Development of Doped Nanoporous Carbons for Hydrogen Storage

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Pittsburgh, PA
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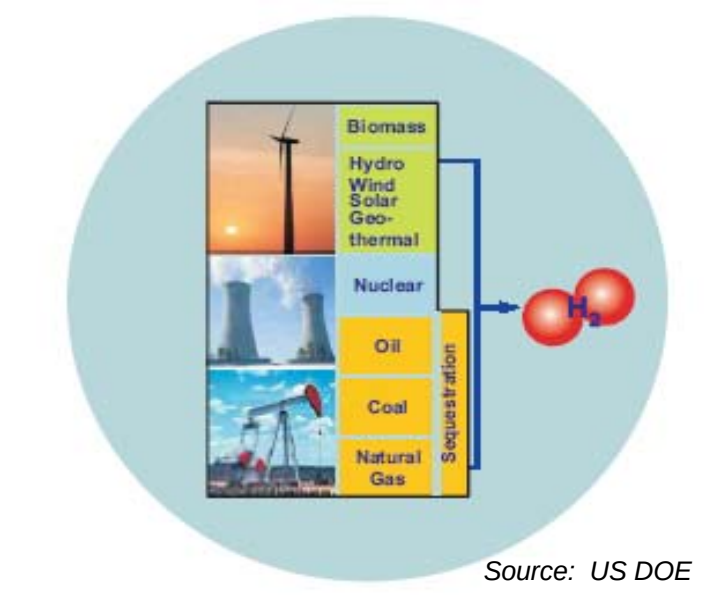
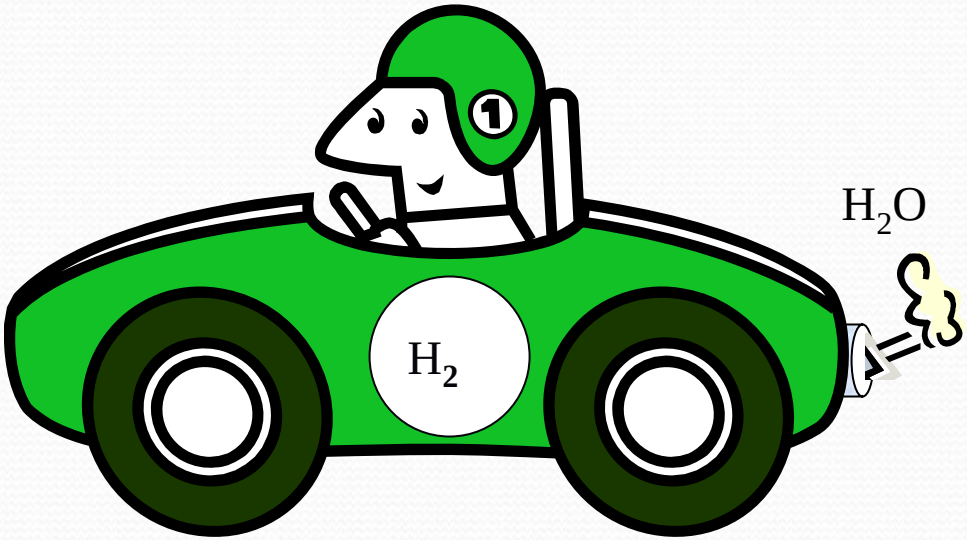
PENNSTATE
1855

Hydrogen,

A brief introduction.

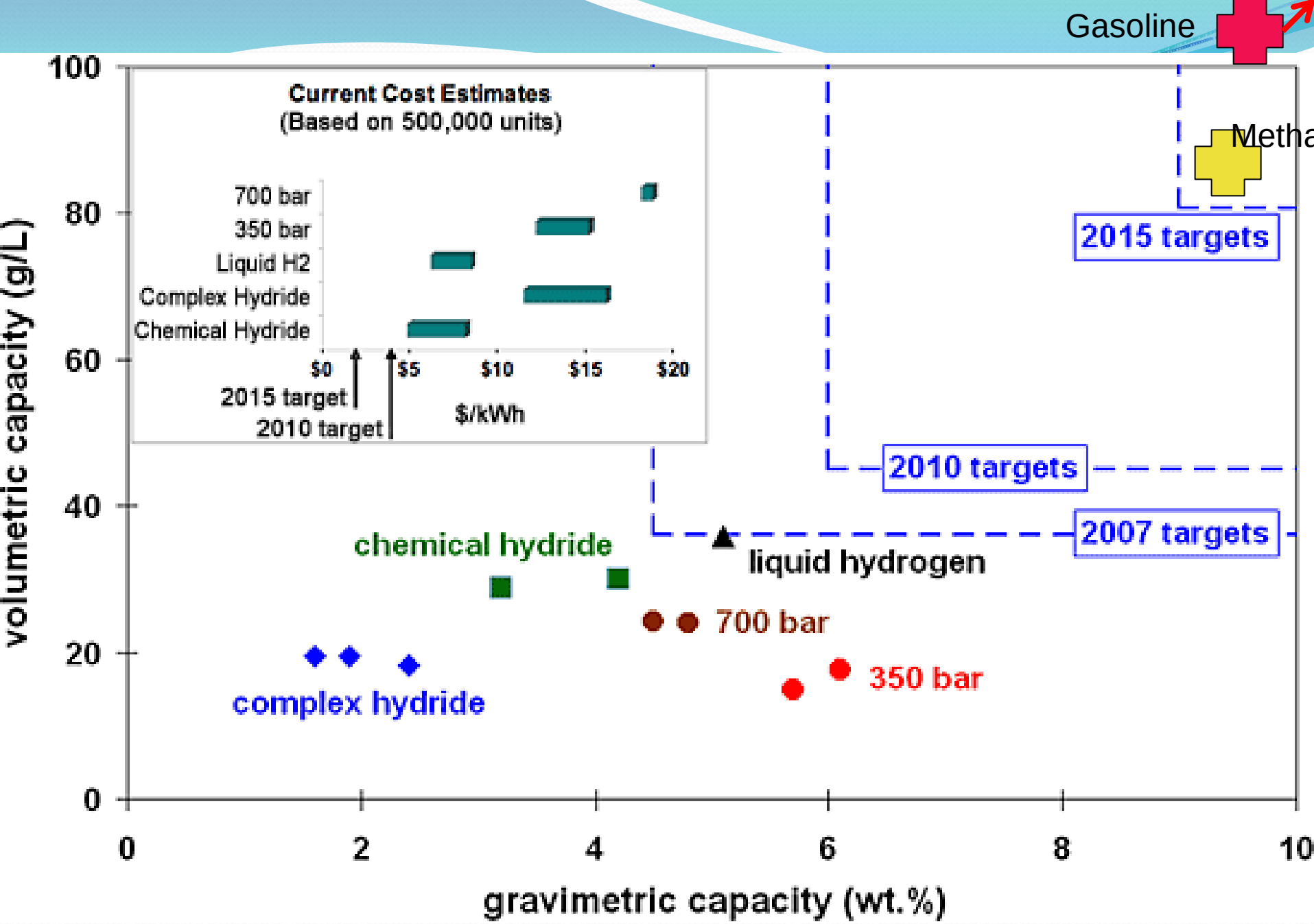


Source: US DOE



Hydrogen easily combines with other elements, and is found naturally as a part of other compounds such as coal, oil, natural gas, plant material, and water.

The 9 million tons of hydrogen currently used per year in the U.S. is enough energy for 20-30 million H_2 cars or 5-8 million homes.
This hydrogen is produced through reforming or gasification.



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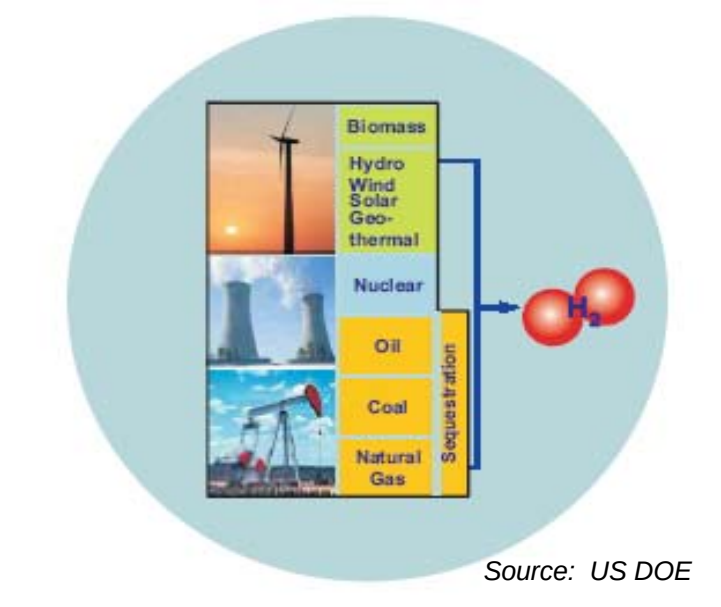

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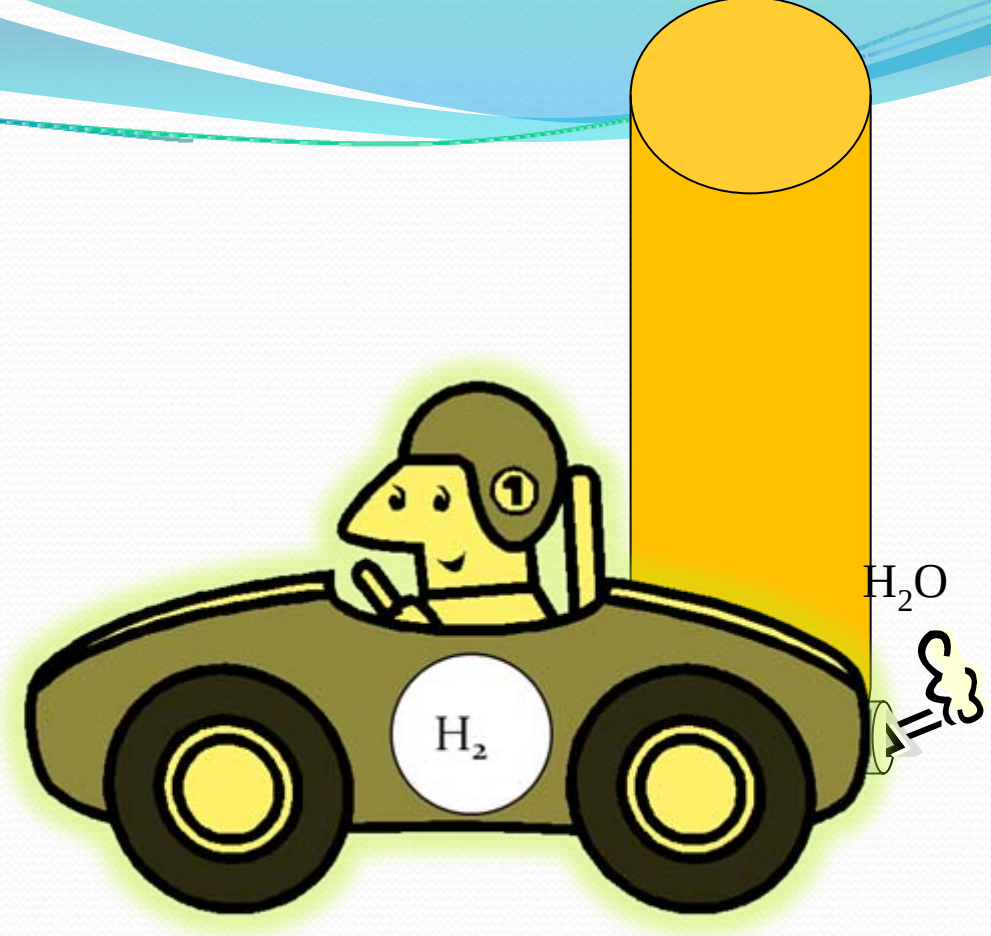

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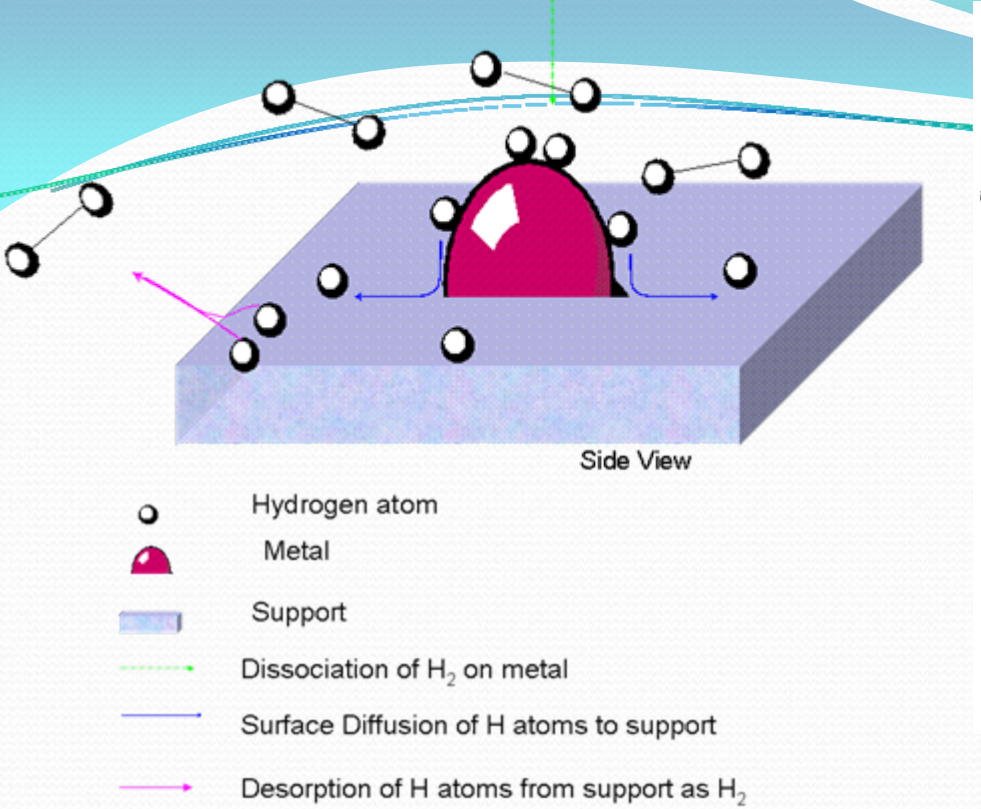
Our Strategies

