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Sorption Properties of a Single Wall Carbon Nanotube

C. Guan, Leslie S. Loo, C. Yang, and K. Wang*

School of Chemical & Biomedical Engineering, Nanyang Technological University, Singapore

The sorption properties of a single wall carbon nanotube were measured for a number of gases. The N_2 and H_2 isotherms were measured at 77 K, while the CO_2 isotherms were measured at 273 K. The data may serve the purpose of design and characterization of carbon nanotubes in sorption applications.

Introduction

Carbon nanotubes (CNTs) have found numerous applications due to their unique mechanical, electrical, and chemical properties. The sorption properties of CNTs were extensively explored in such applications as chemical/biosensors,[1] sorbents for energy storage,[2] and nanofillers in composite membranes,[3] etc. For example, H_2 storage in CNTs has been a much sought-after area, although both encouraging[2] and discouraging[4] results have been reported.

CNTs consist of graphite pores of cylindrical configuration which may present both high sorption potential and selectivity for molecules with specific structure and dimension. Some experimental and simulation studies showed that CNTs have the potential to achieve high H_2 capacity [(5 to 14) % weight percentage] at ambient temperature if the structure is optimized,[5−8] while some other studies show that the optimal temperature for H_2 storage delivery should be much lower at ~ 115 K to meet the DOE (Department of Energy, U.S.A.) standard of 6 wt % at ambient conditions.[9]

The sorption mechanisms in CNTs are also a subject of controversy. While most researchers agree that the cylindrical graphite pores (inner tubes) offer most of the capacities for physical sorption,[5] the role of the external surface, the corners within the tube bundles, the defects, and the functional groups, etc. were not fully understood.[10−12] For example, Lee et al. found the existence of a strong steric barrier for the transport of H_2 in nanotubes.[13] Ye et al. observed a phase transition in single wall carbon nanotube (SWCNT) at 77 K.[14] Lee and Lee reported that excessive H_2 sorption may lead to the breakdown of the tube structure.[7] The NREL (National Renewable Energy Laboratory, U.S.A.) demonstrated the ability for SWCNTs to store substantial quantities of hydrogen at ambient conditions via hydrogenation with reduced binding energies.[15]

This article will report the sorption properties of N_2, H_2, and CO_2 on a high purity, commercial single wall carbon nanotube. These isotherms cover a range of experimental pressures and temperatures.

Experimental Section

The SWCNT was acquired from CheapTube Inc., U.S.A. Table 1 lists the properties of the sample.

A pore and surface analyzer (PSA, Quantachrome, Autosorb-1) was used to measure the N_2 isotherm at 77 K. The specific surface area (S_{BET}) was determined using the Brunauer−Emmett−Teller (BET) method in the relative pressure range of 0.05 to 0.3. The CO_2 isotherm was measured at 273 K with the PSA up to 1 bar. The H_2 isotherms was measured at 77 K in the PSA rig up to 1.05 bar and in a high pressure volumetric rig up to 10 bar. Prior to measurements, the SWCNT samples were degassed at 250 °C overnight under high vacuum.

Table 1. Properties of the SWCNT[a]

purity	ash	OD	surface area	length	EC
> 90 %	< 1.5 %	(1 to 2) nm	> 407 $m^2 \cdot g^{-1}$	(5 to 30) μm	> 10^{-2} $s \cdot cm^{-1}$

[a] Note: OD = outer diameter; EC = electrical conductivity.

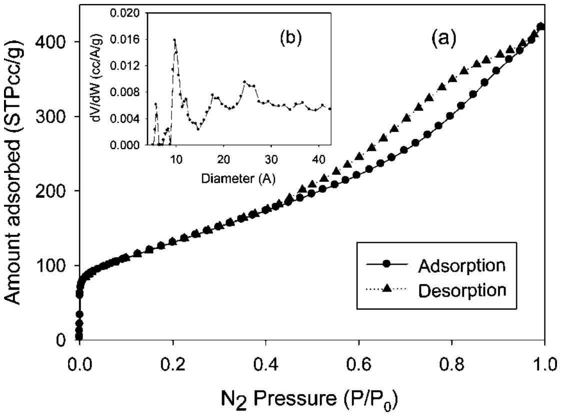

Figure 1. N_2 isotherm (a) and the derived PSD (b) on the SWCNT.

