Butane Adsorption on Multiwalled Nanotubes

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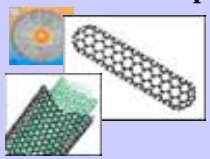
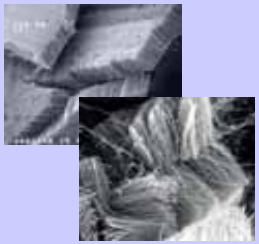
It has previously been shown that a fixed bed of carbon multiwall nanotubes can separate gaseous mixtures of methane and butane. This work proposes a butane sorption model suitable for engineering design of separation systems. MWNT morphology is defined using log-normal distributions for the inner and outer diameter distributions. Butane uptake showed no hystersis, and could be modeled using a modified BET equation. Model coefficients are consistent with butane sorption primarily on the outer surface of the MWNTs. Smaller mean diameter MWNTs give greater uptake, suggesting that MWNTs could be tailored for particular applications.

MWNT Morphology



Length: 50 - 55 µm



- Three samples analyzed
- SEM used to estimate length
- TEM used to estimate diameter distributions

MWNT properties

Sample	Pore volume [m^3/g]	External area [m^2/g]	Internal area [m^2/g]
VGB61	1.33E-9	37.9	0.970
VGB62	1.48E-10	14.8	0.309
VGB63	1.16E-10	11.2	0.0608

- Geometrical properties determined from diameter distributions

The BET equation

BET

$$(P/P_o) / n(1-(P/P_o)) = 1/(c \cdot n_m) + (c-1) \cdot (P/P_o) / (c \cdot n_m)$$

Assumptions:

- Fixed surface sites
- Each bond has the same energy
- No interaction between adsorbed molecules
- Sorption beyond monolayer, but different heat of sorption
- Same conditions for all layers except first
- Adsorption layers $\rightarrow \infty$ as P $\rightarrow$ Psat

APPLICATION

The physical adsorption of gases by non-porous solids give rise to a type II isotherm.
The isotherm for butane uptake on MWNT has the characteristic look of a type II isotherm.

Modified BET

$$k(P/P_o) / n(1-k(P/P_o)) = 1/n_m \cdot c + k(c-1)/(c \cdot n_m) \cdot (P/P_o)$$

Assumption:

- Multilayers @ P_o is finite (~5 - 6)

Results

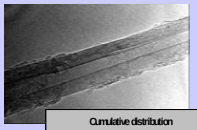
Sample	Total uptake [g/g MWNT]	Pore uptake [g/g MWNT]	Surface uptake [g/g MWNT]	Surface uptake [g/m^2]
VGB61	5.29E-2	7.63E-4	5.21E-2	1.37E-3
VGB62	2.08E-2	8.49E-5	2.08E-2	1.02E-3
VGB63	1.140E-2	6.63E-5	1.13E-2	0.753E-3

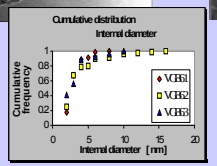
- Butane uptake calculated from adsorption isotherm and MWNT geometry (P/P_o = 0.9)

Sample	No. layers	Monolayer [mole]
VGB61	3.73	1.00E-5
VGB62	3.28	5.11E-6
VGB63	2.47	4.20E-6

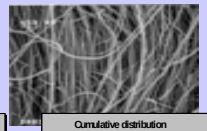
- Number of layers adsorbed on external surface and amount of butane in monolayer calculated from MWNT geometry, butane density (DIPPR), and butane's radius of gyration

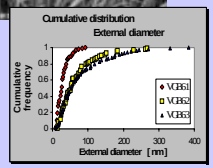
Internal diameter: 2 - 16 nm (Mesoporous)



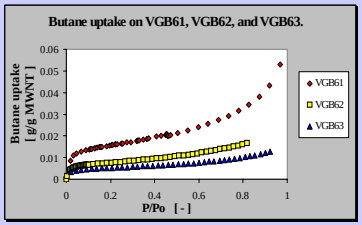


External diameter: 8-380 nm





Butane Adsorption Isotherm



- Hiden instrument (IGA system)
- T = 298 K
- P_o = 2437 mbar (saturated vapor pressure for butane at 298 K)
- m = 45-50 mg
- Isotherms show no hysteresis

BET Parameters

BET model

Sample	k	c	n_m [mole]	Standard deviation
VGB61	1	99	1.01E-5	8.56E-8
VGB62	1	127	5.41E-6	8.73E-10
VGB63	1	184	3.29E-6	2.61E-9

Modified BET model

Sample	k	c	n_m [mole]	Standard deviation
VGB61	0.78	162	1.00E-5	3.19E-11
VGB62	0.72	125	5.35E-6	1.65E-12
VGB63	0.73	136	3.25E-6	2.30E-12

- The modified BET model is valid over P/P_o ~ 0.05 - 0.8
- n_m = monolayer capacity in moles (close to the point of inflection)
- c gives shape of inflection; increasing c $\rightarrow$ sharper slope
- k corresponds to the slope of the isotherm for the multilayer region

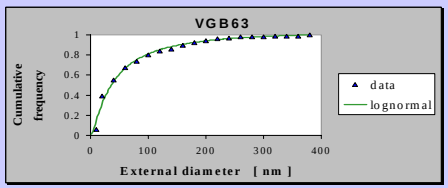
Conclusions and Discussion

- External and internal diameters were fit by a log-normal model
- External area ~11.2-37.9 m^2/g
- Isotherm was fit to modified BET (type II isotherm) and showed no hysteresis
- Parameter n_m and calculated monolayer capacity agree
- Adsorption capacity ~11-53 mg/g. Low compared to activated carbon but no hysteresis
- Surface capacity ~0.75-1.37 g/m^2
- Most uptake on external surface: ~99%
- Number of layers adsorbed ~2.5-3.7 - comparable to reported values for methane uptake on graphite (~3.5)

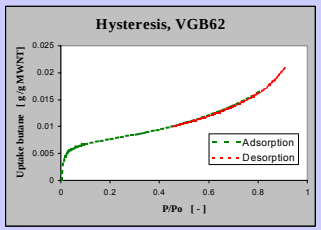
Log Normal Parameters

•log normal curve fits well to external and internal diameter distribution

Sample	Diameter	Mean [nm]	Standard deviation
VGB61	Int.	2.64	0.330
	Ext.	24.3	0.568
VGB62	Int.	2.65	0.601
	Ext.	48.7	0.772
VGB63	Int.	2.40	0.597
	Ext.	53.1	0.898

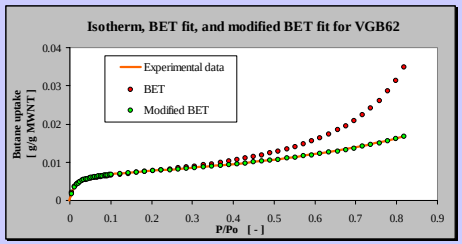


Hysteresis



- An adsorption/ desorption cycle gives an isotherm with no or negligible hysteresis. This is remarkable, since normally adsorption/ desorption isotherms for mesoporous material posess a characteristic hysteresis loop.

BET and Modified BET Fit



Future Work

- Measure sorption of hydrocarbons and hydrocarbon mixtures
- Produce thin films of MWNT assemblies for hydrocarbon, and other, separations

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