

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

Angela D. Lueking,¹ Jing Li,² Milton W. Cole¹

¹Penn State University, ²Rutgers University

June 9, 2010

ST024

Overview

Timeline

- Start - Feb 2009
- End - Aug 2013
- ~25% Complete

Budget

- Total project funding
\$2,038,257
 - DOE Share: \$1,511,367
 - Contractor Share: \$526,890
(\$172,269 Rutgers,
\$354,621 PSU)
- \$350K FY09
- \$300K FY10

Barriers

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

Partners

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

Objectives - Relevance

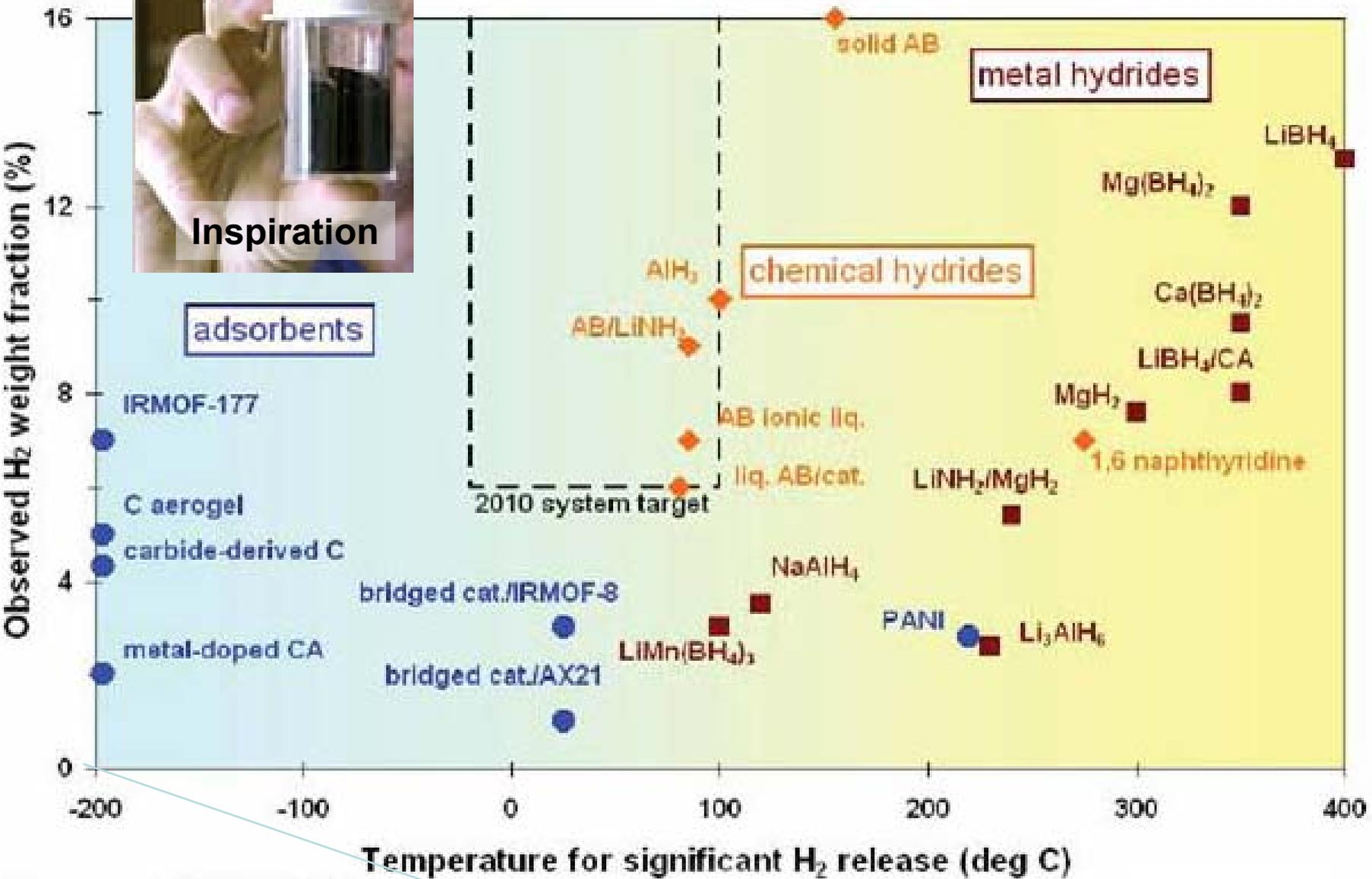
The **overarching objective** is to synthesize designer microporous¹ metal-organic frameworks (MMOFs) mixed with catalysts to enable H-spillover for H₂ storage at 300K-400K and moderate *P*s.

In the past year (June '09.- May '10.), we have:

- A. Synthesized eight MMOF structures with variations in surface chemistry, pore diameter, and pore structure, and surface area measurements (RU)
- B. Adapted volumetric measurements to enable rapid screening tests (RSTs) at high-pressure, towards Go/No-Go Decision Point (PSU)
- C. Validated RSTs against published activated carbon and spillover materials at $P \leq 80$ bar and 298 K (PSU)
- D. Initial screening via RST secondary spillover tests shows 2.4 wt% (excess) achieved at 300K, 80 bar relative to 1.5 wt% benchmark (PSU & RU)
- E. Demonstrated importance of preparation conditions on uptake: 3-fold enhancement in published literature with proper activation (PSU)
- F. Explore methods for pressure-induced hydrogen/gas trapping (PSU & RU)

¹ $d < 2\text{nm}$ (IUPAC)

System weight often not considered.
Pressure considerations affect system weight.



adsorbents

metal hydrides

chemical hydrides

2010 system target

Temperature for significant H₂ release (deg C)

