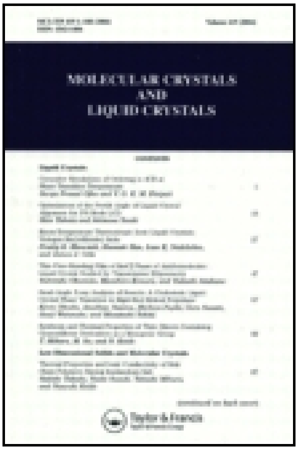

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Comparative Study on Physical Adsorption of Vapor and Supercritical H 2 and Ch 4 on Swnh and Acf

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COMPARATIVE STUDY ON PHYSICAL ADSORPTION OF VAPOR AND SUPERCRITICAL H_2 AND CH_4 ON SWNH AND ACF

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Adsorption isotherms of H_2 and CH_4 on activated carbon fibers (ACF) and single-walled carbon nanohorns (SWNH) were measured at vapor and supercritical conditions. H_2 and CH_4 are adsorbed sufficiently on micropores of ACF

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and SWNH at the vapor conditions and their adsorption isotherms were described by the Dubinin-Radushkevich equation. This shows clearly that even adsorption of H_2 and CH_4 vapors can be described by micropore filling mechanism. However, the adsorption isotherms of supercritical H_2 and CH_4 sensitively depend on the measuring temperature; the higher the measuring temperature, the smaller the amount of adsorption. Although H_2 adsorption isotherm of SWNH at 77 K is of type I and the maximum surface excess adsorption is 0.7 wt.% at 5 MPa, the adsorption isotherm was of Henry type at 300 K and the adsorption amount is less than 0.1 wt.% at 5 MPa.

Keywords: micropore filling; gas adsorption; gas storage; carbon nanotube; activated carbon fiber; hydrogen adsorption; methane adsorption

INTRODUCTION

Storage of H_2 and CH_4 has gathered much attention from urgent demand for clean energy [1–4]. The critical temperatures of H_2 and CH_4 are 33 K and 191 K, respectively. Then, they are supercritical gases at an ambient temperature. Since the supercritical gas cannot be condensed even by application of high pressure, the realization of the high density storage of H_2 and CH_4 is quite difficult. Hence, an optimum assistance method using solid materials has been actively searched. There are four types of the interactions between molecules and solids [5]. An important factor for the molecule-solid interaction is whether a structural change is accompanied or not. Then each molecule or solid has two possibilities, that is, a structural change and no structural change upon the interaction, and thereby there are four combinations, as shown in Table 1. "No" and "Yes" denote the presence and absence of the structural change upon the molecule-solid interaction, respectively. The general concept of storage includes all of four interactions and the narrow meaning of the storage is expressed by occlusion in the Table 1. If we choose the high density storage of H_2 and CH_4 using solid materials without any structural change in the molecule and solid, physical adsorption is a unique choice. Physical adsorption is caused by the dispersion interaction. Then, microporous solids which have an enhanced

TABLE 1 Four Types of Molecule-solid Interaction

	Structural change in molecule	Structural change in solid
Physical adsorption	No	No
Chemisorption	Yes	No
Absorption	No	Yes
Occlusion	Yes	Yes

dispersion interaction of a molecule with solid are good candidates. Here, micropores are the pores whose width w is less than 2 nm.

Carbon microporous materials are expected to satisfy the technological requirements for the storage of H_2 and CH_4, because carbon materials are light, non-toxic, and highly thermal conductive. ACF (activated carbon fiber) has slit-shaped micropores [6], while the micropores of SWNH (single-walled carbon nanohorns) assembly can be approximated by wedge-shaped pores. Although the inner nanospaces of SWNH particles can be opened by oxidation treatment, only the results on the perfectly closed SWNH particles are described here.