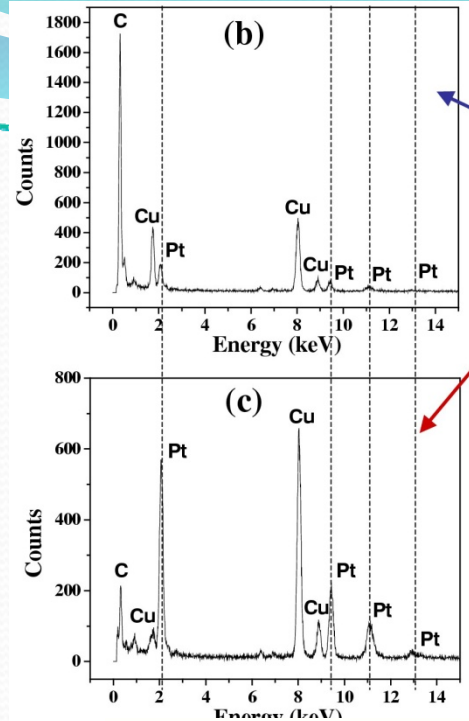
to Maximize H_2 Storage at Moderate T and P

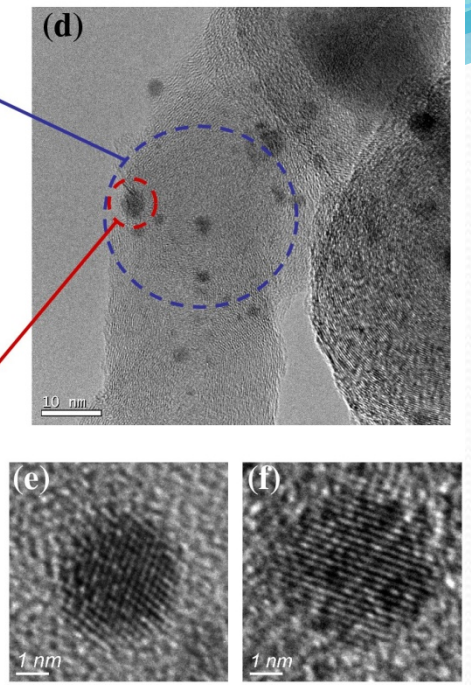
- Utilize Hydrogen Spillover Mechanism for Moderate Temperature Adsorption

- Utilize Advanced Characterization to understand/maximize active Sites

Prof. John Badding, Co-PI







Hydrogen Storage via Spillover in Metal-assisted Carbon:

(Lueking's work at Michigan)

Lueking & Yang, Appl.Catal. A, 265, 259, 2004.

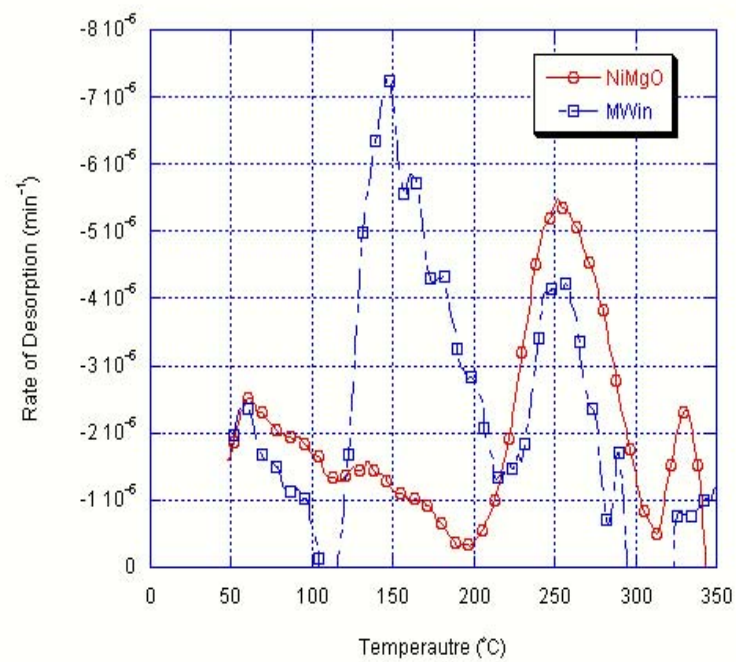
*Lueking & Yang, AIChE J, **49,** 1556, 2003*

*Lueking & Yang, J. Catal. **206**, 165, 2002*

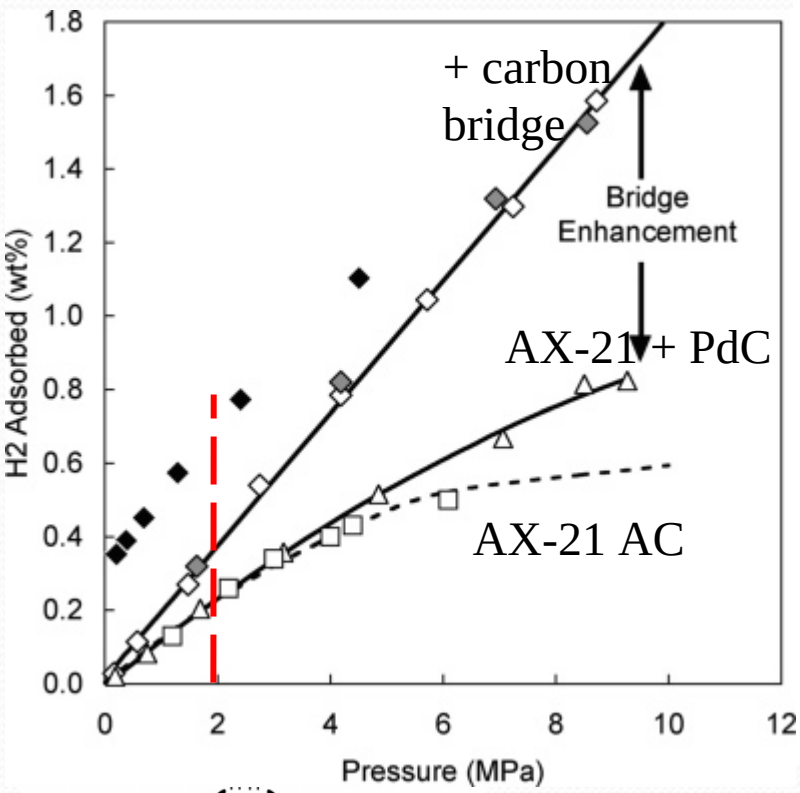
(Lueking's work at Penn State)

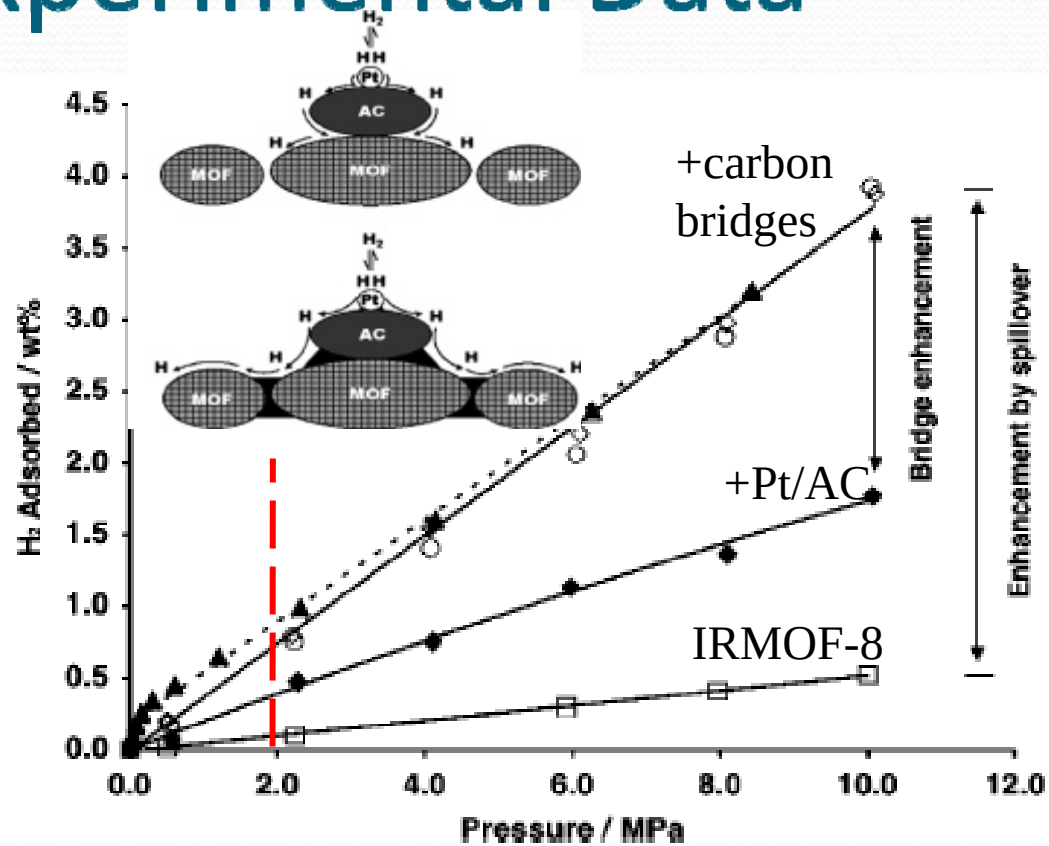
Jain & Lueking, J. Phys. Chem. C. 111, 1788, 2007.

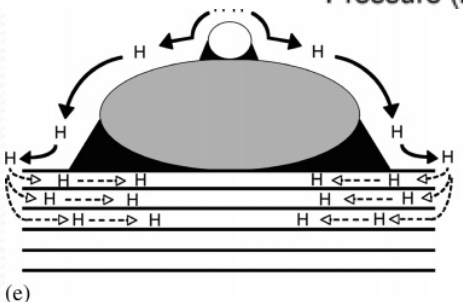
Li, Badding, & Lueking, In Progress



“Benchmark” Experimental Data



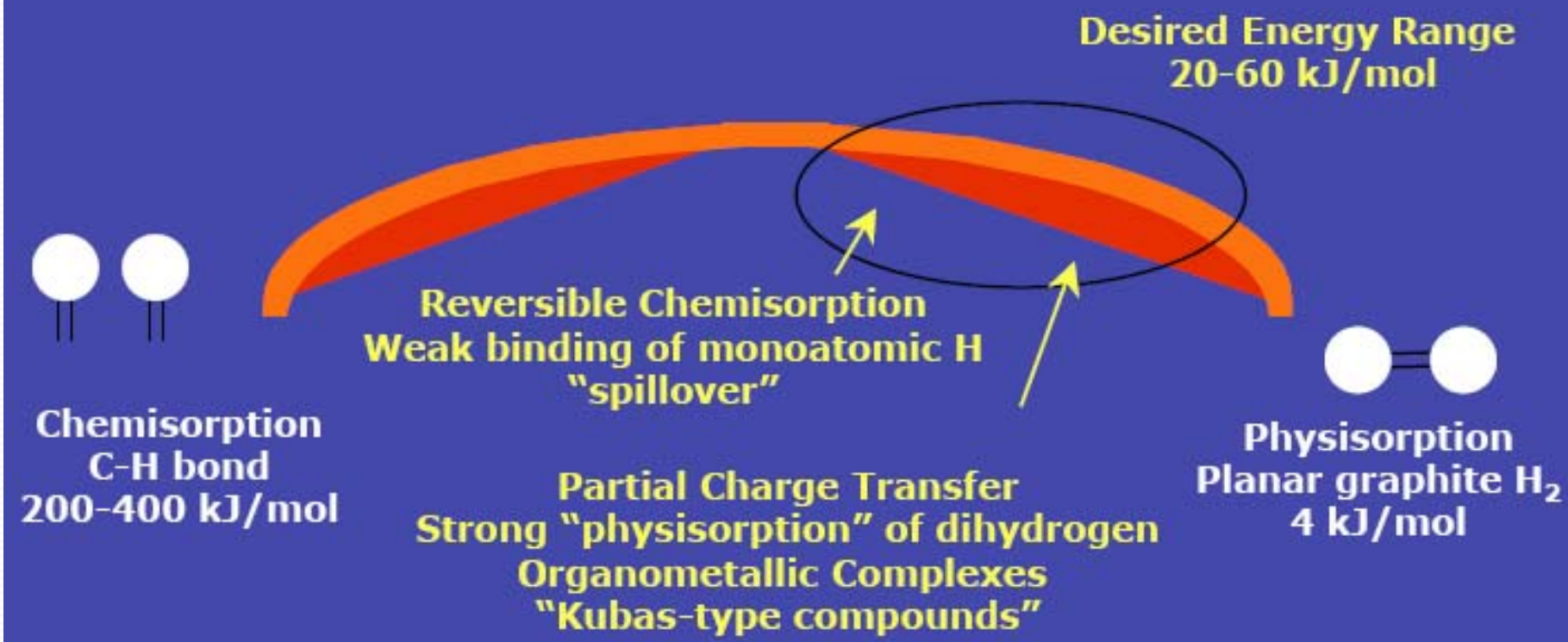




Lachawiec et al., Langmuir, 2005
Li & Yang, JACS, 2006
Yang et al., J. Phys. Chem. B, 2006

