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Methane Adsorption on Multi-Walled Carbon Nanotube at (303.15, 313.15, and 323.15) K

Jae-Wook Lee,[†] Hyun-Chul Kang,[‡] Wang-Geun Shim,[‡] Chan Kim,[‡] and Hee Moon*,[‡]

Department of Environmental and Chemical Engineering, Seonam University, Namwon 590-170, Korea, and Faculty of Applied Chemistry, Chonnam National University, Gwangju 500-757, Korea

Adsorption equilibria of methane on multi-walled carbon nanotube (MWCNT) were measured. For comparison of the adsorption properties, two zeolites (DAY and HSZ-320) were chosen. The isotherm data were obtained using a static volumetric method at 303.15 K, 313.15 K, 323.15 K and at pressures up to 3 MPa. Experimental data of zeolites and carbon nanotube were correlated by the Sips isotherm and the hybrid Langmuir−Sips equations, respectively. Isosteric enthalpies of adsorption were calculated as a function of surface loading.

Introduction

Demand for clean fuels for vehicles of coal and petroleum has been rapidly increasing with the development and progress of modern civilization. Accordingly, hydrogen and natural gas are commonly considered to be suitable nonpollution alternatives to fossil fuel. Thus, the storage of natural gas, whose main component is methane, has become an important subject. In general, the compressed natural gas for vehicles is stored in heavy steel cylinders at higher pressures from (20 to 30) MPa while adsorbed natural gas for vehicles requires a relatively lower pressure (i.e., about 4 MPa) to be stored in a lightweight container. Compared to the compressed natural gas, adsorbed natural gas is a very promising and efficient technology because storage in lower pressure leads to lower cost of fuel.[1,2]

Many studies of methane adsorption on porous media (including molecular sieves, activated carbon, zeolite, etc.) have been reported. Recently, carbon nanotubes have been attracting an increasing interest because of their unique properties including uniform porosity, high tensile strength, electrical conductivity, and relative inertness. Bekyarova et al. investigated the adsorption of methane in a single-walled carbon nanotube (SWCNT).[3] The measured volumetric capacity reached 160 v/v. Kaneko and co-workers also studied the adsorption of methane on SWCNT using a density functional theory method. They found that SWCNT with disordered structure could be applied as storage media for methane and other supercritical gases.[4] Cao et al. optimized the SWCNT arrays for methane storage at room temperature.[5] In contrast to the many works performed on SWCNT, studies on the adsorption of methane on multi-walled carbon nanotube (MWCNT) are very limited. SWCNT can be fabricated in various bundle sizes and lengths (i.e., by changing grinding and other mechanical operations) with containing amorphous carbon. However, MWCNT is capable of making uniform lengths without bundle formation and without amorphous carbon. Thus, the gas adsorption properties on SWCNT and MWCNT seem to be quite different.

In this paper, the adsorption equilibria of methane on MWCNT were measured to gain an understanding of the adsorption mechanisms and to develop adsorption models. The isotherm data were obtained by using a static volumetric method at different temperatures (303.15 K, 313.15 K, and 323.15 K). Experimental data of zeolites and carbon nanotube were correlated by the Sips isotherm and the hybrid Langmuir−Sips equations, respectively. Isosteric enthalpies of adsorption were calculated by Clausius−Clapeyron equation.

Experimental Section

Materials. MWCNT (Nanokarbon Co., Korea) and two zeolites (HSZ-320 and DAY) were chosen for the adsorbent. MWCNT were made using chemical vapor deposition (CVD), which gives homogeneous lengths and well-defined diameters. The adsorbents were used as received without a purification step. The BET surface area of the MWCNT sample was determined as 250 $m^2 \cdot g^{-1}$, and the pore volume was 0.43 $cm^3 \cdot g^{-1}$ from the desorption isotherm of nitrogen at 77 K. Figure 1 shows the SEM and TEM photos of MWCNT demonstrating the uniform diameter distribution without bundle formation. As can be seen in Figure 1b, the pore is centered at the core of the MWCNT, which has a purity of > 95 %. The outer diameter is (70 to 100) nm, the inner diameter is (40 to 60) nm, the wall thickness is (15 to 20) nm, the length is (20 to 30) μm, and the bulk density is (0.005 to 0.006) $g \cdot cm^{-3}$. Prior to measurement, the adsorbent was maintained at 433.15 K in a drying vacuum oven for more than 15 h to remove impurities. Methane of high purity (99.9 %) was used for the adsorbate.

