Hydrogen Trapping through Designer Hydrogen Spillover Molecules with Reversible Temperature and Pressure-Induced Switching

Angela D. Lueking,[1] Qixiu Li,[1] Cheng-Yu Wang,[1] Sarmishtha Sircar,[1] Xiaoming Liu[1]

Co-PIs: Jing Li,[2] Milton W. Cole[1]

[1]Penn State University, [2]Rutgers University

May 12, 2011

ST024

Overview

Timeline

- Start - Sept 2008
- End - Nov 2013
- ~42% Complete

Budget

- Total project funding $2,166,895
  - DOE Share: $1,614,000
  - Contractor Share: $552,895 ($262,862 Rutgers, $290,033 PSU)
- $324K FY10
- $276K FY 11 ($150K to date)

Barriers

- Barriers addressed
  - Gravimetric Capacity
  - Min/max delivery temperature
  - Max delivery pressure from tank
  - Volumetric Capacity

Partners

- Prof. Angela D. Lueking (Penn State—Project Lead)
- Prof. Jing Li (Rutgers) Co-PI
- Prof. Milton W. Cole (Penn State), Co-PI

Other Collaborators

- Profs. John Badding and Vin Crespi (in situ studies; BES project; PSU)
- Institute of Nuclear Energy Research (Taiwan)
- National Renewable Energy Laboratory

Objectives - Relevance

The **overarching objective** is to synthesize designer microporous[1] metal-organic frameworks (MMOFs) mixed with catalysts to enable H-spillover for H_2 storage at 300K-400K and moderate *P*s.

In the past year (May ’10 – March 2011), we have:

A. Focused on Reproducibility Studies / Effect of Preparation Conditions for one MMOF mixed with a Pt/C spillover catalyst (PSU)

B. Improved Uptake and Catalytic Activity of Pt/C Spillover Catalyst (PSU)

C. Synthesized new MMOF structures; focusing on effect of oxygen functional groups (RU)

D. Increased sensitivity/accuracy of volumetric measurements (PSU). Compared single-sided to double-sided volumetric measurements (with NREL).

E. Reproduced literature high-pressure uptake for Pt/C spillover materials at 80 bar and 298 K (PSU)

F. Worked collaboratively with Taiwan institute to verify high and unique spillover results on Pt/ carbon-based sample (PSU & INER)

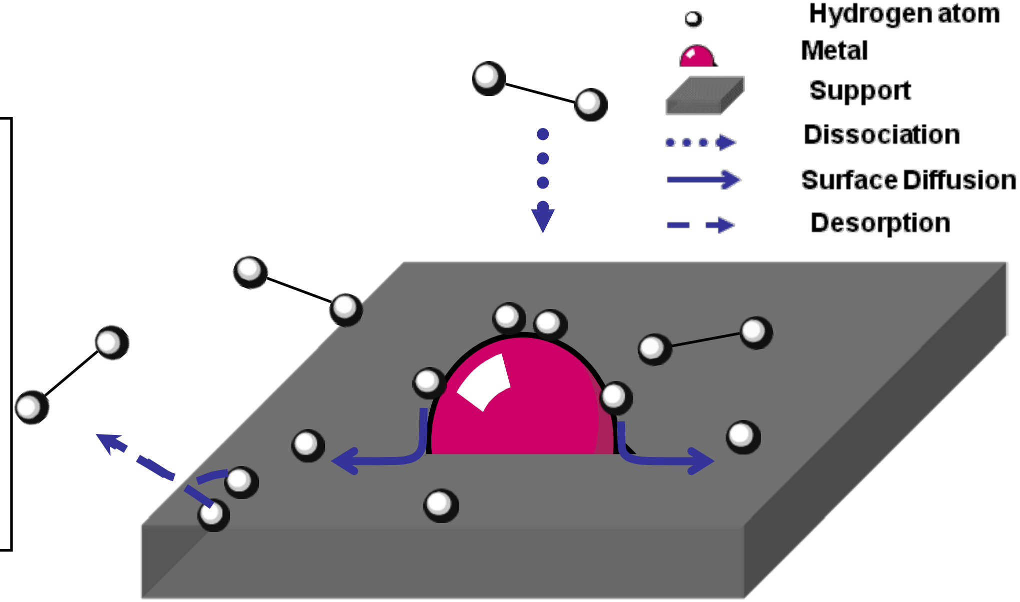
G. Worked collaboratively to obtain in situ spectroscopic validation of spillover to carbon support (PSU; with DOE-BES funding)

[1] d < 2nm (IUPAC)

Hydrogen Spillover

$H_2(g) + 2M \rightarrow 2HM$	(i)
$HM + M' \rightarrow M + HM'$	(ii)
$2HM' \rightarrow H_2(g) + 2M'$	(iii)
$HM' + S \rightarrow H_{sp}S + M$	(iv)
$H_{sp}S + S' \rightarrow S + H_{sp}S'$	(v)
$2H_{sp}S' \rightarrow H_2(g) + 2S'$	(vi)
$H_2 + S'' \rightarrow H_2\text{-}S''$	(vii)

Box 1: Reaction sequence for hydrogen spillover.

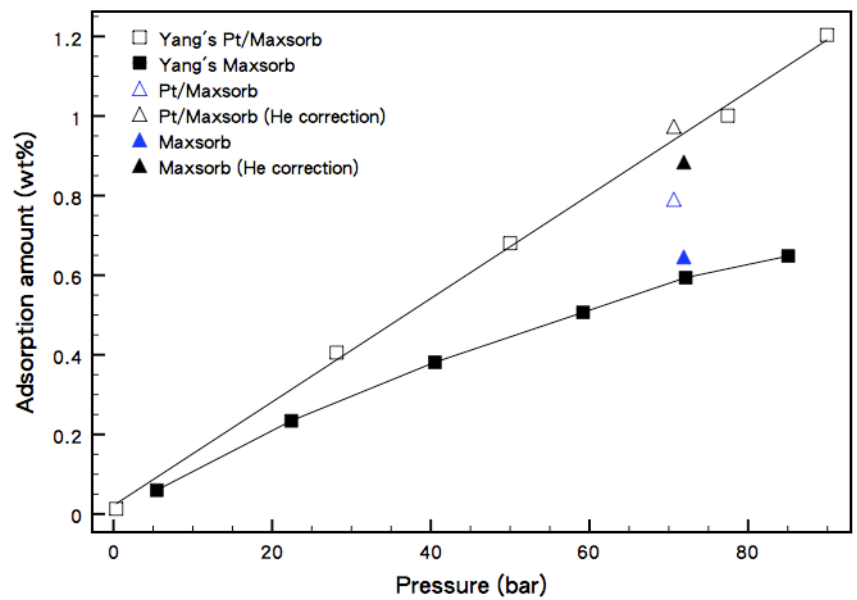


Side View

Reproducibility of spillover called into question in 2009/2010. Weak chemisorption workshop convened in August 2009.

Yang et al. and Tsao et al. report catalyst activation and size is key to spillover.

We've adapted our project to address these issues. Focusing on reproducibility, enhancement, fewer MMOFs.



Benchmark: Li & Yang, JACS, 2006: 1.5 wt% at 80 bar; 2010 workshop recommendation: **25% enhancement.**

Strategies/Approach

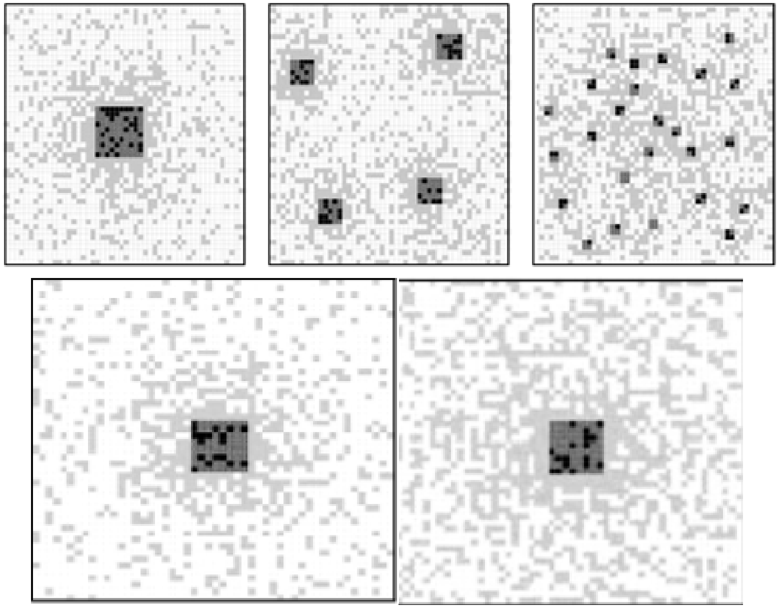
Material Design

To increase uptake via Hydrogen Spillover Mechanism:

- Maximize metal dispersion
- Optimize hydrogen receptors to increase surface residence time → Surface Chemistry
- Change rate limiting step
  - Porosity?
  - Metal-Carbon Interface (Yang et al.)
- MMOFs provide systematic means to alter structure and porosity, however, direct doping is not trivial.

T vs. P switches:

- Is it possible to use pressure to 'adsorb'; T to desorb…?
- Is it possible to use reverse spillover to 'trap' H in the material?



Top: Relative metal dimensions are (a) 11; (b) 6; (c) 2. All have 4% metal surface coverage and equal rates of spillover to desorption. Resulting surface coverage is (a) 25, (b) 32, and (c) 40%.

Bottom: Increasing rate of spillover to desorption by a factor of 100 increases H:M by 50%

Based on: *J. Phys. Chem. C. 111, 1788, 2007.*

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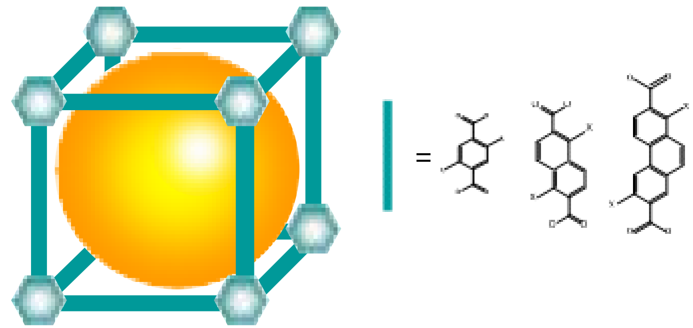
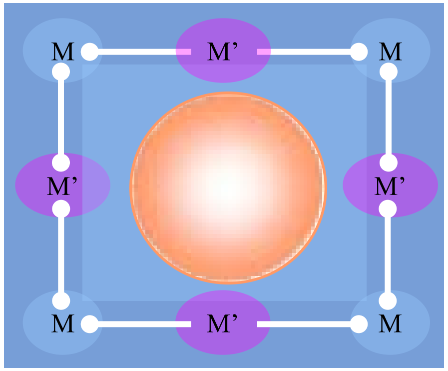
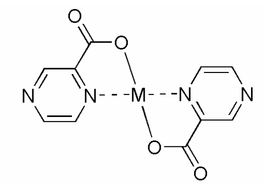
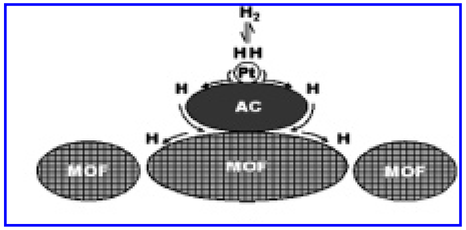
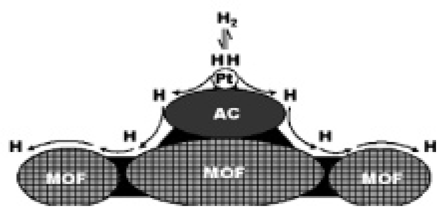










Li & Yang, JACS, 2006

Approach:

Upcoming Milestones

- Correlation between spillover and MMOF functional groups, (Yr. 2-- FY10) leading to:
  - H_2 uptake > 1 wt% at 20 bar and 300K; ★
  - Extrapolation suggests > 4 wt% at 100 bar, or X
  - Pressure savings of >90% relative to the empty tank ★★
- Incorporation of catalytic entities into MMOF framework (Yr. 2-- FY10) leading to:
  - MMOF catalytic activity H-spillover started Jan 2011
  - Improved performance relative to Pt-C catalysts ★★

Go/No-Go Decision Point.

Exceed 5.5 wt% hydrogen storage through the use of the "hydrogen spillover" mechanism, MOF material, or a combination of the two as proposed at moderate temperatures (i.e. 300-400 K) and 100 bar with anticipated system penalties (Go/No Go: 2/29/12).

Technical Barriers

- Project addresses gravimetric uptake, including system weight
- Moderate temperature and pressure
- Track kinetics and capacity of spillover; mechanistic studies and reproducibility

Measurement

High-pressure volumetric used as primary measurement; 1 step ‘rapid screening test’ developed in 2009; improved in 2010.

Low-pressure equipment for dispersion and porosity. Gravimetric used for temperature-programmed desorption.