Continuum of Hydrogen Binding Energies

Affects of bond strain & electronic properties



Source: NREL

Accomplishments (Years 1-2)

Discussed at last year's meeting

- New Materials
  - Exfoliated graphite nanofibers
    - *Goal: Tune porosity*
  - Metal-intercalated graphite nanofibers
    - *Goal: Maximize Metal Dispersion, Carbon-Metal contact*

- New Methods
  - New Adsorption equipment finalized, validated
  - High-pressure, in situ Raman (and other)
    - *Goal: Probe sites that interact with hydrogen at Pressures of Interest*

- "Standard" Materials *Metal-doped Nanocarbons*
  - 1% Pt/GNF
  - 1% Pt/SWNT
  - *Compared to: 5% Pt/Act. Carbon (STREM chemicals)*

Exfoliated graphite nanofibers

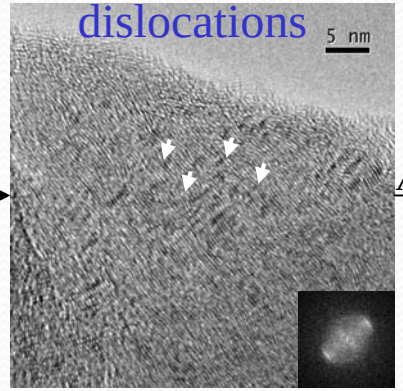
Goal: Tune porosity

0.35 nm; dislocations

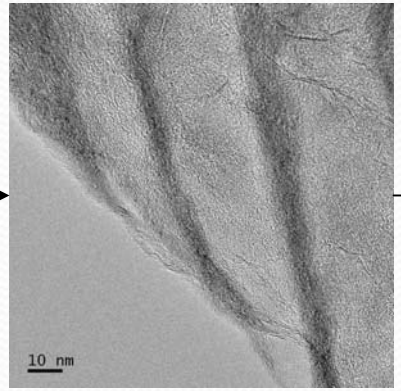
5-50 nm

<0.4 nm

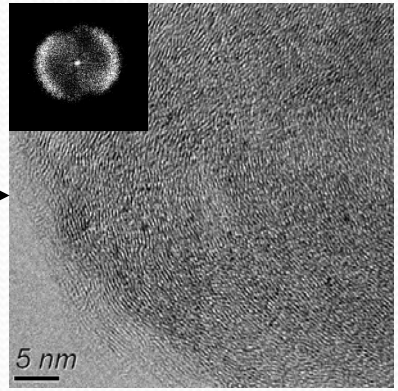
Intercalation
Thermal Shock



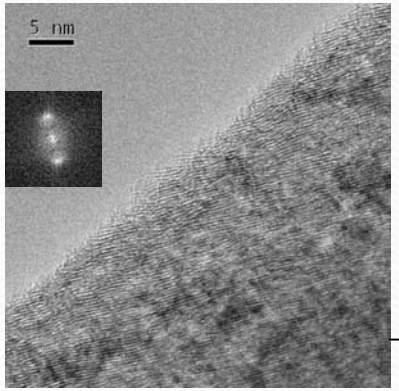
Anneal



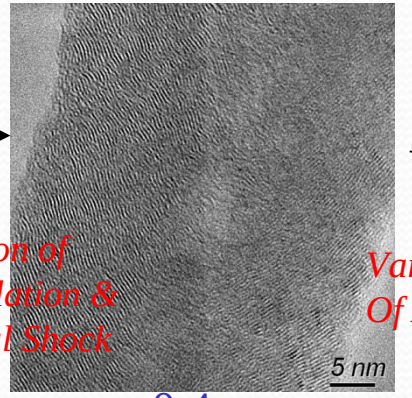
CO2



Start: 0.34 nm

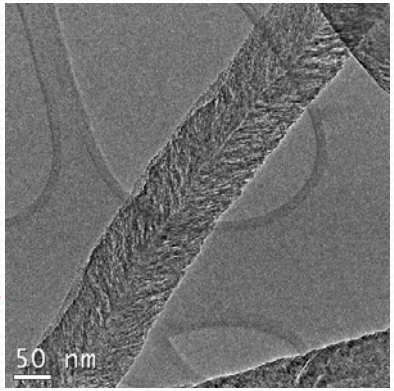


Variation of Intercalation & Thermal Shock



~0.4 nm

Variation Of Anneal

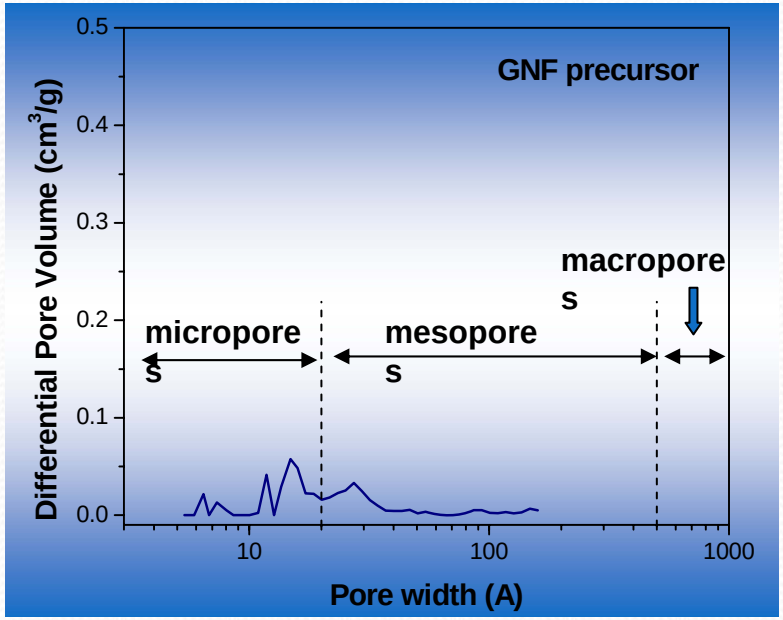


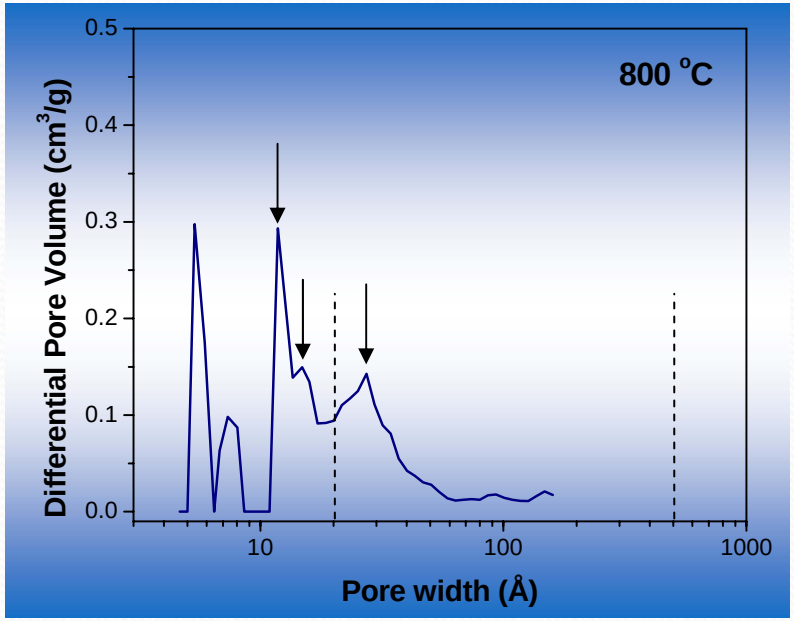
Large pores start to form

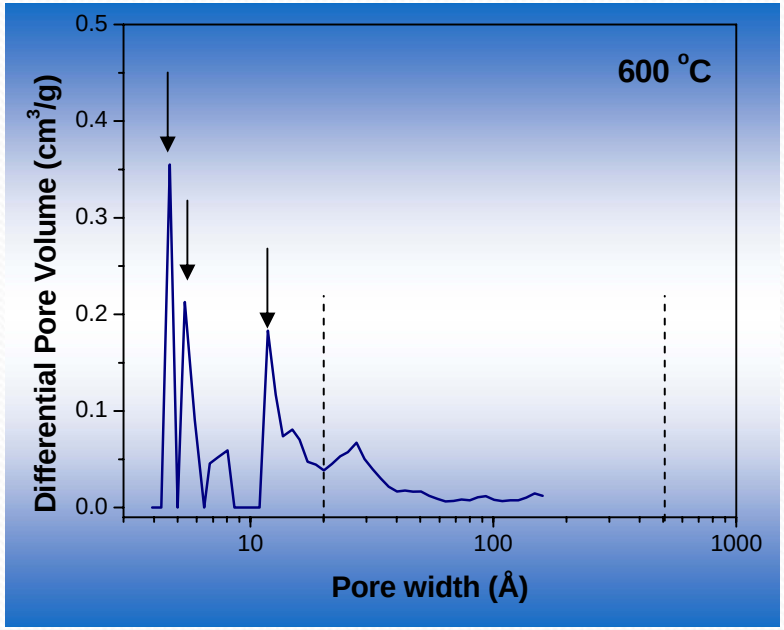
J. Phys. Chem. B, 2005, 109, 12710.

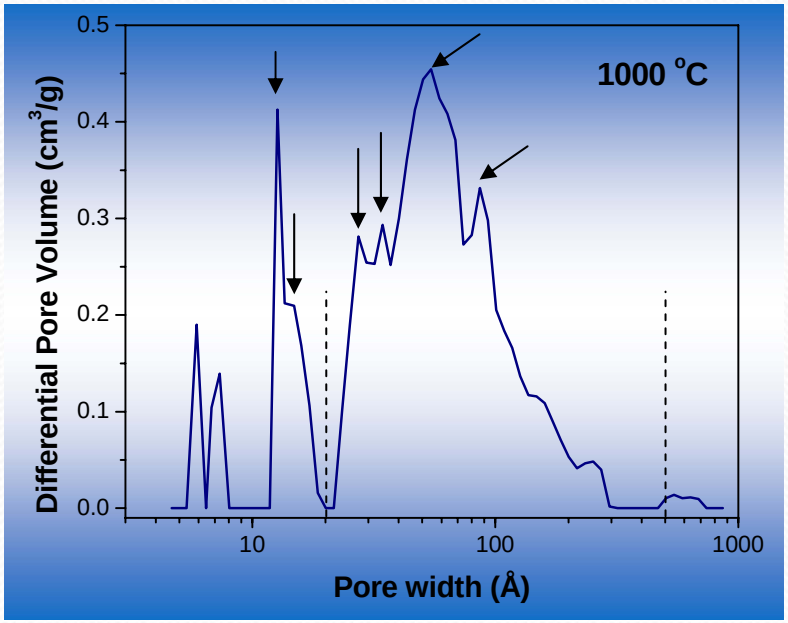
Pore size distribution

Measured by Nitrogen physisorption using DFT









Metal-intercalated graphite nanofibers

Goal: Maximize Metal Dispersion, Carbon-Metal contact

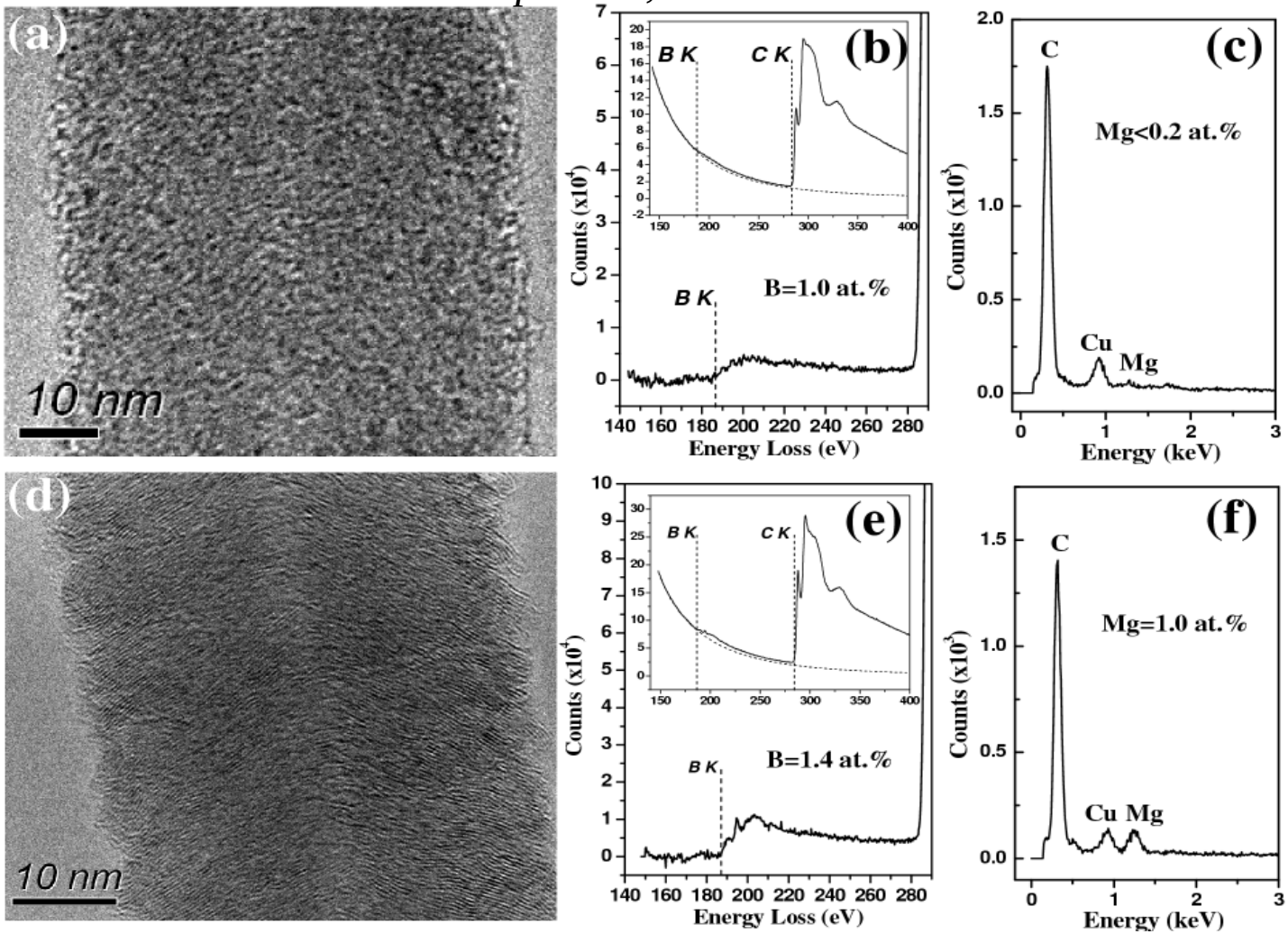


Figure 3: HRTEM (a, d), EELS (b, e) and EDS (c, f) of MgB_2 intercalated GNF. EELS shows a 1 at% of intercalated B while EDS shows a 0.2-1.0 at% intercalated Mg.

