Hydrogen Storage with Carbon Materials – *Quo Vadis?*

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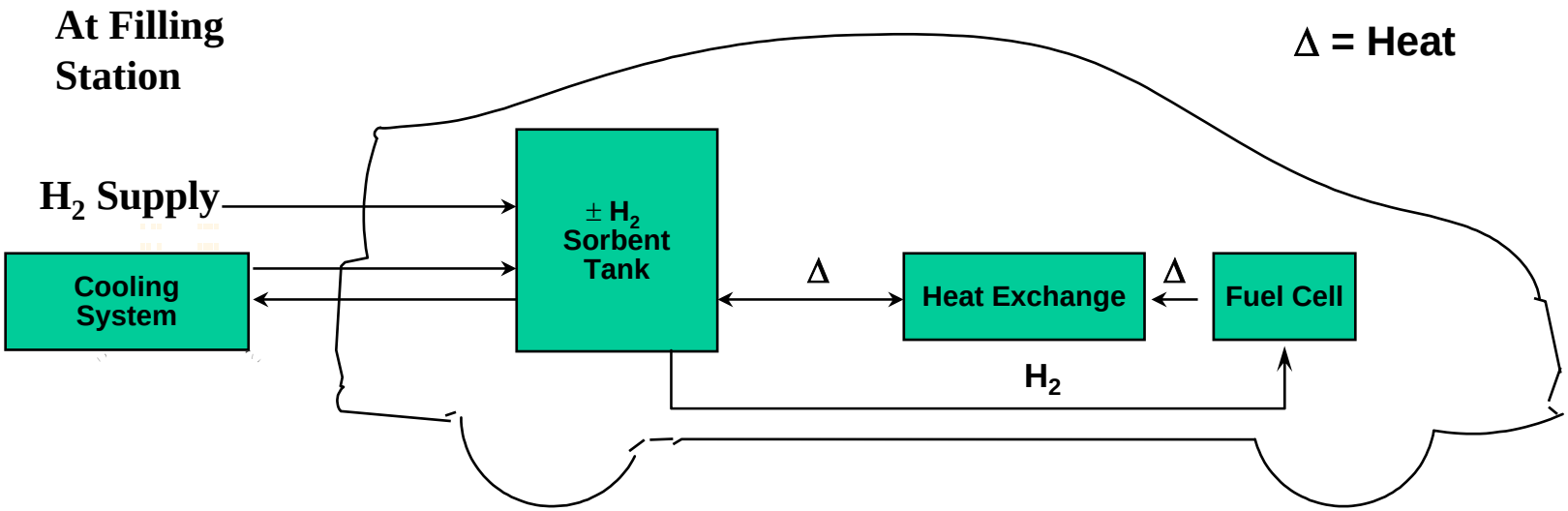
An Overview of the Field of Microporous Carbon Materials

- Single Wall Carbon Nanotubes
- Metal-Organic Frameworks (MOF's)
- Carbon/Metal Hybrid Systems

As reversible H_2 sorbents in the context of a vehicular on-board hydrogen storage model.

With a (personal) prognosis of its path forward

1. The Vehicular Hydrogen Storage Model



- Conformable lightweight tank with pressure/temperature reversible hydrogen sorbent
- Heat exchange capabilities for accommodating H_2 refueling exotherm and heat from fuel cell

System Design: Required ± H_2 Sorbent Properties

Langmuir Model $[S{\cdot}H_2] = K[S_T]P_{H_2}/(1+KP_{H_2})$

for $S + H_2 \underset{}{\overset{K}{\rightleftarrows}} S{\cdot}H_2$ S_T = Maximum loading

Assume S_T = 10 wt%, for [S] = 8 wt% H_2 at 20°C, 50 atm
Thus for isotherm model K = 0.08 atm^{-1}
Estimation of H_2 adsorption entropy (ΔS):
For H_2, S° = 31.2(total), 28.1 (translational) in cal/deg. mole (eu)
For H_2 adsorption $C_{24}K$ at 77K*: ΔH = -2.25 kcal/mole, ΔS= -20.4 eu

From ΔG = -RTlnK = ΔH-TΔS
A ΔS of -20 to -25 eu corresponds to a -ΔH of -4.4 to -5.9 kcal/mole

Require: ΔH ~ -6 kcal/mole or ~ -25 kJ/mole (~10% of LHV for H_2)

* K. Watanabe et al Nature Phys. Sci. 233, 160 (1971)

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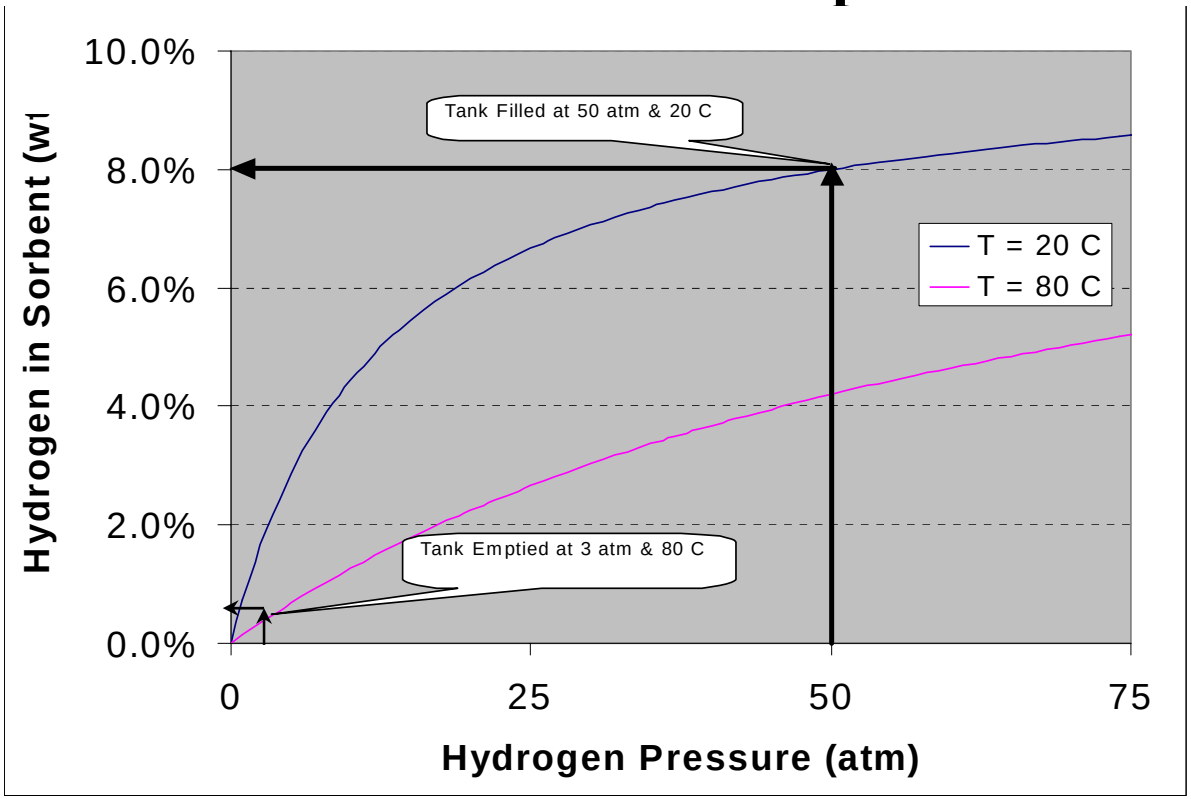
Conceptual System Design: System Engineering Model of Adsorption