G. Thomas, et al., DOE (April 2007)

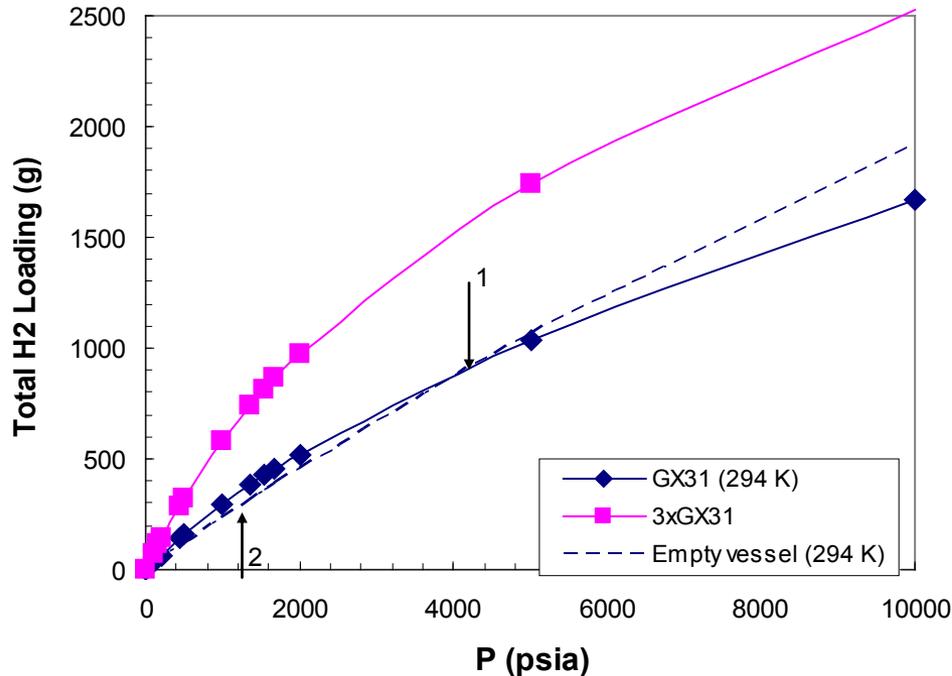
P...??

Source: U.S. DOE

Pressure Savings¹

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

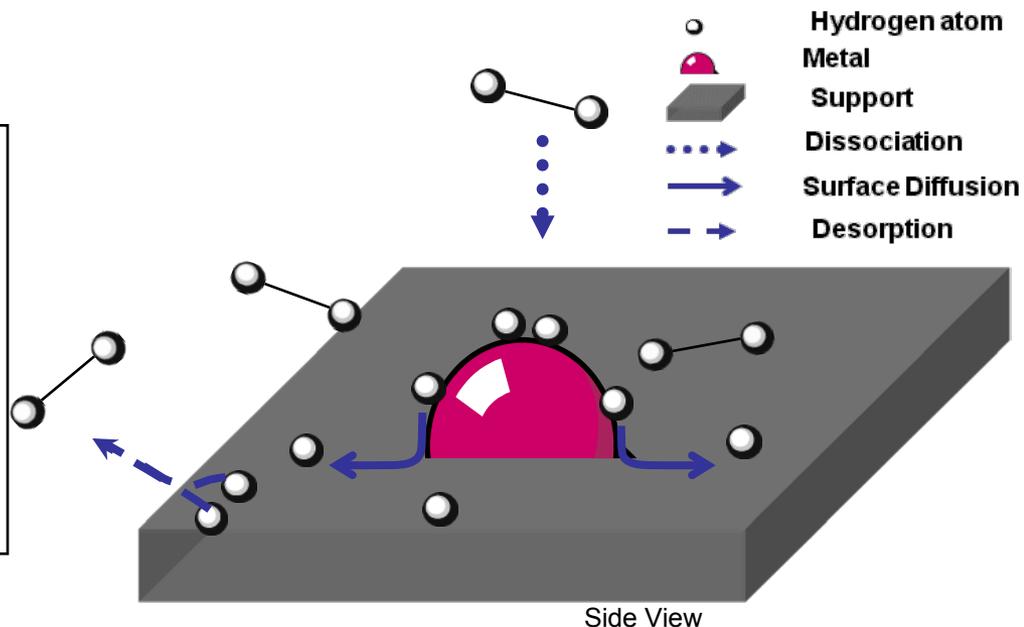
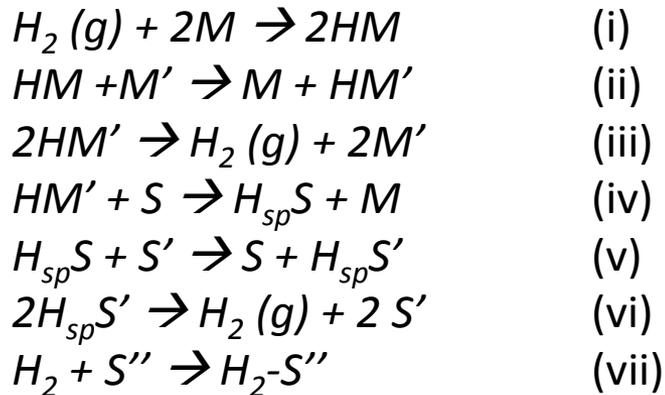
$$n_{H_2} = \frac{PV_E}{zRT} + M_s P \left[K(T, P) - \frac{1}{\rho_s zRT} \right]$$



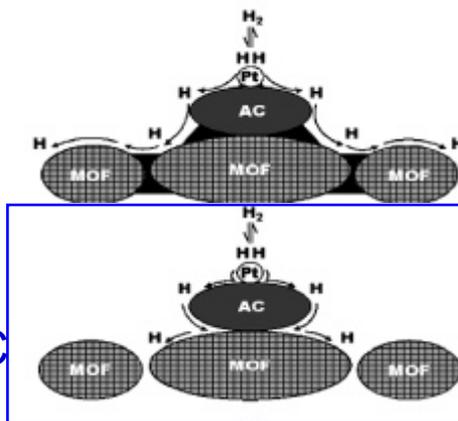
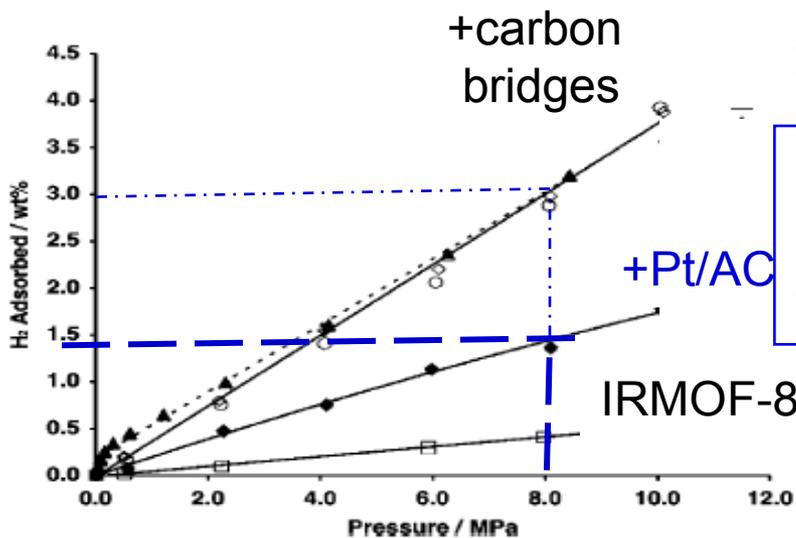
A unique aspect of this work will be consideration of P savings, and consideration of system weight and impacts of isotherm shape.