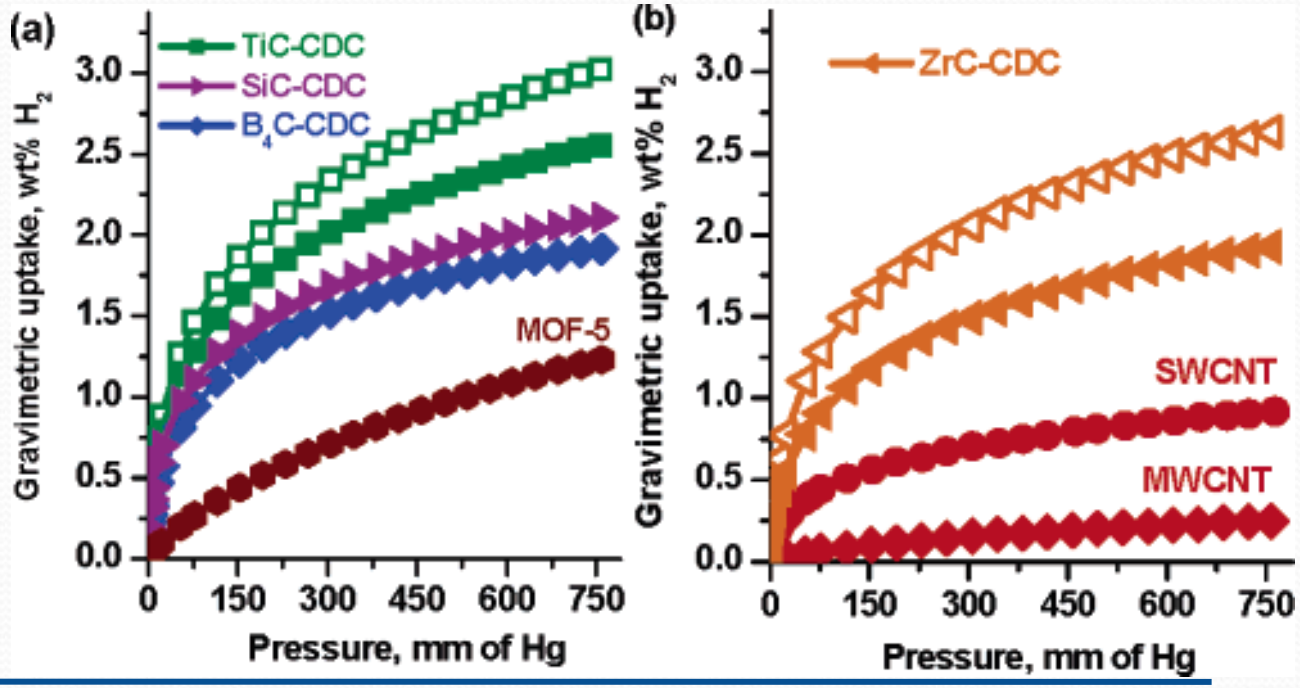
Fonseca, Gutierrez, Lueking, In Preparation, 2007.

This year, a shift in focus…

Carbide-derived carbons (CDC) are produced by high-temperature chlorination of carbides. Metals and metalloids are removed as chlorides, leaving behind a collapsed noncrystalline carbon with up to 80% open pore volume. The detailed nature of the porosity-average size and size distribution, shape, and total specific surface area (SSA)- can be tuned with high sensitivity by selection of precursor carbide (composition, lattice type) and chlorination temperature.

(1) Narrow pore size distribution tunable with better than 0.05 nm sensitivity in the range ~0.5 to ~ 1.5 nm.

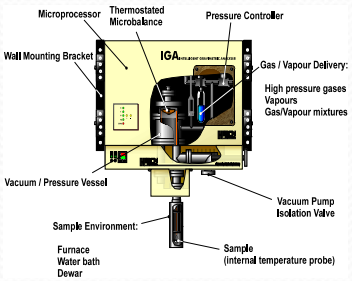
(2) SSA up to 2000 m^2/g.

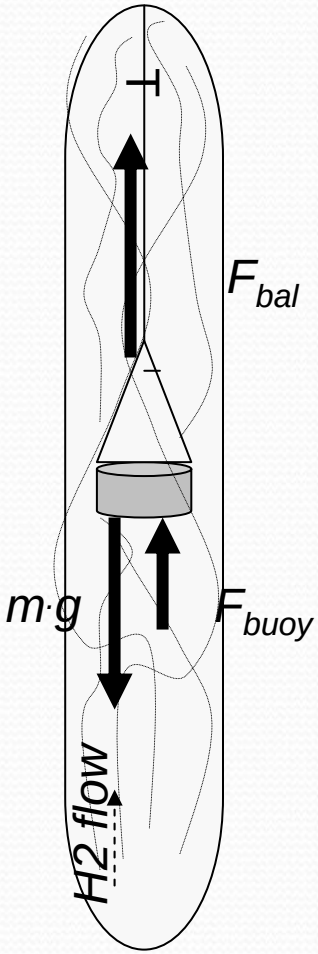


Gogotsi, Y.; Dash, R. K.; Yushin, G.; Yildirim, T.; Laudisio, G.; Fischer, J. E *Journal of the American Chemical Society* **2005,** 127, (46), 16006-16007.

II. H_2 Adsorption Methods

- 1. Gravimetric
  - Hiden Isochema IGA-003
  - Pressures up to 20 bar
  - Temperatures up to 500 C





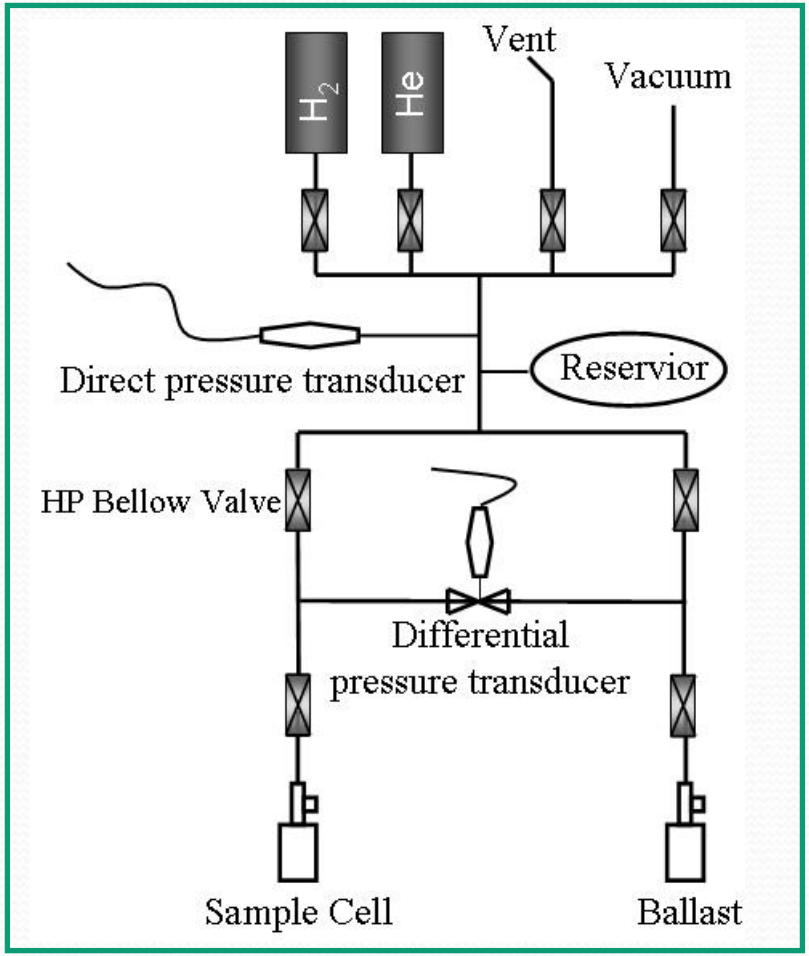
Operating Principle

- Direct measurement of sample mass as adsorption gas contacts the sample
- Precise temperature control
- *In situ* treatments

Potential artifacts

- Buoyancy
- Water contamination
- Contamination of sample

Technique: *Differential* Volumetric Method



Schematic of a differential pressure apparatus

$$dN_{ads} = N_1^o - \frac{\gamma_1 N_2^o}{\gamma_2} + \gamma_1 dP$$

Measure the pressure changes in a fixed volume

Advantages:

High pressure

Differential P increases accuracy by extending pressure range

Simultaneous Blank Experiment

Automatic Control

Assumptions:

Ballast side doesn't adsorb

Pitfalls:

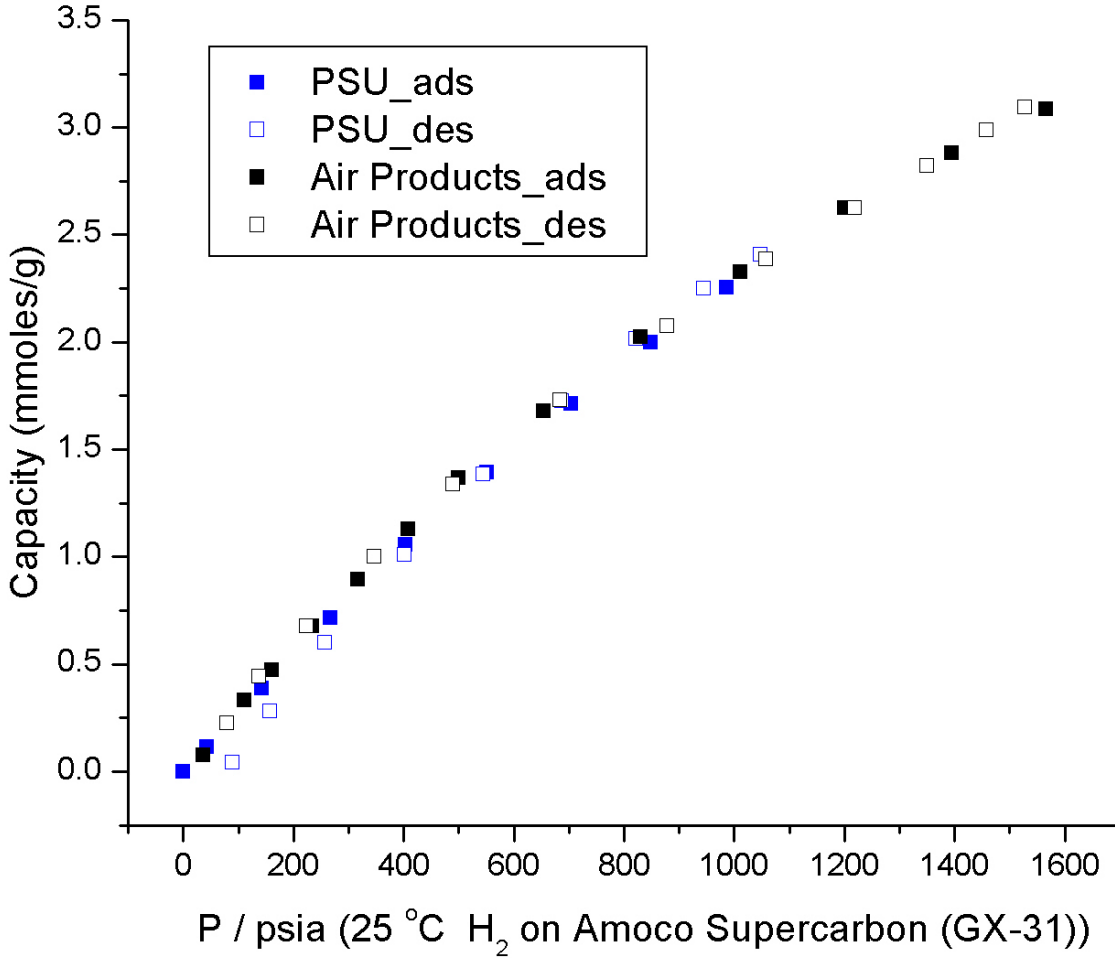
Gas leak

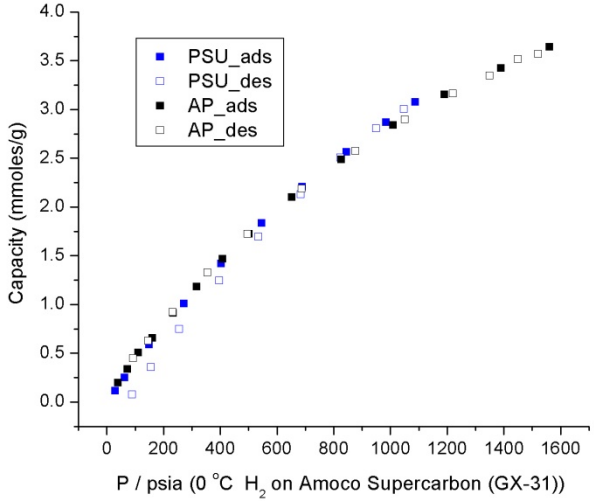
Temperature variation

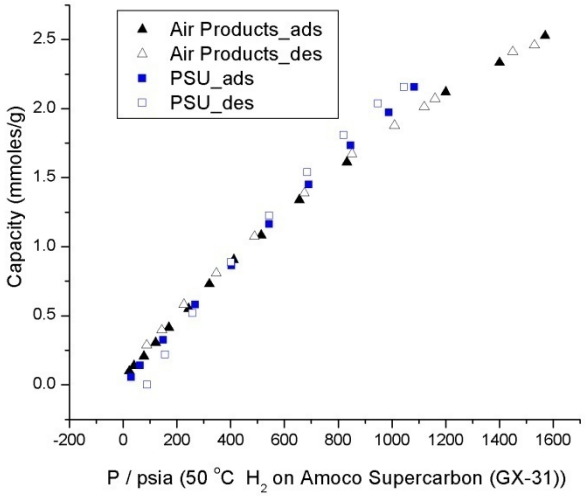
Temperature-dependent compressibility of hydrogen

