it was impossible to obtain such a good simultaneous fit of both isotherms in the full pressure ranges. We found that the simultaneous fit overestimates the experimental N_2 isotherm and underestimates the CO_2 isotherms. This suggests that these carbons contain some micropores that are accessible to the CO_2 molecules but not to N_2 . The observed differences in the pore accessibility may be due to extremely slow diffusion of N_2 at 77 K to some pores and/or certain specific geometrical constraints that allow more access for CO_2 than to N_2 . Actually, a very slow diffusion process was observed directly during adsorption measurements as it took about 85 hours to measure the

initial points of the N₂ isotherm up to about 10^{-3} p/p_0 for PC-Char and 25 hours for PC-5. We believe that in the case of carbons with extremely narrow pores such as these two samples the CO₂ molecules are more reliable than N₂ in probing the sub micropores, but for larger pores at higher pressures CO₂ loses its sensitivity. Consequently, in the analysis of these samples we excluded the N₂ data points at pressures below 1 torr $\cong 10^{-3}$ p/p_0 and the CO₂ points above 1 atm $\cong 3 \times 10^{-3}$ p/p_0 . We will refer to such data as data in shortened pressure ranges. An excellent simultaneous fit of both kernels to such data was obtained for both carbons (Figure 6). The calculated PSDs and pore volumes of these carbons are included in Figure 5 and Table 2 showing systematic change in the carbons pore sizes and volumes upon activation.

Figure 6. Simultaneous fit of the 2D-HS models to the N₂ and CO₂ isotherms (shortened pressure range) measured on two carbons PC-Char (a) and PC-5 (b). Data is represented in linear (upper axis) and logarithmic (lower axis) scale.

Table 2. Cumulative pore volumes of studied samples calculated from the dual gas analysis of N₂ and CO₂ using 2D-HS models

Sample	Burn-off %	Pore volume [cm ³ /g]				
		w < 6 Å	w < 10 Å	w < 15 Å	w < 20 Å	w < 50 Å
PC-Char	-	0.116	0.157	0.158	0.161	0.169
PC-5	5	0.115	0.182	0.195	0.202	0.204
PC-23	23	0.125	0.277	0.388	0.411	0.432
PC-39	39	0.114	0.337	0.491	0.587	0.614
PC-63	63	0.080	0.326	0.553	0.828	1.078
PC-85	85	0.333	0.268	0.497	0.784	1.343
C1021		0.132	0.232	0.272	0.278	0.306

In addition to the family of PC samples we also analyzed a sample of carbon molecular sieve Carboxen C1021 from Supelco. For this carbon we were able to obtain excellent simultaneous fit of N₂ and CO₂ isotherms with the corresponding 2D-HS models in the full pressure range of both isotherms (Figure 7 a). This indicates equal accessibility of this carbon's pores to both gases. In comparison with PC-Char the calculated PSD of C1021 is slightly wider (Figure 7b) i.e. it contains larger micropores. These pores may facilitate access of N₂ molecules to smaller adjacent pores.

Figure 7. PSD analysis of carbon molecular sieve Carboxen C1021 from Supelco. (a) Simultaneous fit of the 2D-HS models to the N₂ and CO₂ isotherms (full pressure range) measured on Carboxen C1021. Data is represented in linear (upper axis) and logarithmic (lower axis) scale. (b) Calculated PSD of C-1021 compared with the PSD of PC-Char.

3.3. Analysis of adsorption isotherms in shortened pressure ranges using dual gas 2D-NLDFT model.

The observation made in the preceding section about partial correlation between N₂ and CO₂ isotherms measured on the same carbon sample suggests that the information about the carbon PSD derived from the low pressure N₂ data may be substituted by the information obtained from the CO₂ data. To test this hypothesis we analyze adsorption data of two representative carbon samples using three procedures: (i) fitting both isotherms in shortened pressure ranges, (ii) fitting both isotherms in full pressure ranges and (iii) fitting only N₂ isotherm in full pressure range. The analyzed two carbon samples are PC-23 and PC-85 obtained from the PC precursor with low and high burn-off percent. The PSDs calculated for these samples according to the three procedures are compared in Figures 8 and 9. Only minor differences between the PSDs calculated using different procedures are observed for each sample. The differences in the cumulative volume plots are even less pronounced, becoming almost indistinguishable for PC-85.

Figure 8. PSD analysis of PC-23 sample. Simultaneous fit of 2D-HS models to N₂ and CO₂ isotherms in shortened pressure ranges (a). Differential PSDs (b) and cumulative volumes (c) calculated using N₂ and CO₂ data in short (i) and full (ii) pressure ranges and using only N₂ data in full pressure range (iii). Color code in part (c) is the same as in part (b).

Figure 9. PSD analysis of PC-85 sample. Notation is the same as in Figure 8.

There are two important advantages of using procedure (i) over procedure (iii) for the characterization of porous carbons containing micropores: 1. Practical - reduced time of the analysis. 2. Fundamental - a confidence that the CO₂ data measured at 273 K are equilibrated.

Our understanding is that this method was developed and tested for “clean” carbon materials (i.e., poor surface chemistry). In cases, where large amount of polar groups are present on the surface, the agreement between the N₂ and CO₂ analysis may not be found [24] due to the occurrence of specific interactions between CO₂ and the surface groups of the carbons (i.e., acid-base and/or polar interactions, hydrogen bonding).

A general idea of using combined adsorption data of different gases as sources of information about the pore structure of carbon materials may be extended to other materials and other means of characterization. The concept of using gas adsorption data in conjunction with mercury porosimetry was recently discussed and the unified method was presented for the PSD determination of hierarchical zeolites from argon adsorption and mercury intrusion [25].

Conclusions

We have shown that the N_2 and CO_2 isotherms of a given carbon measured at 77 and 273 K can be analysed simultaneously with the corresponding 2D-NLDFT models and yield a common PSD that is consistent with both isotherms. This suggests that the information about the carbon PSD derived from the low pressure N_2 data may be substituted by the information obtained from the CO_2 isotherm.

We tested this dual gas analysis approach using the combined N_2 and CO_2 data measured in the pressure range from 1 to 760 torr. It is important to highlight that under such conditions the diffusion into micropores is usually fast and equilibration times are short for both measurements. The unified PSDs obtained from this approach were validated by showing a good agreement with the PSDs derived from the full N_2 isotherm for several samples.

The presented method of simultaneous analysis of adsorption data of the two gases constitutes a useful tool for a comprehensive characterization of activated carbons, and for obtaining detailed and reliable carbon PSDs. The calculated PSDs are robust and consistent with both adsorption isotherms.

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