- Langmuir isotherm model assumes a ΔH of -25 kJ/mol
- The "tank" can deliver 7.56 wt. % H_2 under these modeling conditions
- Vol. Capacity of 75.6 g H_2/Liter d=1g/cc

Gravimetric hydrogen capacity is linked to the heat (ΔH) and the entropy (ΔS) of H_2 sorption, which determine the strength and extent of equilibrium binding to the sorbent, and to the volumetric space per unit mass of sorbent that is accessible to hydrogen capture. The sorbent (S) and H_2 equilibrium is expressed as:

$$S(s) + H_2(g) \underset{}{\overset{K}{\rightleftharpoons}} S \bullet H_2(s) \text{ where } K = [S \bullet H_2] / [S] P_{H_2} \qquad (atm^{-1})$$

System Design: Refueling and H_2 Delivery to FC

Loading of 4 Kg H_2, 20°C
A ΔH of -6 kcal/mole would require a dissipation of 12,000 kcal of heat of sorption + ~ 300 kcal of sensible heat.

For a 3 min. refueling time ≡ 290 kW of cooling
Equivalent to boiling ~ 23 liters of water
A significant engineering challenge!

For H_2 Delivery to Fuel Cell

For 4 Kg H_2 over 6 hours, corresponds to a manageable 2.3kW heat transfer rate, from the FC.

2. Single Wall Carbon Nanotube (SWNT) as H_2 Sorbents

Genesis: Nature Publ. In '97 by A. Dillon, M. Heben[1]
From TPD data; H_2 desorption from C/SWNT at 300 K with Ed = 4.7 kcal/mole
Compare with H_2/AX-21carbon $-\Delta H_{ads}$ = 1-1.3 kcal/mole [2]
Reviews [3-6] on C nanostructure/SWNT + H_2 etc.,

Work on H_2/SWNT rendered difficult by:

- SWNT materials, synthesis and characterization
- Hydrogen adsorption measurements at high H_2 pressures [7]

DOE's SouthWest Research Institute H_2 storage measurement lab.

Refs. 1 A. C. Dillon, M. Heben, *et. al* Nature 386, 377 (1997); 2 G. Pez, W. Steyert, US 4580404 (1986)
3 A. C. Dillon, M. Heben, Appl. Phys. A72, 133 (2001); 4 A. Zuttel, S. Orimo, MRS Bulletin, 27, 705 (2002)
5 M. Hirscher and M. Becker, J. of Nanoscience and Nanotechnology, 3, 3 (2003); 6 M. Becker, M. Haluska *et al*, CR Physique, 4, 1055, 2003; 7 G.G. Tibbetts, G.P. Meisner, and C.H. Olk, Carbon, 39, 2291, (2001)

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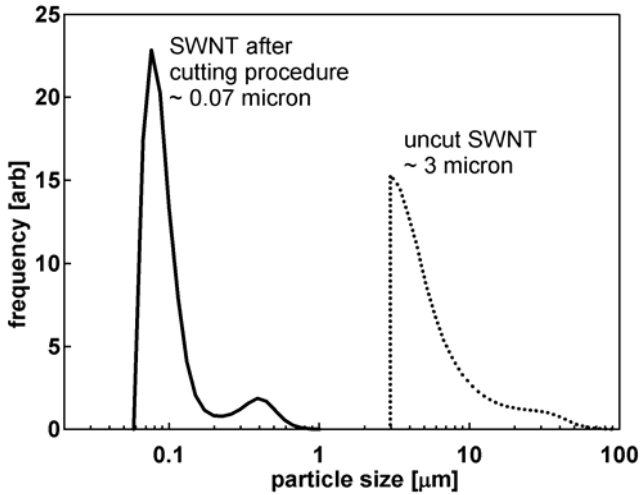
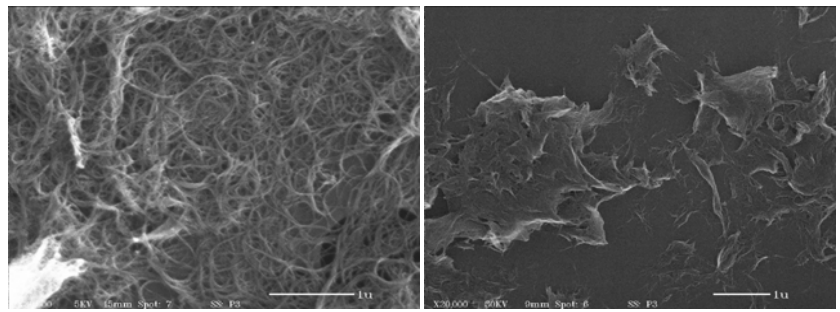
Hydrogen Adsorption by Tailored (cut and uncut) Carbon Nanotubes [1]

1. C Nanotube Samples Preparation
   SWNT Sources: CN Inc., SW Nanotechnologies Inc., T. Swan Co. (UK)
   Purification: Air (250°C), HCl to remove metal
   "Soft" cutting procedure by Chen *et al* [2] using mechanical grinding with beta cyclodextrin/ethanol.
   Raman: d = 7.5Å to 15Å; G/D Ratio 4-7