Apparatus and Procedure. The adsorption equilibrium data of methane were obtained using the static volumetric method (Figure 2). To minimize the dead volume as much as possible, an adsorption cell and a loading cell were connected to small tubes (3.18 mm) and valves (3.18 mm). The loading cell, the adsorption cell, and the dead volumes were measured using helium gas. The loading cell volume was (507 ± 1) mL, and the adsorption cell volume was (505 ± 1) mL. During adsorption, the loading cell, the adsorption cell, and all lines were immersed in a water bath (BS-21, Jeio Tech) that was maintained at ± 0.02 K via a refrigeration circulator (RBC-11, Jeio Tech). Before the adsorbate was introduced into the adsorption cell, the adsorbent mass was weighed within ± 10 mg accuracy after eliminating the impurity traces at 423.15 K and high vacuum for more than 24 h. The impurities in the

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* To whom correspondence should be addressed. E-mail: hmoon@chonnam.ac.kr. Tel.: +82-62-530-1877. Fax: +82-62-530-1899.

[†] Seonam University.

[‡] Chonnam National University.

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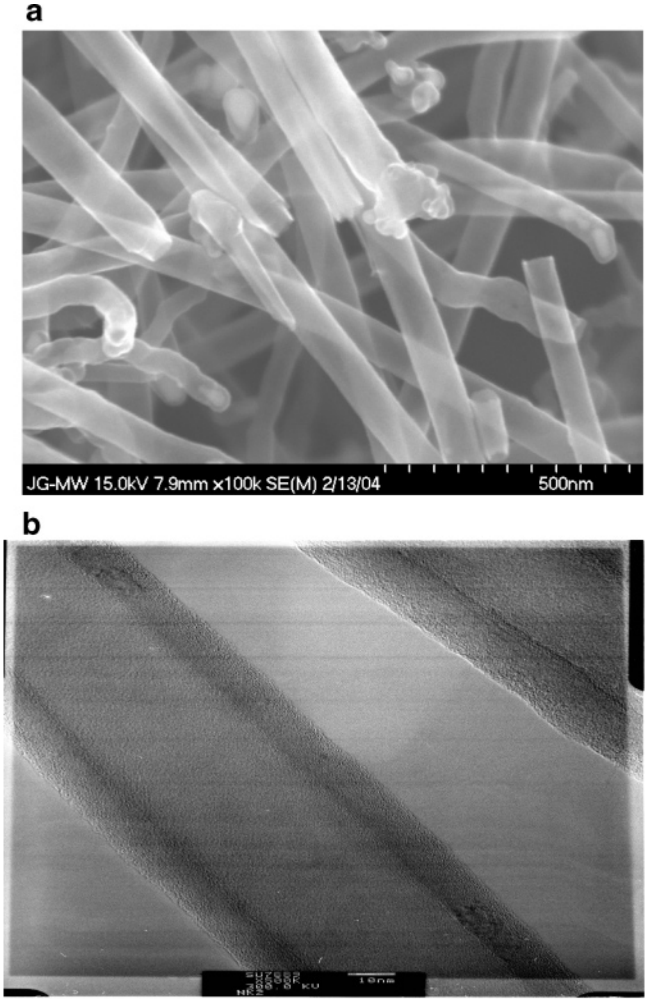

Figure 1. (a) SEM and (b) TEM photos of MWCNT.