EXPERIMENTAL

Pitch-based activated carbon fiber (A20, Ad'all Co.) was used as a representative activated carbon adsorbent having slit-micropores. Single-walled carbon nanohorns (SWNH) of dahlia-like assembly structure were prepared by Iijima *et al.* [7]. The intratube nanospace of the SWNH particle is completely closed and the space is not available for gas adsorption [8]. The gas adsorption occurs on the pores coming from the assembly structure of SWNH particles. The intertube space of the mutually oriented SWNH particle has a strong interaction potential with a molecule [9]. The microporosity of these samples was determined by high resolution N_2 adsorption at 77 K after pre-evacuation. The N_2 adsorption isotherms were analyzed by the SPE analysis for α_s-plot [10,11]. The microporosity is listed in Table 2. The temperature dependence of CH_4 adsorption was measured gravimetrically over 155 to 274 K. H_2 adsorption isotherms of SWNHs were measured at 20 K, 77 K, 196 K, and 303 K. The buoyancy curve of samples was determined gravimetrically at 303 K using He gas up to 10 MPa [12]. Here, the amount of supercritical gas adsorption is expressed by the surface excess mass [13]. The obtained particle density is shown in Table 2, which was used for the correct determination of the surface excess mass of supercritical gas adsorption.

TABLE 2 Microporosity of Samples

	Surface area/ $m^2\ g^{-1}$	Pore volume/ $ml\ g^{-1}$	Average pore width/nm	Particle density/ $g\ ml^{-1}$
ACF	1990	1.08	1.1	2.15
SWNH	308	0.11	0.4*	1.25

(*) evaluated by slit-shaped approximation.

RESULTS AND DISCUSSION

Figure 1 shows the adsorption isotherms of CH_4 on ACF at 114 K. The upper abscissa is expressed by logarithm of P/P_0. The adsorption isotherm is of representative type I, indicating that CH_4 molecules are adsorbed by micropore filling. According to the upper abscissa, adsorption begins below $P/P_0 = 10^{-5}$, being characteristic of micropore filling. Ordinary micropore filling of vapor can be described by the Dubinin-Radushkevich (DR) equation, given by Eq. (1).

$$W = W_0 \exp(-A^2/E^2) \qquad A = RT \ln(P/P_0) \tag{1}$$

Here W and W_0 are the adsorption amount at P/P_0 and micropore volume, respectively. E provides the isosteric heat of adsorption, $q_{st,0.4}$, at the fractional filling of e^{-1} (about 0.4), as given by Eq. (2).

$$q_{st,0.4} = \Delta H_{vap} + E \tag{2}$$

The $q_{st,0.4}$ is a good scale of the interaction strength between a molecule and the pore. The DR plot for the CH_4 adsorption isotherm at 114 K had a good linearity in the wide P/P_0 range. The obtained W_0 and E were $0.75\,ml\,g^{-1}$ and $6.21\,kJ\,mol^{-1}$, respectively. The micropore volume evaluated using the bulk liquid CH_4 density ($0.421\,g\,ml^{-1}$) at the boiling temperature is slightly different from that by N_2 adsorption in Table 2. The $q_{st,0.4}$ of CH_4 is $14.4\,kJ\,mol^{-1}$, being greater than that of N_2 ($11.4\,kJ\,mol^{-1}$). As a CH_4 molecule is larger than an N_2 molecule, the above difference in the $q_{st,0.4}$ is quite reasonable. Thus, CH_4 molecules at 114 K are adsorbed with micropore filling mechanism same as N_2 molecules at 77 K. However,

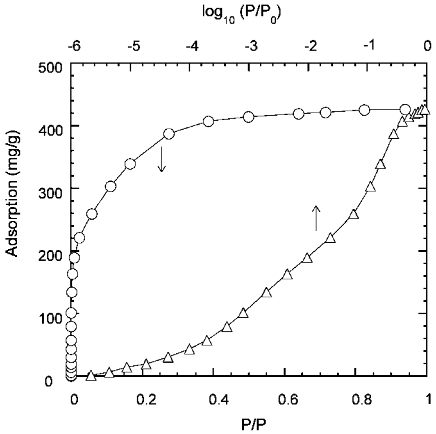

FIGURE 1 Adsorption isotherms of CH_4 on ACF at 114 K.