- 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 H₂ tank loading at 294 K
 - 1: ‘Break Even point’: GX31 carbon and empty vessel have same H₂ 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

Hydrogen Spillover



Box 1: Reaction sequence for hydrogen spillover.



MMOFs exceeding benchmark data (left) will be used for detailed mechanistic studies.

Secondary Spillover studies (box, left) will be used to screen new MMOFs maintaining well-characterized surface and constant H supply.

Measurement

Method Modification to enable rapid screening of new MMOFs.

Down select for more detailed mechanistic studies.

All uptakes reported are excess adsorption.

Proposed
& 2009

Change in
2010
1 step

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

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

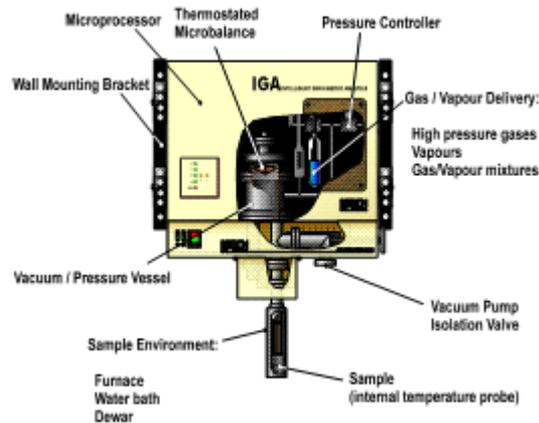
For 100 mg sample: $\pm 0.01 \text{ wt}\%^1$

$\pm 0.1 \text{ wt}\%^2$ [0.2 wt%¹]

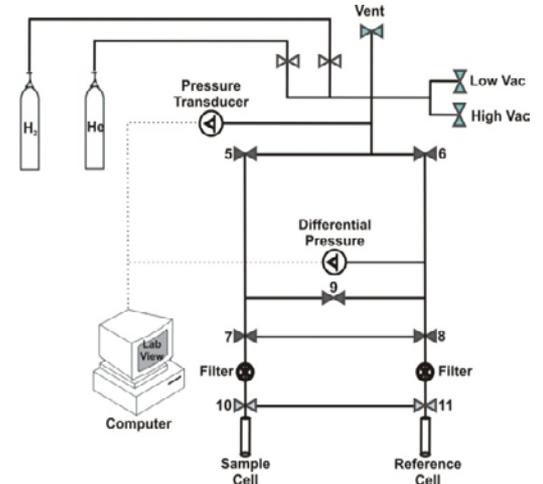
¹Error Propagation
²GX31 Measure



**Micromeritics
Volumetric
2020 (≤ 1 bar)**



**Hidden Gravimetric Analyzer
with In-line Mass
Spectrometer (≤ 20 bar)**



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

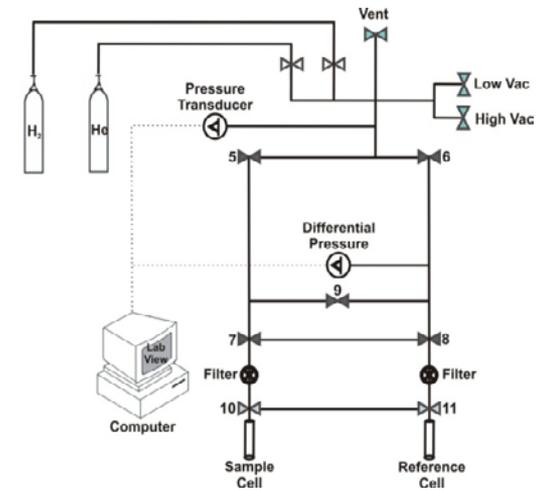
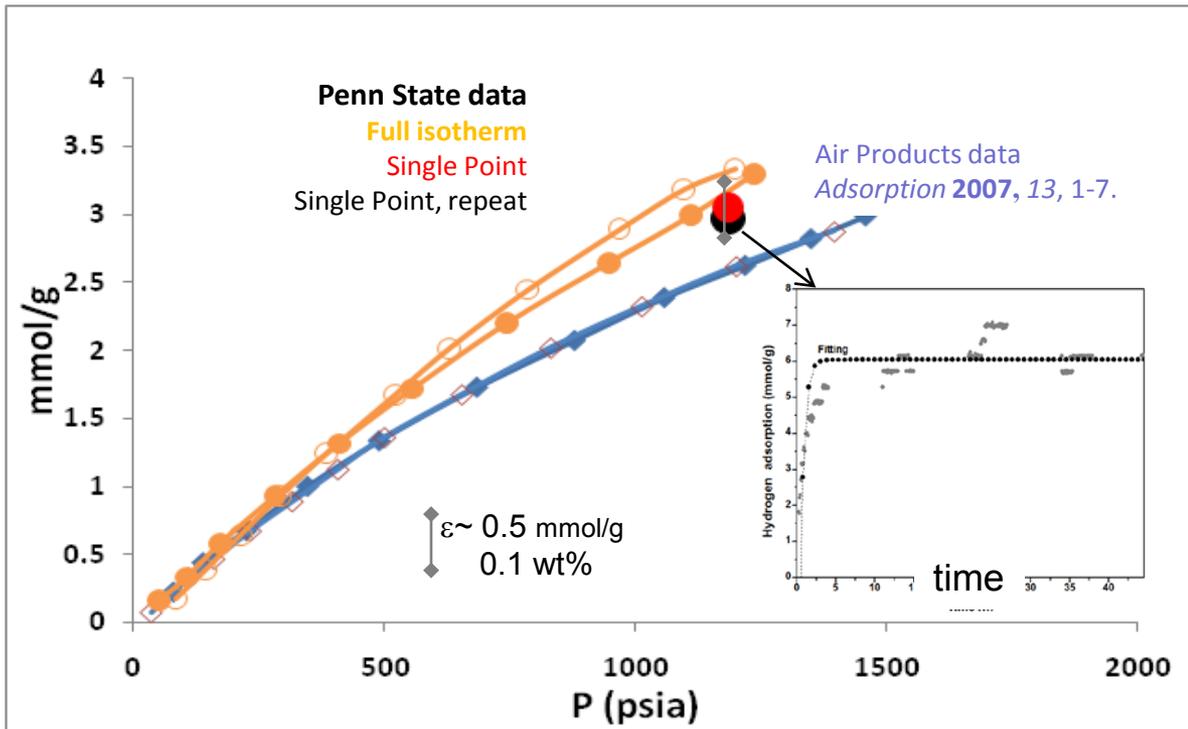
Method adaptation and validation.