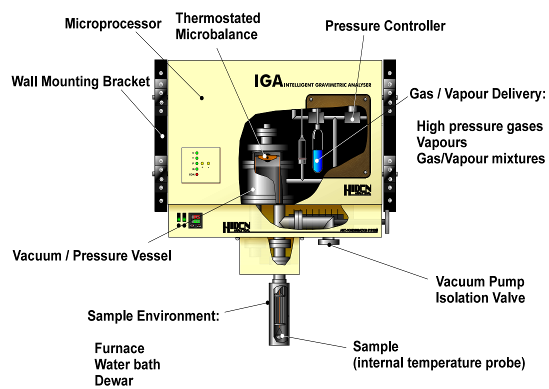
Change in 2011- increased accuracy

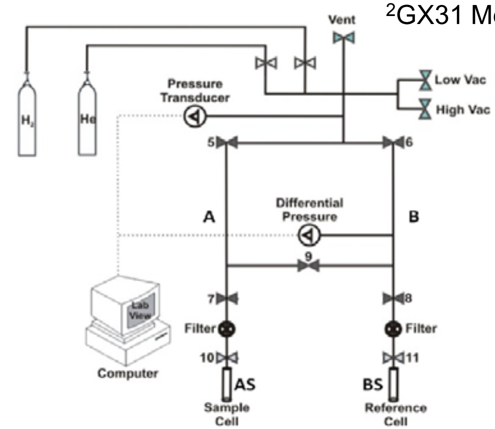
Increased Pressure & Uptake: Used for Rapid-Screening for Go / No-Go

Increased Accuracy and Experimental time; Used for Mechanistic Data and Structure Characterization

For 100 mg sample: +/- 0.01 wt%[1] +/- 0.05 wt%[2] [0.05wt%[1]]

[1]Error Propagation
[2]GX31 Measure





◆ **Micromeritic Volumetric 2020** (< 1bar)

● Hiden **Gravimetric** Analyzer In-line Mass Spectrometer (< 20 bar)

■ **Custom-Built *Differential* Sievert’s Apparatus (< 100 bar)**

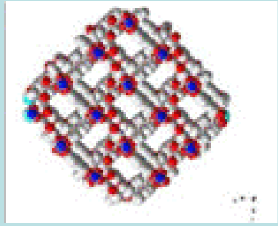
Quality Check

Pd (25°C)	**0.71 wt% (760 mmHg)**	**0.71 wt.% (20 bar) ($HPd_{0.75}$)**	**--**
GX 31 (25 °C)	**0.013 wt% (760 mmHg)**	**0.17 wt.% (20 bar)**	**0.53 wt% (70 bar)**

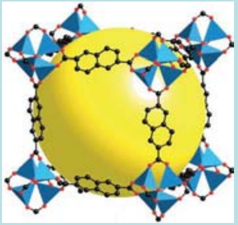
Previous (2009) Results

Explore the effect of surface chemistry, porosity, and structure on hydrogen spillover

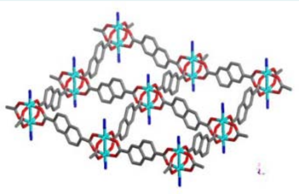
a: MMOF=O
230 m^2/g (BET)



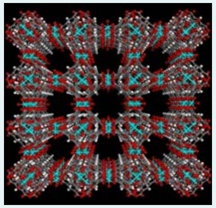
b: IRMOF8
1384 m2/g (BET)



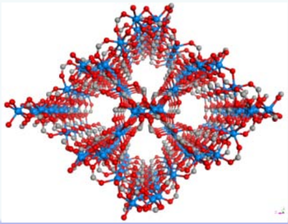
c: $Zn(NDC)(TED)_{0.5}$
2647 m^2/g (L)



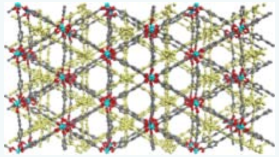
d: $Cu_3(BTC)_2(H_2O)_3$
1641 m^2/g (BET)

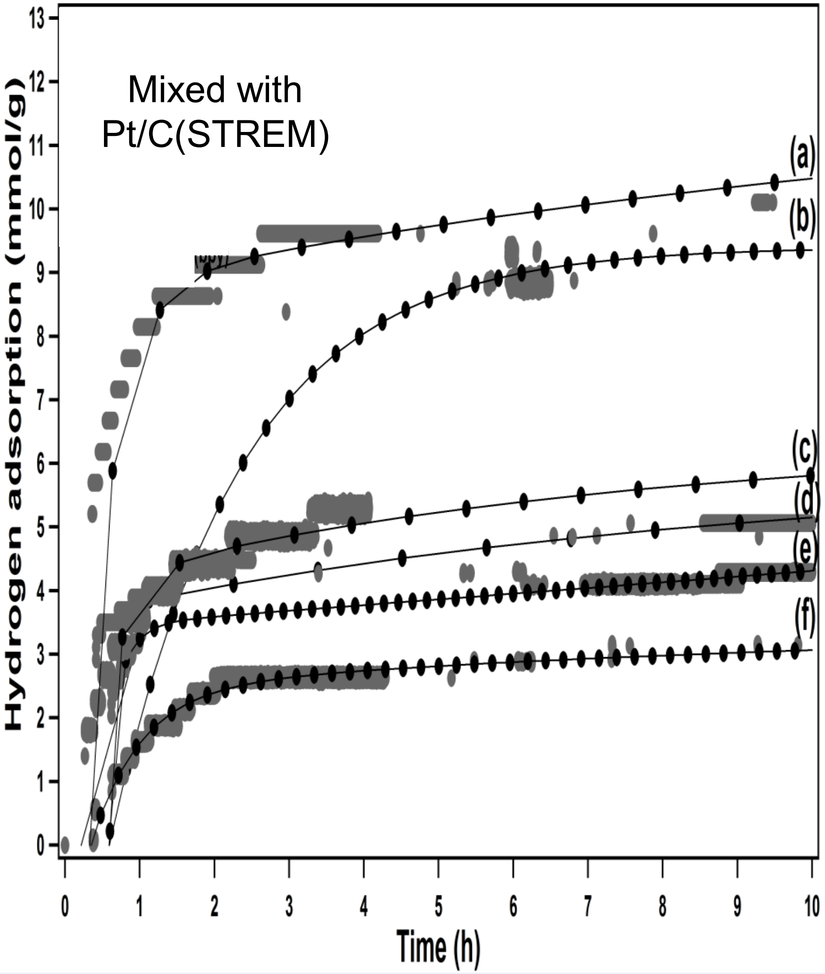


e: $Ni(HCOO)_6$
304 m^2/g (BET)



f: $Zn_3(bpdc)_3(bpy)$
792 m^2/g (BET)



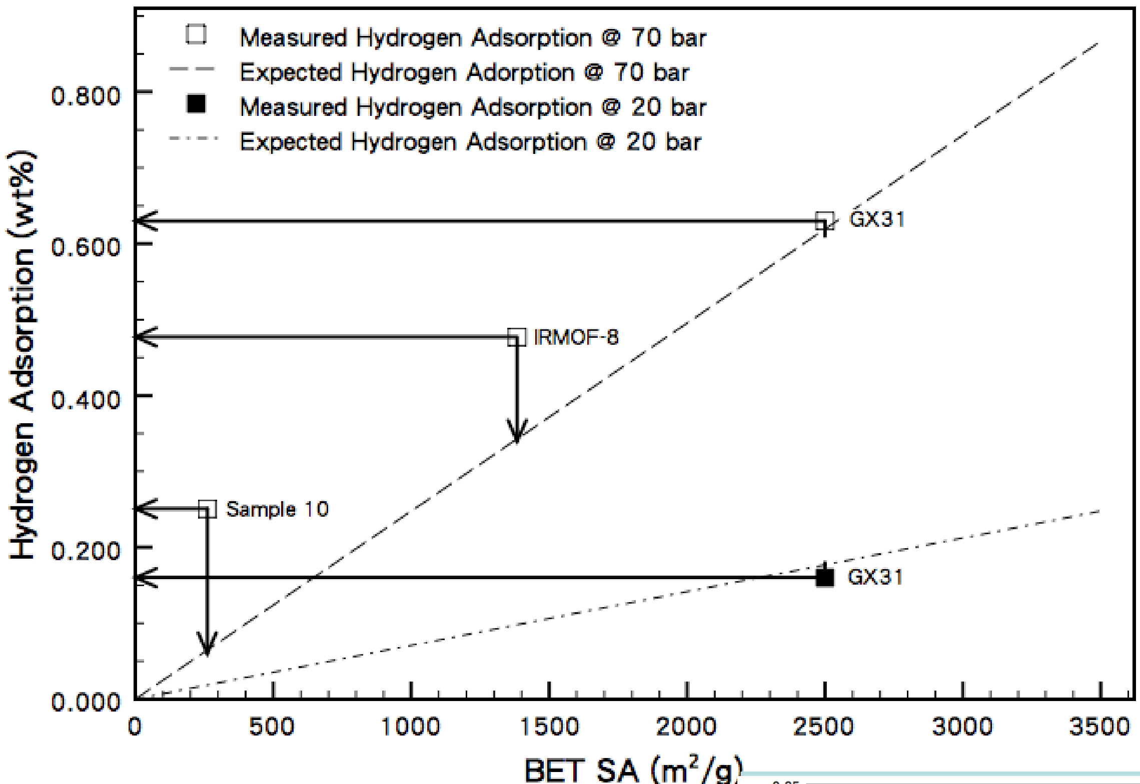


Rapid and increased H_2 uptake after introduction of Carbonyl group. Surface chemistry larger effect than structure; introduction of sp^3 carbon (TED) slows/reduces uptake relative to sp^2 in 3-D (IRMOF-8). Results highly dependent upon preparation and handling.

(1) Panella, B.; Hirscher, M.; and Roth, S. *Carbon.* *2005, 43, 2209-2214.*

Data Comparison: "Expected H_2 Adsorption"

Normalized to BET specific surface area, 0.23×10^{-3}mass%/m^{-2}g at 65 bar. Assumes Henry's Law.



To compare multiple samples, with multiple structures, at multiple Ps, we are currently plotting H_2 uptake via that expected via the "Chahine rule" at 298K (1).

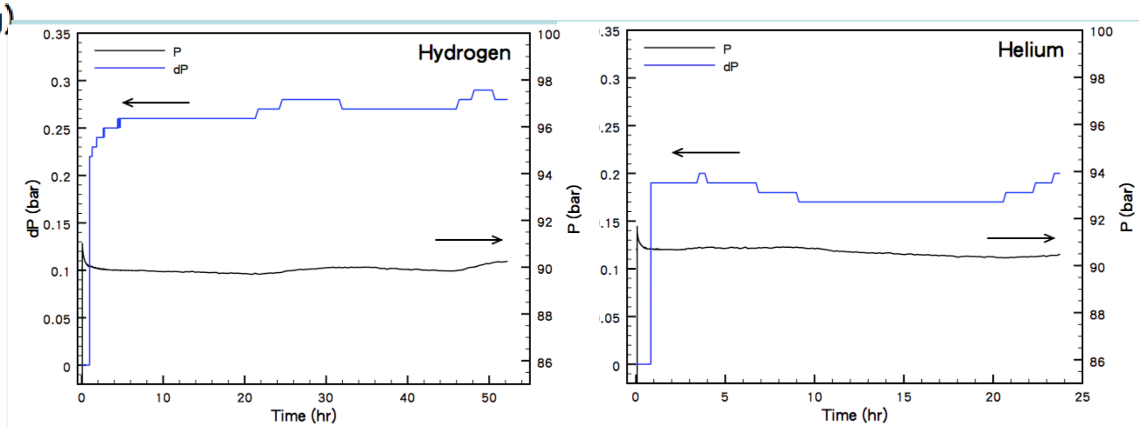
Deviations above the line can be attributed to enhancement due to hydrogen spillover.

Yet, the H_2 uptake on the y-axis still keeps an eye on gravimetric targets.

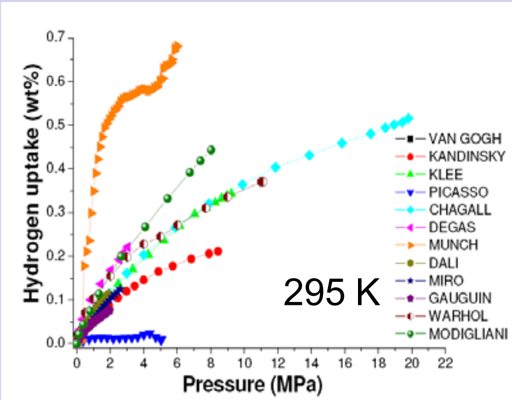
Kinetic data tracked for >=24 hours. Slow uptake is.not seen unless otherwise specified.

Isolated pressure reading (isolated from sample cell) shows T stability.

Select samples selected for repetition/cylability tests and full reproducibility seen.



Significant increase in volumetric accuracy
Minimization of Effect of Volume Errors; Valve volume



NESSHY Round-Robin Testing Results for High Surface Area Carbon Material

Courtesy of Mike Miller, SwRI

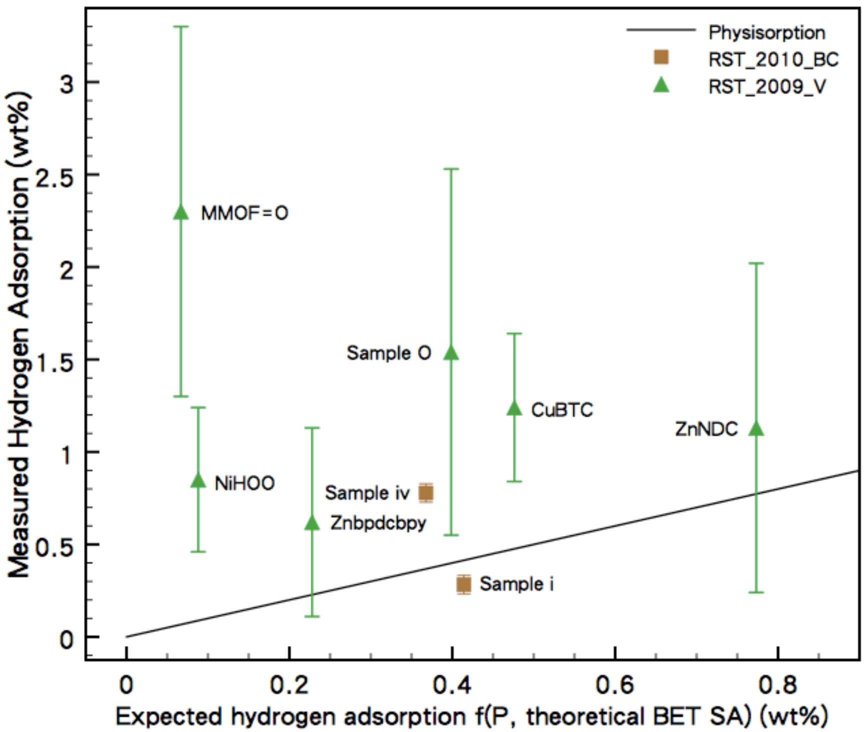
With improvements, 2010 data has significantly less error (via propagation) compared to 2009 methods.