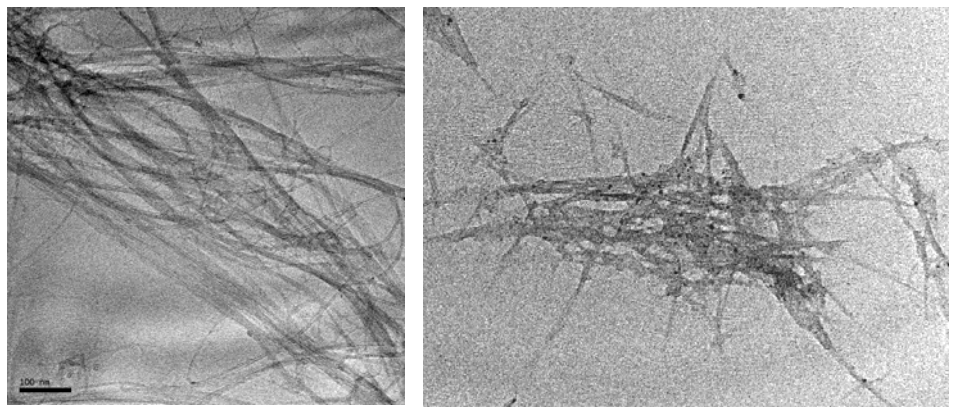


Laser light scattering profile of cut and Uncut SWNT

Uncut Cut



SEM



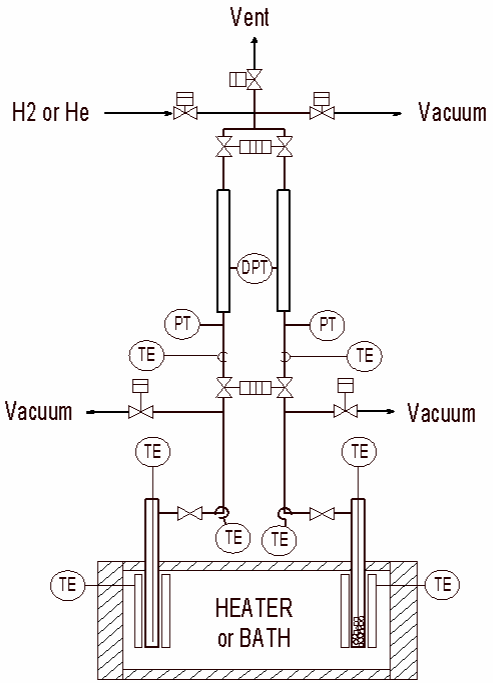
TEM

100 nm

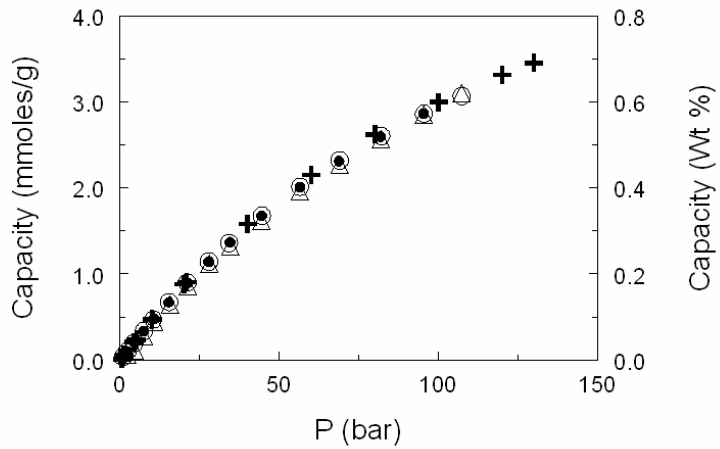
100 nm

1 M. Haas, J. Zielinski, G. Dantsin, C. Coe, G. Pez, and A. Cooper, J. Mater. Res., submitted.
2 T. Chen, M. T. Dyer, M. F. Foo, J. Am. Chem. Soc. 123, 620 (2001)

2. H_2 Adsorption Equipment and H_2/Carbon "Certification" Data



Schematic of differential gas Adsorption apparatus[1]



Hydrogen isotherms (25°C) on Amoco GX-31 activated carbon with 112 mg (Δ) and 580 mg (O, •) samples and a Rubotherm adsorption balance[2] with a 1014 mg Sample (+)

1 Browing, D. J.; Gerrard, M. L.; Lakeman, J. B; Mellor, I. M.; Mortimer, R. J.; Turpin, M. C.; Nano Lett.; 2002; 2(3); 201-205

2 F. Dreisbach, Rubotherm Präzisionsmeβtechnik GmbH, Germany (2004)

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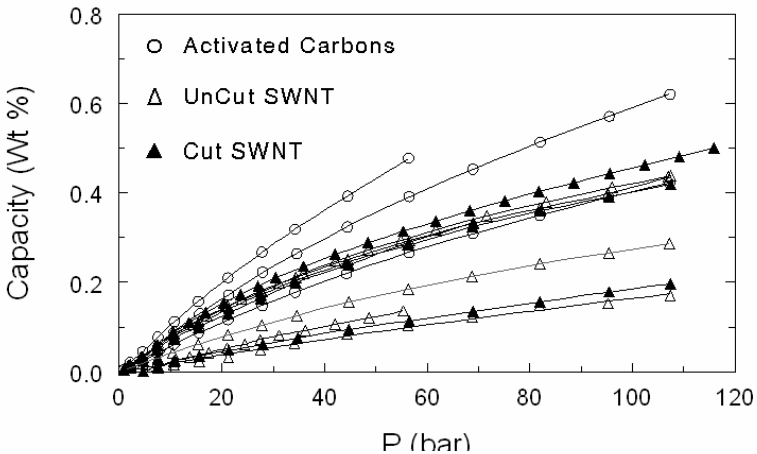
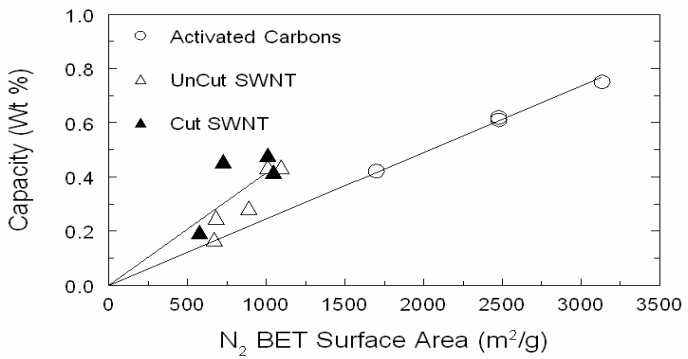
3. SWNT H_2 Isotherms at 25°C to 120 bar (no correction for He adsorption)