adsorption cell were eliminated by a vacuum pump for 5 h after the adsorbent was placed in the adsorption cell. When the temperatures in the loading and adsorption cells reached the required levels, the experiment was initiated. The adsorption equilibrium state was considered when the temperatures and the pressures per cell were constant. The pressure in each cell was measured with a pressure transducer. The temperature was measured by a K-type thermocouple that operated within ± 0.01 K accuracy. Pressures and temperatures were recorded with a mobile recorder (MV100, Yokogawa Co.). The adsorption capacity was calculated using the mass balance (eq 1) on the basis of the temperature and pressure measured before and after the adsorption equilibrium state:

$$\left.\frac{PV}{zRT}\right|_{\mathrm{L}_1} + \left.\frac{PV}{zRT}\right|_{\mathrm{A}_1} = \left.\frac{PV}{zRT}\right|_{\mathrm{L}_2} + \left.\frac{PV}{zRT}\right|_{\mathrm{A}_2} + NM \tag{1}$$

where P is pressure, T is temperature, V is volume, R is the gas constant, M is the molecule weight, z is the compressibility factor, and N is the amount adsorbed, 1 represents the state prior to the adsorption equilibrium, and 2 represents the final equilibrium state.

Results and Discussion

The adsorption data for methane on MWCNT and two zeolites were obtained at 303.15 K, 313.15 K, and 323.15 K and pressures up to 3 MPa. The experimental data are represented in Tables 1 to 3 and graphically shown in Figures 3 to 4. It can be seen that the adsorption equilibrium of two zeolites and MWCNT are quite different. The adsorption isotherm of zeolites and MWCNT are of type I and type IV as Rouquerol et al.[6] demonstrated. The adsorption capacity of methane on zeolites and MWCNT is significantly dependent on temperature.[7,8] Unlike zeolites, the adsorption of methane on MWCNT is weakly favorable at a low pressure (i.e., < 1.5 MPa), while capillary condensation occurs at a higher pressure. In addition, the pressure responsible for capillary condensation of methane increased with temperature.

Table 1. Adsorption Isotherm Data for Methane onto HSZ-320

T = 303.15 K		T = 313.15 K		T = 323.15 K	
P	N	P	N	P	N
MPa	mmol·g^{-1}	MPa	mmol·g^{-1}	MPa	mmol·g^{-1}
0.045	0.075	0.023	0.033	0.038	0.047
0.098	0.140	0.058	0.066	0.087	0.091
0.163	0.246	0.111	0.131	0.173	0.163
0.282	0.391	0.186	0.223	0.302	0.272
0.466	0.563	0.279	0.320	0.490	0.399
0.606	0.673	0.443	0.456	0.790	0.553
0.748	0.758	0.639	0.593	1.038	0.657
0.949	0.859	0.787	0.689	1.341	0.733
1.201	0.961	0.968	0.770	1.710	0.8200
1.517	1.050	1.207	0.850	2.153	0.8864
1.920	1.127	1.583	0.924	2.618	0.9436
2.632	1.231	2.082	1.013		
		2.696	1.076		

Table 2. Adsorption Isotherm Data for Methane onto DAY

T = 303.15 K		T = 313.15 K		T = 323.15 K	
P	N	P	N	P	N
MPa	mmol·g^{-1}	MPa	mmol·g^{-1}	MPa	mmol·g^{-1}
0.029	0.029	0.053	0.053	0.038	0.015
0.069	0.074	0.125	0.122	0.089	0.058
0.119	0.126	0.206	0.208	0.133	0.101
0.206	0.225	0.324	0.317	0.207	0.168
0.312	0.349	0.438	0.426	0.278	0.229
0.416	0.462	0.633	0.593	0.390	0.332
0.552	0.597	0.992	0.866	0.558	0.461
0.740	0.773	1.169	0.994	0.790	0.634
1.001	0.988	1.584	1.204	1.095	0.840
1.291	1.197	1.851	1.333	1.422	1.011
1.653	1.416	2.141	1.451	1.873	1.196
2.079	1.588	2.568	1.611	2.533	1.449
2.607	1.774				

Table 3. Adsorption Isotherm Data for Methane onto MWCNT

T = 303.15 K		T = 313.15 K		T = 323.15 K	
P	N	P	N	P	N
MPa	mmol·g^{-1}	MPa	mmol·g^{-1}	MPa	mmol·g^{-1}
0.032	0.019	0.041	0.033	0.038	0.043
0.081	0.136	0.113	0.154	0.092	0.064
0.156	0.227	0.227	0.185	0.169	0.091
0.255	0.256	0.388	0.263	0.292	0.175
0.367	0.403	0.598	0.416	0.441	0.224
0.559	0.438	0.862	0.438	0.627	0.244
0.798	0.518	1.196	0.523	0.878	0.341
1.114	0.698	1.570	0.611	1.189	0.336
1.546	0.862	1.979	1.084	1.551	0.378
1.948	1.481	2.408	1.498	1.968	0.684
2.376	1.818	2.838	1.698	2.507	1.252
2.745	1.886			2.836	1.350