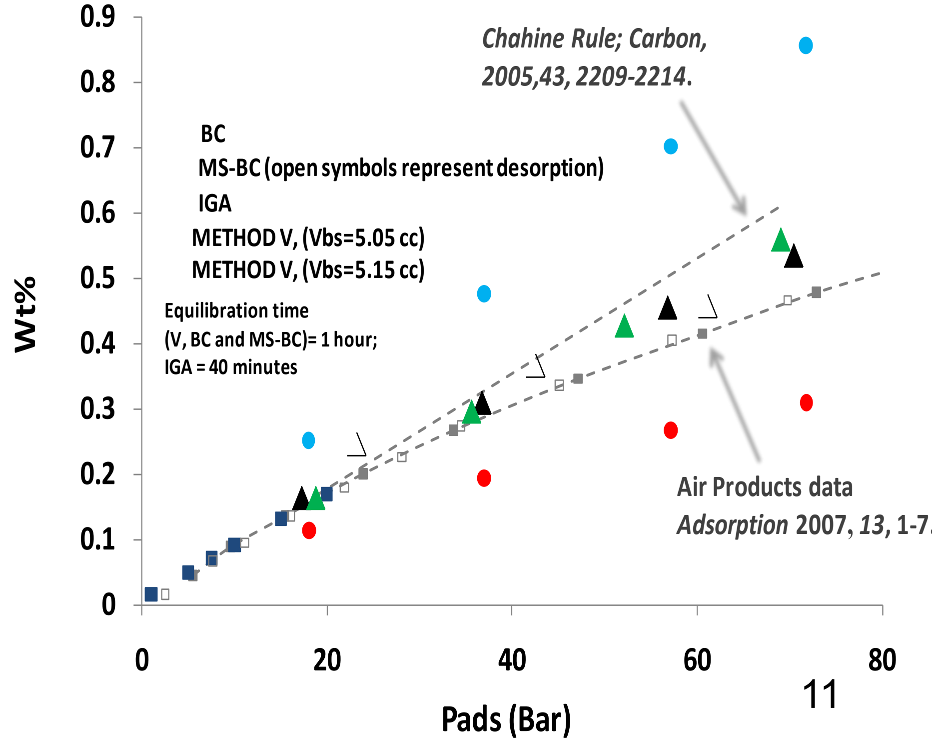
At 80 bar, 298 K, 100 mg sample, RST:

Single Sided : 1 ± 0.6[1] wt%

Method V (2009): 1 ± 0.1[1] wt%

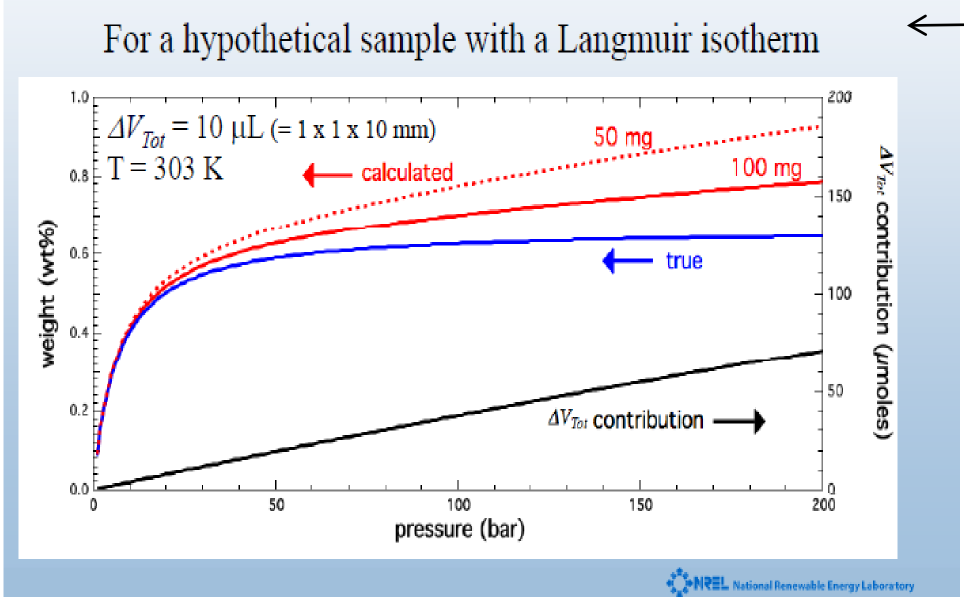
Method BC (2010): 1 ± 0.05[1] wt%





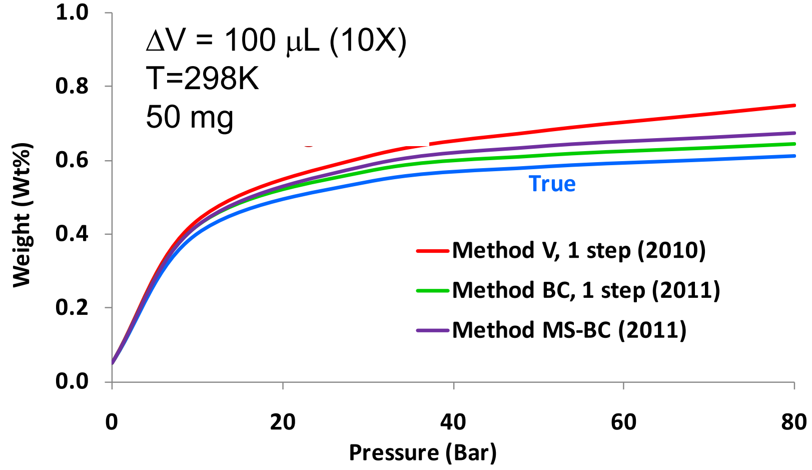
[2009 surface area taken prior to ball milling.] See also supplementary information.

Significant increase in volumetric accuracy
Minimization of Effect of Volume Errors; Valve volume



NREL's analysis; Courtesy of Parilla

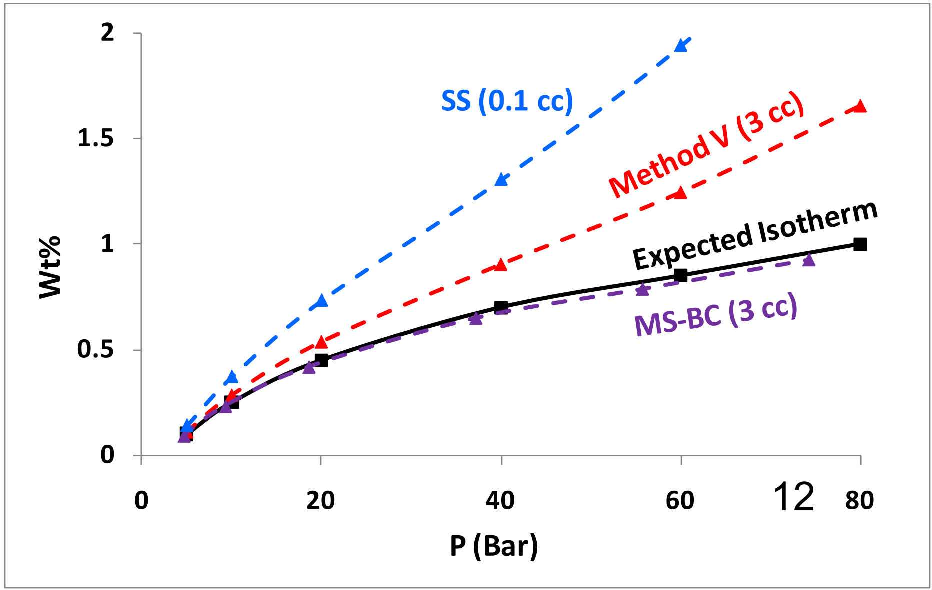
Similar analysis for differential



Although Differential provides improvements over single-sided, Method "V" used in 2009 is still fairly sensitive to volume calibrations.

Methods "BC" and "MS-BC" developed in 2010 are insensitive to volume calibrations. Even with a 10-fold increase in volume error , error is less than single-sided.

Differential less error than single-sided with 30-fold increase in valve volume error. BC and MS-BC insensitive.



Full details in supplementary information.

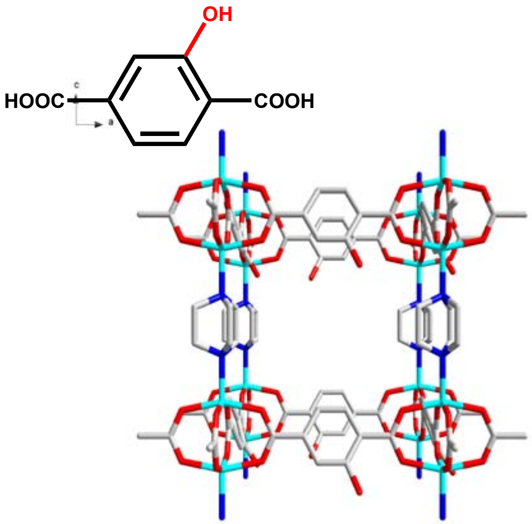
Focus on Reproducibility, Preparation, and Introduction of Oxygen Functional Groups