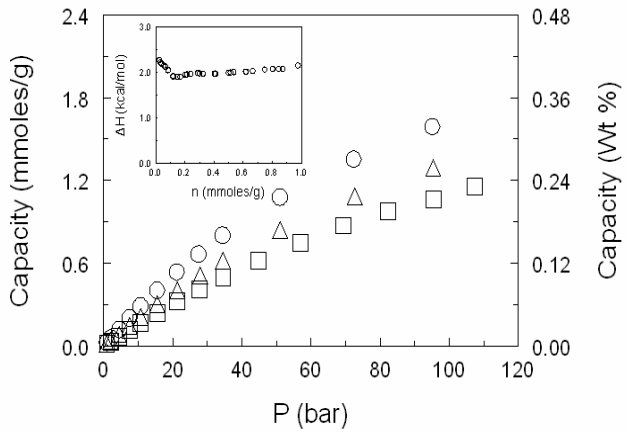




H_2 capacity at 25°C and 107 bar for SWNT and AC samples as a function of N_2 BET surface area.

* H_2 Capacities <1wt% at 25°C, 100 bar

* No <u>obvious</u> contrast between cut and uncut tubes!



H_2 Isotherms SWNT at 0°C, 25°C and 50°C. Insert: Isoteric heat of a function of coverage, ΔH = -2 kcal/mole.

Prognosis for H_2/SWNT adsorbents

Summary: H_2 Capacities <1 wt% at 100 atm

Capacities consistent with others' recent data: eg. 0.5 wt% at 100 bar [1,2] and 0.3 wt% at 90 bar [3], 0.9 wt% at 300 bar [5]; and 0.7 wt% at ~100 bar [4] for carbon nanofibers

But with ΔH -2 kcal/mole *vis-à-vis* -1 kcal/mole for carbons

Path Forward: Look to a fundamental understanding of SWNT…H_2 interactions using quantum mechanics.

Key: "Bent carbon" in SWNT

VIDEO – [NEXT SLIDE] Quantum Molecular Dynamics of SWNT, 0.47 wt% H_2

1 R. Basca *et al*, J. Phys. Chem. B, 2004, 108, 12718; 2 A. Zuttel *et al*, J. Alloys and Compds, 2002, 330-332, 676
3 M. Shiraishi, T. Takenobu, M. Ata, Chem. Phys. Lett, 367, 633 (2003); 4 E. Painer, R. Chahine *et al*, Int. J. of Hydrogen Energy, 2001, 26, 831; 5 J. Lawrence and G. Xu, Appl. Phys. Lett. 84, 918, (2004); 4 H. Cheng, G. P. Pez and A. Cooper, J. Am. Chem. Soc., 2001, 123, 5845

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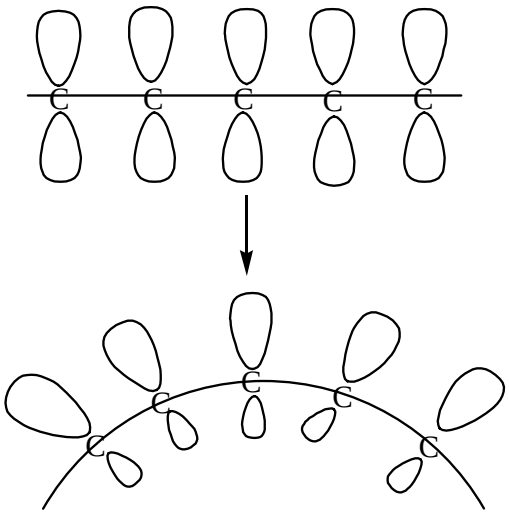
Modelling of H_2 ····SWNT Interactions

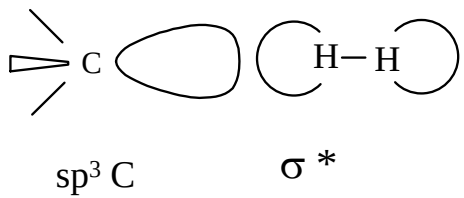
Classical molecular dynamics model of H_2 interacting with an SWNT using a curvature dependent force field [1,2]

Graphene sheet
(sp^2 carbon)
ε ($C\cdots H_2$) = 0.0517 kcal

Bent carbon
(limit: sp^3C)
ε ($C\cdots H\text{-}H$) = 0.25 kcal (end-on)
ε ($C\cdots H_2$) = 0.092 kcal (side-on)