Results and Discussion

Figure 1a shows the N_2 isotherm measured at 77 K on the SWCNT. The measured S_{BET} derived from the N_2 is 420 $m^2 \cdot g^{-1}$. The total pore volume of the sample is ~ 0.70 $cc \cdot g^{-1}$, and the micropore volume is ~ 0.12 $cc \cdot g^{-1}$. The embedded Figure 1b shows the pore size distribution (PSD) of the SWCNT derived from the N_2 isotherm via the NLDFT (nonlocal density functional theory) which assumes a cylindrical graphite pore geometry. It is seen that the sample has a sharp volume peak at the pore diameter of ~1.1 nm and a minor peak at ~2.0 nm, which is consistent with the information in Table 1 that tube OD = (1 to 2) nm. Meanwhile, a large portion of the pore volume (as well as surface area) was seen to be contributed by tubes with a diameter above 2 nm. This apparent discrepancy with the product specifications (confirmed by the SEM/TEM images) is probably due to the sorption at the external surface of the tubes and the void space formed among the CNT bundles,

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* Corresponding author. E-mail: mkwang@ntu.edu.sg.

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Table 2. Isotherm Data on SWCNT

pressure bar	adsorbed $STPcc \cdot g^{-1}$	pressure bar	adsorbed $STPcc \cdot g^{-1}$	pressure bar	adsorbed $STPcc \cdot g^{-1}$	pressure bar	adsorbed $STPcc \cdot g^{-1}$
N_2 ($T = 77$ K)							
$3.000 \cdot 10^{-5}$	3.089	0.09944	109.5	0.7485	274.9	0.6011	245.3
$3.600 \cdot 10^{-5}$	3.298	0.1256	115.2	0.7724	286.4	0.5757	234.7
$6.200 \cdot 10^{-5}$	3.508	0.1512	120.5	0.7973	299.8	0.5516	225.4
$6.200 \cdot 10^{-5}$	3.927	0.176	125.7	0.8214	313.5	0.5255	216.1
$8.300 \cdot 10^{-5}$	4.595	0.2008	130.9	0.847	329.2	0.5	208
$1.660 \cdot 10^{-4}$	12.1	0.2254	136	0.8716	344.8	0.4789	201.6
$5.120 \cdot 10^{-4}$	21.36	0.2499	141.1	0.8967	360.6	0.4513	190.6
$8.320 \cdot 10^{-4}$	33.42	0.2745	146.3	0.924	376	0.4286	182.5
$9.940 \cdot 10^{-4}$	59.45	0.299	151.5	0.9469	387.7	0.4037	175.7
$1.081 \cdot 10^{-3}$	62.66	0.3235	156.7	0.9726	401.7	0.3764	169.1
$2.392 \cdot 10^{-3}$	70.84	0.3479	162	0.992	419.8	0.3528	163.9
$3.609 \cdot 10^{-3}$	74.33	0.3725	167.3	0.9769	409.8	0.3241	157.6
$5.221 \cdot 10^{-3}$	77.22	0.4004	173.4	0.9525	397.9	0.3009	152.6
$6.239 \cdot 10^{-3}$	78.64	0.4225	178.3	0.9253	388.6	0.2762	147.3
$7.490 \cdot 10^{-3}$	80.05	0.4495	184.3	0.9039	382.7	0.2512	142
0.01345	84.67	0.4746	190	0.8741	375.4	0.225	136.6
0.01896	87.61	0.4993	195.8	0.8537	369.4	0.1994	131.2
0.02553	90.34	0.5233	201.7	0.8263	360.3	0.1739	125.8
0.02938	91.72	0.5489	207.8	0.8015	349.7	0.1237	115.2
0.03959	94.95	0.5721	213.9	0.7788	338.6	$9.920 \cdot 10^{-2}$	109.8
0.05069	98.01	0.5961	220.4	0.7514	324.2	$7.470 \cdot 10^{-2}$	104.2
0.06185	100.8	0.6233	228.3	0.7289	311.4	$5.080 \cdot 10^{-2}$	98.37
0.06854	102.5	0.6479	236.1	0.7029	297	$2.590 \cdot 10^{-2}$	90.79
0.0748	103.9	0.6716	244.2	0.6765	282.6	$1.990 \cdot 10^{-2}$	88.33
0.08064	105.3	0.6985	254	0.6532	270.1	$1.780 \cdot 10^{-2}$	87.34
0.09267	108	0.7232	263.7	0.6277	257.4	$1.260 \cdot 10^{-2}$	84.41
CO_2 ($T = 273$ K)							
$6.315 \cdot 10^{-4}$	0.067	0.2641	8.02	0.8477	19.22	0.7307	17.22
$1.053 \cdot 10^{-3}$	0.097	0.3273	9.448	0.9004	20.1	0.6256	15.36
$1.264 \cdot 10^{-3}$	0.11	0.3741	10.43	0.9527	20.99	0.5727	14.39
$5.792 \cdot 10^{-3}$	0.331	0.4261	11.53	1.0056	21.85	0.5206	13.38
0.0575	2.848	0.4734	12.48	1.0520	22.63	0.4583	12.18
0.0820	3.729	0.5313	13.58			0.4145	11.28
0.0938	4.103	0.5841	14.61	0.9939	21.68	0.3719	10.39
0.1276	5.117	0.6374	15.57	0.9405	20.8	0.3138	9.144
0.1415	5.491	0.6896	16.5	0.8876	19.91	0.2598	7.917
0.1824	6.056	0.7428	17.43	0.8351	19.01		
0.2099	6.725	0.7955	18.33	0.7824	18.11		
H_2 ($T = 77$ K)							
$1.000 \cdot 10^{-4}$	0.3136	0.238	32.1	0.531	47.13	0.953	60.21
$6.000 \cdot 10^{-4}$	0.9408	0.247	32.68	0.583	49.1	1.01	61.62
$1.100 \cdot 10^{-3}$	1.456	0.252	33.04	0.636	50.98		
$5.300 \cdot 10^{-3}$	4.01	0.26	33.64	0.689	52.77	1.11	59.45
$8.440 \cdot 10^{-3}$	18.61	0.323	37.43	0.741	54.32	2.58	77.35
0.152	25.45	0.381	40.45	0.793	55.84	4.89	84.43
0.194	28.92	0.422	42.49	0.844	57.32	6.8	93.54
0.223	31.02	0.481	45.11	0.901	58.96	10.62	94.66