Single step isotherm at 80 bar designed to allow tracking of **full kinetics** of adsorption and desorption. Kinetics anticipated to shed light on mechanism and rate limiting step.

Modification after detailed error analysis to optimize design.

Validation against published data for GX-31 activated carbon (below) and Pt/C + IRMOF-8 (slide 17).

Change in
2010
1 step



Custom-Built Differential Sievert's Apparatus
($< 100 \text{ bar}$)

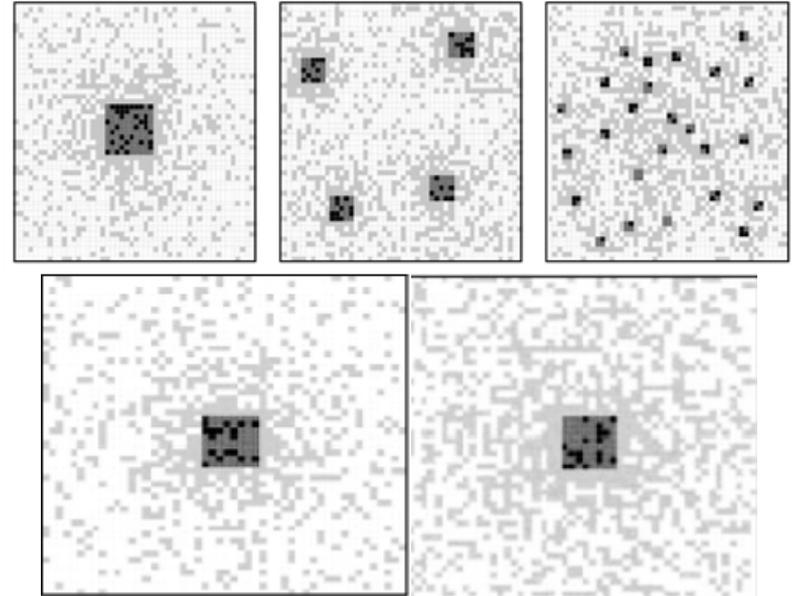
Material Design

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.)

To enable P savings:

- Build in T- and P- switches into material to separately optimize adsorption vs. desorption



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.

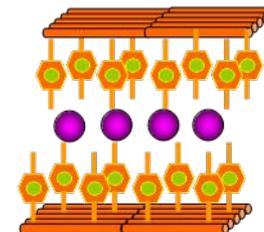
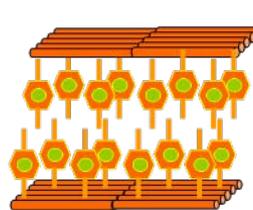
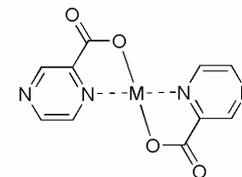
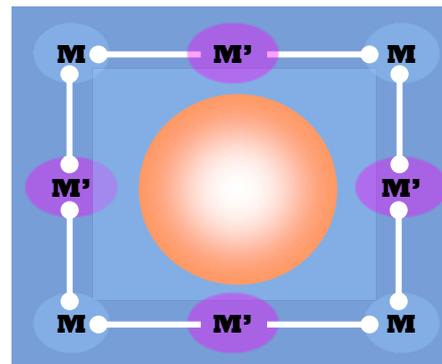
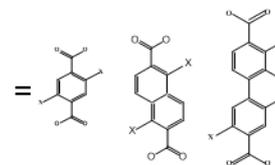
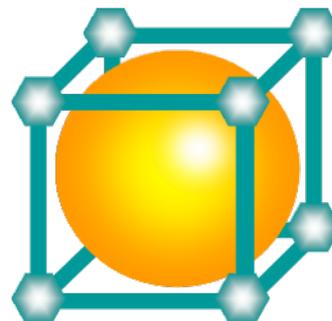
Material Design

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.)

To enable P savings:

- Build in T- and P- switches into material to separately optimize adsorption vs. desorption



Material Design

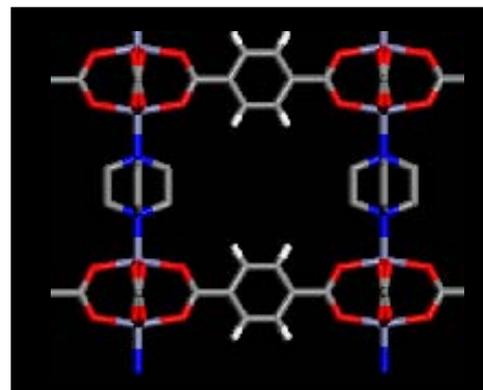
To increase uptake via Hydrogen Spillover Mechanism:

- Maximize metal dispersion
- Optimize hydrogen receptors to increase surface residence time → Surface Chemistry
- Change rate limiting step
 - Porosity?
 - Metal-Carbon Interface (Yang et al.)

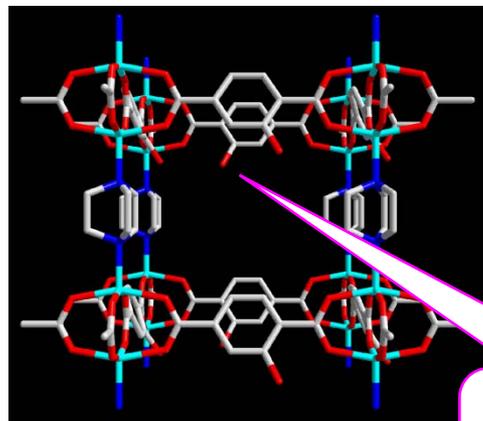
To enable P savings:

- Build in T- and P- switches into material to separately optimize adsorption vs. desorption

Specific Example: Introduction of O functional group expected to increase residence time of metastable H species. Ligand stability prevents H₂O formation.



MMOF



MMOF-O

Internal surface is modified by oxygen atoms

Approach:

Upcoming Milestones

- Correlation between spillover and MMOF functional groups, (Yr. 2-- FY10) leading to:
 - H₂ uptake > 1 wt% at 20 bar and 300K;
 - Extrapolation suggests > 4 wt% at 100 bar, or
 - 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
 - Improved performance relative to Pt-C catalysts

Go/No-Go Decision Point.