ε is L. J. potential well depth
from t-butyl radical $\cdots H_2$
sp^3C model

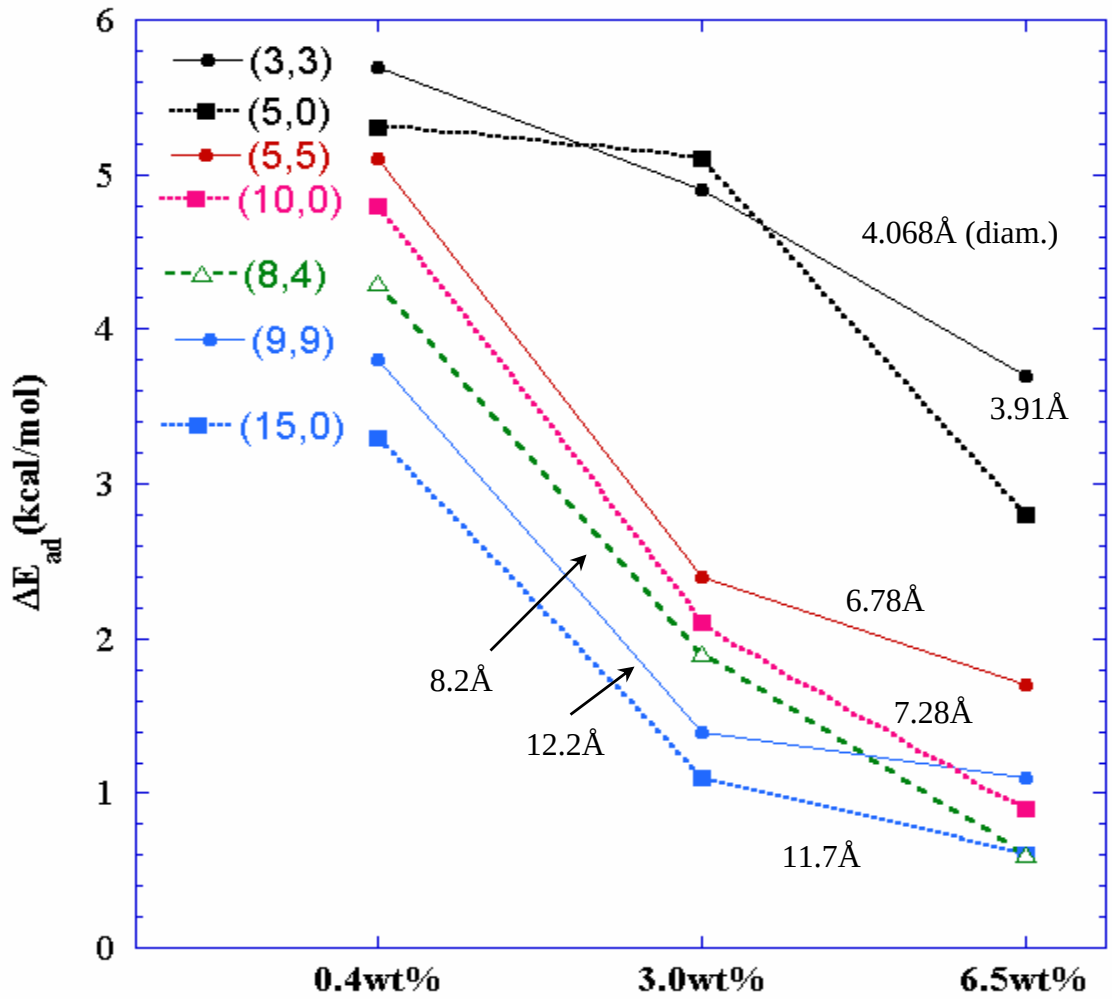




sp^3 C σ *

1 M. K. Kostov, H. Cheng, A. C. Cooper, G. P. Pez, Phys. Rev. Lett., 89, 146105, 2002
2 H. Cheng, A. C. Cooper, G. P. Pez, M. Kostov, P. Piotrowski, S. H. Stuart, J. Phys. Chem. B., 109, 3780, (2005)

Hydrogen adsorption energies for SWNT lattices as a function of tube type, and H_2 loading



VIDEO CLIP: Next Slide - For 9,9 tube, 25°C and 6.5 wt% H_2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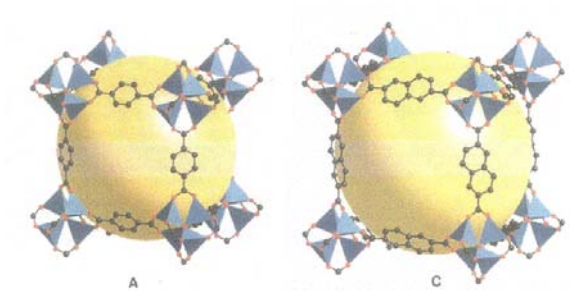
H_2 Sorption by Porous Metal-Coordination Framework Structures

IRMOF-1, IRMOF-8: Cube with $[OZn_4(CO_2)_6]$ O-centered Zn_4 tetrahedron bridged by 6 aromatic dicarboxylates O.M.Yaghi *et al* [1,2]



IRMOF-1 IRMOF-8

Ref.	Material	SA(m^2/g)	H_2(wt%), 1 atm, 77K	H_2 (wt%) at 25°C
1, 2	IRMOF-1	3362	1.32 (1.5*)	1 at 20 bar (0.15)*
1,2	IRMOF-8	1466	1.50	2 at 10 bar
3	IRMOF-1	572	~1.3	0.05 at 20 bar
4	GX-31	2500		0.2 at 20 bar
5	AX-31	3300	2.6	

*Prediction by molecular dynamics simulation (for H_2) with rigid framework. [6]
See also X. Zhao, for a hysteretic adsorption/desorption of H_2 by MOF's. [7]

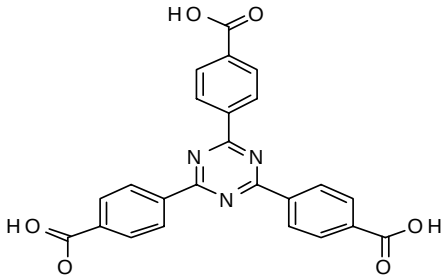
1 N. L. Rosi, O. M. Yaghi *et al*, Science, 300, 1127 (2003); 2 J. L. C. Rowsell, O. M. Yaghi *et al*, J. Am. Chem. Soc., 2004, 126, 5660 3 B. Panella and M. Hirscher, Advanced Materials, 2005, 17, 538; 4 M. Haas et al, J. Materials Res. (see slide 8); 5 G. Pez, W. Steyert, US 4580404 (1980); 6 G. Garberoglio, A. Skoulidos and K. T. Johnson, 2005, J. Phys. Chem. B. (in press); 7 X. Zhao, A. J. Fletcher, K. M. Thomas *et al*, Sciencepress, 14 Oct. 2004

H_2 Capacity and Heat of Adsorption for $Cu_3(TATB)_2$ [1] porous solid (PCN-6)

$[Cu_3(TATB)_2(H_20)_3 \bullet 3DMSO \bullet 11H_2O$

↓ Solv. exchange

$[Cu_3(TATB)_2]$ as a 3D porous coordination network (PCN-6)



4,4',4"-s-triazine-2,4,6-triyl-tribenzoic acid

H_3TATB

Scheme 1. The acid form of the TATB ligand.

