Pore Structure Analysis based on Helium Adsorption under Cryogenic Condition

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Introduction

Microporous solids like an activated carbon are in widespread use as functional materials, adsorbents, catalyst carriers and electrodes. A molecular sieving carbon is used as a PSA (pressure swing adsorption) material for nitrogen concentration and methane purification. Nowadays, the extension of their use has been actively studied, for example, as a material for separation and recovery of carbon dioxide from flue gases. As the performance of adsorption processes using these microporous solids are significantly controlled by adsorption characteristics of these solids, it is valuable to make clear the structural characteristics of the microporous solid (e.g. specific surface area, pore volume and pore size distribution) for advancement of adsorption processes. Some methods such as gas adsorption method, X-ray diffraction and electron microscope observation have already been applied to the micropore characterization. However, it is very difficult to clarify the micropore structure less than 1nm by means of these well-known methods. Therefore, applying helium to probe molecule for assessment of the ultramicroporosity, a new helium cryostat was designed. Then, a volumetric method applying the helium adsorption with the helium cryostat is proposed. Adsorption equilibria of helium on some microporous solids can be measured at a temperature around its boiling point and the adsorption isotherms obtained by the helium adsorption were compared with those values obtained by the nitrogen adsorption. The possibility of the application of this method to the characterization of the micropore is discussed on the basis of these results.

Experimental

A schematic diagram of a helium adsorption apparatus and details of a helium cryostat are shown in Figs. 1 and 2, respectively. The helium adsorption apparatus contains the helium cryostat, a calibrated volume chamber and an analyzing system (Micrometirics ASAP-2000, Shimazu).

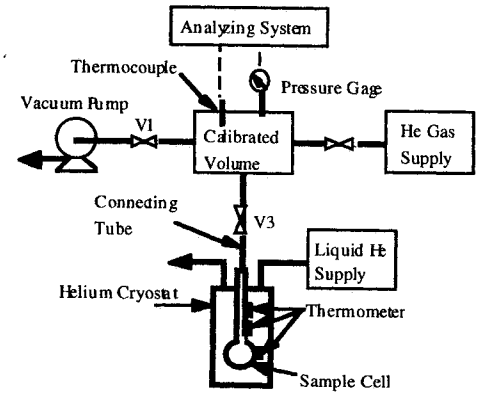

Fig. 1 Schematic diagram of helium adsorption apparatus

The helium cryostat has three vacuum insulation layers. A glass sample cell having a volume of 17.0 cm^3 is inserted into the center of the cryostat and is cooled to a temperature around the boiling point by exchanging the heat with liquid helium. On the other hand, when measuring the nitrogen adsorption equilibrium, the sample cell was cooled by a Dewar's vessel filled with liquid nitrogen. The measurement were automatically conducted. Five kinds of samples, activated carbon fiber (ACF), super activated carbon (SAC), activated carbon produced by us, carbonized mesocarbon microbead (MCMB) and graphitized MCMB were used for the measurement of adsorption equilibria of helium and nitrogen. Here, carbonized MCMB and graphitized MCMB are nonporous solid and applied to adsorbent in order to analyze by means of t-plot. The mass of each sample was about 1 g. Before measurement, samples were evacuated for a few hours at 423 K to remove any impurities.

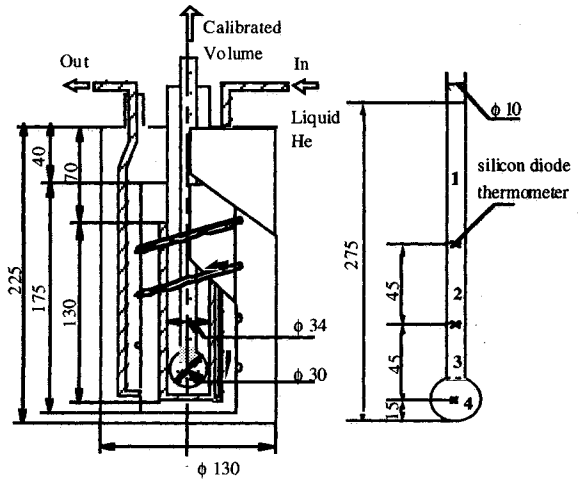

Fig. 2 Details of helium cryostat

Results and Discussion

The amount of adsorbed helium is calculated from the helium adsorption data following the example of Duband, Ravex and Chaussy.