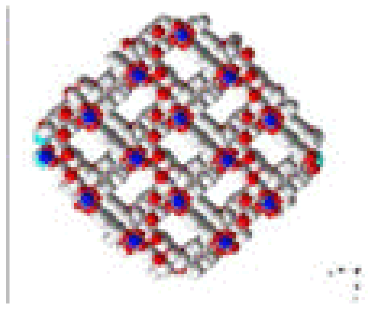
$Zn(BDC\text{-}OH)(TED)_{0.5}$
MMOF-OH

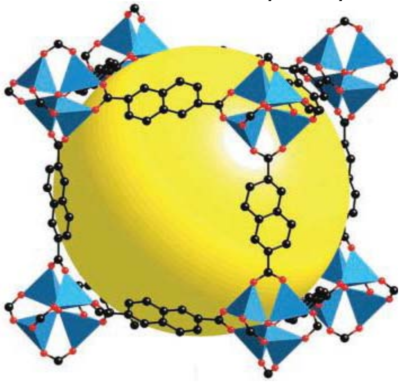
MMOF=O

$Zn_4O(NDC)_3$
IRMOF-8

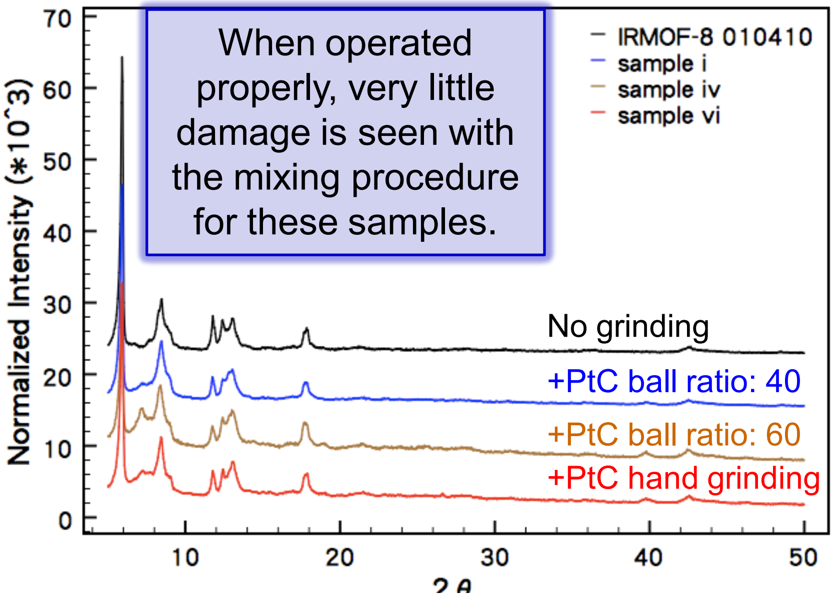
JACS 2004, 126, 5666-5667

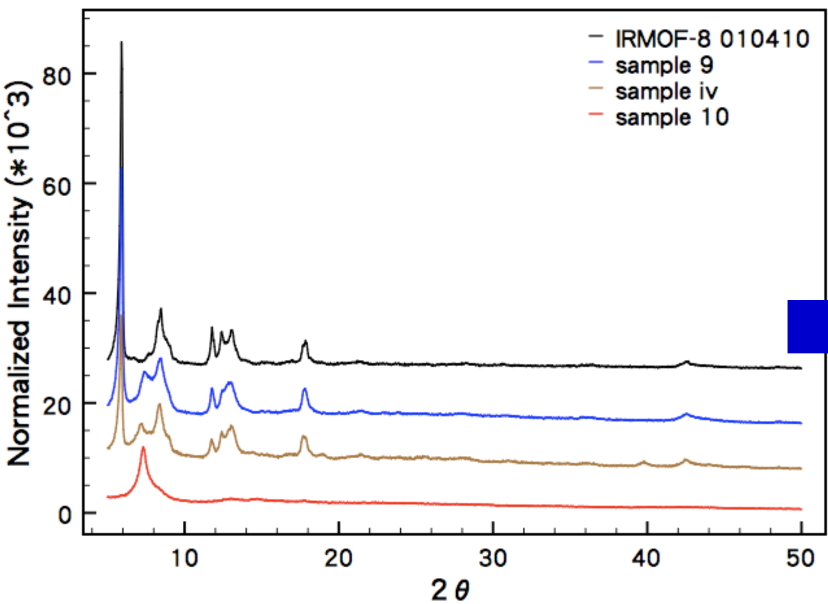






Focus on Preparation





$Zn_4O(NDC)_3$

IRMOF-8

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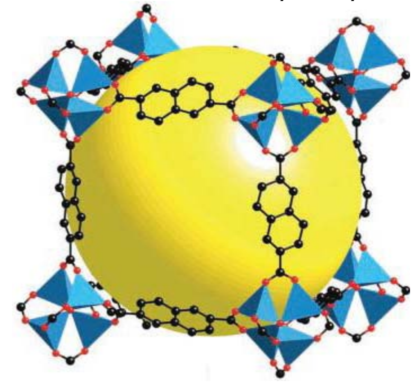
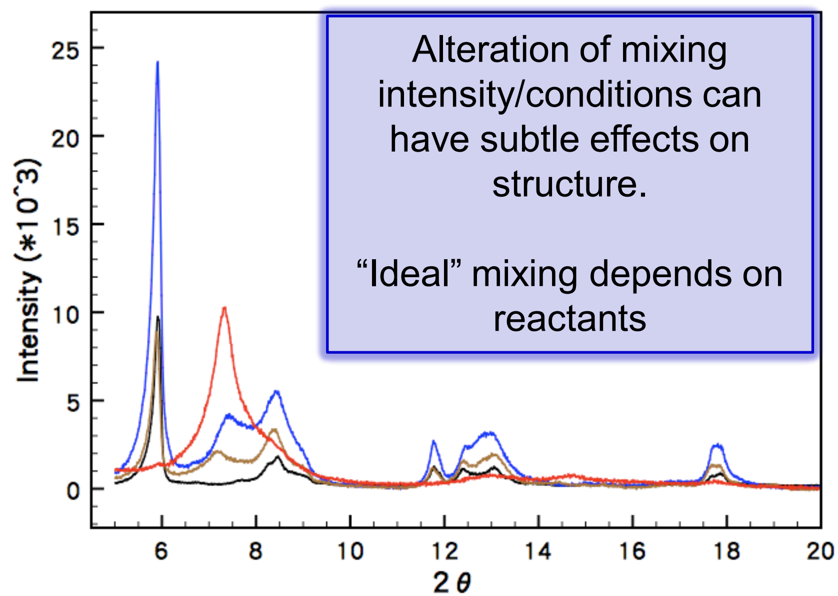


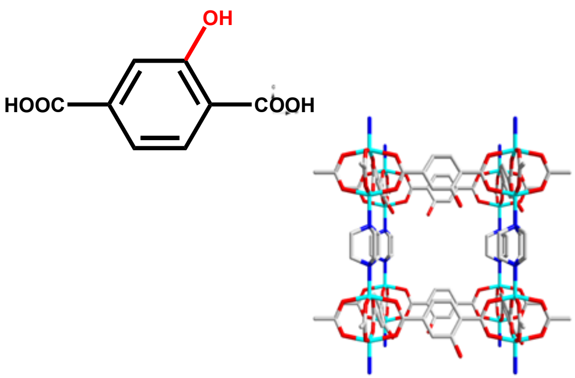


Technical Accomplishments

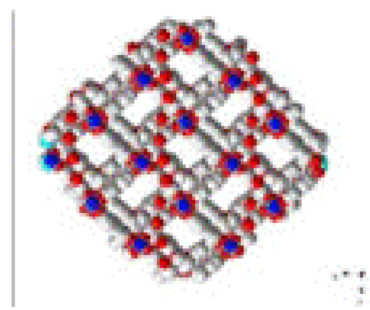
Focus on Preparation / Surface Chemistry

$Zn(BDC\text{-}OH)(TED)_{0.5}$

MMOF-OH

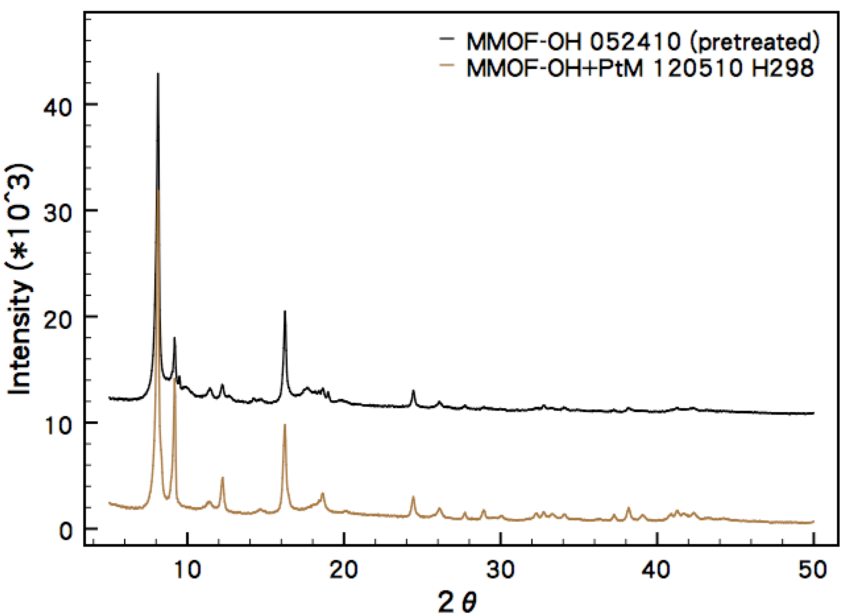


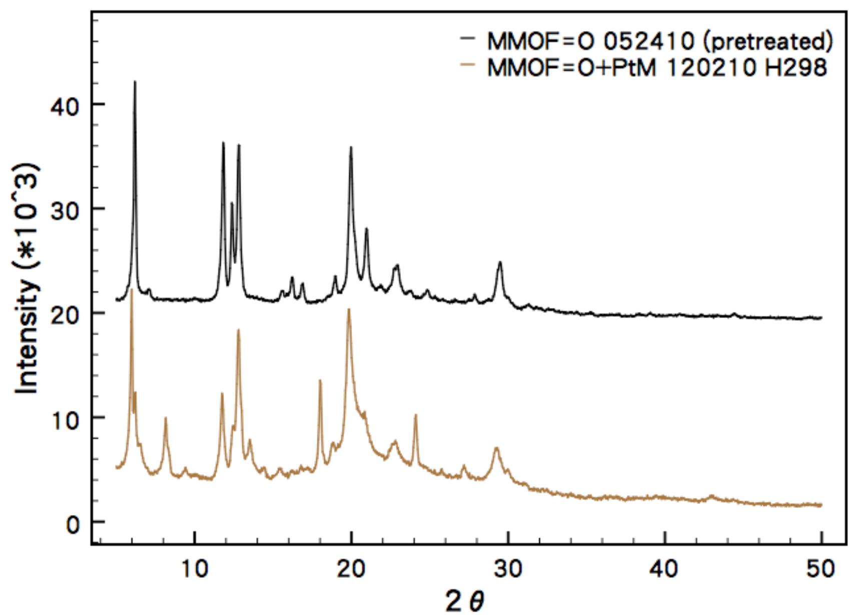
MMOF=O



With mixing, subtle changes are seen in structure, but MMOF remains largely intact...

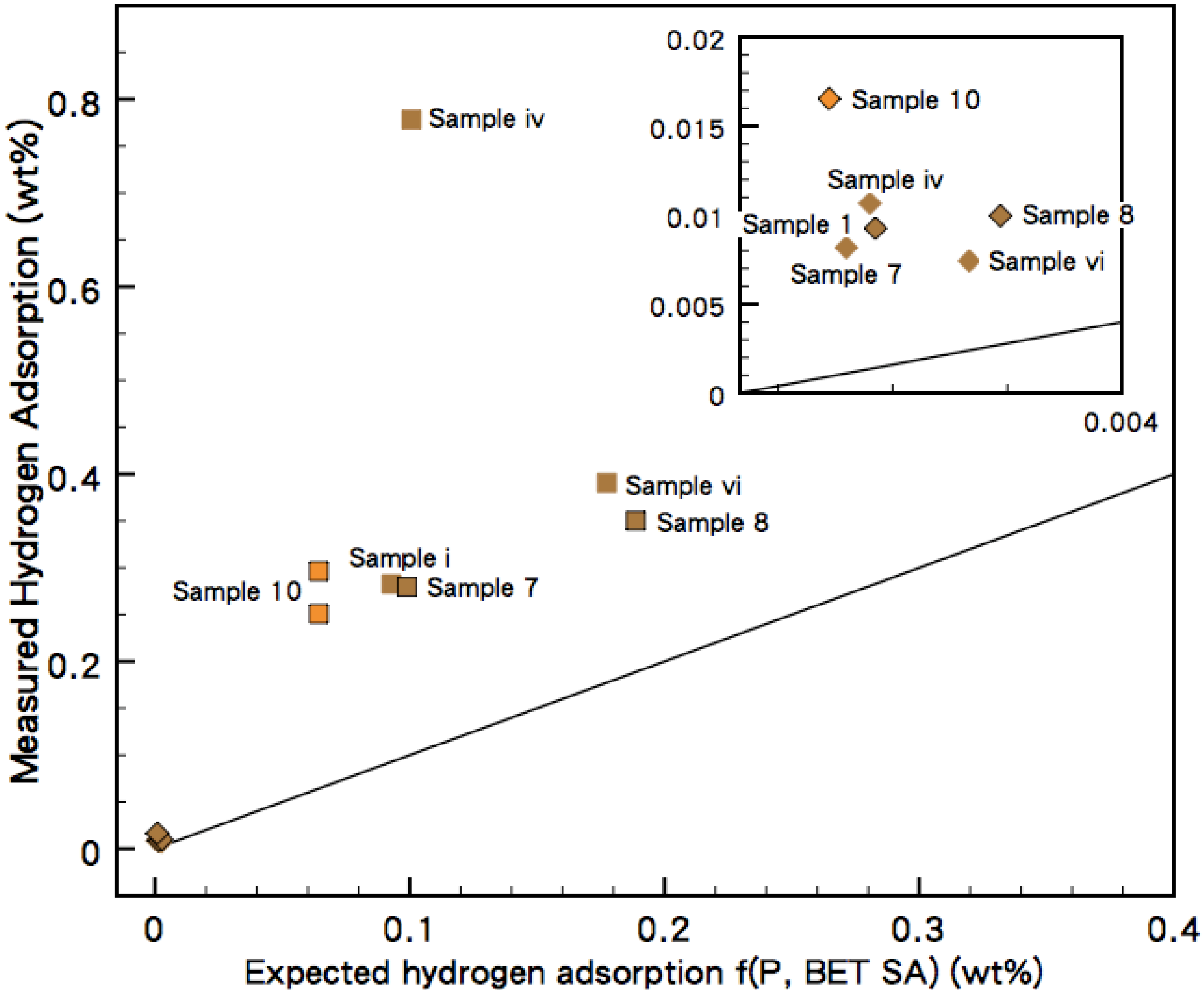
(This shortcoming to be addressed in future work.)





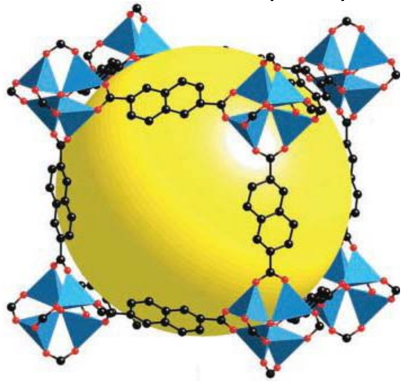
Effect of Preparation on H_2 uptake

298K



$Zn_4O(NDC)_3$
IRMOF-8

JACS 2004, 126, 5666-5667



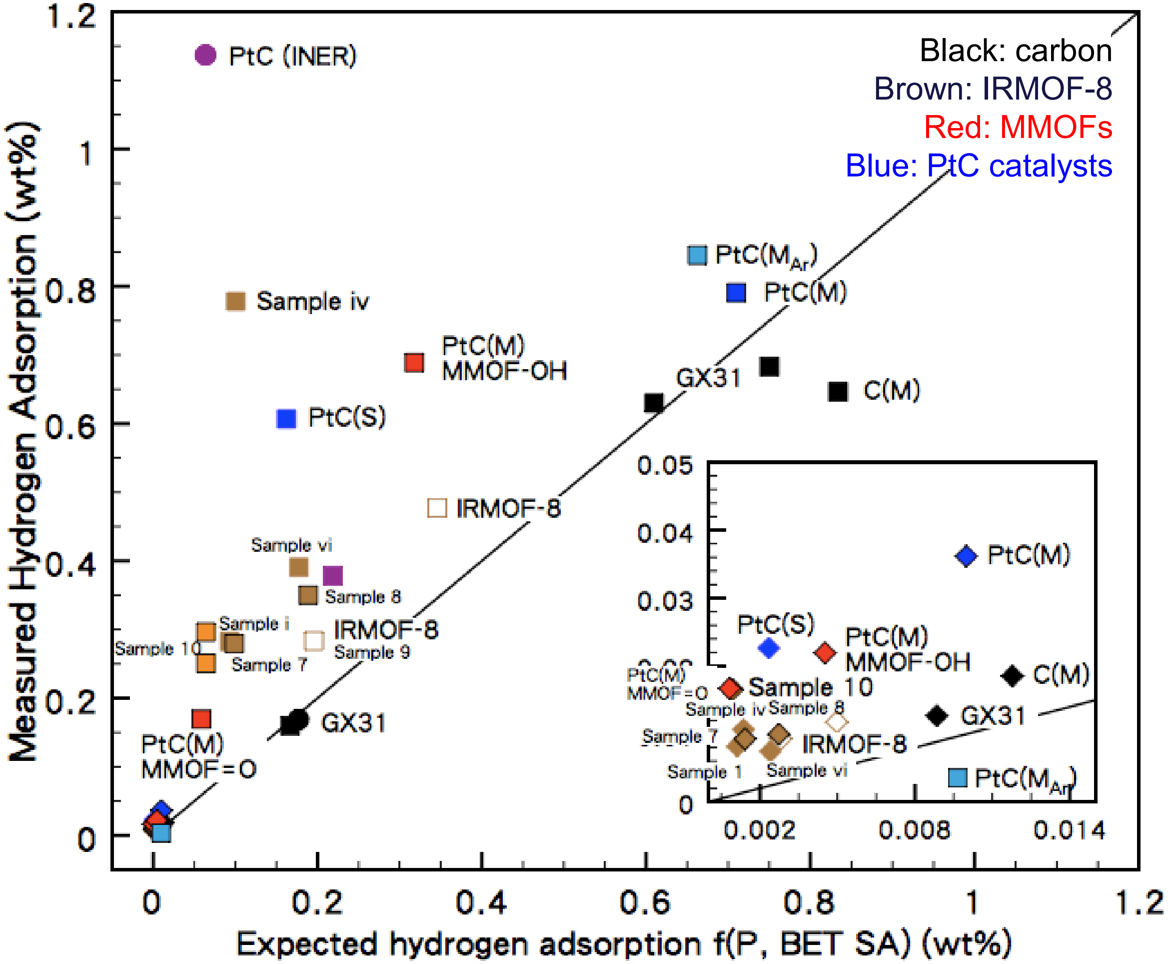
#	IRMOF8+ [ball:sample]
9	ball milling [25]
i	+PtC(S) [40]
iv	+PtC(S) [60]
6	+ PtC(S) (hand)
7	+ PtC(M)* [60]
8	+ PtC(M)* [25]
10	+ PtC(M)* + sucrose(2) [20]

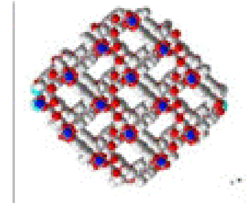
•PtC(M) 2841 m^2/g vs. 652 m^2/g for (S); and dispersion increased ~3-fold.