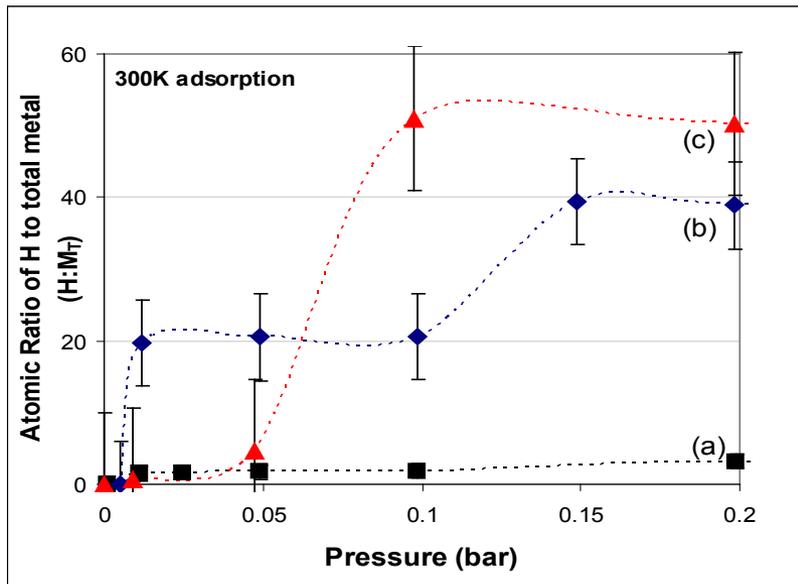
Exceed 5.5 wt% hydrogen storage through the use of the “hydrogen spillover” mechanism, MOF material, or a combination of the two as proposed at moderate temperatures (i.e. 300-400 K) and 100 bar with anticipated system penalties (Go/No Go: 3Q Year 2).

Technical Barriers

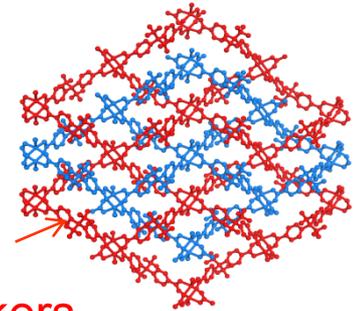
- Project addresses gravimetric uptake, including system weight
- Moderate temperature
- Track kinetics and capacity of spillover; mechanistic studies and reproducibility

Previous (2009) Results

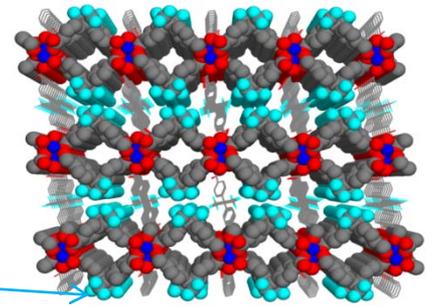
Explore the effect of surface chemistry, porosity, and structure on hydrogen spillover



(c)
+Zn(bdc)(ted)
Carbon-based linkers



(b)
+ Cu(hfipbb)
Incorporated
surface
sites for increased
H-bonding



(a) 5% Pt/C catalyst

Use of a spillover catalyst (5% Pt/C, mixed 9:1 with grinding) increases T_{ads} to 300K. MMOFs can increase the uptake by providing specific H-bonding sites that accept spilled over H* when mixed 9:1 with Pt/AC. Above, (b) surface chemistry may play a role at very low pressure, then (c) enhanced porosity may dominate.

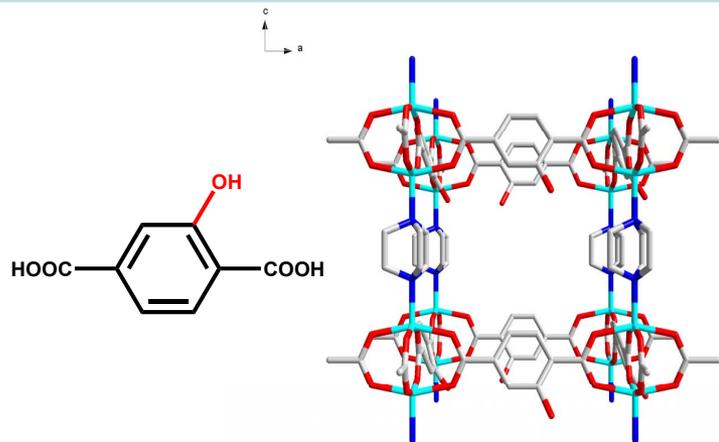
Technical Accomplishments

Synthesis of Eight MMOFs—Illustrative examples

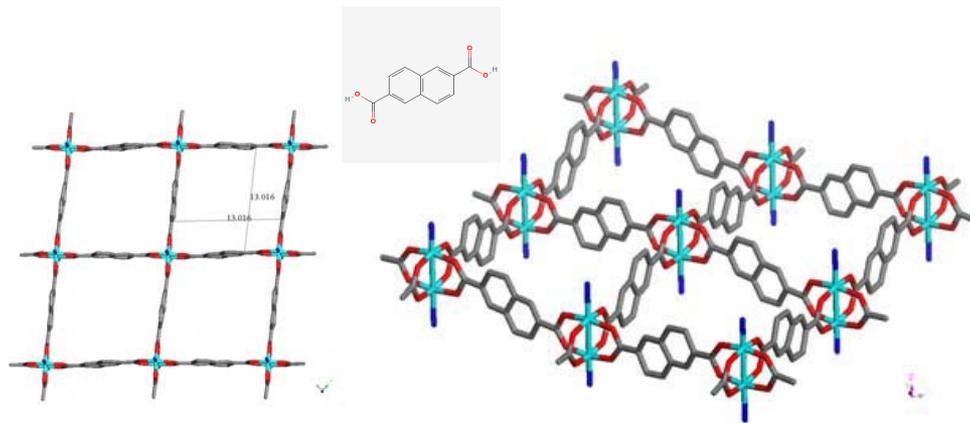


1023 m²/g (L)

1133 m²/g (BET)

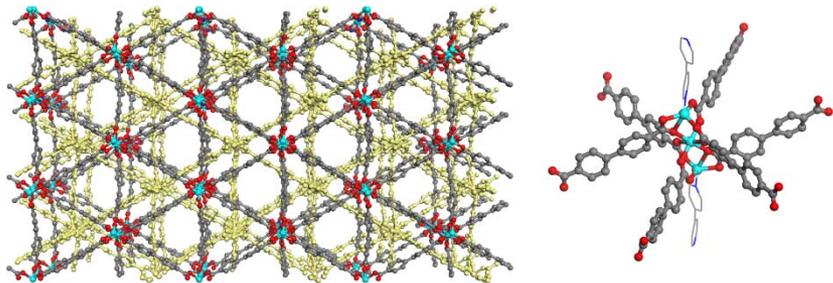


2647 m²/g (L)



792 m²/g (BET)

Adv. Mater. 2005, 17, 2703

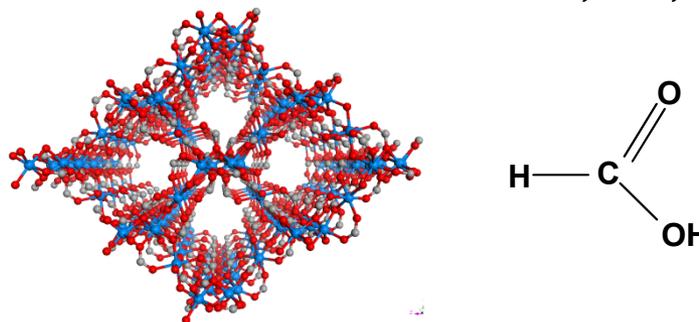


354 m²/g (L)



304 m²/g (BET)

Adv. Func. Mater. 18, 2008, 2205



Suite of Eight MMOFs synthesized with variations in surface chemistry, pore diameter, structure.
Used in initial down-select (now in process).