which constitutes a major volume contribution of mesopores. The desorption hysteresis confirms the existence of mesopore volume in the sample. The data are listed in Table 2.

Figure 2 shows the sorption isotherm of CO_2 measured on the sample at 273 K (the sample cell was submerged in an ice bath during the experiment). As the sorption pressure is low ($P_0 = 1.05$ bar), CO_2 adsorbed moderately, and no hysteresis was observed between the adsorption and desorption isotherms. A small hump was seen at $P/P_0 = 0.18$, which may be related to the transition of adsorption from the internal tubes to the external voids/surfaces.[12] Simulation studies are needed to understand the underlying mechanisms at this point. The experimental data are listed in Table 2.

Finally, the H_2 isotherm measured on the SWCNT at 77 K is shown in Figure 3, which combines the data from the PSA ($P < 1.05$ bar, solid circles) and the high pressure volumetric rig (1.05 bar $< P <$ 10 bar, open circles). It is seen that the isotherm data measured with the two rigs agree with each other reasonably well. The H_2 isotherm data are listed in Table 2 and were fitted to the Langmuir equation [$C_\mu = C_{\mu s}bP/(1 + bP)$, where b is the sorption affinity, P is the pressure, and $C_{\mu s}$ is the saturation capacity of the SWCNT]. The fitting parameters are listed in the caption of Figure 3. The isotherm data revealed

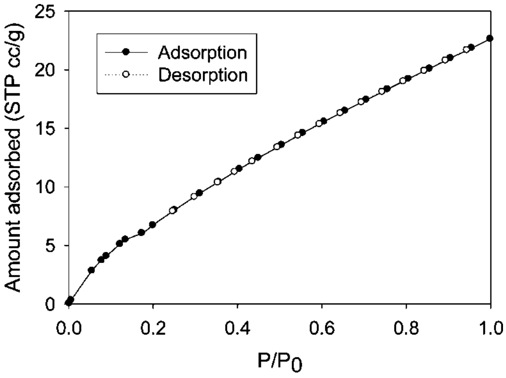

Figure 2. CO_2 isotherm at 273 K on the SWCNT ($P_0 = 1.05$ bar).

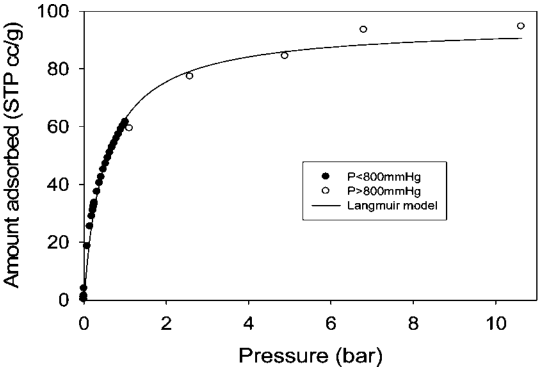

Figure 3. H_2 isotherm on SWCNT at 77 K. The fitting parameters of the Langmuir isotherm are: $C_{\mu s} = 95$ ccSTP·g^{-1}, $b = 1.93$ bar^{-1}.

that the SWCNT presents an H_2 sorption capacity of ~ 0.9 wt % at 77 K and 10 bar. This capacity is mainly determined by the micropore volume and the tube sizes of the SWCNT sample.

Conclusion

The sorption isotherms of N_2 and H_2 were measured for a SWCNT at 77 K, while the CO_2 isotherm was measured at 273 K. The SWCNT was found to have a major tube diameter distribution at 0.11 nm, but the external surface and the void space among the CNT bundles constitute the major contribution of mesopore volume. The H_2 sorption capacity of the sample is found to be ~ 0.9 wt % at 77 K and 10 bar.

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