Subtle differences seen in XRD affect uptake in few cases. (O, iv) Improving catalyst* has little effect, suggesting poor contact.

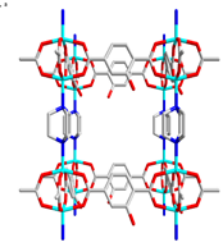
Technical Accomplishments

Alter Surface chemistry

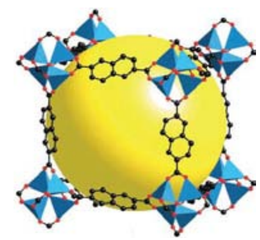




MMOF=O



MMOF-OH



IRMOF-8

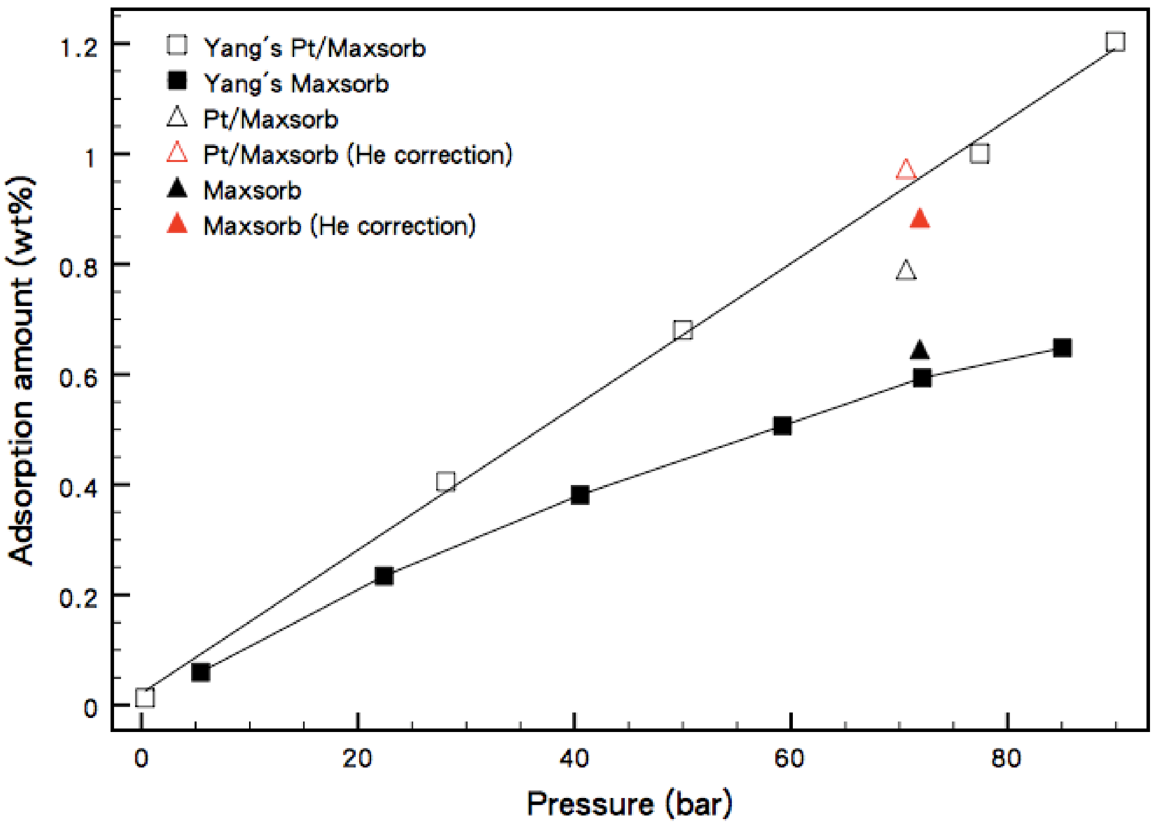
All MMOF mixed with better PtC(M)

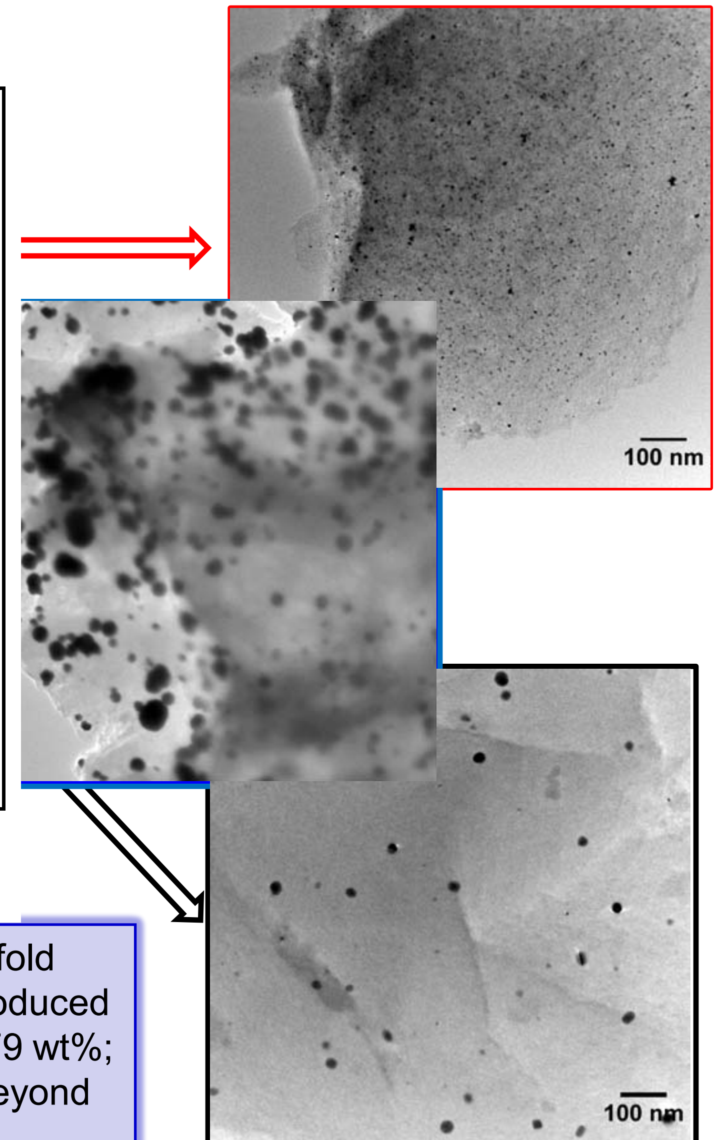
Of 2010 secondary spillover data, one out of 8 PtC/IRMOF samples has high uptake (iv). Difficult to separate out effect of surface chemistry vs. structure vs. interface.

Primary spillover has best uptake. Although moving toward direct doping was our ultimate goal, doping of MOFs and/or systematic study of surface chemistry on carbon is more difficult.

(1) Chen H; Yang RT. Langmuir. 2010 Oct;26(19):15394-8.

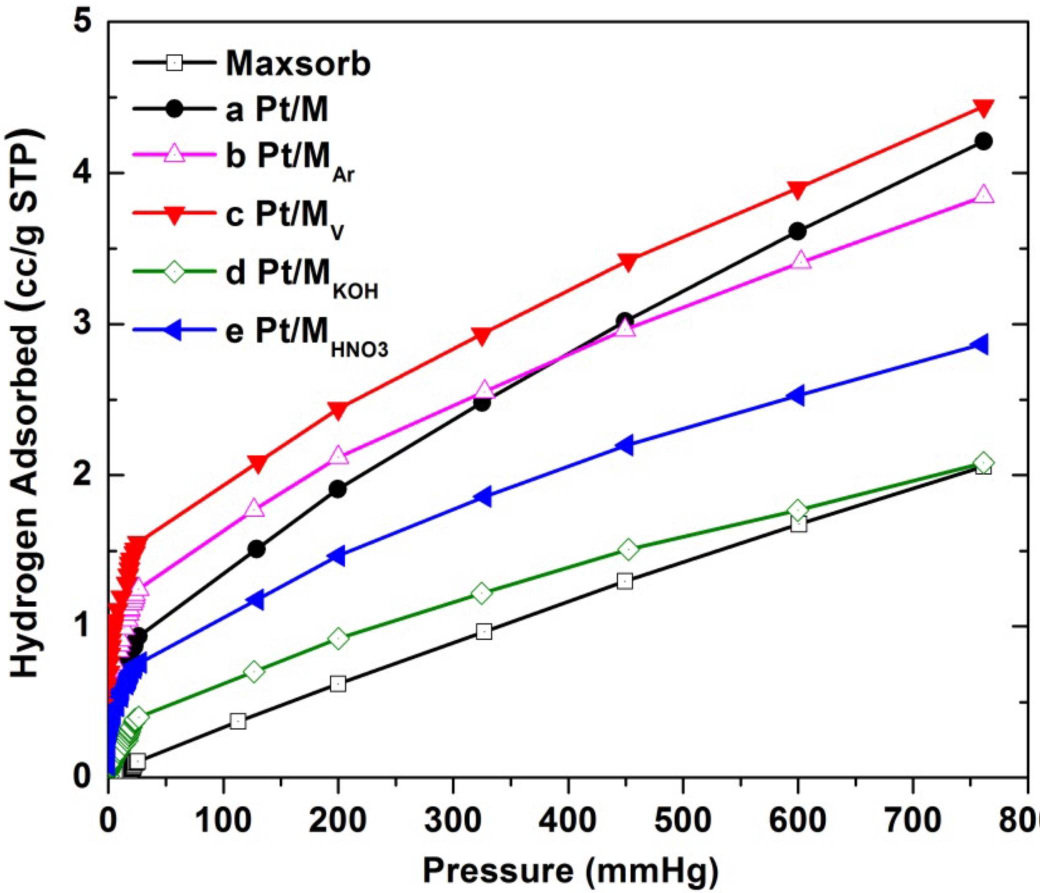
Shift Focus to Primary Spillover: Effect of Carbon Support, Catalyst Dispersion





Following Michigan doping procedure (1) increased dispersion ~3-fold and low-pressure H_2 uptake. High–pressure (71 bar) uptake reproduced from literature. Uptake of Maxsorb increased from 0.65 wt% to 0.79 wt%; beyond the margin of error, despite a decrease in surface area. Beyond margin of error, increase is 22%.

Effect of Carbon Support, Catalyst Dispersion

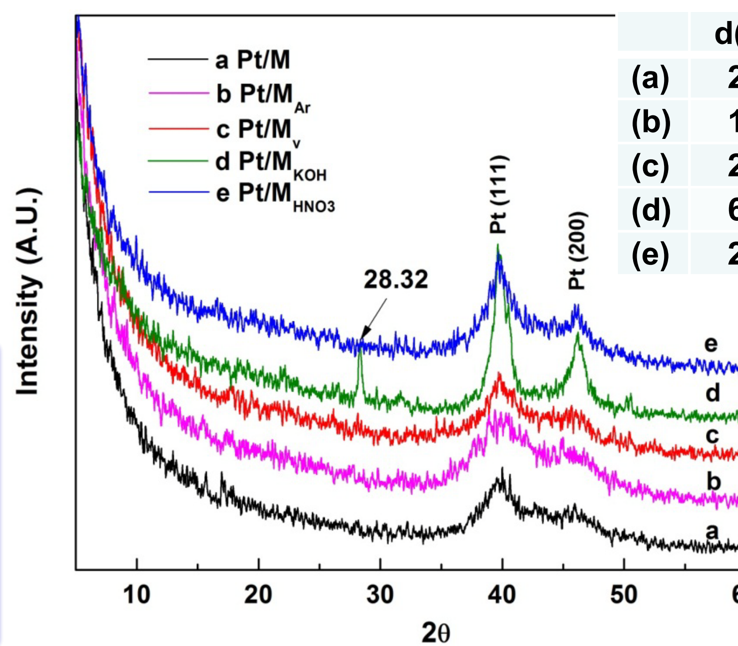


Task 1: Explore surface chemistry

Now: Explore effect on catalyst dispersion and primary spillover.

