

Characterization of Carbon Micro and Ultramicropores Using Adsorption of Hydrogen and Other Simple Gases

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Introduction

Micropores and ultramicropores play the most significant role in carbon applications aimed for hydrogen and natural gas storage. Development of carbon materials for these applications requires accurate and reliable methods for the characterization of carbon microporosity usually described in terms of pore size distribution (PSD). Traditionally, the PSD of a porous carbon is evaluated from the analysis of nitrogen adsorption isotherms measured at 77 K. This method, however, will not account for a certain range of the smallest pores which may be accessible to CO₂ at 273K and to H₂ molecules but not to N₂ at 77 K.

Recently, it was proposed [1] to use H₂ adsorption isotherms measured at cryogenic temperatures (77 or 87 K) for the characterization of carbon ultramicropores. Hydrogen at 77 K is above its critical point and its adsorption isotherms are sensitive to the pore sizes in the range of very small pores. This sensitivity, however, diminishes gradually for increasing pore sizes and almost disappears for pores larger than 10 Å. To describe carbon pore size distribution in a wider range of pore sizes it is proposed to use H₂ adsorption isotherms in conjunction with N₂ or Ar isotherms.

For the calculation of carbon PSDs the Non Local Density Functional Theory (NLDFE) is used. Methods based on this approach have become widely applied for the characterization of pore structure of activated carbons and other porous materials [2-5]. The evaluation of the PSD is based on the theoretical isotherms calculated using NLDFE for individual pores of a given adsorbate-adsorbent system. Mathematical procedure used to calculate the PSD can be described as fitting of a combination of the theoretical isotherms to the experimental data. Usually, one or more isotherms of a single adsorbate are used for such calculations. Here, a set of isotherms measured for different adsorbates is fitted simultaneously by their corresponding models to yield a single PSD as a solution for all carbon-adsorbate systems used in the analysis. Including H₂ isotherms in the PSD analysis allows extending the range of the analysis to ultramicropores which are vital for hydrogen storage applications.

Experimental

Several porous carbon samples representing different pore structures were studied using adsorption isotherms of N_2 , Ar and H_2 . Selected results obtained for carbon molecular sieve Takeda 3A (Takeda Co.) and activated carbon fiber ACF10 (Nippon Kynol, Japan) are reported in this abstract. Adsorption isotherms were measured in the pressure range of 0.001–760 torr using an Autosorb 1 MP [Quantachrome Instruments, Boynton Beach, Florida, USA]. Prior to the adsorption measurements the samples were outgassed for 12 hours at 520 K under high vacuum.

Results and Discussion

The theoretical adsorption isotherms were generated using the NLDFT of Tarazona [3] with gas-gas interactions described by the Lennard-Jones potential. The slit pore model was assumed for carbon pores and the carbon-gas interactions were described by the Steele potential [6]. Interaction parameters for carbon- N_2 and carbon-Ar systems were taken from reference [5]. Gas-gas interaction parameters for H_2 were taken from reference [7] and carbon- H_2 interaction parameters were calculated by applying Lorentz-Berthelot combining rules. Sets of theoretical isotherms calculated for given carbon-adsorbate systems were used as kernels in the SAIEUS [8] numerical algorithm to calculate PSD from the appropriate experimental data. The SAIEUS algorithm utilizes the regularization procedure and imposes non-negativity constraints on the solution. This algorithm is applied in an interactive manner which allows stable and meaningful solutions to be obtained. A more detailed description of the method is given elsewhere [8, 9].

