Study of Nitrogen Adsorbed on Open-Ended Nanotube Bundles

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The adsorption of N_2 on the open-ended single-walled carbon nanotube bundles was studied. The amount corresponding to the first coverage adsorbed on open-ended carbon nanotube bundles is three times larger than the amount adsorbed on closed-ended nanotube bundles. The isosteric heat of adsorption was obtained from the adsorption isotherm measurement performed at temperatures ranging from 117 to 130 K. The estimated heat of adsorption of nitrogen on the open-ended nanotube bundles is about twice as great as that on the closed-ended nanotube bundles. This leads directly to the conclusion that the binding energy of nitrogen on the open-ended nanotube is greater than that of nitrogen on the closed-ended nanotube bundles.

Introduction

Carbon nanotubes (CNTs), which have fine pores and lower dimensionality, are useful materials in both nanoscale and macroscale applications such as ultra-fine probes,[1,2] field emission devices,[3,4] and gas storage devices.[5−8] Studies concerning the adsorption of molecules on the single-walled carbon nanotubes (SWNTs) especially, are, attracting fundamental interests and offer important technological information such as separation of mixtures and hydrogen storage. The report by Pederson et al.[5] suggests that carbon nanotubes with a few nanometer-sized diameter should be able to draw liquids up by capillarity. Also, the report by Dillon et al.[7] showing that hydrogen gas can condense to a high density inside SWNTs implies that SWNTs have a large storage efficiency for hydrogen-fueled vehicles. This is a consequence of the higher binding energy inside the nanotube caused by the curvature of the tube's interior.

Recently, some theoretical calculations have been done for the binding energy of H_2, He, and Ne on the interstitial channel of the nanotube bundles and for the attractive potential energy of H_2 inside the nanotube.[9−11] Some theoretical studies have also predicted the increased adsorption capacity and adsorption binding energy of the open-ended nanotubes.[5,10−12] Weber et al.[13] have shown experimentally that the binding energy of CH_4 on the closed-ended nanotube is 76% larger than that on planar graphite. In our earlier report,[14] the binding energy of nitrogen on closed-ended single-walled carbon nanotubes at lower coverage was also studied. However, it is interesting that there have not yet been any experimental results related to the calculation of the binding energy of the adsorbates inside nanotubes.

In this paper, an experimental study of the adsorption of nitrogen on the open-ended SWNTs is reported. Comparison of the amount adsorbed on SWNTs related to the acid treatment and related to the annealing temperature after the acid treatment will be discussed. The isosteric heat of adsorption and the binding energy from isotherm adsorption experiments on open-ended SWNTs below the first coverage were estimated.

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Experimental Section

The apparatus for the isotherm adsorption experiments was composed of a gas handling system and a refrigerator. The gas handling system consisted of 1/4" VCR valves (Nupro) and a capacitance pressure gauge (MKS Baratron 127). A He-recycled refrigerator (CTI model 22 refrigerator) was used.

The nanotubes used as a substrate in this experiment were produced at Rice University by the pulsed laser vaporization method.[15] To remove the half-fullerene caps at the ends of the nanotube, an acid treatment was done in the mixture of H_2SO_4 and HNO_3 with the ratio of 3 to 1 under a sonicating process for 24 h.[16] The acid-treated nanotube samples experienced a filtering process with a membrane filter with the mesh size of 0.45 μm. To compare annealing effects, nanotubes were divided into two pieces. A piece of nanotube was annealed at 873 K and another was annealed at 1073 K for 12 h in a vacuum of 10^{-6} Torr pressure, respectively. The nanotube samples were transferred into a copper cell in air and evacuated at 350 K for 24 h before measurements were taken. The mass of the nanotubes used in the experiments was 30 mg. The mean tube diameter of SWNT was 1.2 nm.[15] Temperatures were controlled using a temperature controller (Lakeshore DRC-93CA) with 0.01 K precision. Measurements to obtain the heat of adsorption were performed at five different temperatures; 117.25, 120.28, 123.55, 126.51, and 129.95 K.

Results and Discussion

Figure 1 shows the isothermal adsorption of nitrogen on the closed-ended SWNTs and the open-ended SWNTs measured at 71 K. The amount adsorbed, *y*-axis, was represented in mmol/g. The amount of molecules related to the first coverage, which is believed to correspond to the monolayer of the plane graphite, on the closed-ended SWNTs is about 1 mmol/g. Different from the case of the planar graphite, a clear-cut distinction is not