Modification of Maxsorb:

- M_{Ar}: Ar anneal 950 °C in Ar, 3 hr
- M_{V}: Vac anneal 730 °C, 3 hr
- M_{KOH}: KOH oxidation (298K)
- M_{HNO3}: HNO_3 oxidation (298K)



	d(Å)
(a)	20
(b)	16
(c)	21
(d)	63
(e)	27

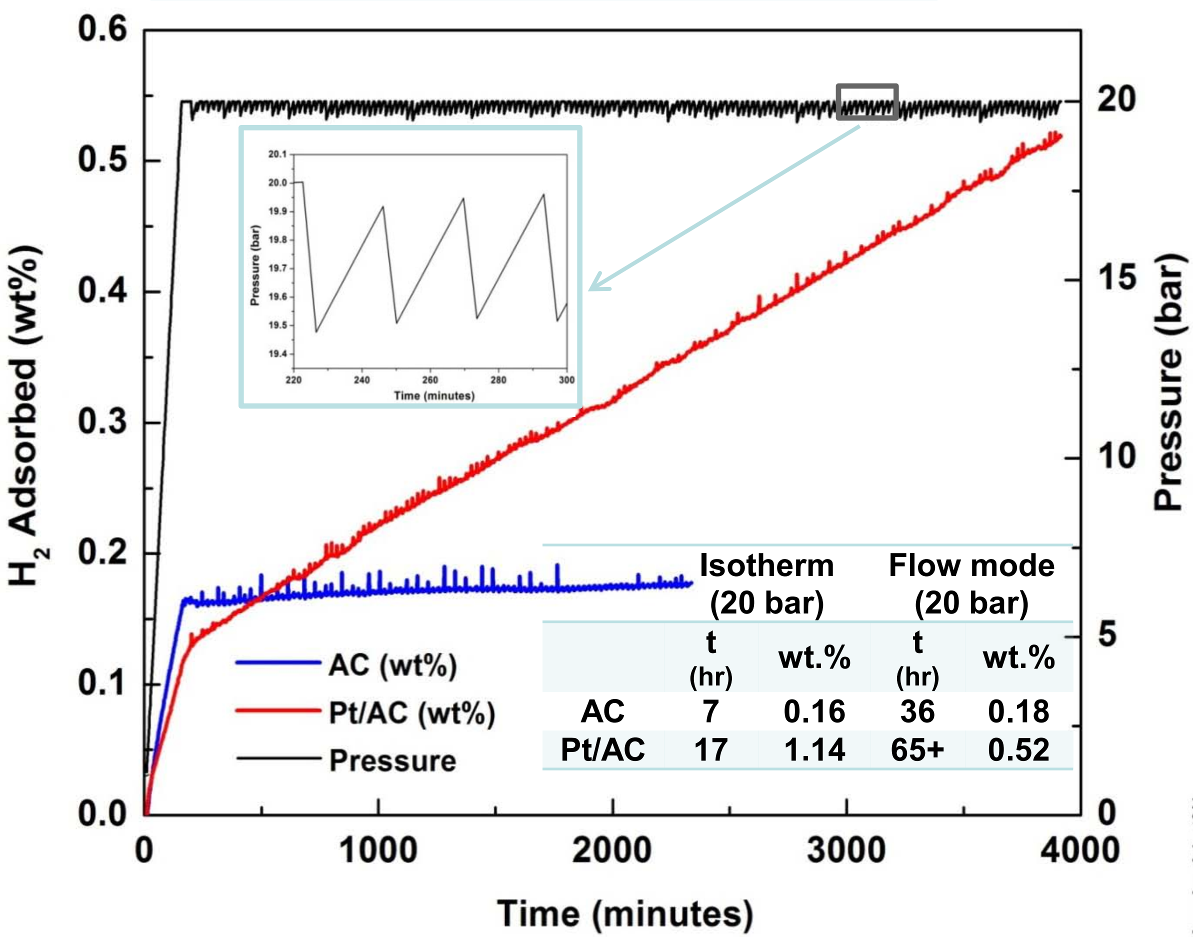
Surface chemistry of carbon support affects metal dispersion (i.e. low-pressure knee in H_2 isotherm); metal particle size (right), and slope of H_2 isotherm.

Oxidation found to increase metal particle size / lower dispersion

Strategies/Approach

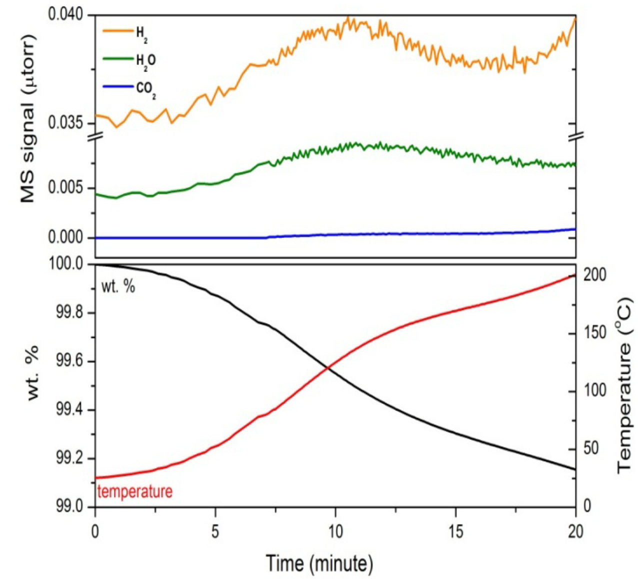
Collaboration with INER (Taiwan)

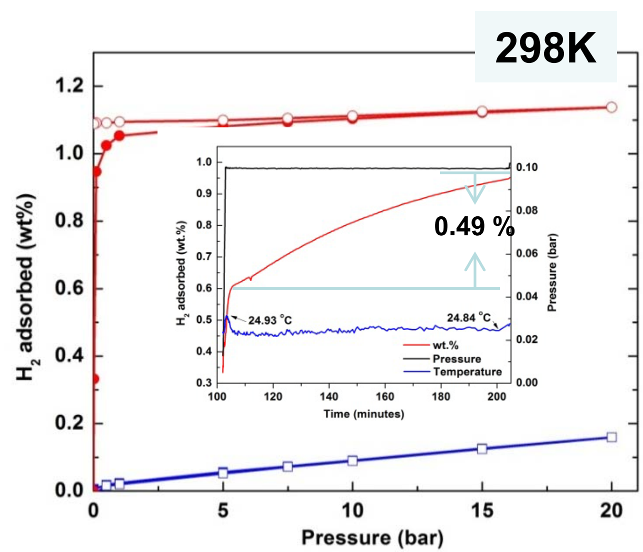
H_2 adsorption in flow mode at 25 °C



	Isotherm (20 bar)		Flow mode (20 bar)	
	t (hr)	wt.%	t (hr)	wt.%
AC	7	0.16	36	0.18
Pt/AC	17	1.14	65+	0.52

TPD-MS after 'flow' 0.5 wt%

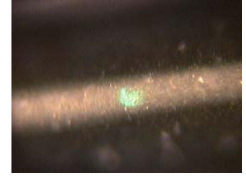


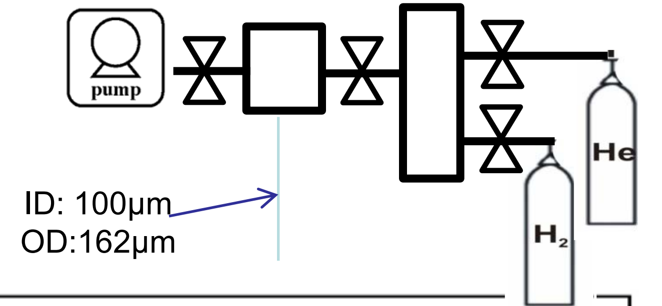


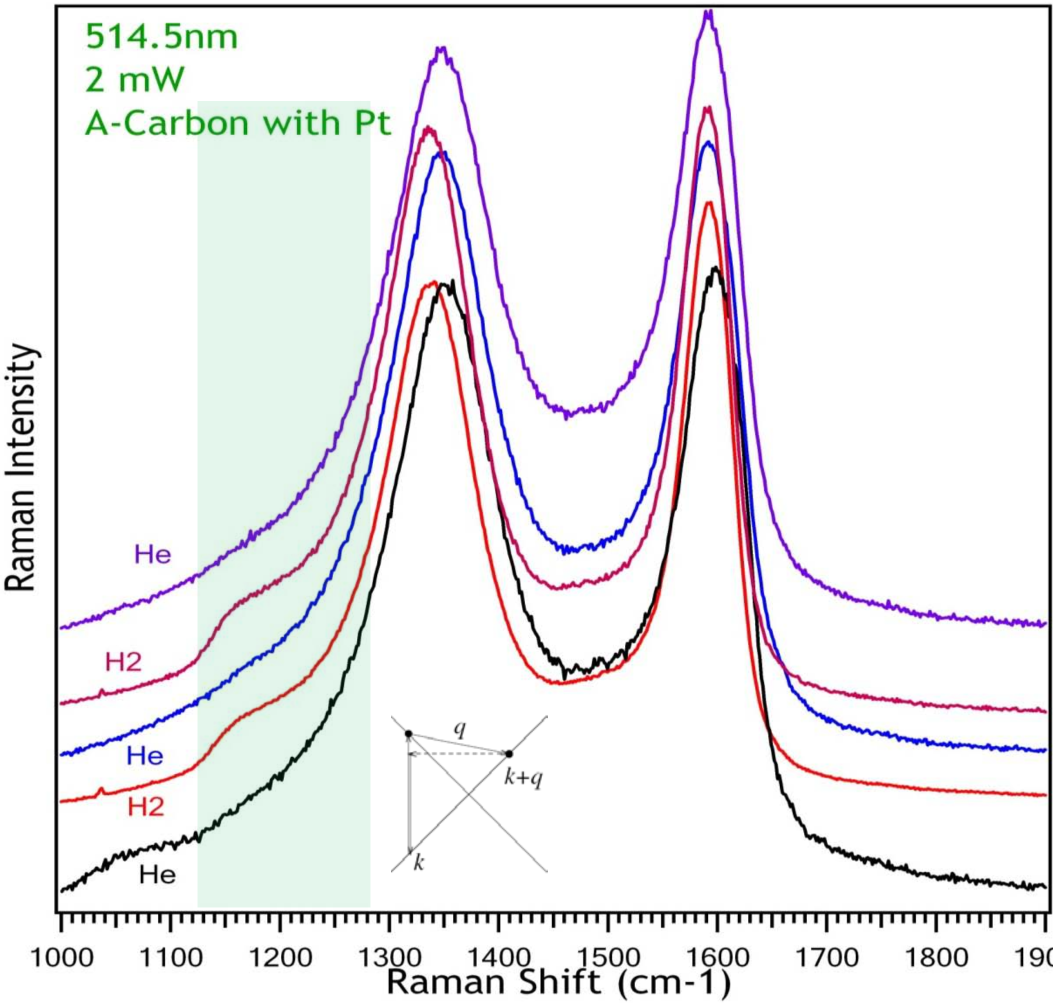
Pt/C provided by INER has unusual adsorption behavior.
Uptake is rapid at low pressure; slow at high pressure.
Continues in excess of 65 hours at 20 bar (100 cc/min).
Uptake highly dependent upon activation and age.

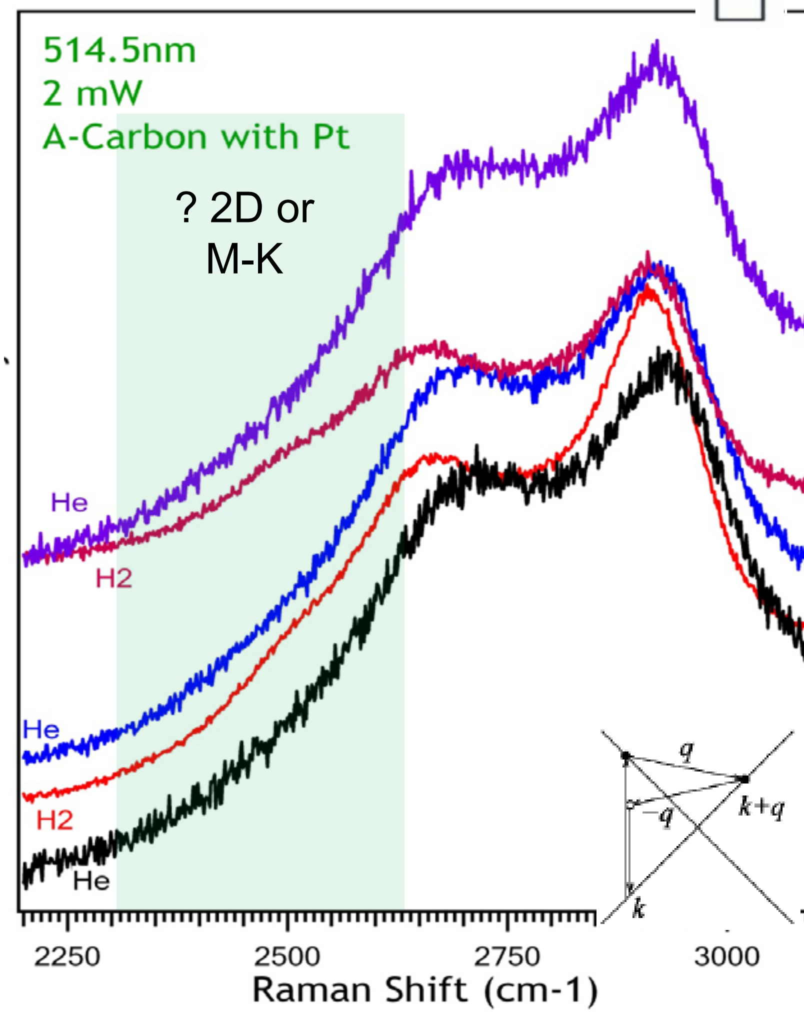
Technical Accomplishments

In Situ High-Pressure Spectroscopy *(with INER, Badding, Crespi)*









Pt/C shows Raman feature at 1200 cm^{-1} in H_2 only when activated.
Not seen for Pt, AC precursor, unactivated Pt/AC, or fiber.