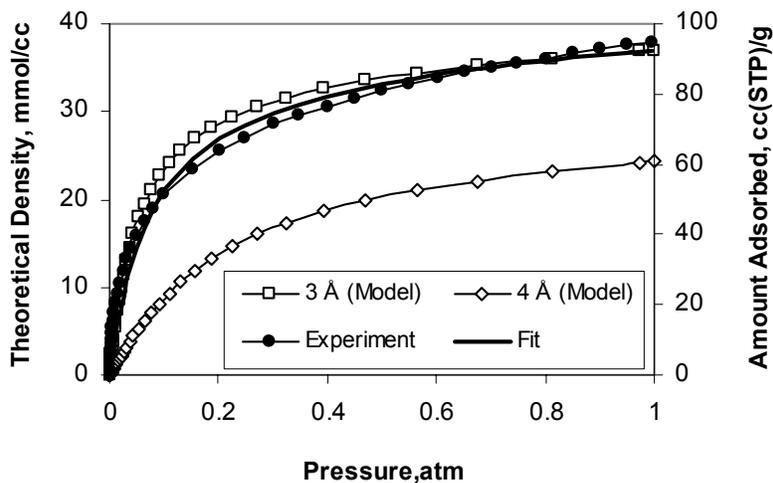


Figure 1. Experimental H_2 isotherm measured at 87 K for the Takeda 3A sample compared with the NLDFT isotherms calculated for the 3 and 4 Å pores and with the curve fitted by SAIEUS.

Figure 1 presents examples of NLDFT isotherms calculated for H₂ adsorption in the 3 and 4 Å carbon pores at 87 K compared with the experimental H₂ isotherm measured at the same temperature on the Takeda 3A sample. The curve fitted to the experiment by SAIEUS is also included in the figure. It can be seen without calculations that the experimental isotherm is very similar to the theoretical one calculated for the 3 Å pore. Based on this observation and on the fact that N₂ adsorption on this sample at 77 K is negligible one would expect a narrow PSD centered near the value of 3 Å. Indeed, this type of PSD is obtained from the calculations (Figure 2).

The result obtained from this analysis is in quantitative agreement with the molecular sieving properties of Takeda 3A carbon which is used for the separation of CO₂ from CH₄ and thus has pores in the range of 3-4 Å [10]. This result can be treated as a critical test of the method. It agrees very well with the PSD reported from CO₂ adsorption at 273K [10], confirming the usefulness of H₂ at 77K or 87K and of CO₂ at 273K [11, 12].

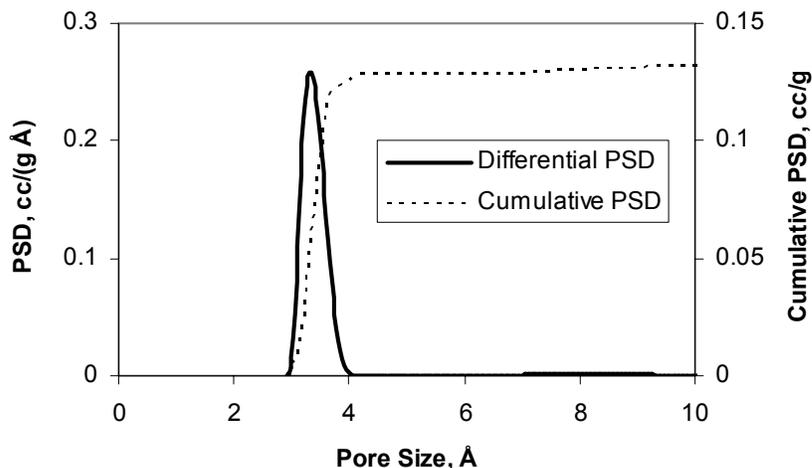


Figure 2. Differential and cumulative PSDs of Takeda 3A sample calculated from H₂ isotherm measured at 87 K.

To accurately characterize carbons containing larger pores in addition to ultramicropores one can use a combination of adsorption isotherms including a hydrogen isotherm. An example of such data set measured for activated carbon fiber ACF10 is presented in Figure 3. The data for this carbon were analyzed in two ways:

1. All three isotherms (N₂, Ar and H₂) were simultaneously fitted by one PSD function using appropriate NLDFT kernels.
2. Two isotherms (N₂ and Ar) were simultaneously fitted by another PSD function.

A satisfactory fit is obtained to all three experimental isotherms (Figure 3). The PSD function shown in Figure 4 represents a common solution for all three isotherms. This means that each of the isotherms can be calculated by integration of this function with the appropriate kernel. Lower integration limits used for H₂ are 2.9 Å and 3.6 Å for N₂ and Ar. The PSD obtained from the simultaneous analysis of N₂ and Ar isotherms (Figure 4) represents range of pores accessible to these molecules. Using this distribution one can calculate isotherms for N₂ and Ar but not for H₂.