Contamination of gas

Quality Check



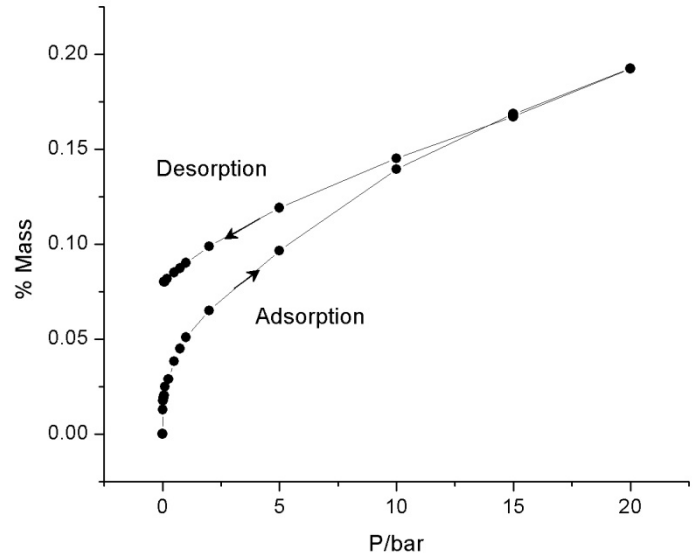


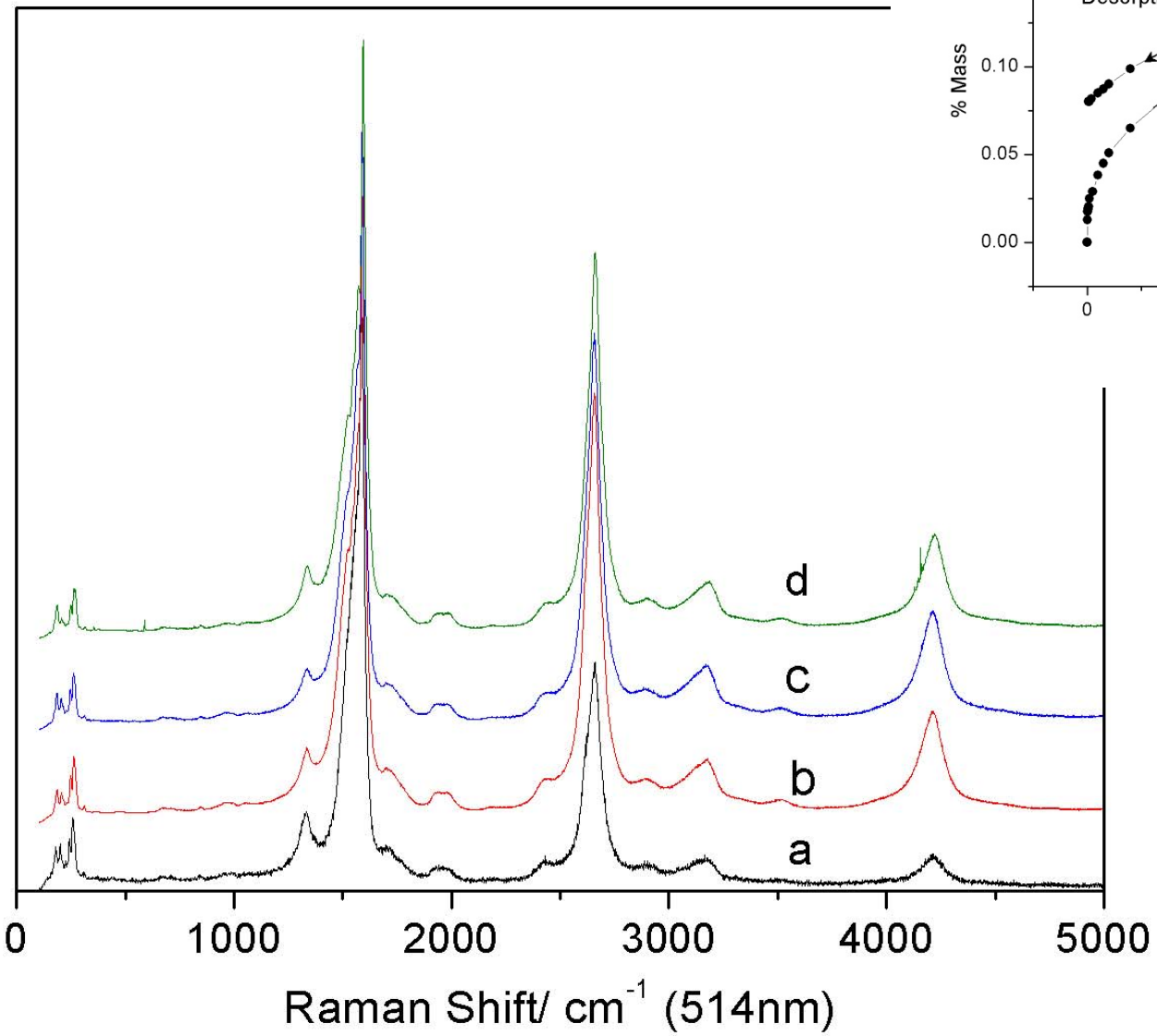


Our Strategies

to Maximize H_2 Storage at Moderate T and P

- Utilize Hydrogen Spillover Mechanism for Moderate Temperature Adsorption
- Utilize Advanced Characterization to understand/maximize active Sites





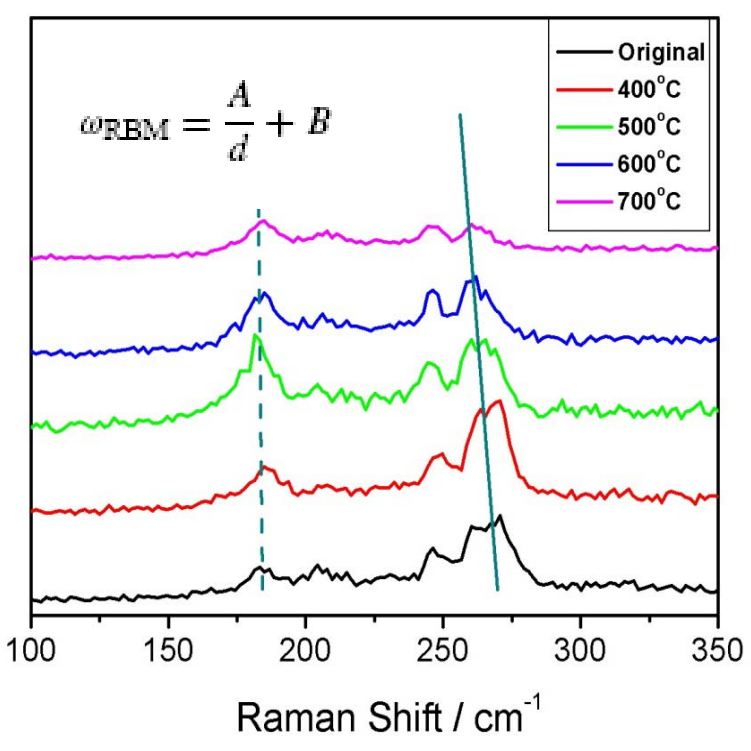
Pt/SWNT , 100 bar H_2

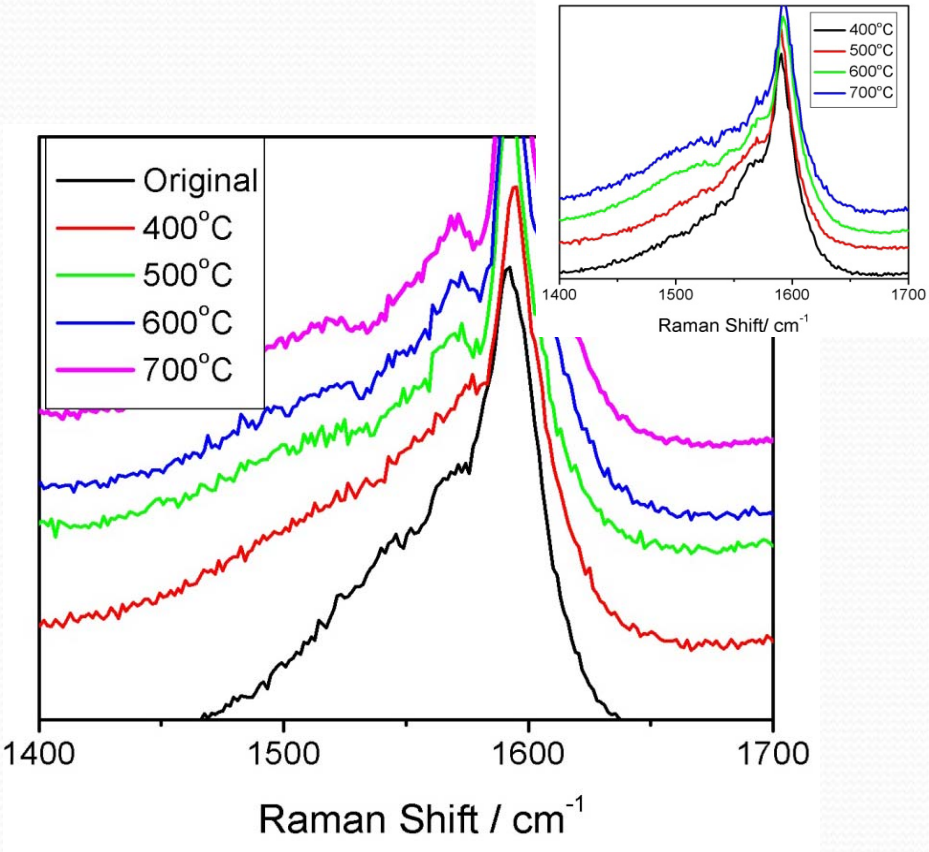
Pt/SWNT , heated in H_2

Pt/SWNT , heated in He

SWNT (HiPCO) + 1%Pt

In situ Raman Results

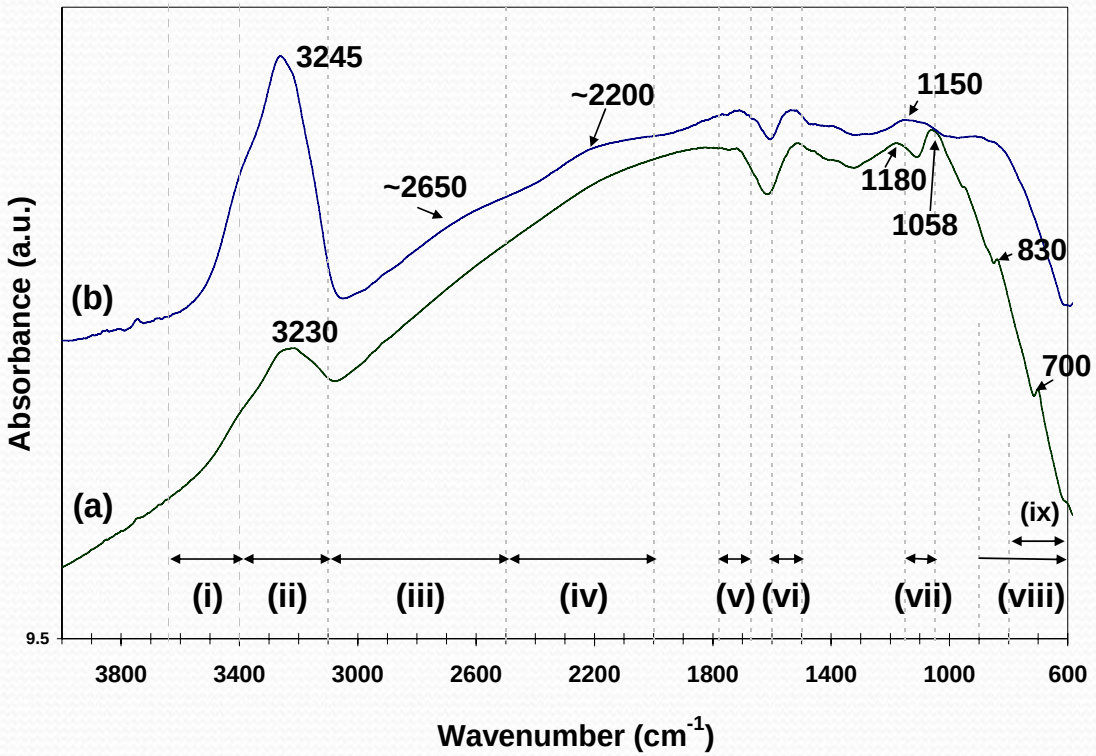




- Radial breathing mode (RBM) of SWCNTs heated at different temperatures in high pressure H_2 atmosphere (E_{laser}=2.41 eV).

