

COMPARATIVE PORE STRUCTURE ANALYSIS USING SMALL-ANGLE X-RAY SCATTERING (SAXS), BJH, AND DFT ANALYSIS METHODS

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Introduction

The adsorption capacity of porous carbon depends significantly on its pore structure. Consequently, it is very important to know as much detailed information as possible of pore characteristics of porous carbon [1-4]. Thus many different kinds of methods have been used in analyzing pore characteristics. Conventionally, the isotherm analysis of N₂ adsorption/desorption has been adopted, however, in recent SAXS technique has also been tried to analyze the pore structures [5-8]. SAXS measurements can have some advantages in that it can provide us with the information about structure of several orders in length scale. So, we tried in this study to compare the pore characteristics obtained from different analysis methods, i.e. SAXS and BJH and DFT for N₂ adsorption isotherms using the four standard samples, initially distributed for the purpose of worldwide round-robin tests for the pore structure analysis using DFT for N₂ adsorption isotherms. For the obtained SAXS data, the Porod's law, the surface and mass fractal analysis, and the power law were adopted to figure out the pore structures as detailed as possible.

Experimental

The four standard samples (HP, PCO, F400 and ACF10) that were prepared for the worldwide round-robin test of the pore structure analysis of activated carbons using the conventional BET method and the recent DFT method were used in this study.

Small-angle X-ray scattering (SAXS) measurements were performed on a pinhole collimated Nanostar (Bruker, Germany) operating at 40 kV and 35 mA. To investigate scattering over a wide range of q values ($q=4\pi\sin\theta/\lambda$ where 2θ is scattering angle and λ is the wavelength), two different experimental setups were used: the sample-to-detector (STD) distance was 106cm ($0.05 < q < 2 \text{ nm}^{-1}$) and 22cm ($1 < q < 10 \text{ nm}^{-1}$), respectively, with the x-ray wavelength of 1.54184 Å. The samples were pulverized in an agate mortar and pestle and held between two tapes attached to both side of a hole (5-mm-diameter and 0.5 mm thick) in a brass plate. And N₂ adsorption/desorption

experiments were made on ASAP2010 (produced by Micrometric, U.S.A.) under conventional conditions.

Results and Discussion

Figure 1 shows N₂ adsorption/desorption isotherms of the samples, and Figure 2 shows pore size distribution (PSD) obtained from SAXS data. Figure 3 contrasts the features of each analysis method, i.e. BJH, DFT, and SAXS, in terms of pore size distribution.

For the analysis of SAXS data obtained from the two STD distance set-ups, the scattering profiles at each STD were converted to a master SAXS profile by considering the intensity-scaling factor calculated on the basis of the solid angle concept. For the obtained master SAXS profiles, pore structural analyses were carried out for various viewpoints of pore structures using appropriate functions such as the surface and mass fractal analysis, the power law, and the Porod's law, particularly the Porod Invariant (PI) as shown in Eqn. (1). We considered PI in discontinuous way, i.e. range by range of q rather than in overall continuous way, in order to calculate the porosity at a particular pore size.

$$Q = \int_0^{\infty} q^2 I(q) dq = \sum_n \int_{q_n}^{q_{n+1}} q^2 I(q) dq \quad (1)$$

It can be seen in Figure 3 that the overall profiles of PSD obtained from each method are quite similar each other, but the details are somewhat different. That is, in the case of SAXS analysis, pore size distribution tends to become broader, especially in micro- and mesopore region (<10nm). In contrast to BJH and DFT methods, the microporosity is relatively under-estimated but macroporosity is over-estimated in SAXS analysis. This phenomena may result from the followings: while nitrogen adsorption method defines distribution curve by the amount of the adsorbed N₂ gas molecules and hence by the number of accessible pores, SAXS method considers nearly almost all kinds of pores that show the electron density fluctuation within carbon matrix. This fact is speculated responsible for the broader PSD profile in SAXS method than in the other methods. The details of the analyzes are under study to have the more precise pore structure from the combined analyzing techniques.