Technical Accomplishments

Synthesis of Eight MMOFs—Illustrative examples

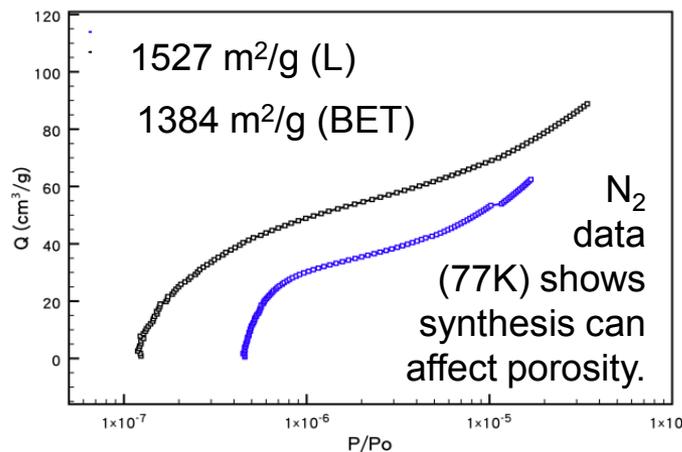
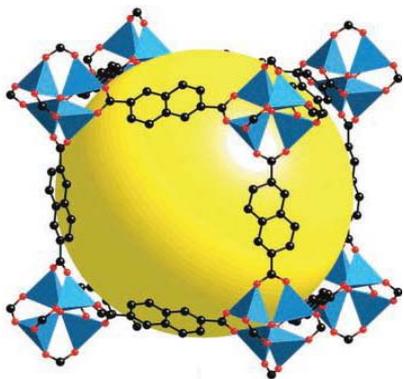


1527 m²/g (L)



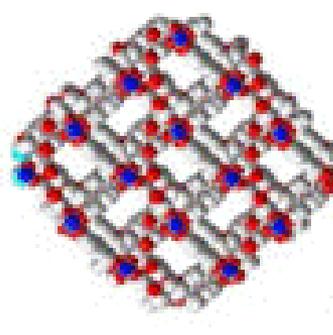
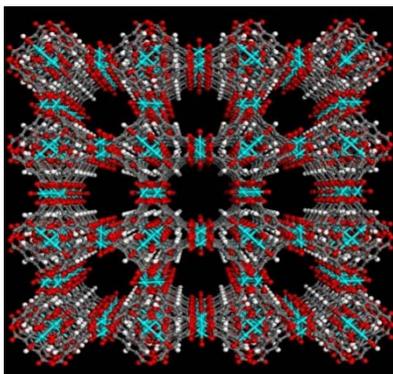
1384 m²/g (BET)

JACS 2004, 126, 5666-5667



1874 m²/g (L)

1641 m²/g (BET)



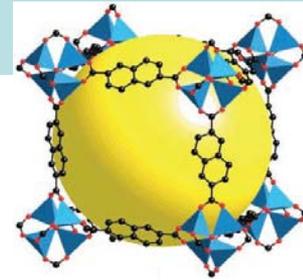
Suite of MMOFs synthesized with variations in surface chemistry, pore diameter, structure. Used in initial down-select (now in process).

Structure Characterization

	Zn ₃ (BPDC) ₃ (BPY)	Co(FA)*	Ni(NDC)(TED) _{0.5} *	Zn(BDC-OH)(TED) _{0.5}
Large Cage dimensions	(~ 10.6 Å × 10.6 Å × 5 Å)	~ 5-6 Å	7.5 Å × 7.5 Å (c) 4.8 Å × 3.2 Å (a-b-) 7.8 Å (Ar)	5.0 Å (N ₂)
Window size (Å)	~ 8 Å	1.4 × 5.3	Same as cage	Same as cage
Pore volume (cm ³ /g)	0.33	0.14	0.73	0.56
Surface area (m ² /g)	792 (BET)	354 (Langmuir) 304 (BET)	2015 (Langmuir)	1111 (Langmuir) 1023 (BET)
Activation Temperature	100 °C	150 °C	100 °C	170 °C
Thermal Stability (TGA)	> 200 °C	> 250 °C	> 200 °C	Up to 250 °C
Reference	<i>Advanced Materials</i> 2005 , 17, 2703	<i>Advanced Functional Materials</i> 2008 , 18, 2205		

*Isostructural compounds used as preliminary reference

Suite of MMOFs synthesized with variations in surface chemistry, pore diameter, structure. Used in initial down-select (now in process).