- G mode of SWCNTs heated at different temperatures in high pressure H_2 atmosphere (E_{laser}=2.41 eV).
- At right, heated in He atmosphere

FTIR Characterization of surface sites



FTIR spectra for (a) CDC-600 and (b) CDC-1000.
Regions of interest include (i) alcohol O-H stretching; (ii) adsorbed water (O-H stretching); (iii) carboxylic acids O-H stretching; (iv) triple-bond stretching; (v) carbonyl C=O stretching; (vi) aromatic stretching; (vii) alcohol C-O stretching; (viii) C-H out of plane bending; (ix) C-Cl stretch.

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- Utilize Advanced Characterization to understand/maximize active Sites
  - *Changes are extremely subtle and not likely to be the DRIVER to maximize adsorption.*

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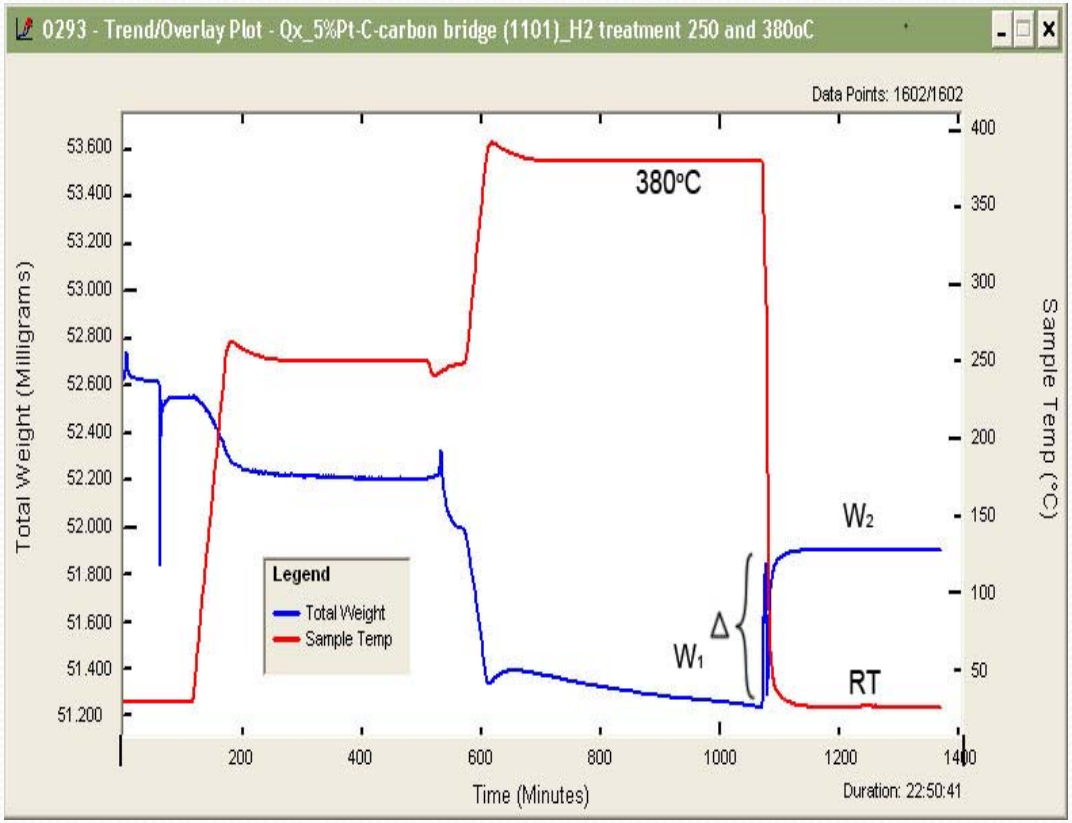
Our Strategies

to Maximize H_2 Storage at Moderate T and P

- Utilize Hydrogen Spillover Mechanism for Moderate Temperature Adsorption
- Utilize Advanced Characterization to understand/maximize active Sites
- Think in terms of Total Pressure Savings, particularly Shape of Adsorption Isotherm

Observation during pretreatment



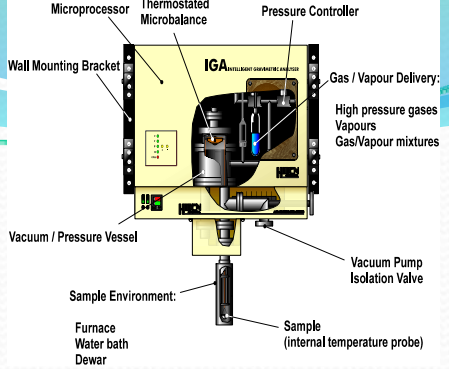
Δ_{qtz}=0.5mg
$\Delta_{Pt\text{-}C}$=0.6–1.0 mg

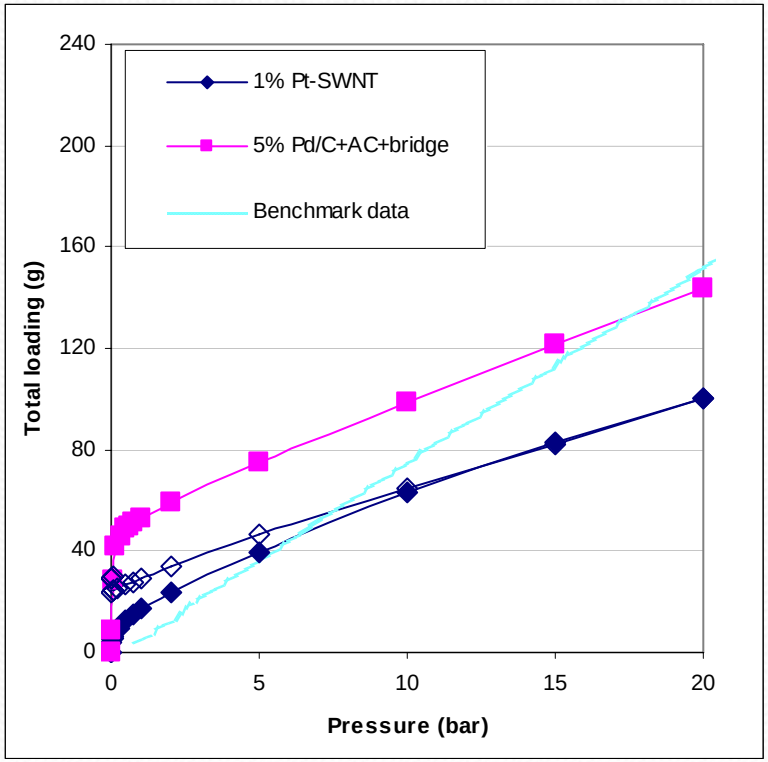
$$W_1 - W_2 = -m_s^o\left(\frac{\rho_{g,1}}{\rho_s} - \frac{\rho_{g,2}}{\rho_s}\right) + m_{ads} - k_p^o\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

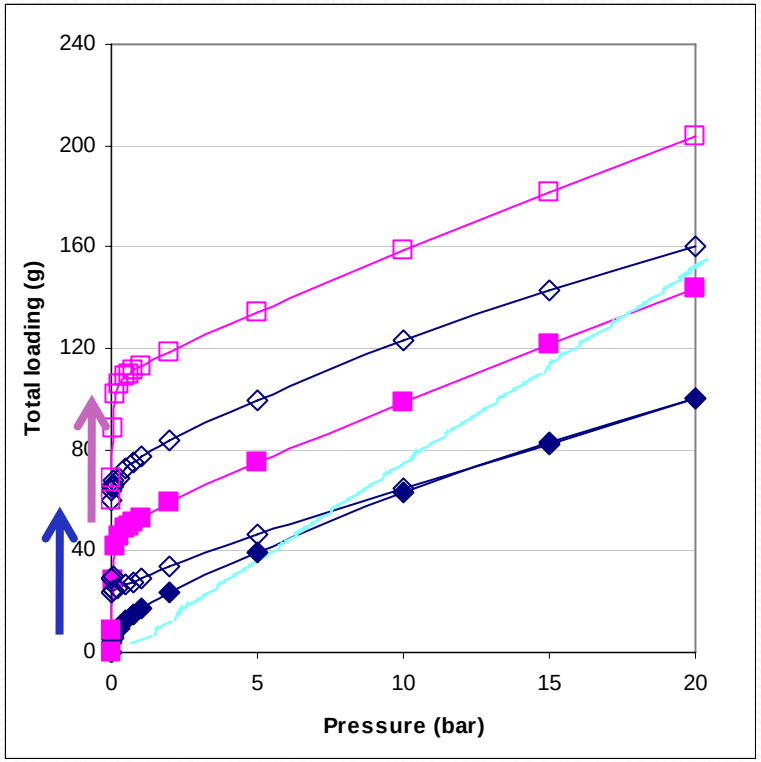
~ 0

Sample	W_2 (380oC)/mg	W_1 (25oC)/mg	m_s^o (mg)	m_{ads} (mg)	H2 adsorbed / wt%	Metal content (g/g)	H:M ratio (mol/mol)
Quartz	68.9091	69.4706	69.4706	0.00	0.00%	0	0.00
Activated Carbon	48.9427	49.4867	49.5042	-0.02	-0.04%	0	NA
5%Pt-C+AC+carbon bridge (1:8:1)	51.2357	51.9022	51.7972	0.10	0.20%	0.50%	79.10
5%Pd-C+AC+carbon bridge (1:8:1)	54.2781	54.899	54.8396	0.06	0.11%	0.50%	23.05
5%Pd-C	49.7549	50.7636	50.3164	0.45	0.88%	5%	18.91

Significance I







"Standard" analysis

Considering Low P data

T (K)	294
Ve (L)	42.2
Ms (g)	29936.94
rhos (g/cc)	2
packing	0.71

Status: Waiting on Mass Spectrometry Confirmation

Significance II: Pressure Savings[1]

- DOE system targets include tank weight, etc.

- Most H2 reports are based on *excess adsorption*
  - (Solid-bound H2, in excess of He pore penetration).

- Not only not accounting for total tank weight…
- But not accounting for total H2 weight!
  - For nanoporous adsorbents, H2 in pores can be significant.

[1]Zielinski, J. M.; McKeon, P.; Kimak, M. F., *Ind. & Eng. Chem. Res.* **2007,** *46*, 329-335.

Pressure Savings[1]

- To be advantageous, solid-state adsorbent must
  - Sorb more H2 than its own weight, and
  - Sorb more H2 than the gas it displaces

$$n_{H_2} = \frac{PV_E}{zRT} + M_s P\left[K(T,P) - \frac{1}{\rho_s zRT}\right]$$

[1]Zielinski, J. M.; McKeon, P.; Kimak, M. F., *Ind. & Eng. Chem. Res.* **2007,** *46,* 329-335.

Pressure Savings[1]