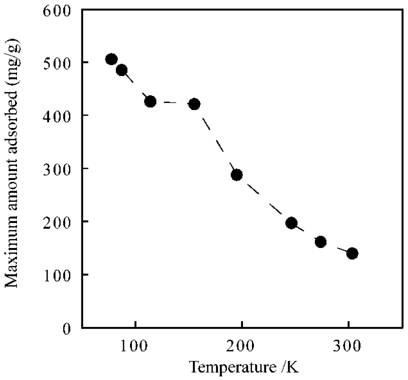

FIGURE 2 Temperature dependence of CH_4 adsorption amount.

the amount of CH_4 adsorption decreased remarkably with the increase of the temperature. The surface excess adsorption isotherm of CH_4 above 191 K had a maximum at 5 MPa. This maximum stems from the increase of the bulk gas phase CH_4 density. Figure 2 shows the temperature dependence of the maximum of the surface excess maximum adsorption of CH_4 on ACF. There is a gradual change below 191 K of the critical temperature, which suggests the presence of the highly compressed structure. However, the maximum decreases with the increase of temperature above 191 K; that at 303 K is about one fourth of that below 191 K. Then the adsorption of supercritical CH_4 is not easy compared with adsorption of CH_4 vapor.

Figure 3 shows the adsorption isotherm of H_2 on SWNHs at the boiling temperature of H_2 (20 K). The adsorption isotherm is of typical type I,

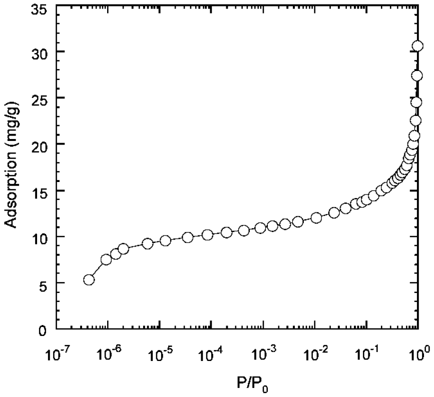

FIGURE 3 Adsorption isotherm of H_2 on SWNH at 20 K.

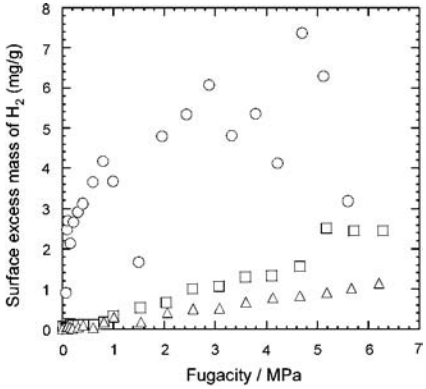

FIGURE 4 Adsorption isotherm of H_2 on SWNH at different temperatures: (○) 77 K; (□) 196 K; (△) 303 K.

indicating that even H_2 molecules are adsorbed by the micropore filling mechanism. The adsorption begins below $P/P_0 = 10^{-7}$, suggesting the presence of the physical adsorption sites having quite strong interaction potential, which originate from the regional orientation structures. The DR plot for the adsorption isotherm was linear in the wide pressure range, providing that W_0 (H_2) $= 0.17\,\mathrm{ml\,g^{-1}}$ and $q_{st,0.4} = 5.0\,\mathrm{kJ\,mol^{-1}}$. Figure 4 shows the surface excess adsorption isotherms of H_2 on SWNH at 77 K, 196 K, and 303 K. The adsorption isotherm at 77 K is Langmuirian and it has depression points near 1.5 and 4.2 MPa. The maximum adsorption at 77 K is 0.75 wt. % at best. The adsorption isotherms at 196 K and 303 K are almost of Henry type, indicating that the interaction of an H_2 molecule and SWNH is not sufficient for adsorption. The surface excess amount at 303 K is only 0.1 wt.%, being quite different from the great values in the literature [1–3]. Thus, the adsorption of supercritical H_2 on pure SWNH is not remarkable. However, the depression feature in the adsorption isotherm at 77 K suggests the association of the structural change upon adsorption.

Although supercritical H_2 cannot be adsorbed sufficiently on SWNH, the possibility of the assembly structural change during adsorption suggests the direction for future research on the hydrogen storage with nanocarbon materials.

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