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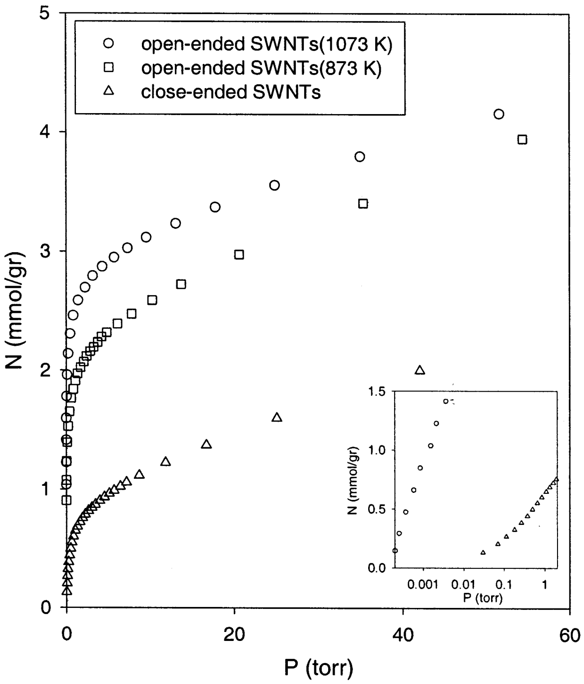

Figure 1. Isotherm adsorption data of nitrogen on SWNTs at 71 K. Inset shows the isotherm adsorption of nitrogen on both the closed-ended and the open-ended nanotubes at low coverage in semilog scale.

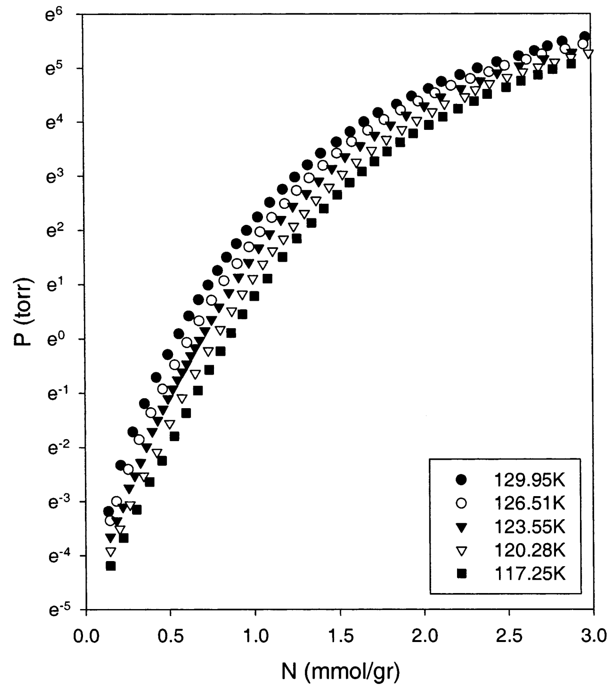

Figure 2. Adsorption data below the first coverage for all the temperatures in this study. The pressure (*y*-axis) was given in natural log scale.

shown between the regions below and above the one coverage, which represents the two-phase coexistence,[17] because the geometrical shape of the nanotube bundles is different from that of the planar graphite. The interstitial channel, the ridge, and the outer surface are the theoretically possible sites where molecules could be adsorbed on the closed-ended SWNTs.[18] Talapatra et al.,[18] however, found experimentally that adsorption occurs only on the ridge and the outer surface for CH_4, Ne, and Xe. The possible adsorption sites for nitrogen are expected to be the same as in the cases of the above gases. Because the ridge, which is the region between two adjacent nanotubes, has greater binding energy than that of the outer surface, the gas tends to be adsorbed on the ridge first in the case of closed-ended nanotubes.

The process by which the nanotubes were opened enhanced the adsorption on the inner sites of the nanotubes. This is supported by the fact that, as shown in Figure 1, the amount of adsorbates on the open-ended SWNTs is much larger than that of adsorbates on the closed-ended SWNTs. The acid treatment, however, also causes the oxidation of the nanotube surface.[19] Oxidized groups such as C−O, O═C−O, and other oxidized groups are formed at the nanotube ends and at defect sites on the walls, and these prevent the enhancement of the inner site adsorption. Kuznetsova et al.[19] have shown that the thermal treatment of nanotubes causes these groups to be decomposed and thus enhances adsorption in nanotubes. Figure 1 also shows the adsorption of nitrogen on open-ended nanotubes having different thermal treatment temperatures of 873 and 1073 K, respectively. Nanotubes annealed at 1073 K have about 50% larger adsorption capacity than those annealed at 873 K and have about 200% larger adsorption capacity than nanotubes without the acid treatment. This means that thermal treatment followed by the acid treatment enhances the adsorption on the inner sites of the nanotubes, consistent with the report by Kuznetsova et al.[19]

Not only does the opening process provide more sites for adsorption, but also it provides higher binding sites, which is strongly related to the advantage of nanotubes as a gas storage material. The inset in Figure 1 shows the isotherm adsorption of nitrogen on both the closed-ended and the open-ended nanotubes annealed at 1073 K at low coverage in semilog scale. Adsorption on the open-ended nanotubes occurs at lower pressure regions than on the closed-ended nanotubes. This is caused by the higher binding energy of inner sites due to a larger number of nearest neighbor carbon atoms inside the nanotube which interact with adsorbates. In view of the extent of the coverage, the nitrogen gas is adsorbed on the inner sites of the nanotubes prior to the outer sites of the nanotube bundles up to a coverage about 1.5 mmol/g. Nitrogen molecules begin to be adsorbed on the outer sites above 1.5 mmol/g.

