FINE CHARACTERIZATION OF PORE STRUCTURE OF POROUS CARBONS WITH SUPERWIDE PRESSURE RANGE-ADSORPTION TECHNIQUE

M. Sunaga, T.Ohba, T.Suzuki, and K.Kaneko
Physical Chemistry, Material Science,
Graduate School of Natural Science and Technology, Chiba University
1-33 Yayoi, Inage, Chiba 263-8522, Japan

Introduction

Microporous carbons has gathered much attention from scientific interests and applications for energy storage and environmental technologies[1]. In particular, the microporous carbons whose pore width is smaller than 1 nm have a remarkable enhanced adsorption property owing to the overlap of molecule-pore wall interaction potential from opposite pore walls. Then, a substantial adsorption in such small micropores begins below low relative pressure of 10^{-4} in case of N_2 adsorption on carbon slit pores at 77K. Hence, adsorption researchers have tried to develop an N_2 adsorption equipment from low P/P_0 range[2].

Recently even commercial adsorption equipments have provided the N_2 adsorption isotherm from $P/P_0=10^{-6}$~10^{-5}. However, the adsorption measurements in the pressure range of $P/P_0=10^{-6}$ is not easy due to the vacuum quality of the ordinary high vacuum system. Also molecular simulation studies predict the important adsorption in small micropores[3]. Accordingly we need to determine the reliable adsorption isotherm of N_2 on microporous solid from less than $P/P_0=10^{-6}$. This paper reports the adsorption isotherms of N_2 on activated carbon fiber (ACF) from $P/P_0=10^{-9}$ to 1, stressing the importance of the adsorption data in P/P_0 range of 10^{-8} to 10^{-6}.

Experimental and Molecular Simulation

Pitch-based ACFs (P5 and P20) and phenol-resin based activated carbon were used as microporous carbon samples. The gravimetric adsorption equipment is composed of a laser sensing gravimeter and the ultrahigh vacuum system having three Baratron gauges of different pressure range and an ion gauge. This newly developed adsorption system is denoted by a superwide pressure range adsorption (SWPAd) equipment. The ACF samples were pre-evacuaed at 393K and 10^{-9}Pa for 24h. The N_2 adsorption isotherms were measured at 80 K below 10^{-6}Pa and at 77 K above 10^{-6}Pa . For comparison, the N_2 adsorption isotherms were measured at 77K using the high

vacuum gravimetric system (HVAd) after preheating at 373K and 10^{-3} Pa for 2h. The N_2 adsorption isotherms of graphite slit pores with heterogeneity were simulated with grand canonical Monte Carlo (GCMC) technique using the established procedures.

Results and discussion

Figure 1 shows the N_2 adsorption isotherms of P5 and P20 determined by two methods. The abscissa and ordinate of Figure 1 are expressed by the logarithm of P/P_0 and the adsorbed N_2 per unit weight of carbon sample. The solid and open symbols denote the adsorption

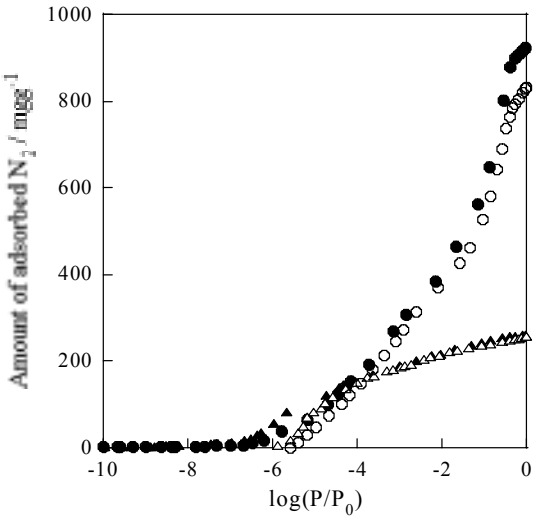

Fig. 1. N_2 adsorption isotherms of pitch-based ACFs at 77 K.
(▲,□): P5 and (○,●): P20
Solid symbols: By HVAd method
Open symbols: By SWPAd method

isotherms obtained by SWPAd and HVAd systems, respectively. In the case of P5, both adsorption isotherms are almost overlapped each other except for the pressure range below 10^{-5}. On the other hand, the adsorption amount determined by SWPAd is larger than that by HVAd in both of low and high pressure ranges. The adsorption isotherms below $P/P_0 = 10^{-6}$ are not explicitly shown in this figure.

Figure 2 shows N_2 adsorption isotherms of P5 and P20 whose ordinate is shown by the logarithm of the amount of adsorption. These log-log isotherms show a distinct difference of the adsorption isotherms by SWPAd and HVAd methods below $P/P_0 = 10^{-5}$, although errors in the adsorption amount are not negligible below $P/P0 = 10^{-8}$. The log-log expression of the adsorption isotherm by SWPAd method shows clearly the rising pressure; the adsorption begins at $P/P_0 = 10^{-8}$ for P5 and $P/P_0 = 10^{-7}$. The rising pressure of the adsorption isotherm by SWPAd method shifts to a low pressure range by order of about two. Therefore, this new technique is quite effective to evaluate the microporosity precisely. In particular, the average pore width w of P5 is 0.7 nm, being the bilayer thickness of an N_2 molecule and thereby the blocking effect near the pore entrance must be taken into account. This SWPAd method provides a more reliable

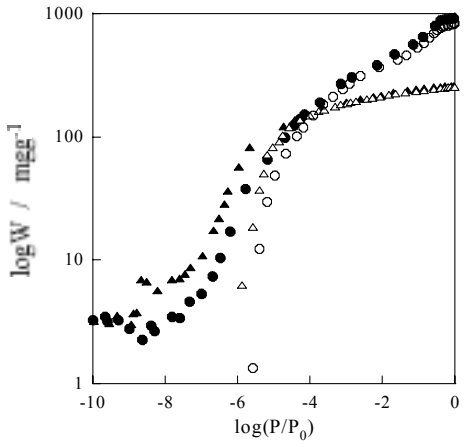

Fig. 2. Logarithm expression of N_2 adsorption isotherms of pitch-based ACFs at 77 K.
(▲,□): P5 and (○,●): P20
Solid symbols: By HVAd method
Open symbols: By SWPAd method

adsorption behavior for small micropore systems.

These adsorption isotherms observed with SWPAd method were compared with the simulated adsorption isotherms. The SWPAd method gives a reliable adsorption isotherm having a clear adsorption rising below $P/P_0 = 10^{-6}$. Then the SWPAd method should accelerate the progress of molecular simulation study. Also the SWPAd method provides a new insight for the stability of activated carbon. The adsorption capacity change observed in P20 by two measuring methods should be associated with the structure stability of ACF. The pre-evacuation of P20 samples creates new micropores, leading to a higher adsorption amount near $P/P_0 = 1$.

Acknowledgements

This work was supported by the Grant-in-Aid from Japan Science and Technology and Fundamental Gramt-in-Aid for Scientific Research (B) from Ministry of Education and Science.

References

[1] Kaneko K. Adsorption on New and Modified Inorganic Sorbents. In Dabrowski A, VA Tertykh, Amsterdam, Elsevier, 1996, p.635-657.

[2] Kakei K, Ozeki S,Suzuki T, Kaneko K. J. Chem. Soc. Faraday Trans.I,1990;86,371-376.

[3] Bandosz T J, Buggs M J, Gubbins K E, Hattori Y, Iiyama T, Kaneko K, Pikunic J, Thomas K. In Thrower PA and Radvic L, editors. Chemistry and physics of carbon, in press.