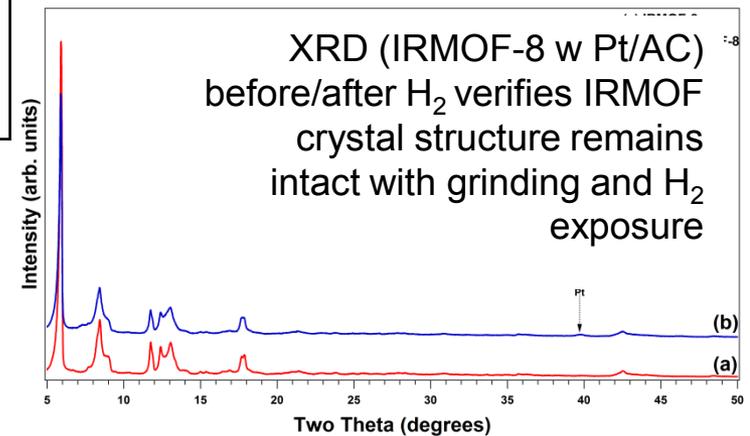
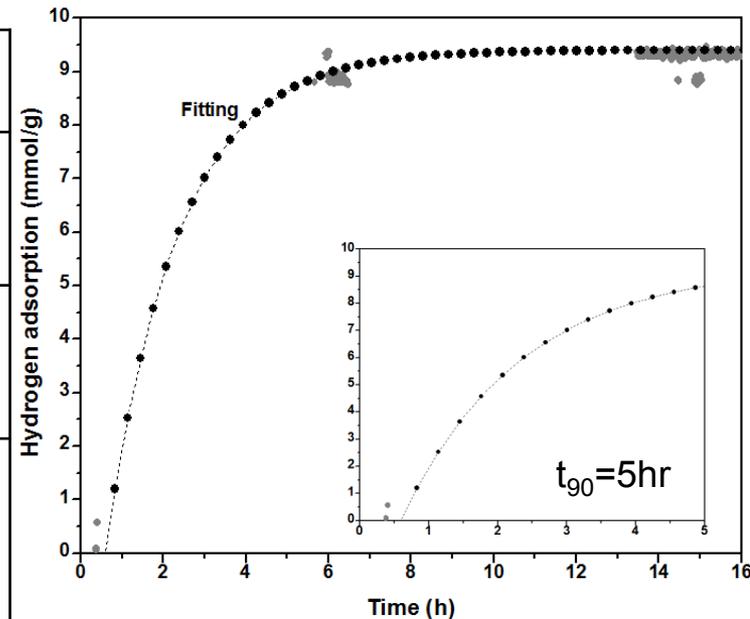


Technical Accomplishments

Validation and Establishing a Benchmark

Literature data for Spillover to IRMOF8 (298K)

Sample	Pressure (bar)	Wt.% of Hydrogen	Reference
IRMOF-8 +5%Pt/AC +Bridge	20,70, & 100 20,80, & 100 20,70, & 100	0.09,0.37,0.52 0.38,1.4,1.80 0.74,2.68,3.94	Yang et al. JACS. 2006,128,8136
IRMOF-8 +5%Pt/AC +Bridge	20 & 70	0.70,2.35	Miller et al. J. Phys. Chem. C 2009,113,3222
IRMOF-8 +5%Pt/AC +Bridge	70	4.70 (72h)	Tsao et al. JACS. 2009, 131,1404
5%Pt/AC +IRMOF-8	80	1.5	Ours



Benchmark data

Meets or exceeds benchmark

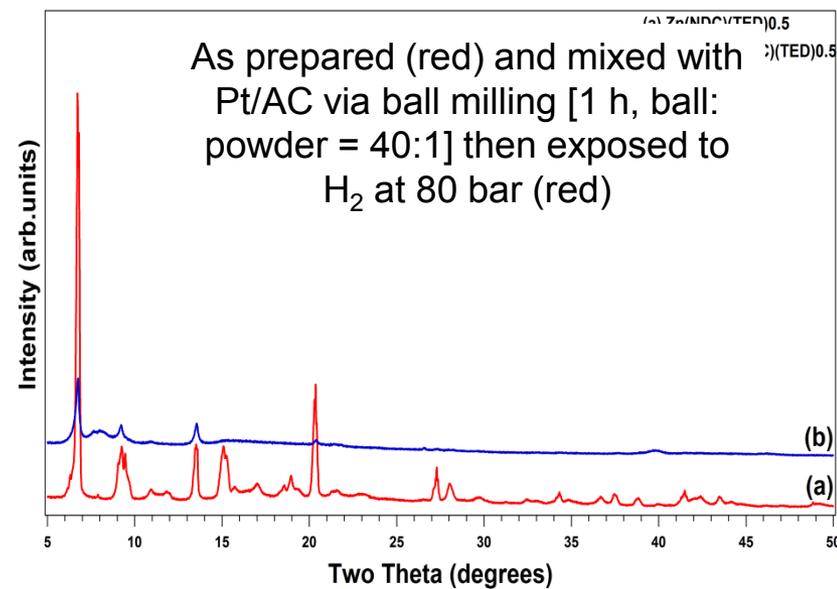
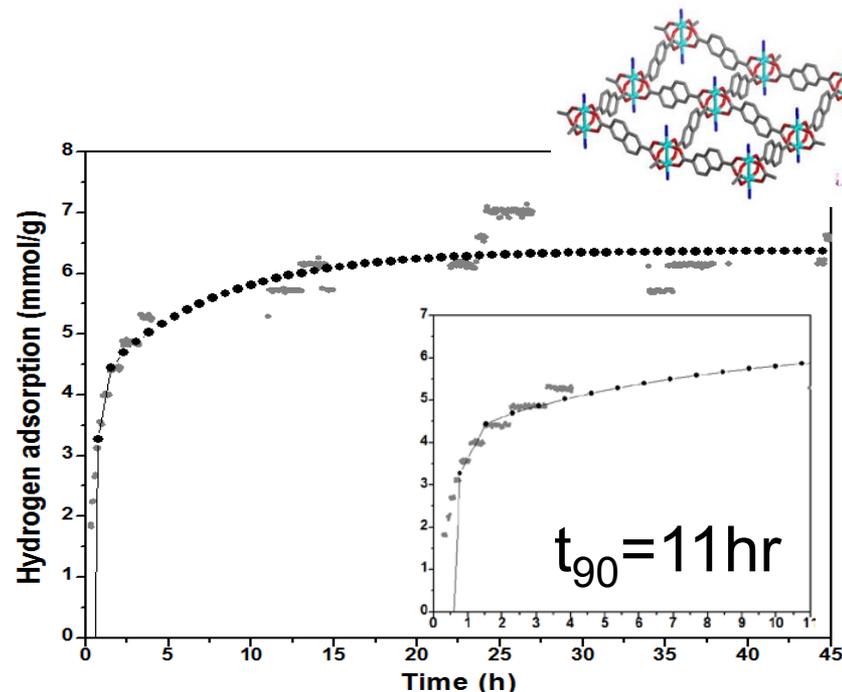
Technical Accomplishments

Screening with Pt/C catalyst

Mixed 9:1; T_{ads}=298 K;

20: full isotherm IGA; 80: volumetric RST

Sample	Pressure (bar)	Wt.% of Hydrogen
5%Pt/AC +IRMOF-8	80 (V)	1.5
+Zn(NDC)(TED)	20 (G) 82 (V)	0.59 1.12