Collaborations

University:

- Prof. Angela D. Lueking (Penn State) PI
- Prof. Jing Li (Rutgers) Co-PI
- Prof. Milton W. Cole (Penn State), Co-PI

Collaborations in 2011

- Prof. Ralph Yang, University of Michigan, (synthesis training)
- Tsao, INER (Taiwan Federal Laboratory)
- National Renewable Energy Laboratory (spillover, blind tests, and measurements)
- Badding and Crespi (PSU, in situ characterization)

Pending Collaborations / On-going discussions

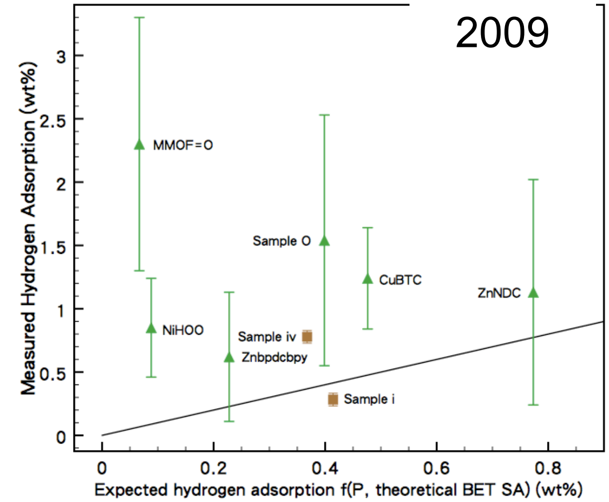
- Prof. Adri Van Dunn, Penn State (Multi-scale modeling)

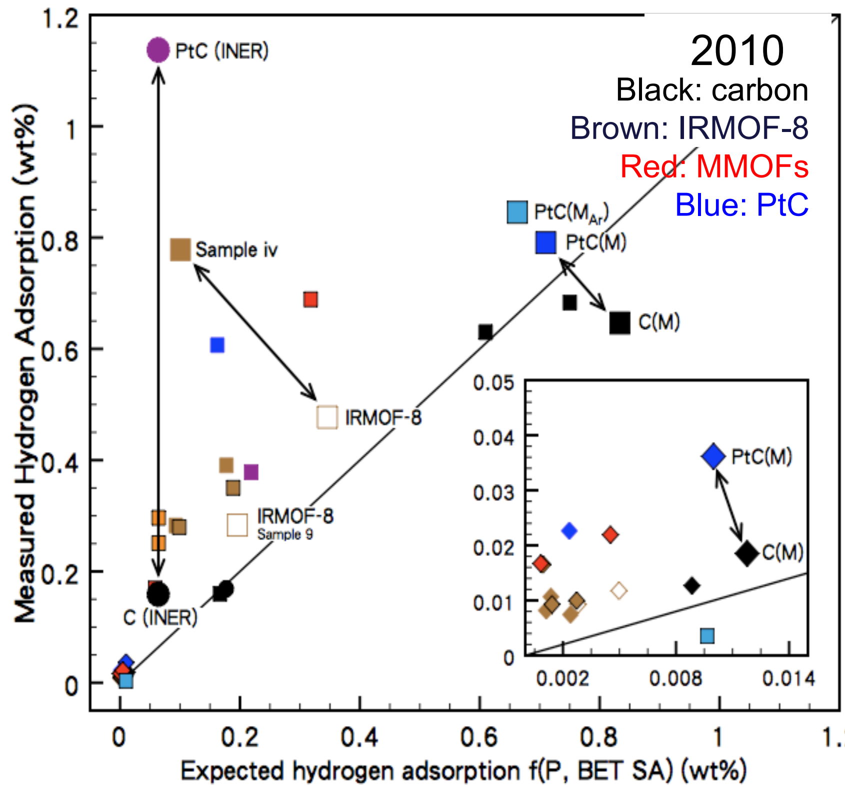
Summary

- Improvements made in differential volumetric measurements. Error propagation and analysis shows new Method BC and MS-BC have minimal effect of valve volume, temperature, and potential volume errors
- Most promising *reproducible* results of the past year are for primary spillover directly to carbon.
  - Mixing MMOF and catalyst may be more of an art than a science. Subtle structure changes in PtC/MMOF samples with high uptake.
  - Improvements in primary spillover catalyst did not translate to improvements in secondary spillover to MMOF, suggesting poor contact
  - *2009 data of 2.5 wt% cannot be discounted, but* synthesis *is not completely reproducible.*

For Primary Spillover:

- PtC(M_{Ar}) 0.85 wt% ; 1.03 wt% (He) at 70 bar
  - *Studies on-going; PtC(M_V) expected improvement*
- PtC(INER) 1.14 wt% at 20 bar
  - *TPD on-going*





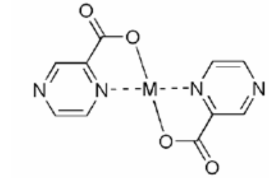
Arrows represent samples showing >20% enhancement due to spillover.

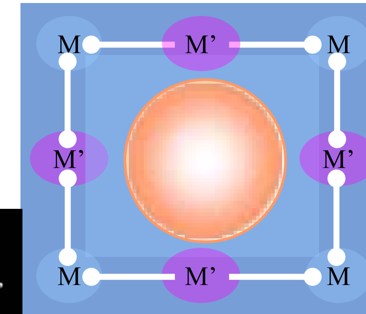
Future Work

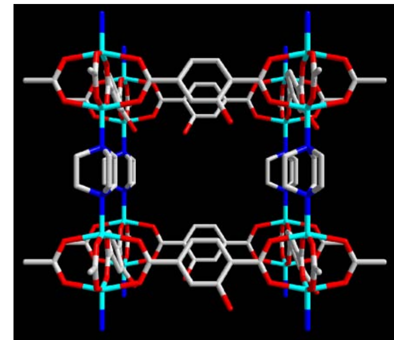
- Direct catalytic doping of MMOF
- New ways to approach carbon-MMOF-catalyst mixing
- Resolve effect of O vs. C on spillover vs. doping
- Resolve gravimetric and volumetric discrepancies seen for *spillover samples only*
- Incorporate TPD into gravimetric studies
- Write paper on volumetric improvements

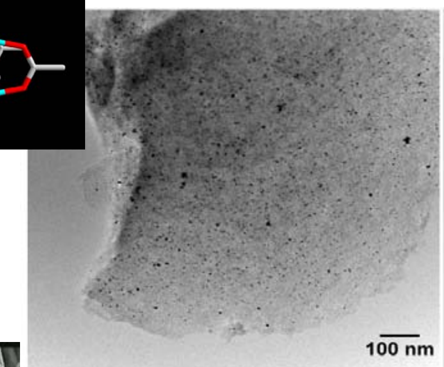
Related Collaborative Work

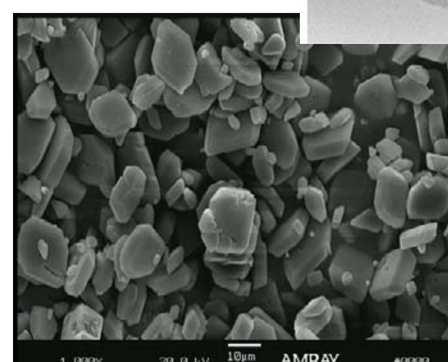
- Continued measurement of Tsao et al. sample.
- Confirm in situ measurements with D_2 and theoretical calculations
- Multi-scale modeling of spillover

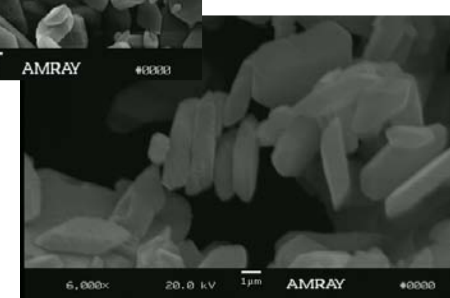










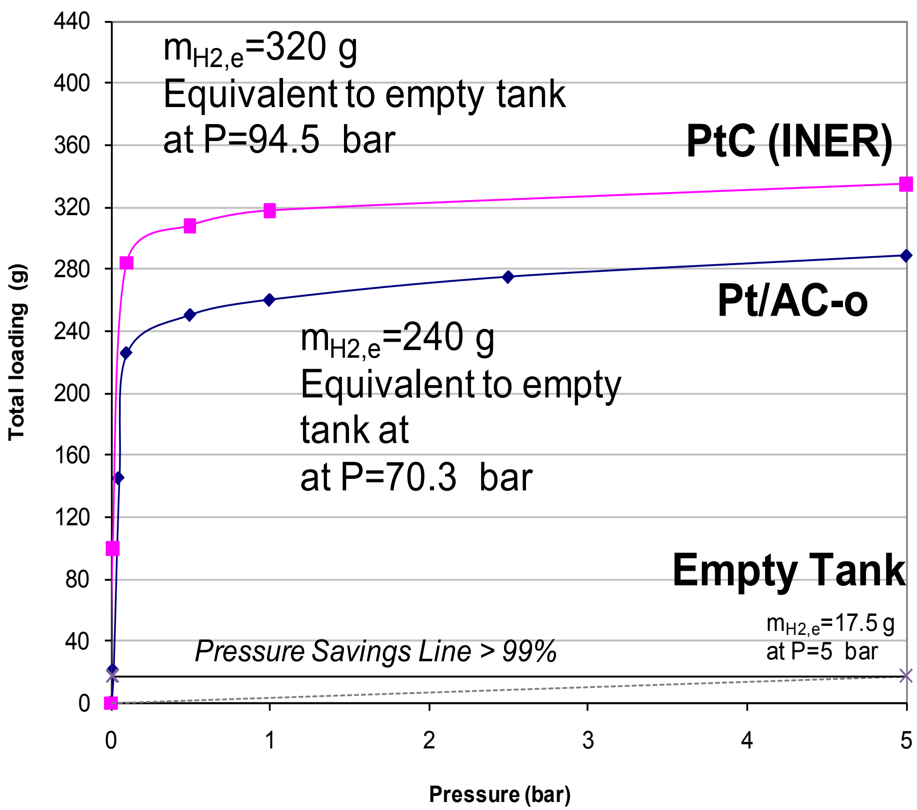


Technical Back-Up Slides

Strategies / Approach:

Pressure Savings[1] Offered by Spillover

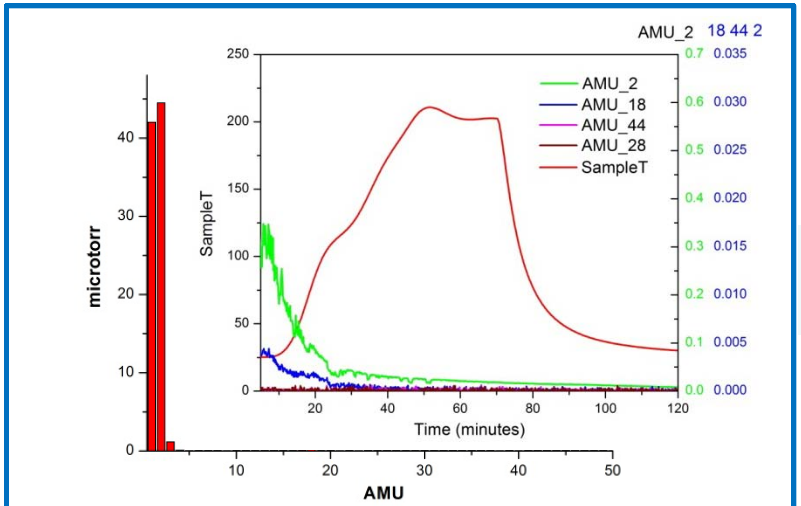
[1]Zielinski, J. M.; McKeon, P.; Kimak, M. F., *Ind. & Eng. Chem. Res.* **2007,** *46,* 329-335



- Introduced to account for system weight
- Lower P enables reduced wall thickness meaning and less robust, lighter container.
- Also accounts for isotherm shape: Consider (left) total H_2 tank loading at 294 K
  - 1: 'Break Even point': GX31 carbon and empty vessel have same H_2 loading
  - >1: Detrimental to add GX31
  - 2: Pressure at which the sorbent is most advantageous
  - Projected 3-fold improvement (■) in adsorbent provides advantages over much larger P range

A unique aspect of this work will be consideration of P savings, and consideration of system weight and impacts of isotherm shape. *Must be accompanied by TPD.*

H_2O & gravimetric measurement (IGA)

