GCMC Simulation of N_2 Adsorption Isotherm of Microporous Carbon: Effect of the Interlayer Spacing

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1. Introduction

The measurement of the N_2 adsorption isotherm has been widely used to characterize activated carbon. X-ray diffraction (XRD) is not so effective for determination of the activated carbon structure compared with well-crystalline microporous solids such as zeolite. Therefore, the N_2 adsorption analysis is indispensable to understand the pore structure of activated carbon. However, analysis of the N_2 adsorption isotherm of activated carbon is not fully established yet, because adsorption by micropores of activated carbon, which is called micropore filling, is different from both multi-layer adsorption and capillary condensation. In the past several years computer simulation using statistical mechanics has been applied to elucidate the adsorption mechanism of N_2 by graphitic micropores. Those simulation researches have contributed to understand adsorption of N_2 by activated carbon. The model of a slit-pore between perfect crystalline graphite slabs is used in ordinary simulations[1-4]. However, real activated carbon is composed of micrographites of which structure is more disordered. For example, the stacking height of real micrographites is several nm at best and the interlayer spacing is greater than 0.335nm. We must take into account these factors in simulation. Also information on the more real micropore-space of activated carbon should be used in molecular simulation for comparison with the experimental isotherm, even if the micropore structure of activated carbon has some distribution. In this work, we simulated the N_2 adsorption isotherm of activated carbon using the observed interlayer spacing.

2. Characterization of ACF

We used pitch-based activated carbon fiber (ACF). The adsorption isotherm of N_2 was obtained gravimetrically at 77 K and it was analyzed by Sing's α_S-plot using the SPE method [5]. The average pore width of the sample was 1.02 nm.

XRD of ACF was measured (Cu Kα, 35kV, 10mA) in atmosphere. It has a very broad (002) peak with a small angle scattering background because ACF has micrographitic structures of very small crystallite size. We determined an accurate peak position of the (002) peak using the background correction [6]. The interlayer sapcing, d_{002} was 0.36±0.01 nm.

3. Simulation Model

For the adsorbate-adsorbate interaction potential, we used the Lennard-Jones 12-6 pair potential. The solid-fluid interaction potential $\phi_{sf}(z)$ for nitrogen interacting with a single graphite slab is described by the Steele's 10-4-3 potential [4].

$$\phi_{sf}(z) = A\left[\frac{2}{5}\left(\frac{\sigma_{sf}}{z}\right)^{10} - \left(\frac{\sigma_{sf}}{z}\right)^{4} - \frac{(\sigma_{sf})^4}{3\Delta(0.61\Delta+z)^3}\right],$$

where A is $2\pi\sigma_{sf}^2\varepsilon_{sf}\rho\Delta$, z is a vertical distance from the graphite surface, ρ is the solid number density, ε_{sf} and σ_{sf} are fitted parameters for the nitrogen-carbon potential well depth and an effective diameter. Δ in this equation corresponds to d_{002}. Parameters except Δ and ρ used here were taken from Steele's work [7] (nitrogen: ε_{ff}/k=95.2K, σ_{ff}=0.375nm, graphite: ε_{ss}/k=28.3K, σ_{ss}=0.340nm).

4. Calculation

GCMC simulation was performed for the experimental pore width; 1.0nm. The size of unit cell was 6nm × 6nm. We calculated N_2 adsorption for six different Δ value; 0.335, 0.36, 0.40, 0.50, 0.60 and 0.70 nm. The ρ value corresponding to each d_{002} was calculated. GCMC simulation was

