

NEW METHOD FOR CHARACTERIZATION OF ACTIVATED CARBONS USING CARBON DIOXIDE ADSORPTION

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Introduction

The application of CO₂ adsorption at ambient temperatures has some advantages over N₂ adsorption in studies of microporous carbons and allows to test the most narrow micropores, which may be not accessible at cryogenic temperatures [1,2]. Considerable progress in characterization and prediction of adsorption properties of micro- and nanoporous materials can be achieved by using the molecular theories of adsorption such as the Density Functional Theory (DFT) [3-9]. The present work focuses on the application of the DFT for adsorption characterization using CO₂ adsorption with a prominent example of two typical samples of activated carbon catalyst supports.

Method

To model carbon dioxide adsorption in carbon slit pores we employed the non-local density functional theory (NLDFT) of Tarazona [3] which was used earlier for the description of nitrogen and argon adsorption in carbons [4-6] and nanoporous siliceous materials [7-9].

Parameters of the fluid-fluid interactions were chosen to reproduce the liquid-gas coexistence of bulk carbon dioxide at 273.2 K. Carbon-CO₂ interactions were modeled with the Steele 10-4-3 potential with the parameters of the potential calculated according to the Lorentz-Berthelot combining rules. With these parameters, the NLDFT model reasonably reproduced the CO₂ isotherm on non-porous carbon [10] for up to 1 atm.

The CO₂ adsorption isotherms were calculated using the NLDFT in carbon slit pores with the *internal* pore width ranging from 3 to 20 Å. The theoretical isotherms were further used for fitting the

experimental CO₂ isotherms using the integral adsorption equation. The pore size distributions were calculated by inverting the integral adsorption equation. A detailed description of the NLDFT model for CO₂ and the numerical method will be presented elsewhere.

The experimental adsorption isotherms of CO₂ at 273.2 K were measured with the Autosorb-1C adsorption apparatus (Quantachrome Corp., USA) within the pressure range of up to 1 atm.

Results and Discussion

The experimental adsorption isotherms and corresponding theoretical fits are shown in Fig.1.

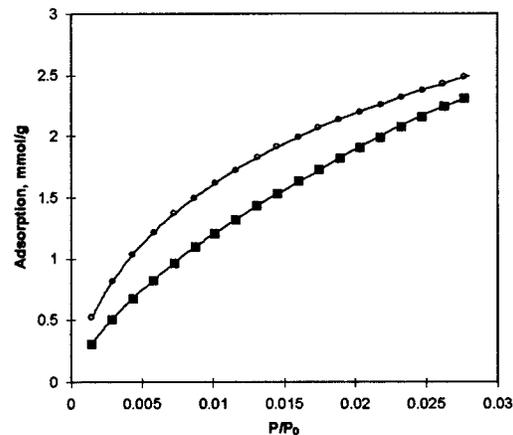


Figure 1. CO₂ adsorption isotherms on two activated carbon catalyst supports at 273.2 K. Open circles, experimental data on sample 1; squares, experimental data on sample 2; Lines, integral isotherms calculated using NLDFT.

The calculated pore size distributions shown in Fig. 2 are essentially bi-modal for both carbon samples. While the positions of the peaks observed at

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ca. 5.4-5.7 Å and ca. 8-8.4 Å are quite similar for both samples, the magnitudes of these peaks are different. The structure of the sample 1 is more uni-modal, while that of the sample 2 is prominently bi-modal.

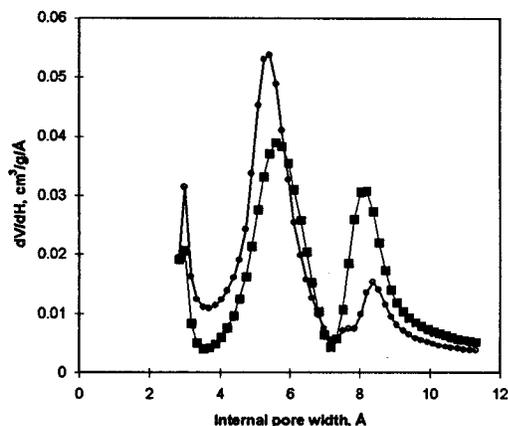


Figure 2. Pore size distributions of two activated carbons. Circles, sample 1; Squares, sample 2. Lines are shown to guide the eye.

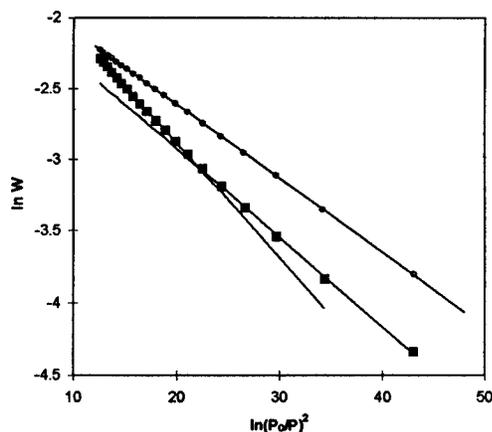


Figure 3. Dubinin-Radushkevich plots. Circles, sample 1; Squares, sample 2.

For comparison, we used the conventional Dubinin-Radushkevich (DR) equation to elucidate the structural information from the adsorption data. According to the Dubinin's approach [11], in the case of the uni-modal pore structure (sample 1) we may expect the adsorption isotherm to be linear in the coordinates of the DR plot. The Fig. 3 shows that this is indeed the case. In the case of the bi-

modal pore structure (sample 2) the adsorption isotherm in the DR coordinates should be well-approximated by two lines with different slopes. The slopes are related to the characteristic adsorption energies and the pore widths of the corresponding pore structures. Fig. 3 shows that the DR plot for sample 2 exhibits two linear regions. However, the characteristic pore widths calculated by using the Dubinin's approach were considerably larger than those calculated by using the NLDFT model.

Conclusions

The new NLDFT model for carbon dioxide adsorption at 273 K has been applied to calculate the pore size distributions of two activated carbon catalyst supports. It was found, that the results obtained with the NLDFT model agree qualitatively with the predictions of the DR method, however, the NLDFT model is capable of yielding more detailed information about the activated carbons structure.

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