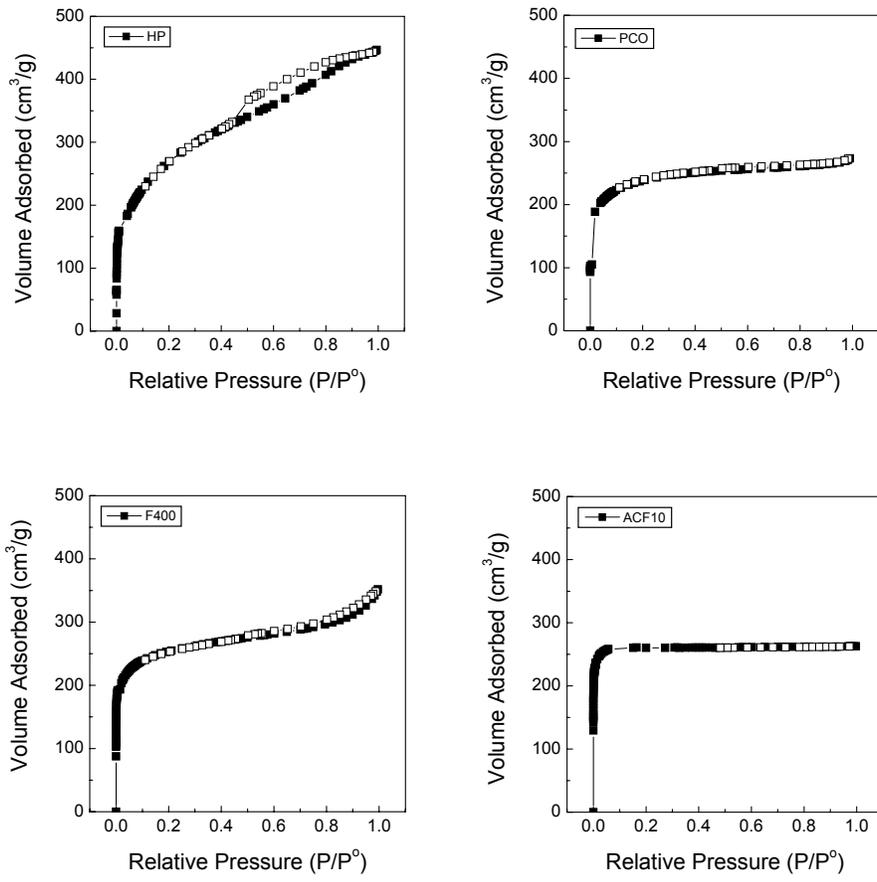


Figure 1. N₂ adsorption/desorption isotherms

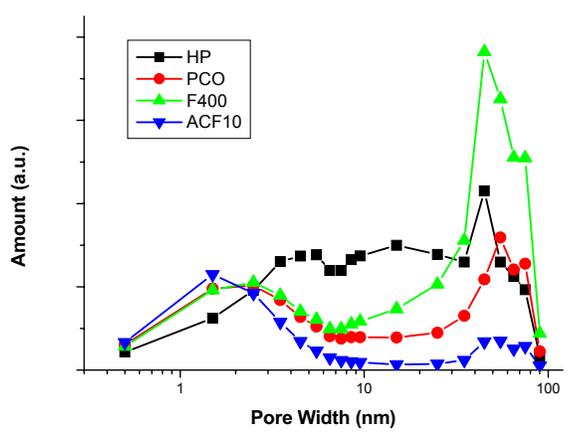


Figure 2. Pore size distribution calculated from SAXS data

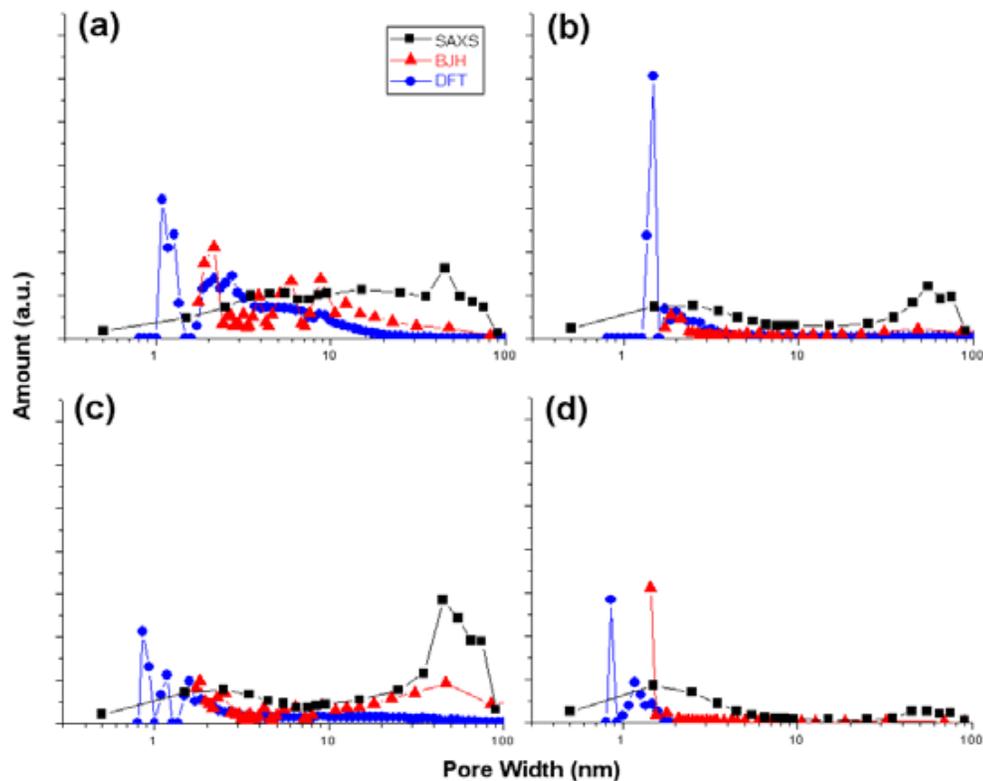


Figure 3. Comparison of Pore Side Distribution of (a) HP, (b) PCO (c) F400, (d) ACF10.

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