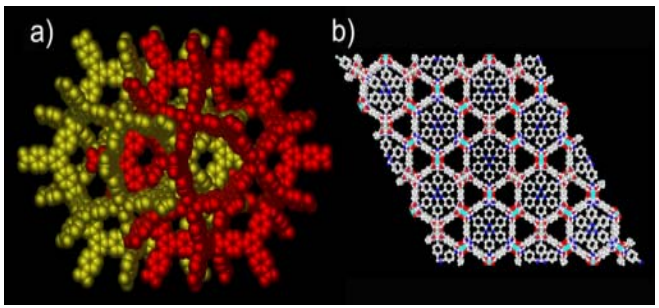
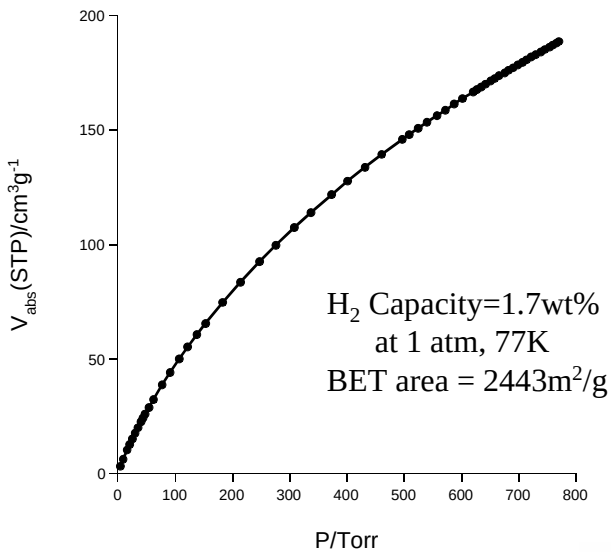


Figure 4. a) The two identical interweaving nets represented by two cuboctahedral cages. The red cage can be generated by a translation of the gold one by *ca.* 1/5 of a unit cell along [0 0 1] (the horizontal direction). b) A view of the packing of PCN-6 from [0 0 1] direction. The projection on the [0 0 1] plane has idealized *p6mm* 2D symmetry. The channels are 9.2 Å across the edge of a triangle.



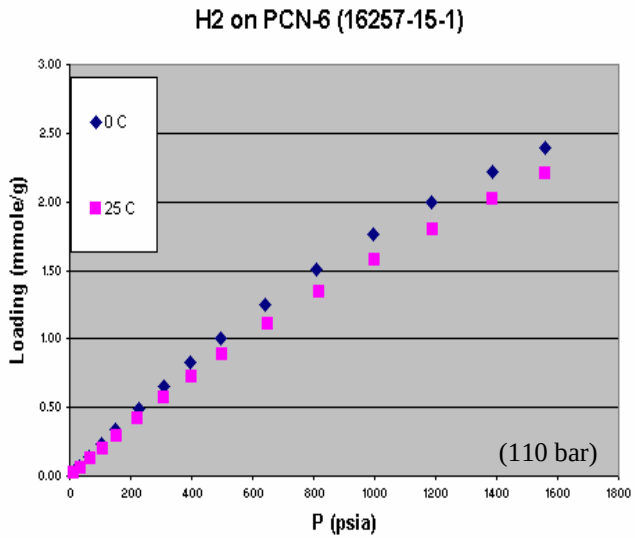
H_2 Adsorption on PCN-6 at 77K

1 Private Communication from Prof. Hongcai Zhou, Miami Univ., Oxford, OH, USA

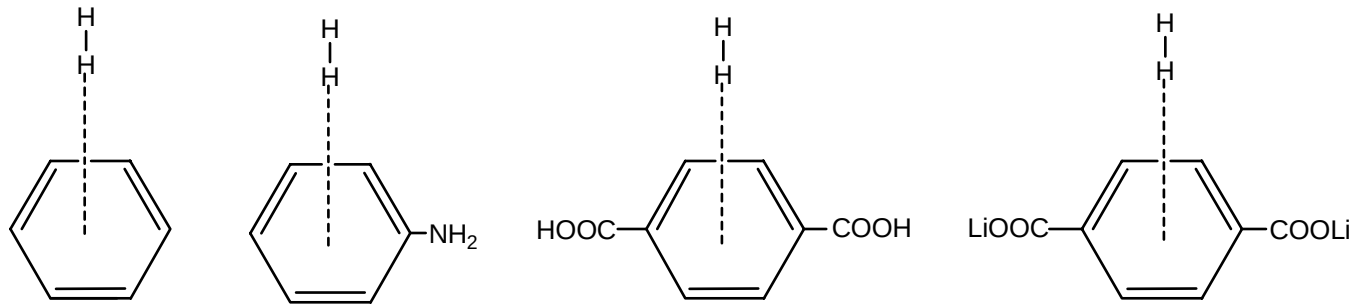
Ambient Temps H_2 Capacity and ΔHads for PCN-6 [1]

H_2 Capacity = 0.44 wt% at 100 bar, 25°C

ΔH_{ads} (isosteric heat) = -1 kcal mole
(at from 0.1 to 0.44 wt% H_2 coverage)



Aromatic rings-H_2 interaction energies. [2] (MP2/TZVPP calc)



ΔE(kcal/H_2)	0.94	1.08	0.87	1.03

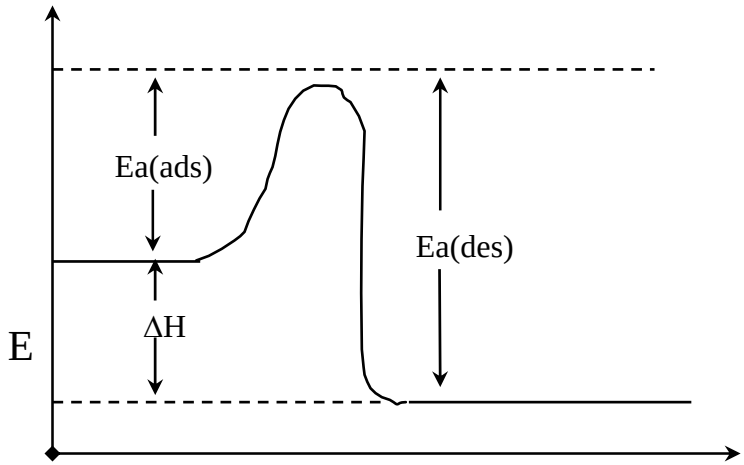
For MOF's (PCN's) need hydrogen ΔH_{ads} >> ΔH for H_2 ··· aromatic molecules!

