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} to 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 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 $P/P_0 = 10^{-8}$. 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.

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References