Using an ideal gas law approximation, the amount of helium introduced into the sample cell and the connecting tube is given by

$$m_f = \frac{(P_d - P_e)V_c M}{RT_c} \qquad (1)$$

where $P_{e,r}$ is the equilibrium pressure at room temperature. The amount of residual helium in the sample cell and the connecting tube is calculated dividing it into four parts; the connecting tube, upper and lower cylindrical parts of the cell and the spherical part of the cell. Assuming a linear temperature gradient in each part except the spherical part of the cell, the corresponding amount is expressed by the sum total

$$m_b = \sum_{j=1}^{3} \left\{ \frac{P_{e,j} V_j M}{R(T_{h,j} - T_{l,j})} \ln \frac{T_{h,j}}{T_{l,j}} \right\} \quad (2)$$

where $P_{e,j}$ is the value considered a thermal transpiration effect according to the following equation.

$$\frac{(P_{e,j}/P_e) - 1}{\sqrt{T_j/T_c} - 1} = \frac{1}{A^* X^{*2} + B^* X^* + C^* \sqrt{X^*} + 1}$$
$$X^* = \frac{2 P_e d}{(T_j + T_c)} \left(T_c > T_j = \frac{T_{j,h} + T_{j,l}}{2} : j = 1, 2, 3 \right) \quad (3)$$

The amount of residual helium in the spherical part of the sample cell is calculated using an intergranular volume and a density of helium at the measuring pressure and temperature. Therefore, the amount of helium adsorbed at the standard condition is estimated by

$$q = \frac{RT_0(m_f - m_b - \rho V_i)}{P_0 M m_a} \quad (4)$$

Table 2 shows measuring temperatures and corresponding saturated vapor pressures calculated by the Antoine equation.

Table 2 Experimental conditions

	He		N_2	
Adsorbent	T_m [K]	P_s [kPa]	T_m [K]	P_s [kPa]
ACF	4.49	130.7	77.35	101.3
SAC	4.49	130.7	77.35	101.3
Act. carbon	4.68	159.2	77.35	101.3
MCMB(gra.)	4.48	129.6	77.35	101.3
MCMB(car.)	4.53	135.2	77.35	101.3

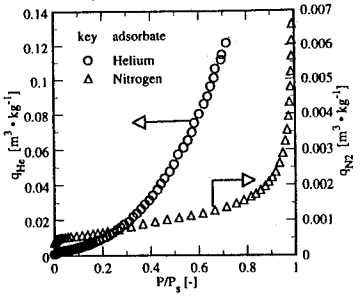

Fig. 3 Helium and Nitrogen adsorption isotherms for graphitized MCMB

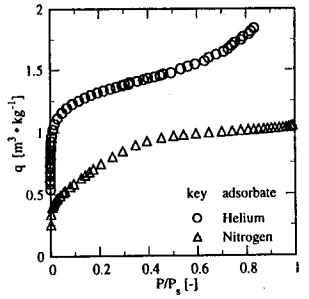

Fig.4 Helium and Nitrogen adsorption isotherms for Super Activated Carbon

Helium and nitrogen adsorption isotherms, for instance, for the graphitized MCMB and the SAC are shown in Figs. 3 and 4, respectively. Since the sample cell could not be kept at a temperature around the boiling point of helium for a long time, complete helium adsorption isotherms in the whole relative pressure region were not obtained.

From these figures, it can be seen that the amounts of helium adsorbed are much greater than those of nitrogen adsorbed under the whole relative pressure region for all adsorbents. Also, the shape of the adsorption isotherm of helium for the graphitized MCMB is different from the nitrogen; according to Brunauer, the former can be classified as type II and the later as type I. Beside, the shapes of adsorption isotherms are roughly similar for SAC and can be classified as type I. From these results, it is suggested that the SAC is a microporous material. For the graphitized MCMB, the shape of adsorption isotherm is expected to be type II because of non-porous material. Helium adsorption isotherm, however, is not in agreement with this. As the amount of helium adsorbed is much greater than that of nitrogen, it is considered that the adsorbed films of helium are very thick compared with those of nitrogen. This is why it is difficult to fit the helium adsorption isotherm with B.E.T. equation.

The validity of Frenkel-Halsey-Hill (F.H.H.) equation may be investigated by plotting $\log(\ln(P_s/P))$ in terms of $\log(t)$ which will yield a straight line relationship for the multilayer adsorption. For the graphitized MCMB, the following relations were obtained:

i) For helium adsorption

$$\ln\left(\frac{P_s}{P}\right) = \frac{3.18}{t^{0.476}} \quad (5)$$

ii) For nitrogen adsorption

$$\ln\left(\frac{P_s}{P}\right) = \frac{0.396}{t^{2.30}} \quad (6)$$

Here, t is the statistical thickness of the adsorbed film. Based on these adsorption isotherms for the SAC, t-plot of SAC calculated by means of the t-method is shown in Fig. 5.

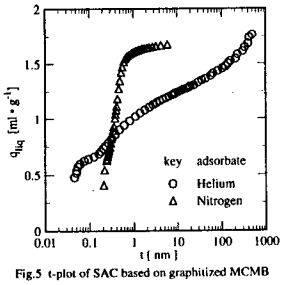

Fig.5 t-plot of SAC based on graphitized MCMB

The t-plot based on nitrogen adsorption isotherm indicates that the SAC has micropores less than 0.6 nm of pore radius. The t-plot based on helium adsorption isotherm, however, corresponds to that of nitrogen and covers a wider range than that of nitrogen.

Conclusions

A helium cryostat which can accurately measure the equilibrium pressure of helium around its boiling point was proposed and the obtained adsorption data were evaluated by applying a t-plot to the helium as well as nitrogen adsorption isotherms.