1 Data by C. Coe, J. Zielinski (Air Products) on behalf of Prof. H. Zhou
2 O. Hubner, A Glöss, M. Fichtner and W. Klopper, J. Phys. Chem. A, 2004, 108, 3019

Carbon/Metal Hybrid Systems

For metal-free SWNT -ΔH ads ~2 kcal/mole (bulk meas.)
Yet: activation energy for desorption Ea(des), 4.7 [1], 4.8 [2] (300K)

Assumed a non-activated
Adsorption ("physisorption") where:
Ea(des) = ΔH_{ads}



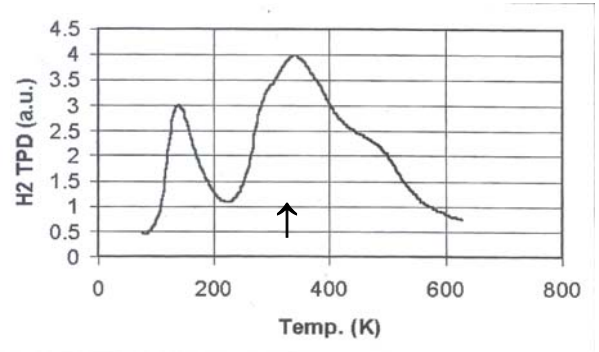
Adsorption: $H_2 + S \rightarrow S \bullet H_2$

For an "intimate" multi-wall nanotube/Fe sample: H_2 desorption peak at 350K with (Ea(des) = 13 kcal/mole). With H_2 capacity ~0.035 wt% (Dillon *et al*, NREL [3])
Here ΔH must be < Ea(des), since desorption is seen at 350K, not at higher temperatures.

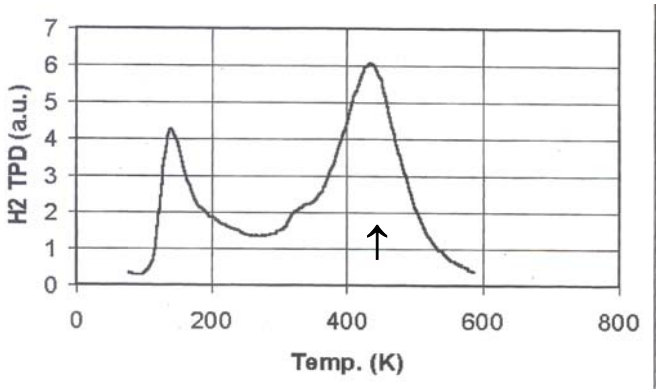
THESIS: Possibility of an enhanced H_2 storage by an *interfacial carbon/metal composition.*

1 A. C. Dillon, M. Heben *et al*, Nature, 386, 377 (1997); 2 M. Shiraishi, T. Takenobu, M. Ata, Phys. Lett, 367, 633 (2003)
3 A. C. Dillon, J. L. Blackburn *et al*, MRS Proceedings (in press)

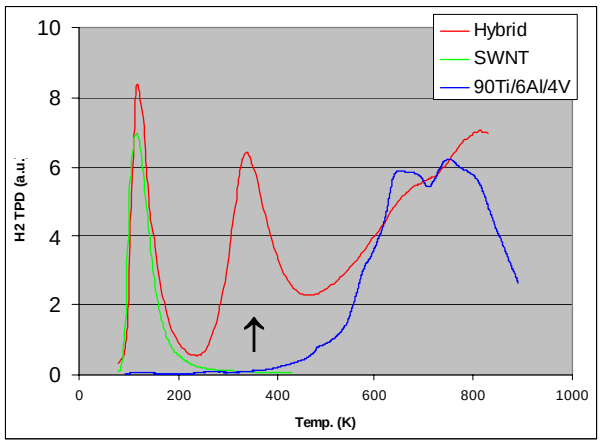
Temperature Programmed Desorption of Metal-Carbon Hybrid Materials



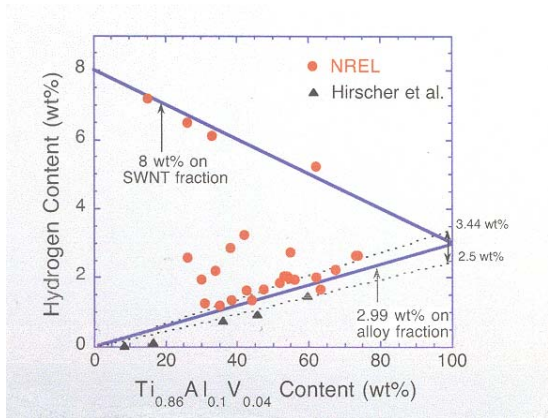
Graphite/Ni (1:1)[1]



Graphite/Pt (1:1)[1]



SWNT/TiAlV alloy metal hybrid vs. pure SWNT and TiAlV alloy[2]

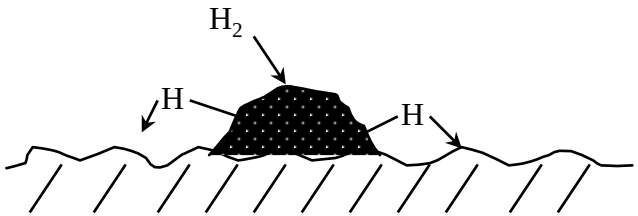


SWNT/TiAlV alloy. Total sample H_2 content following sonication[3] and data from Hirscher[4].

Active interfacial C/M composition with T(des) at 300-350K. But how to amplify this phenomenon, isolate the active interface?

1 A. C. Cooper and G. P. Pez US 6,596,055; 2 G. P. Pez, DOE Workshop, May 2003, www.eere.energy.gov/hydrogenandfuelcells/pdfs/solid_liquid_carriers_pres_air_prod.pdf; 3 M. Heben, A. Dillon *et al*, in "Hydrogen in Materials and Vacuum Systems", G. R. Nyneni Ed. American Inst. Phys. Proceedings No. 671, 77-89 (2003); 4 M. Hirscher, M. Becker, Appl. Phys. A72, 129-132 (2001)

Metal/Carbon Hybrids and Hydrogen Spillover



Hydrogen spillover eg. From Pt to carbon [1] at 350°C (Boudart [1]).