It is seen from Figure 4 that for this carbon:

1. Differential distributions calculated for both cases merge for pores larger than 5 Å.
2. More than 10% of pores accessible to H₂ molecules are not accessible to N₂ and Ar.

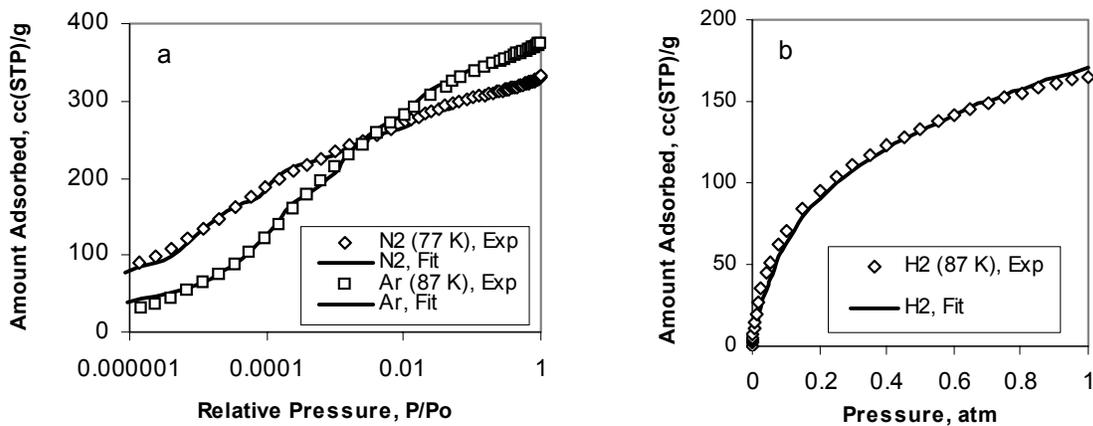


Figure 3. Experimental isotherms of N₂, Ar and H₂ measured at 77 at 87 K compared with their fits obtained by fitting all three isotherms simultaneously with a single PSD.

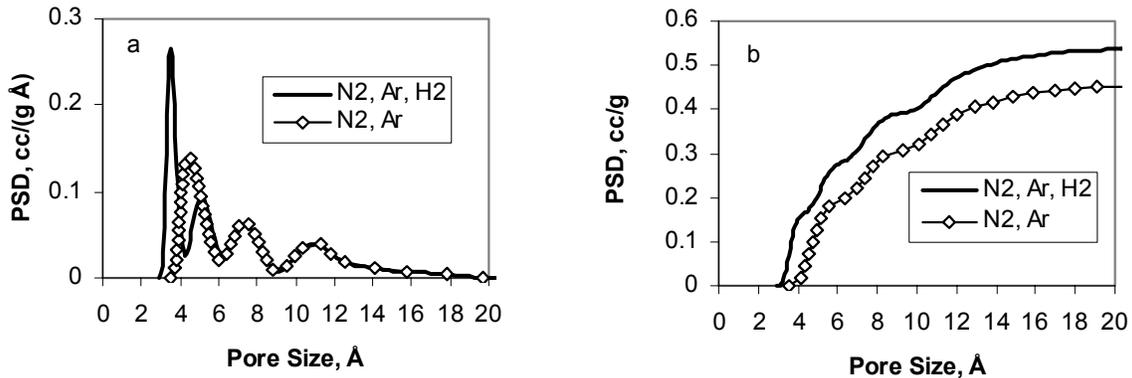


Figure 4. Differential (a) and cumulative (b) PSDs of ACF10 sample calculated (1) from N₂, Ar, H₂, and (2) from N₂, Ar isotherms

Conclusions

1. The result obtained from the H₂ adsorption analysis of the Takeda 3A carbon is in quantitative agreement with the molecular sieving properties of this carbon. This result demonstrates that H₂ can provide meaningful information about ultramicropores.
2. It is shown that the simultaneous analysis of multiple adsorption isotherms can be used to confirm the consistency of the carbon PSD for different adsorbates.
3. Including H₂ isotherms in the PSD analysis allows extending the lower limit of the analysis to pore sizes of about 3 Å. This pore size range may be useful for hydrogen storage applications.

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