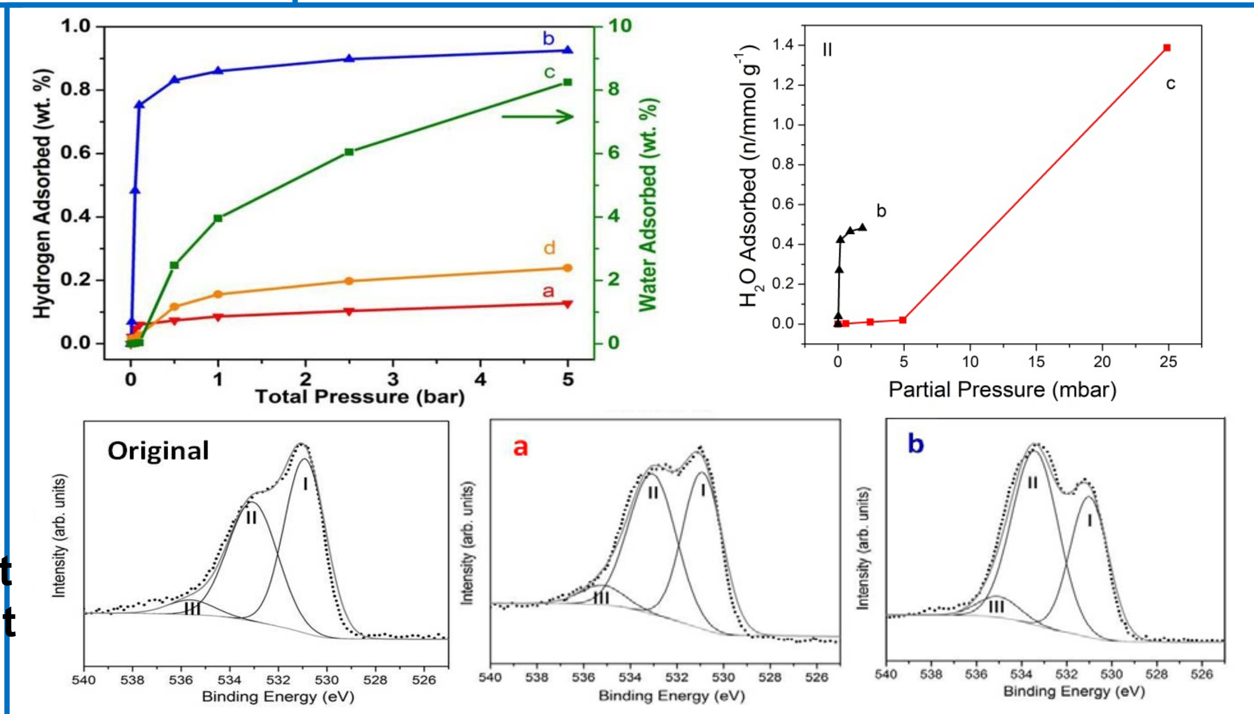


1. 99.9999 purity H_2 and T-purge valve

2. MS check before and after H_2 isotherm

3. H_2O adsorption on Pt/AC *

***Li&Lueking, JPCC, 2011**



Plot a: with "dry" treatment
Plot b: with "wet" treatment
Plot C: H_2O adsorption

Measurement- Operating Equations & Error

Single-Sided

$$dN_{SS} = P_A^o v_A + P_{AS}^o v_{AS} - P_A v_{AAS}$$

$$\Delta n_{ads\,err} = \frac{P\,\Delta V_{Tot}}{R\,T\,z(P,T)}$$

*NREL

Method V

$$dN_V = \mathrm{X} + v_{AAS} dP$$

$$\mathrm{X} = P_A^o v_A + P_{AS}^o v_{AS} - \frac{v_{AAS}}{v_{BBS}}(P_B^o v_B + P_{BS}^o v_{BS})$$

$$\varepsilon_V \sim \left(\frac{dP}{v_A * RTz} * v_{AAS} \right) \varepsilon_{v_A} + \frac{v_{AS}\varepsilon_{dP}}{RTz}$$

Method BC

$$dN_{BC} = v_{AAS}(dP - dP_{BC})$$

$$\varepsilon_{BC} = \frac{(dP - dP^{BC})\varepsilon_{v_{AAS}}}{RTz}$$

Method MS-BC

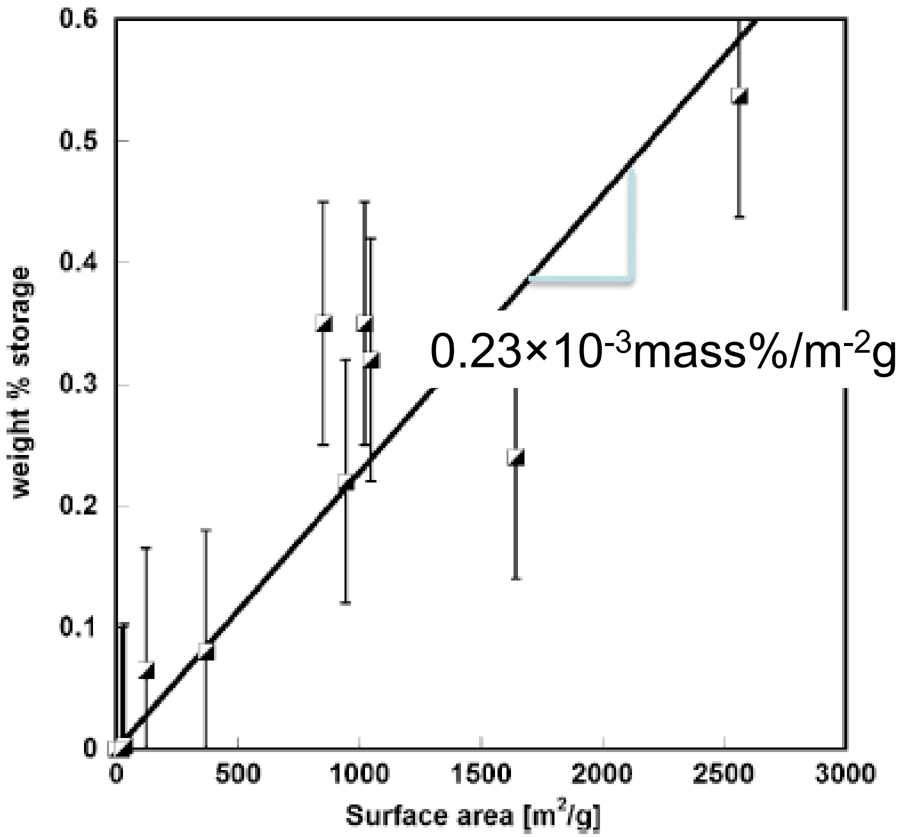
$$dN_{MS-BC} = v_{AAS}(dP^i - dP_{BC}^i) - v_{AS} * (dP^{i-1} - dP_{BC}^{i-1})$$

$$\varepsilon_{MS-BC} = \frac{(dP^i - dP_{BC}^i)\varepsilon_{v_{AAS}} - (dP^{i-1} - dP_{BC}^{i-1})\varepsilon_{v_{AS}}}{RTz}$$

Differential equipment may have different ways of processing the data.

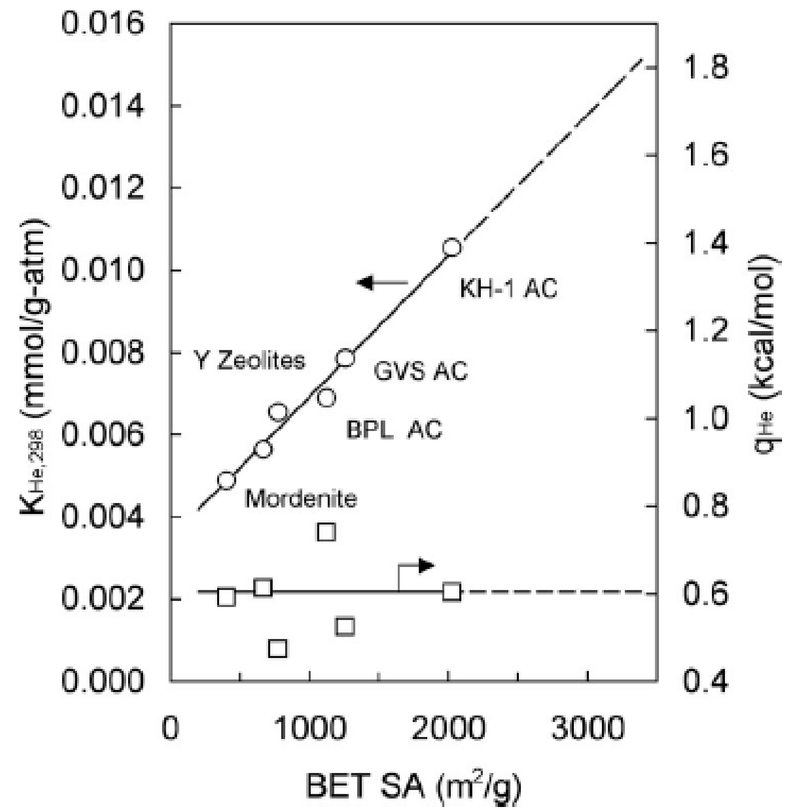
Calculations

Expected H_2 adsorption



(1) Panella, B.; Hirscher, M.; and Roth, S. *Carbon. 2005, 43, 2209-2214.*

He corrected adsorption

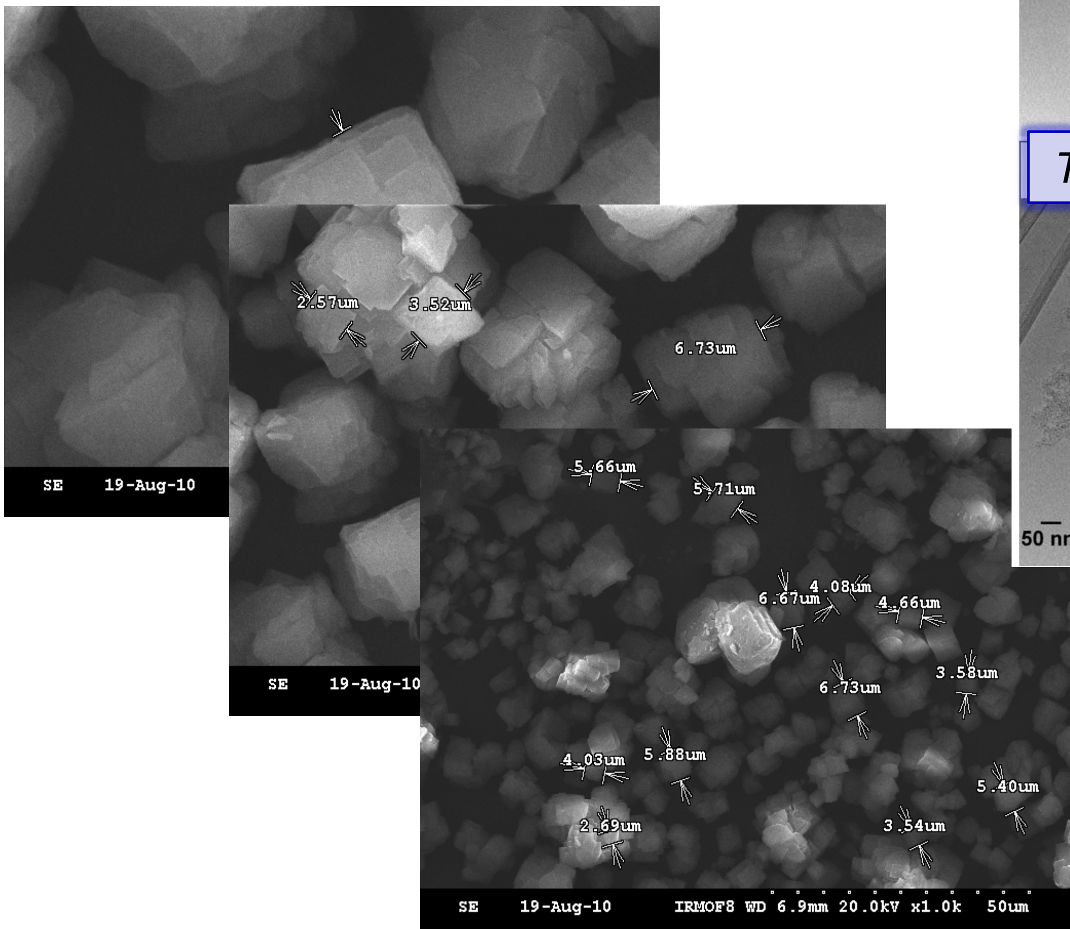


$$K_{He,298} = 3.44 \times 10^{-6} SSA + 3.49 \times 10^{-3}$$

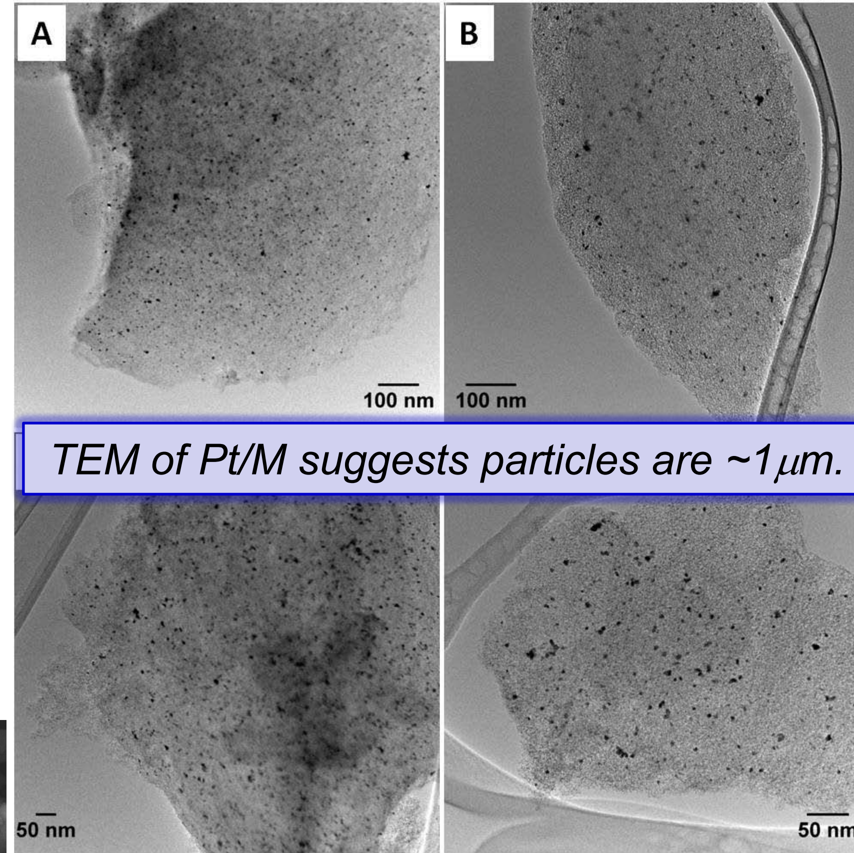
(2) Lachawiec Jr, A. J.; DiRaimondo, T. R.; and Yang, R. T. *Review of Scientific Instruments. 2008, 79, 063906.*

Supplemental Slides

Particle Size



The SEM of IRMOF-8 is from PSU; roughly cubic with size ranging from 3-10μm.



TEM of Pt/M suggests particles are ~1μm.

The SEM of MMOF=O is from RU; roughly 1x10μm rods.