Reversible in $H_2 + WO_3 \overset{Pt}{\rightleftharpoons} H_{0.35}WO_3$

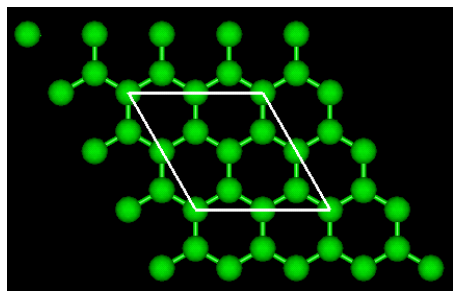
Hydrogen spillover to enhance H_2 storage (Lueking andYang [2,3])

MW nanotube/NiMgO: from 0.42 wt% to 3.6 wt% desorption
- Depending on H_2(T,P) pretreatment. Isotherm 3.6 wt% at 69 bar (K ~ 0.1 atm 1).
  "Ongoing reproducibility studies"
- Carbon nanofibers/catalyst: 3.8 wt% H_2 (max) [3]

H_2 Spillover Mechanism – THESIS: A reversible chemical hydrogenation of graphite?

VIDEO: Next Slide - Pt_4/Graphite + H_2

Hydrogenation of unit cell of graphite:
ΔE (electronic energy) = -7.25 kcal/mole H_2
Accounting for ΔH^o ~ -4 kcal/mole H_2 and
$\Delta G°$~ +5 kcal/mole H_2 (v. unfavorable!)



Hydrogenation Energy: Graphite + *n* H_2

n	1	2	3	4
ΔE* (kcal/mole H_2)	24.58	4.21	0.28	-7.25

1 A. T. Robell, M. Boudart *et al*, J. Phys. Chem. 68, 2748 (1964); 2 A. Lueking, R. T. Yang, AlChE Journal 2003, 49, 1557
3 A. Lueking, R. T. Yang, N. M. Rodriguez and R. T. Baker, Langmuir, 2004, 20, 714

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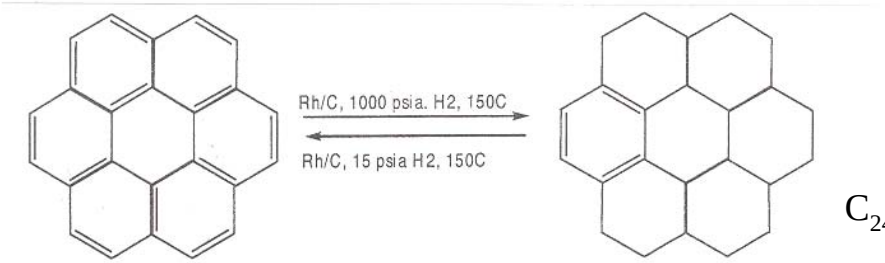
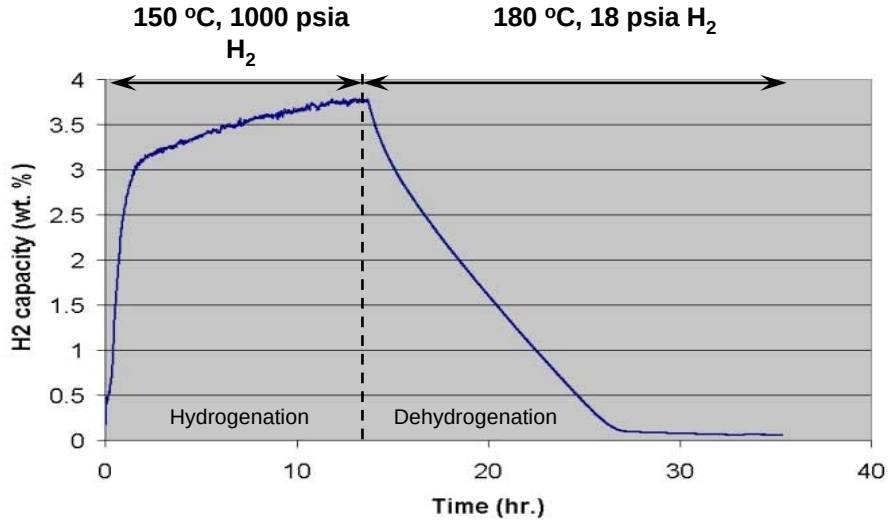
Reversible Catalytic Hydrogenation of Coronene – a "Microcosm" of Graphite, In the Solid State



$C_{24}H_{12}$ $C_{24}H_{30}$

Mixture of 2:1 Coronene: (5% Rh/C) +18H (75%), +14H (23%)

ΔH^o = -11.5 kcal/mole H_2
$\Delta G(150°C)$ = 0.85 kcal/mole H_2



3.6 wt% capacity
(including catalyst)
5.1 wt% theoretical

A reversible – and thermodynamically favorable "spillover" of H_2 from Rh ↔ C ↔ coronene
Reactions are slow – we went to aromatic liquids for better H-transfer. Genesis of our "H_2 Storage with Liquid Carriers" work; A. Cooper's talk tomorrow.

AIR PRODUCTS

VARCARE LA SOGLIA DELLA SPERANZA

Giovanni Paolo II (1994)

VARCARE LA SOGLIA DELLA SPERANZA

Giovanni Paolo II (1994)

Crossing the threshold of hope.
John Paul II 1994

Prospectives for H_2 Storage with Carbons – *Quo Vadis*?

- Have clear goals – DOE's 2010, 6+wt% system target, model with $-\Delta H_{ads}$ ~6 kcal/mole H_2
- Can do reliable measurements for determining H_2 isotherms, ΔH_{ads} etc.
- Need to tailor SWNT materials in diameter, electronic properties etc.
- Need to prepare MOF's with more strongly H_2-interactive functions
- Devise carbon-metal hybrid materials that maximize the active C/M interface.

- With computational modelling – as a leading indicator

Capabilities, research avenues of DOE's Carbon Center[1] and those of many international investigators in this field.

- Need: Surprises – what we never dreamed of!

1 "DOE Carbon-based Materials Center of Excellence – Overview" by M. J. Heben *et al* and collection of poster papers at 2005 DOE H_2 Program Review. www.eere.energy.gov/hydrogenadnfuelcells/annual_review05_storage.html

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Air Products and Chemicals and now DOE's support for the Carbon Center