Among the many isotherms tested for the simulation of methane on MWCNT, we found that the hybrid isotherm model of the Langmuir and Sips isotherms with four parameters nicely fitted the experimental adsorption data.[9−12] The proposed isotherm model is as follows:

Langmuir−Sips:

$$N = q_{\mathrm{m}}\left(\frac{b_{\mathrm{L}}P}{1 + b_{\mathrm{L}}P} + \frac{b_{\mathrm{S}}P^{1/n}}{1 + b_{\mathrm{S}}P^{1/n}}\right) \tag{2}$$

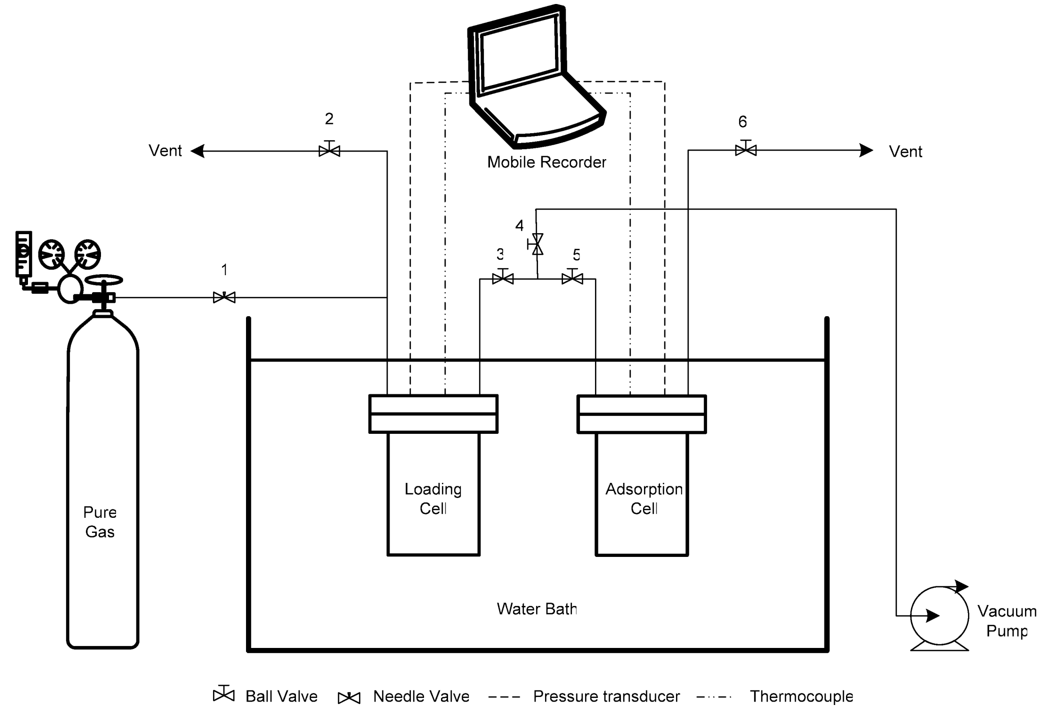

Figure 2. Schematic diagram of the adsorption apparatus.