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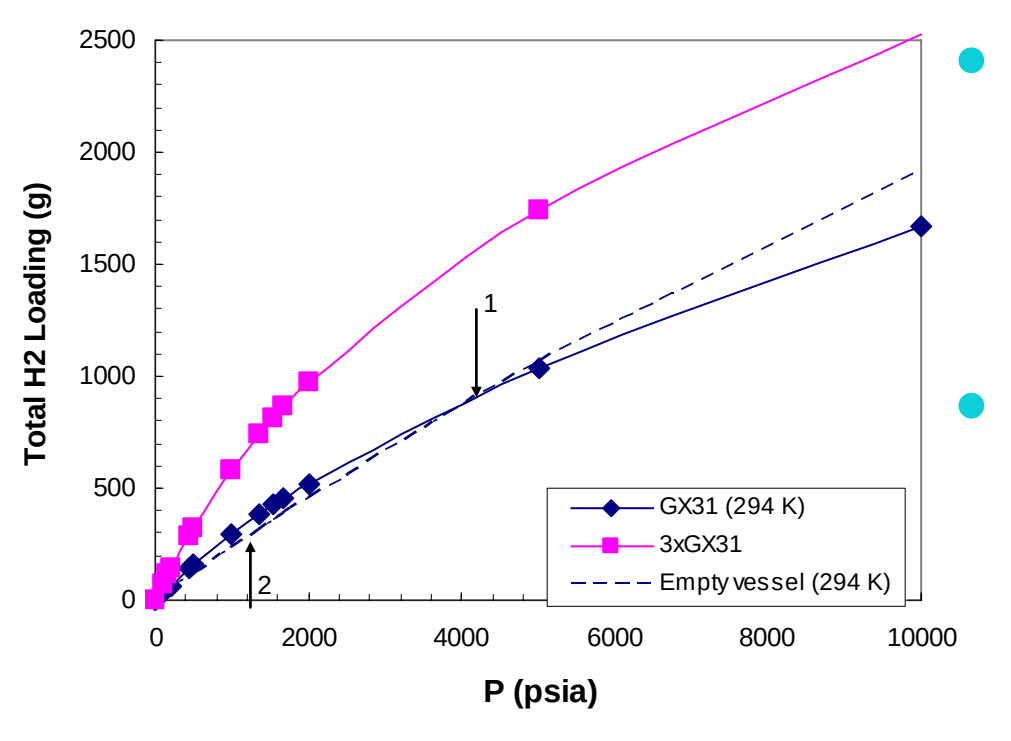
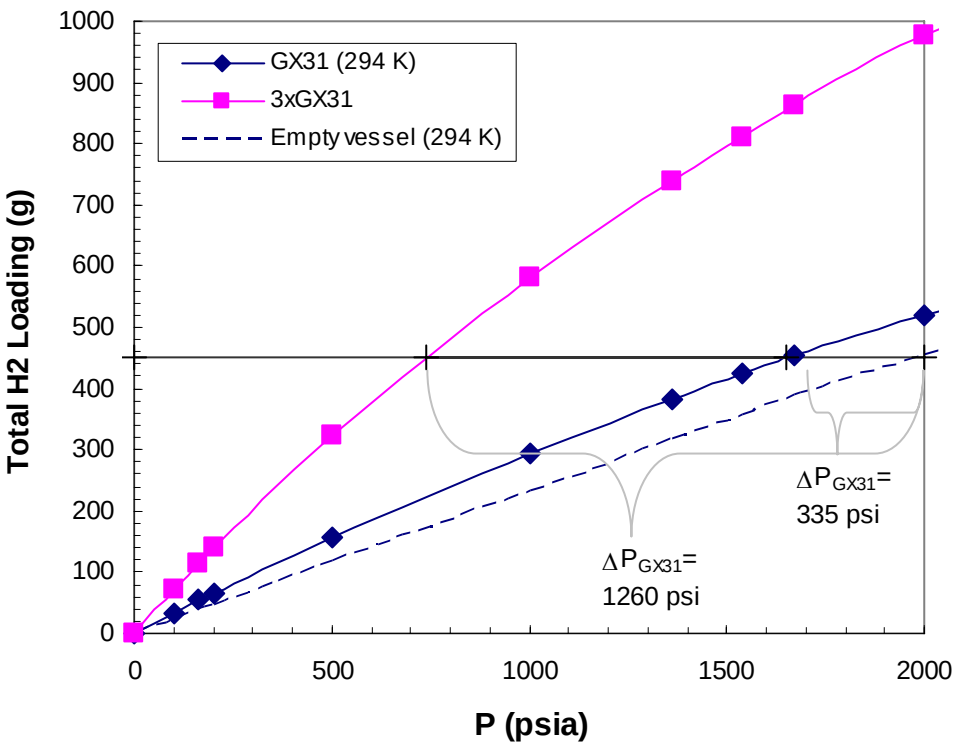


- 1: 'Break Even point'
  - Adsorbent and empty vessel have same H2 loading
- 2: Pressure at which the sorbent is most advantageous

[1]Zielinski, J. M.; McKeon, P.; Kimak, M. F., *Ind. & Eng. Chem. Res.* **2007,** *46*, 329-335.

Pressure Savings[1]

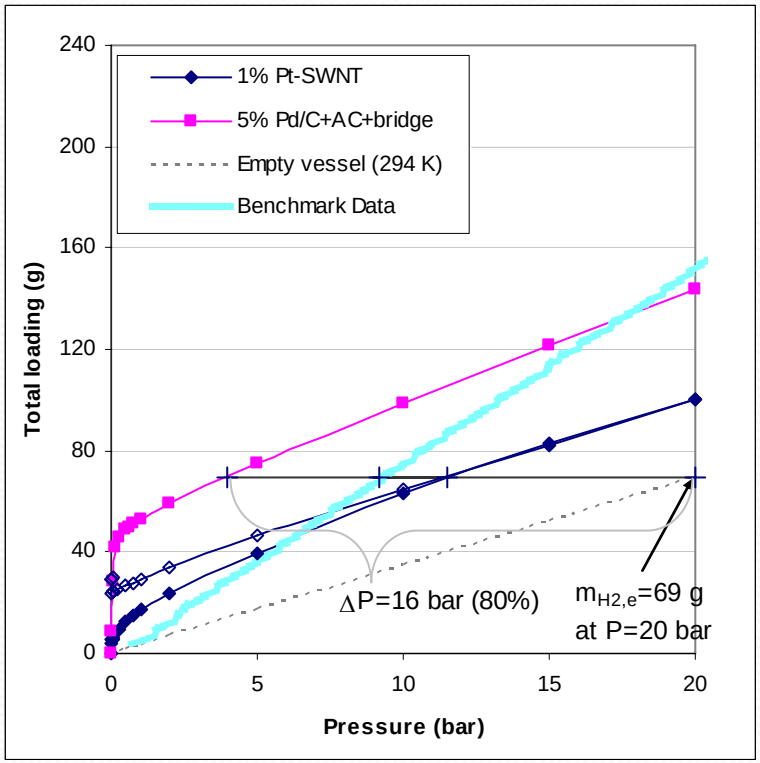
$$n_{H_2} = \frac{PV_E}{zRT} + M_s P\left[K(T,P) - \frac{1}{\rho_s zRT}\right]$$



- The GX31 adsorbent contains 450 g of H_2 at 1665 psia, a pressure savings of 335 psia. This pressure saving may translate to a reduction in wall thickness meaning that a less robust, and thus lighter, container may be used.

[1]Zielinski, J. M.; McKeon, P.; Kimak, M. F., *Ind. & Eng. Chem. Res.* **2007,** *46,* 329-335.

Spillover systems already exhibit significant pressure savings



"Standard" analysis

Status: Working to Employ Strategies to Maximize Low P Uptake;
TPD (with mass spec) needed to determine desorption temperatures

Our Strategies

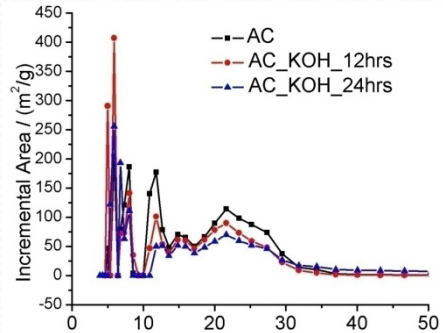
to Maximize H_2 Storage at Moderate T and P

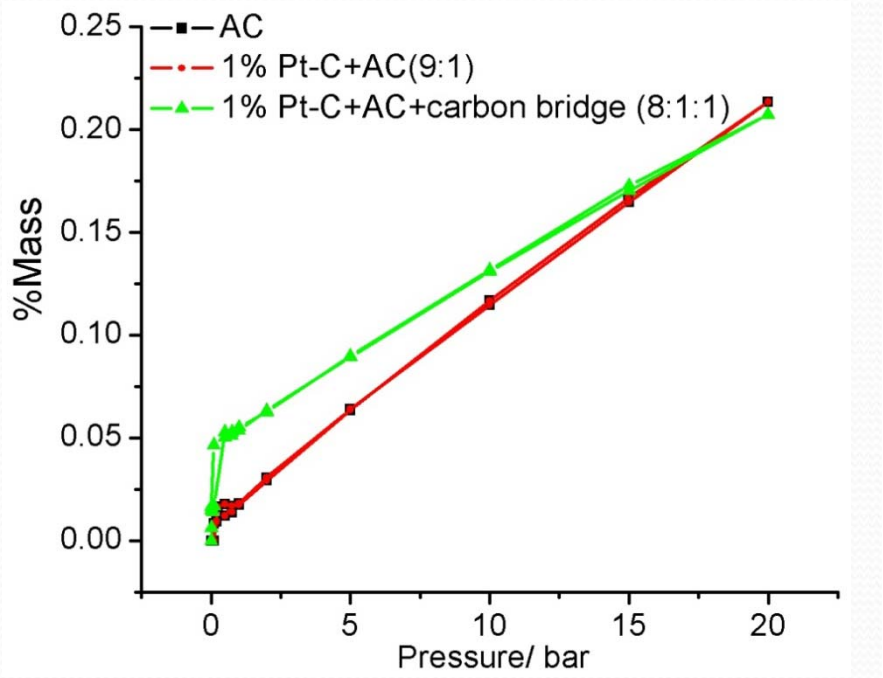
- Utilize Hydrogen Spillover Mechanism for Moderate Temperature Adsorption
  - Maximize metal dispersion
  - Maximize hydrogen receptors
    - Surface Chemistry
    - Porosity
    - Metal-Carbon Interface
- Utilize Advanced Characterization to understand/maximize active Sites
- Think in terms of Pressure Savings, particularly total H2 loading and shape of adsorption isotherm

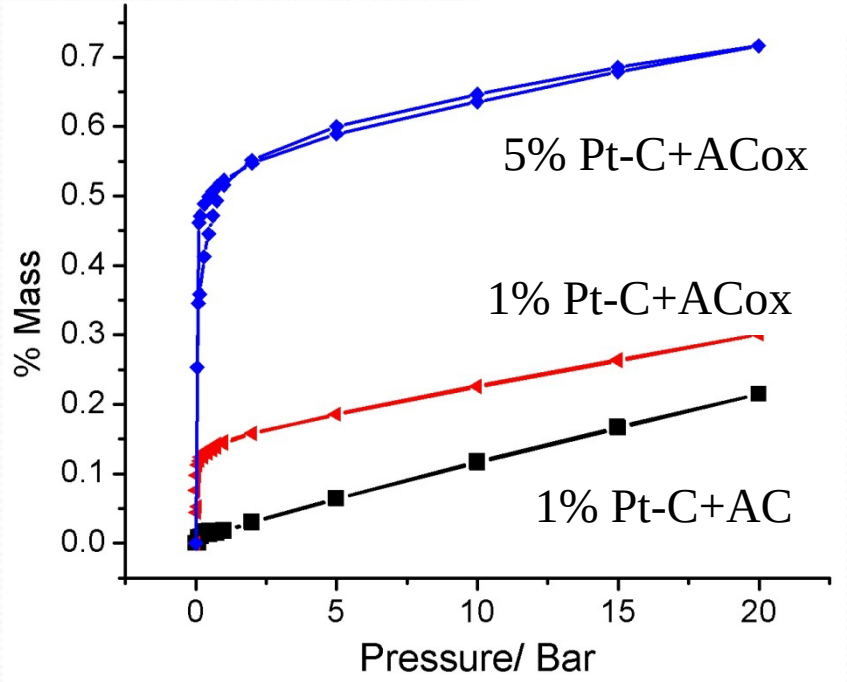
Maximize hydrogen receptors:

Explore oxygen functional groups

Introduction of oxygen groups as surface receptors more effective than bridging technique

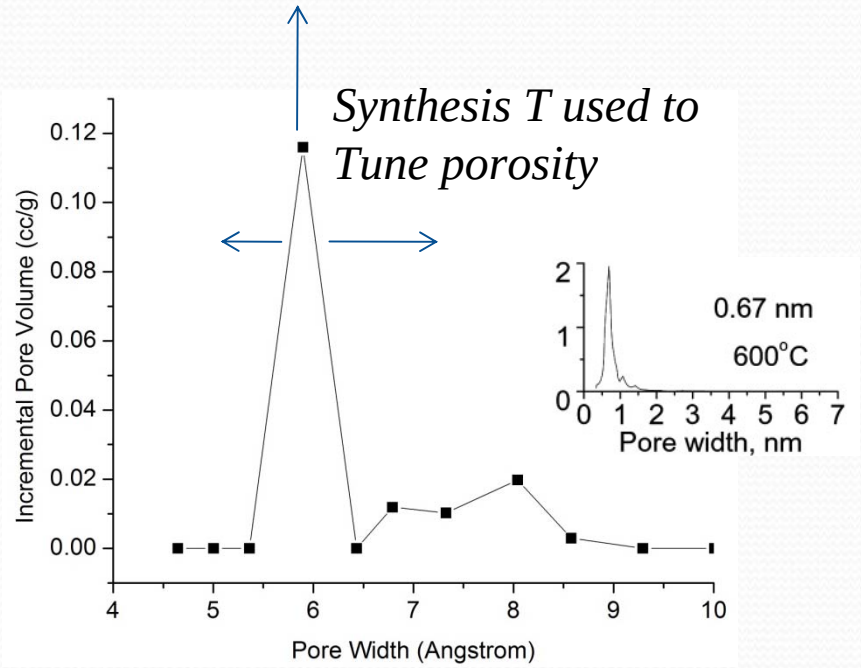


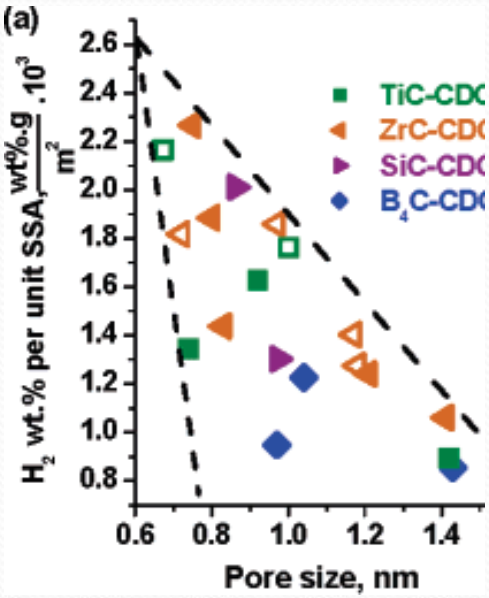




Maximize hydrogen receptors:

Explore high porosity materials

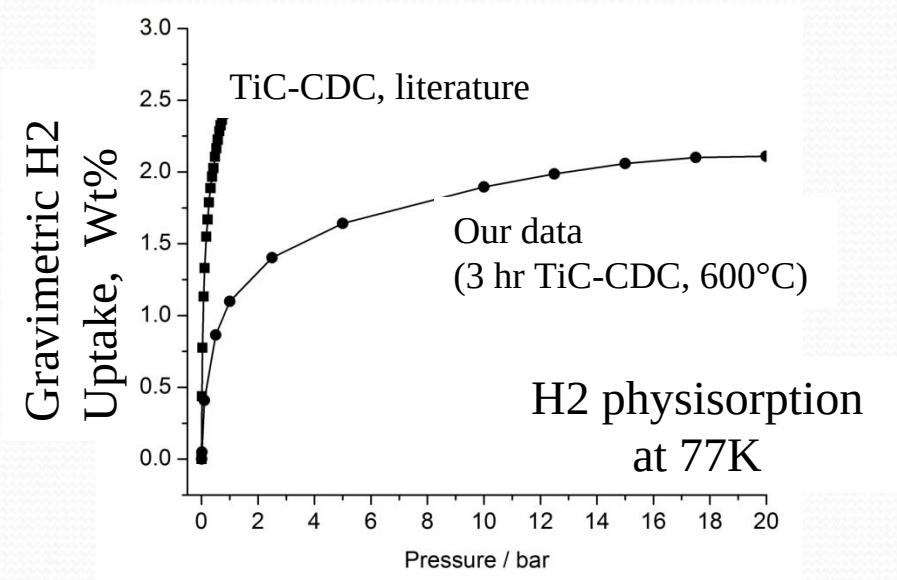


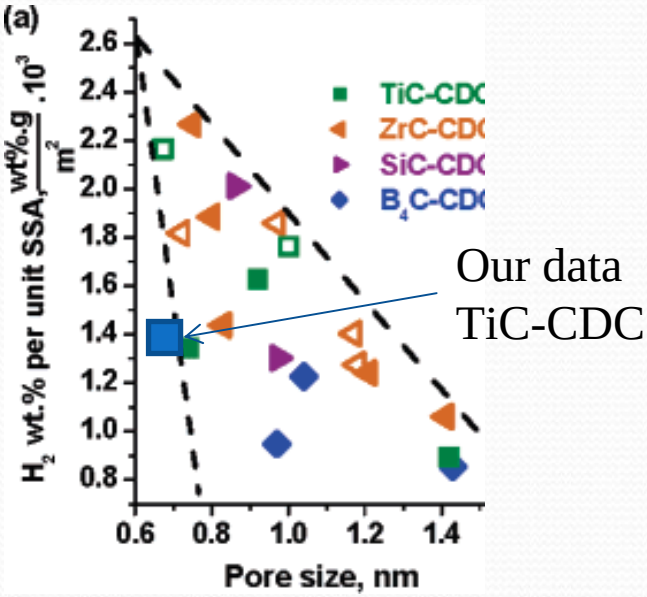


H2 physisorption at 77K, 1 bar

- Utilizing Carbide derived carbons (CDCs)
- Anticipate Ability to:
  - Tailor porosity, and
  - Introduce surface functional groups
  - Incorporate metals directly into material by partial extraction

Explore high porosity materials





H2 physisorption at 77K, 1 bar

A work in progress…

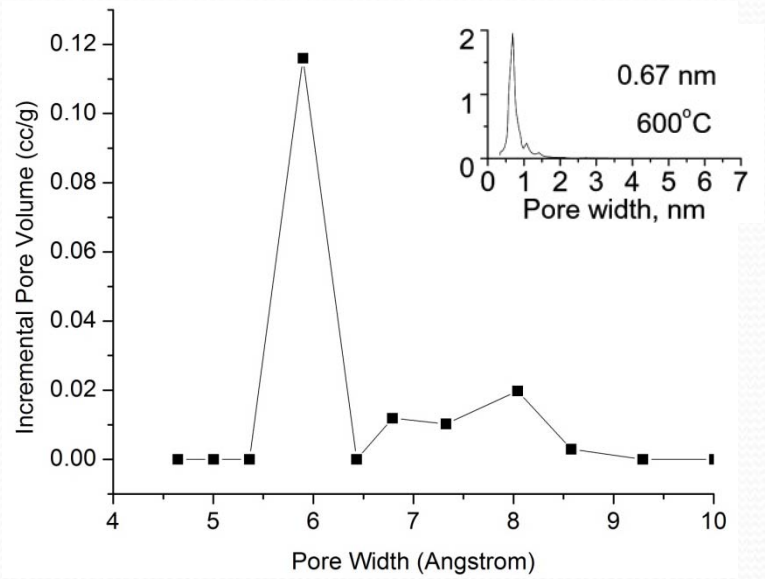
BET surface area

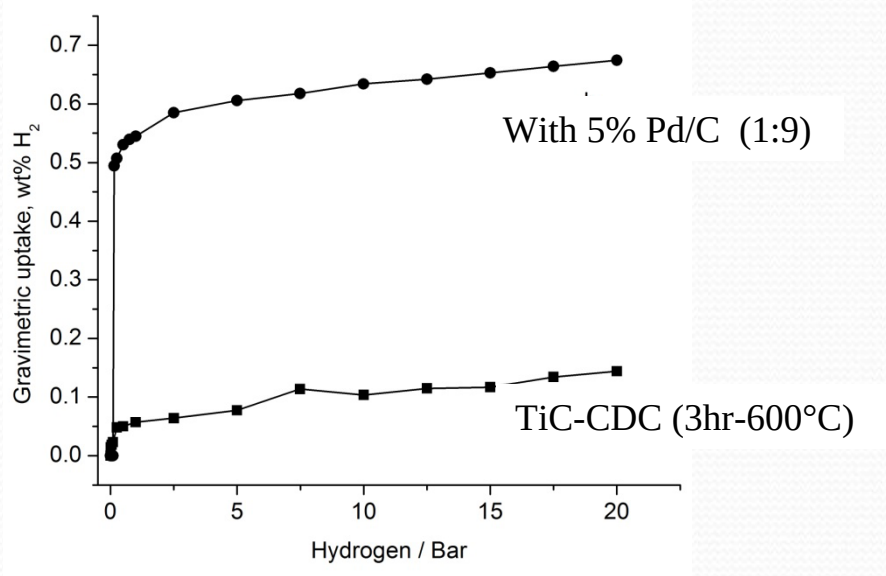
805.4 m^2/g vs. 1058 m^2/g (literature)

Total DFT pore volume

0.3 cc/g vs. 0.82 cc/g (literature)

Explore high porosity materials





- Utilizing Carbide derived carbons (CDCs)
- Anticipate Ability to:
  - Tailor porosity, and
  - Introduce surface functional groups
  - Incorporate metals directly into material by partial extraction

Comparison of Various Samples

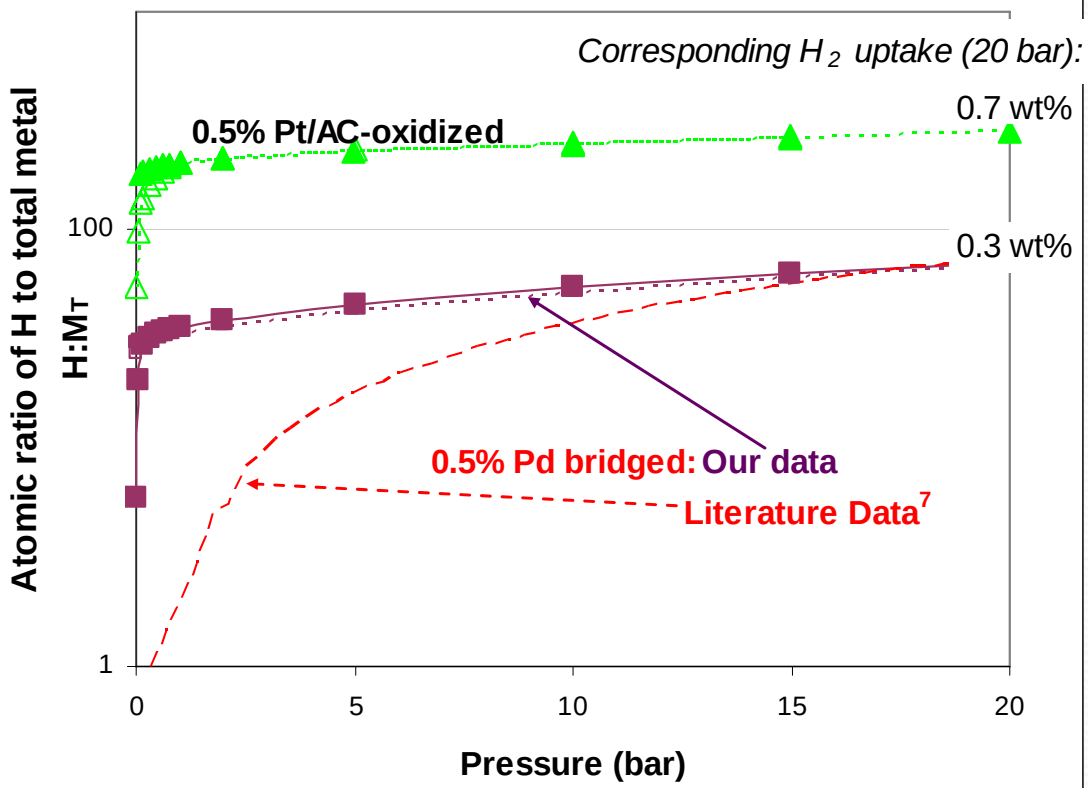
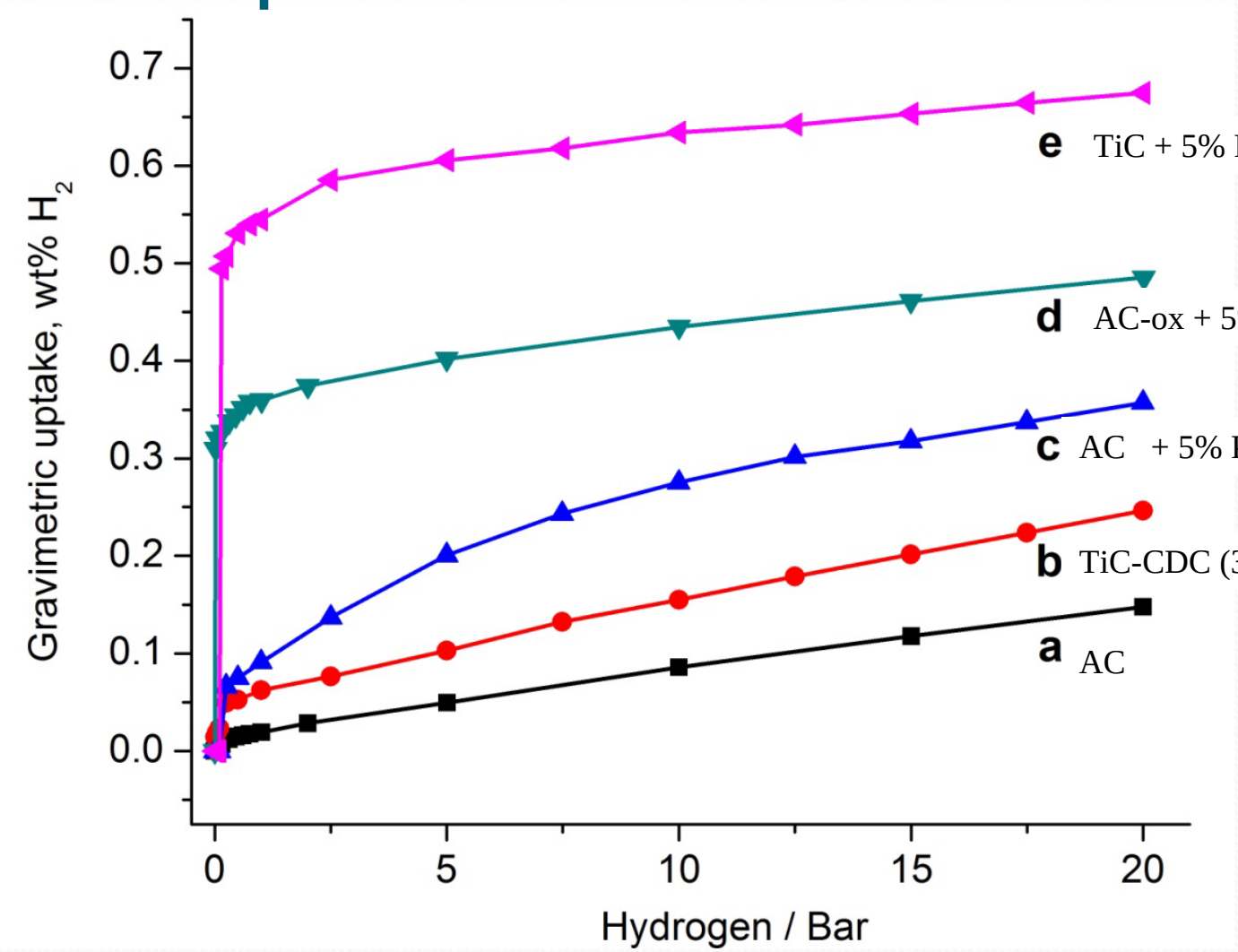


Fig. 1: H_2 uptake data for spillover materials at 300K.

Comparison of Various Samples



16 bar pressure
Savings (80%)

Summary and Conclusions

- Hydrogen spillover materials provide appreciable hydrogen uptake at 300K and moderate pressures
- Low pressure uptake leads to significant pressure savings

Goals for Remaining Project

- Validate low pressure spillover ($P \rightarrow 10^{-6}$ bar) with mass spec
- Incorporate TPD and MS measurements in to "pressure savings"
- Utilize CDCs *and* oxidation (best results to date)
  - Tune/optimize porosity, Introduce Surface Chemistry, Selective metal extraction
- Produce a Ph.D. Student and Thesis
  - Mechanistic Model to Describe Data