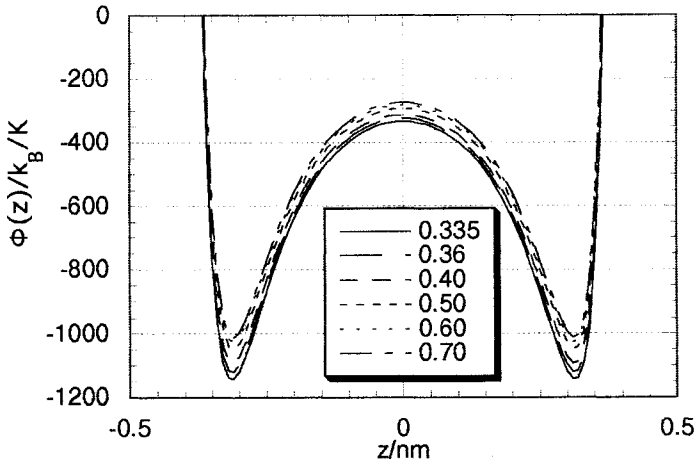

Figure 1; The interaction potential profiles of a nitrogen molecule with graphite-slit pore of the pore width of 1nm.

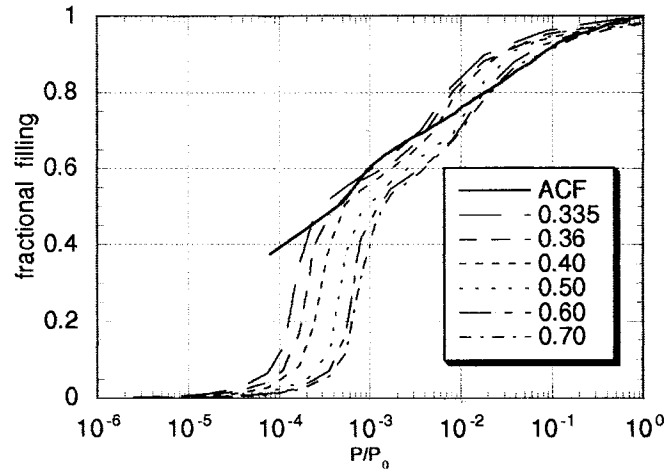

Figure 2; Comparison of simulated nitrogen adsorption isotherms with an observed isotherm of ACF.

basically run for 2×10^6 configurations to get equilibrium (3×10^6 configurations around the critical points on adsorption isotherms), using a Hewlett Packard 735 work station.

5. Results and Discussion

Potential curves calculated using the different Δ values are shown in Fig. 1. Origin of z is shifted to the ceter of the micropore in Fig. 1. There are two minima in each potential curve at 0.32 nm from the center of micropore and the depth of the minima decreases with increase of Δ. The position of the potential minima for Δ=0.70 is higher than that for Δ=0.335 by 150K. Thus, the effect of Δ is quite important for simulation.

The simulated and experimental adsorption isotherms for ACF are shown in Fig. 2. Each simulated isotherm has a steep jump and a gradual uptake in the P/P_0 regions of 10^{-4}–10^{-3} and 4×10^{-3}-2×10^{-2}, respectively. The greater Δ value shifts the adsorption isotherm to the higher P/P_0 side.

The simulation explicitly showed that the steep jump come from adsorption on each micropore-surface and the gradual uptake is caused by adsorption in the residual space between pre-adsorbed nitrogen layers on both micropore surfaces. So far ACF has a slight pore size distribution and thereby a strict comparison of the simulated isotherm with the observed isotherm of ACF is not conclusive. We believe that the simulated isotherm using Δ=0.36-0.40 is close to the observed one. In future, we must take into account the pore size distribution for the simulation.

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Reference

[1] Seaton, N.A.; Walton, J.P.R.B.; Quirke, N., *Carbon,* **1989**, *27,* 853.
[2] Matrange, K.R.; Myers, A.L.; Glandt, E.D., *Chem. Eng. Sci.,* **1992**, *47,* 1569.
[3] Lastoskie, C.; Gubbins, K.E.; Quirke, N., *J. Phys. Chem.,* **1993**, *97,* 4785.
[4] Kanko, K.; Cracknell, R. F.; Nicholson. D., *Langmuir,* **1994**, *10,* 4606.
[5] Kaneko, K.; Ishii, C., *J. Colloid Interface Sci.,* **1992**, *67,* 203.
[6] Suzuki, T; Kaneko, K., *Carbon,* **1993**, *31,* 1359.
[7] Steele, W.A., *Surf. Sci.,* **1973**, *36,* 317.