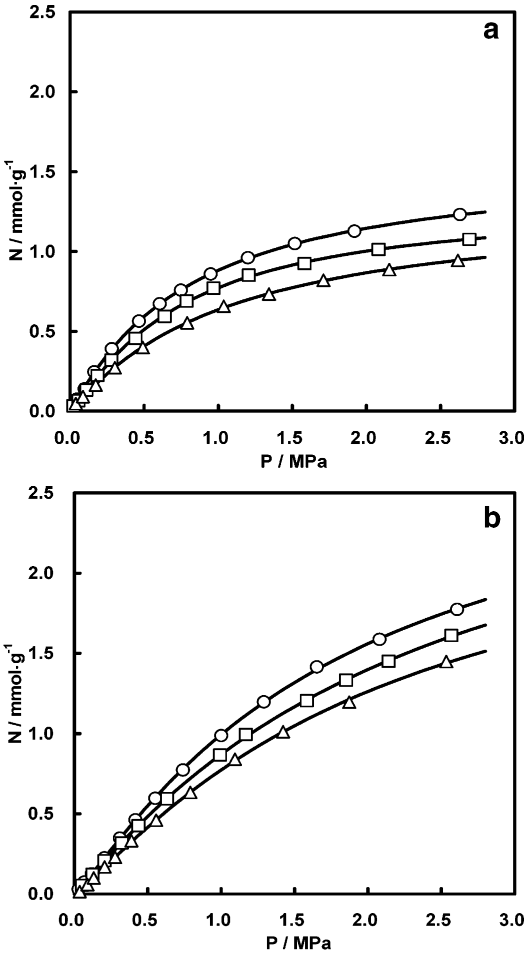

Figure 3. Adsorption isotherms of methane on (a) HSZ-320 and (b) DAY: ○, 303.15 K; □, 313.15 K; △, 323.15 K; —, Sips isotherm (Table 4).

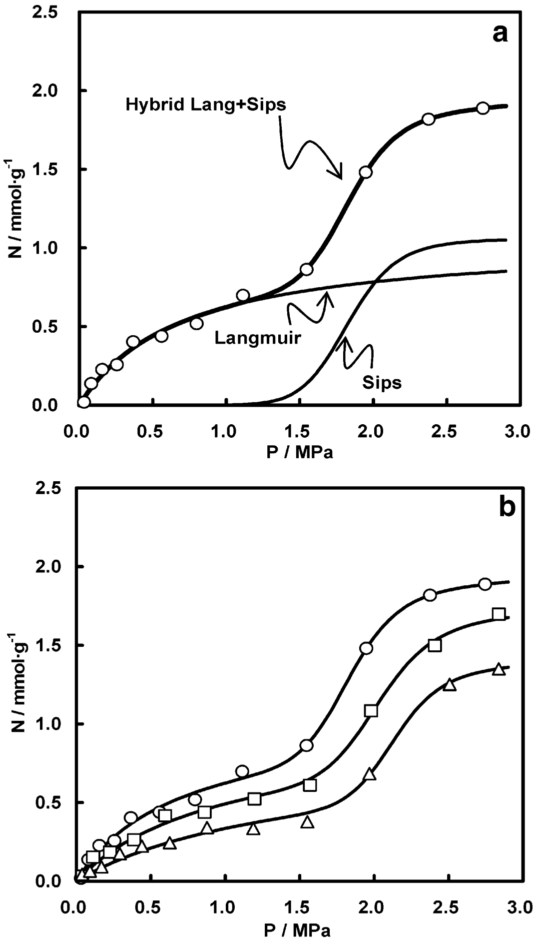

Figure 4. (a) Validation of the hybrid isotherm model for the adsorption of methane on MWCNT at 303.15 K. (b) Adsorption isotherms of methane on MWCNT: ○, 303.15 K; □, 313.15 K; △, 323.15 K; —, hybrid Langmuir−Sips isotherm (Table 5).

where N is the amount adsorbed; P is the equilibrium pressure of methane; and q_m, b_L, b_S, and n are the isotherm parameters. Four isotherm parameters (q_m, b_L, b_S, n) of the hybrid isotherm were determined by a nonlinear least-squares fitting routine of the Nelder−Mead simplex method. On the other hand, the Sips

Table 4. Sips Isotherm Parameters for Methane onto HSZ-320 and DAY

adsorbate	T K	q_m mmol·g^{-1}	b MPa^{-1}	n	error %
HSZ-320	303.15	1.567	1.288	0.928	0.022
	313.15	1.315	1.426	0.857	0.062
	323.15	1.299	0.958	0.940	0.026
DAY	303.15	2.923	0.514	0.867	0.049
	313.15	3.049	0.400	0.921	0.036
	323.15	2.616	0.420	0.869	0.067