The energetics of the adsorption process can usually be described in terms of the heat of adsorption. It is the amount of the heat released when an atom is adsorbed on a substrate. It also reflects the interaction between the gas and the substrate at finite temperature and coverage. It can be determined from the isotherm adsorption data measured at different temperatures, which is defined as[20]

$$q_{\mathrm{st}} = kT^2\left(\frac{\mathrm{d}\ln P}{\mathrm{d}T}\right)_N \tag{1}$$

Here, k is Boltzmann's constant, N is the amount of gas adsorbed on the nanotubes, P is the pressure of the coexisting unadsorbed gas, and T is the average value of the temperature. Figure 2 is the plot of N vs ln P at five different temperatures. In Figure 2, a limited range of data below the first coverage is plotted. Using these data and the above equation, an estimate for the isosteric heat of adsorption of N_2 for different N values was done, and the results are shown in Figure 3. The heat of adsorption (*y*-axis) in Figure 3 represents the average value of the heat of adsorption obtained at different temperatures of Figure 2. The *Y*-axis was represented in two different units: meV and kJ/mol. The open triangle represents the isosteric heat of adsorption on the closed-ended nanotubes below the first coverage.[14] In the latter case, the adsorption sites were the ridges and the outer surfaces, which are the secondary preference sites in the

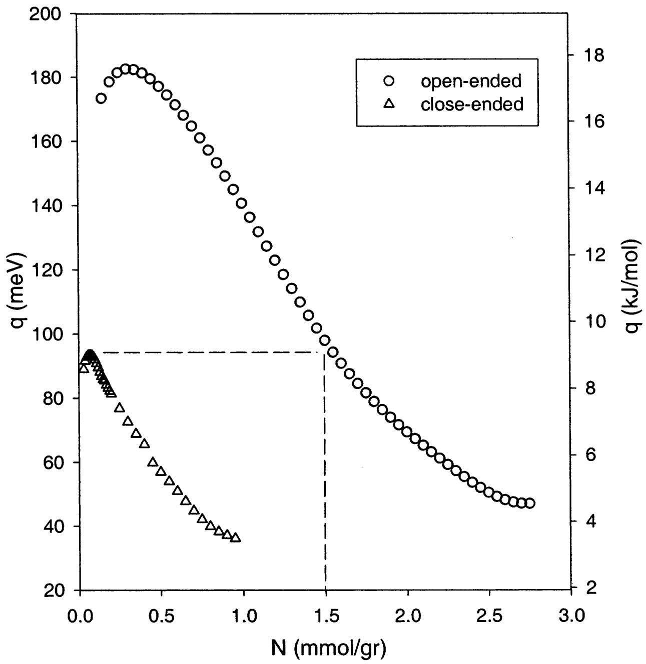

Figure 3. Average value of the isosteric heat of adsorption over all different pairs of temperatures.

adsorption on open-ended nanotubes. The maximum value of the isosteric heat of adsorption for the closed-ended nanotubes is the same as that for the open-ended nanotubes at $N = 1.5$ mmol/g, as indicated by a dash-line in Figure 3. This indicates that the gases start to be adsorbed on these outer sites at the coverage of 1.5 mmol/g as mentioned above.

The small bump of the heat of adsorption at a low coverage was also shown in the graph of the heat of adsorption on closed-ended nanotube bundles. The maximum value of the heat of adsorption of N_2 is about 182.6 meV. The heat of adsorption was inclined to decrease after the maximum value with increasing coverage. The degree of the decrease is affected by the heterogeneity of the substrate. With increasing coverage, the adsorption sites on open-ended nanotubes change from the inner site of the nanotubes to the ridge, and then to the outer surface. The abrupt decrease of the heat of adsorption implies that the sites have much different binding energy from each other. It causes the nanotube bundles to have a role of substrate with heterogeneous property.

At low coverage, the adsorbed system can be regarded as a one-dimensional system, then the binding energy, E, and the heat of adsorption have a relation of[13]

$$q_{st} = E_b + 2kT \tag{2}$$

The average value of the binding energy near the small bump is about 161.4 meV, which is twice as great as the value of the binding energy (78.5 meV) for the closed-ended nanotube bundles.[14] This means that the binding energy of the nitrogen adsorbed on the inner sites of the nanotubes is about two times greater than that of the nitrogen adsorbed on the ridges and the outer surfaces of the nanotube bundles. This leads to the conclusion that it is possible to adsorb the same amount of gases in the case of open-ended nanotubes with lower pressure than in the cases of closed-ended ones and the planar graphite, which coincides with the result shown in inset of Figure 1.

Conclusions

The adsorption isotherm of nitrogen molecules on the open-ended nanotube bundles was measured and showed that the adsorption capacity increases with both an acid treatment and annealing process. An estimate for the isosteric heat of adsorption and the binding energy was also given. The binding energy at low coverage on open-ended nanotubes is about two times greater than that on closed-ended nanotube bundles, and three times greater than that on planar graphite. This supports also the usefulness of the open-ended nanotubes for gas storage.

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