Table 5. Langmuir−Sips Isotherm Parameters for Methane onto MWCNT

parameters	T = 303.15 K	T = 313.15 K	T = 323.15 K
q_m	1.056	0.967	0.824
b_L	1.436	1.025	0.686
b_S	1.145×10^{-3}	3.886×10^{-4}	3.042×10^{-5}
n	11.180	11.070	13.700

equation (eq 3) was used to fit the isotherm data of HSZ-320 and DAY in terms of temperatures of (303.15, 313.15, and 323.15) K. The Sips equation is as follows:

Sips:

$$N = \frac{q_m b P^{1/n}}{1 + b P^{1/n}} \tag{3}$$

where q_m, b, and n are the isotherm parameters. The Sips isotherm parameters for two zeolites are listed in Table 4, and the hybrid Langmuir−Sips parameters for MWCNT are summarized in Table 5. As shown in Figures 3 and 4, a good correlation was observed.

Figure 4a illustrates a comparison of three isotherms in MWCNT. The thickest solid line is the predicted result by the hybrid Langmuir−Sips isotherm parameters (q_m, b_L, b_S, n) in eq 2. The thin solid lines are the simulated results only by Sips parameters and Langmuir parameters of the determined hybrid isotherm parameters, respectively. The Langmuir isotherm describes only the surface adsorption region at relatively lower pressure, while the Sips isotherm explains the capillary condensation region at higher pressure. From an engineering point of view, the Sips isotherm, capable of explaining the capillary condensation, was superior to flexible fit of isotherm data although its physical meaning is arguable. As shown in Figure 4b, the hybrid Langmuir−Sips isotherm successfully fit the isotherm data of methane on MWCNT in terms of temperatures (303.15 K, 313.15 K, and 323.15 K).

The isosteric enthalpies of adsorption can be calculated by the Clausius−Clapeyron equation:[6]

$$Q_{st} = -R\left[\frac{\partial \ln P}{\partial(1/T)}\right]_N \tag{4}$$

where P is the pressure, T is the temperature, R is the gas constant, and Q_{st} is the isosteric enthalpy. The isosteric enthalpy is a measure of the interaction between adsorbate molecules and adsorbent lattice atoms, and it may be used as a measure of the energetic heterogeneity of a solid surface. For the heterogeneous adsorption system, the isosteric enthalpy curve varies with the surface loading. It has been recognized that surface heterogeneity may come from the energetic, structural, and geometric heterogeneity.[13] Our experimental results showed that the isosteric enthalpies of adsorption with the surface loading varied in the range from −15 kJ mol^{-1} to −50 kJ mol^{-1} for MWCNT and from −10 kJ mol^{-1} to −40 kJ mol^{-1} for HSZ-320 zeolite and showed a nearly constant value of −15 kJ mol^{-1} for DAY zeolite (Figure 5). A strong adsorption energetic heterogeneity of MWCNT and HSZ-320 zeolite was observed. Especially, the MWCNT adsorbents for the experiment had an energetically heterogeneous surface.

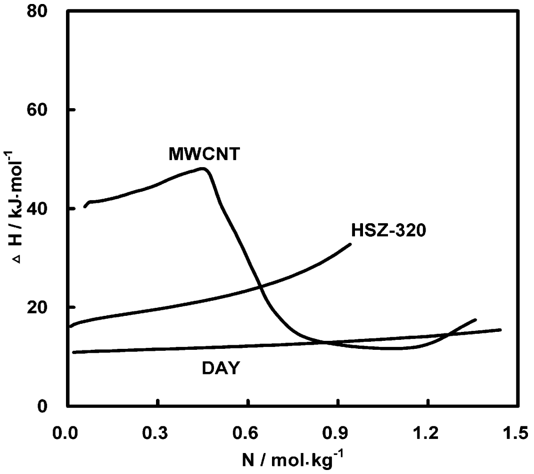

Figure 5. Isosteric enthalpy of adsorption as a function of loading.

Conclusions

The adsorption equilibrium data of methane on MWCNT and two zeolites were obtained at 303.15 K, 313.15 K, and 323.15 K and at pressures up to 3 MPa. The experimental data of zeolites were well-correlated by the Sips isotherm while those of MWCNT were explained by the hybrid Langmuir−Sips equation. The isosteric heats of adsorption of the MWCNT calculated by the Clausius−Clapeyron equation were found to be an energetically heterogeneous surface.

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