Benchmark data

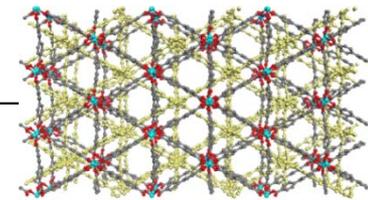
Meets or exceeds benchmark

Screening with Pt/C catalyst

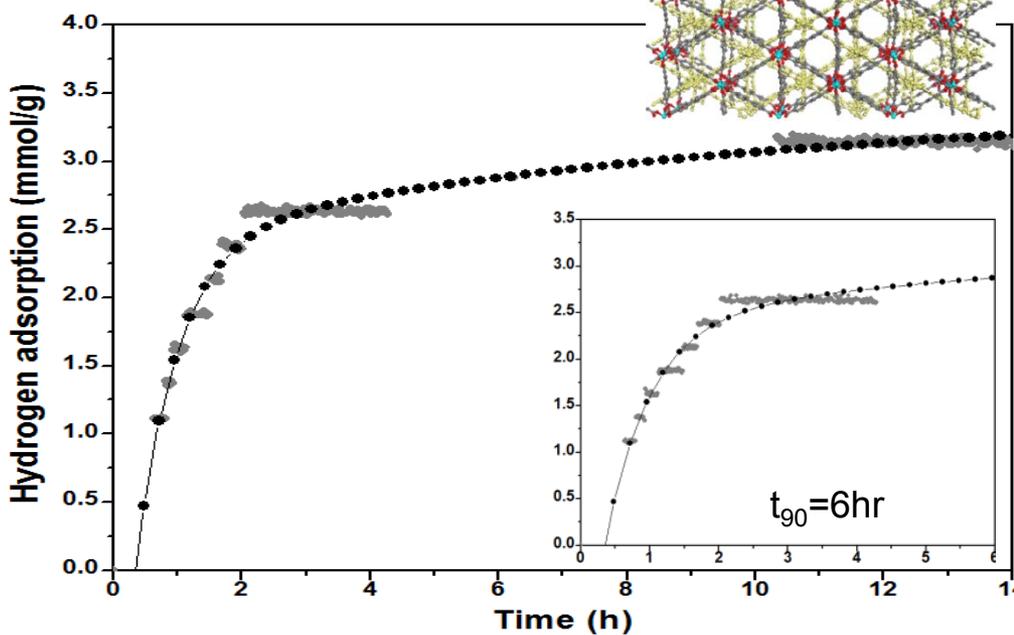
Mixed 9:1; T_{ads}=298 K;

20: full isotherm IGA; 80: volumetric RST

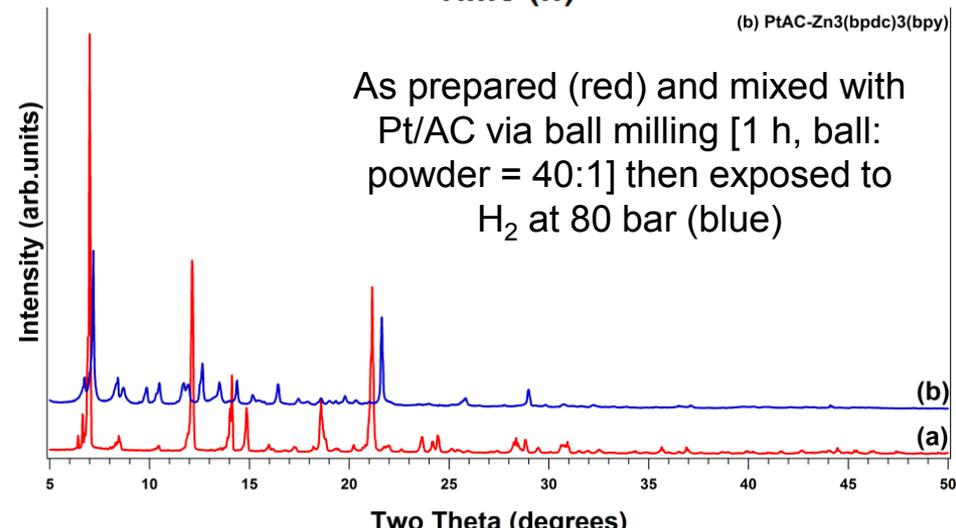
Adv. Mater. 2005, 17, 2703



Sample	Pressure (bar)	Wt.% of Hydrogen
5%Pt/AC +IRMOF-8	80	1.5
Zn(NDC)(TED)	82	1.12
+Zn₃(bpdc)₃(bpy)	20 80	0.09 0.63



(b) PtAC-Zn₃(bpdc)₃(bpy)



As prepared (red) and mixed with Pt/AC via ball milling [1 h, ball: powder = 40:1] then exposed to H₂ at 80 bar (blue)

Benchmark data

Meets or exceeds benchmark

Screening with Pt/C catalyst

Mixed 9:1; $T_{ads}=298$ K;

20: full isotherm IGA; 80: volumetric RST

Sample	Pressure (bar)	Wt.% of Hydrogen
5%Pt/AC +IRMOF-8	80	1.5
+Zn(NDC)(TED)	82	1.12
+Zn ₃ (bpdC) ₃ (bpy)	20	0.09
	80	0.63
+Ni(HCOO)₆ [+Ni-FA]	20	0.17
	80	0.93

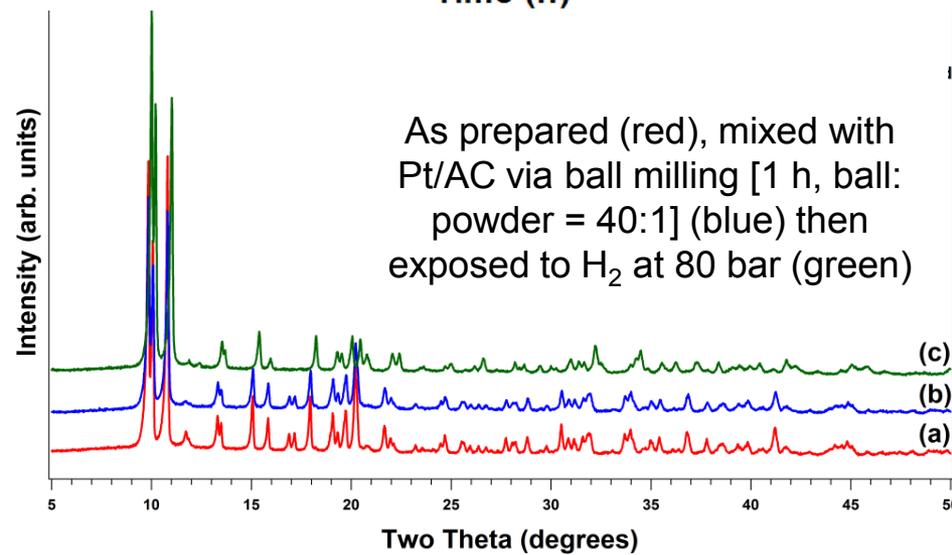
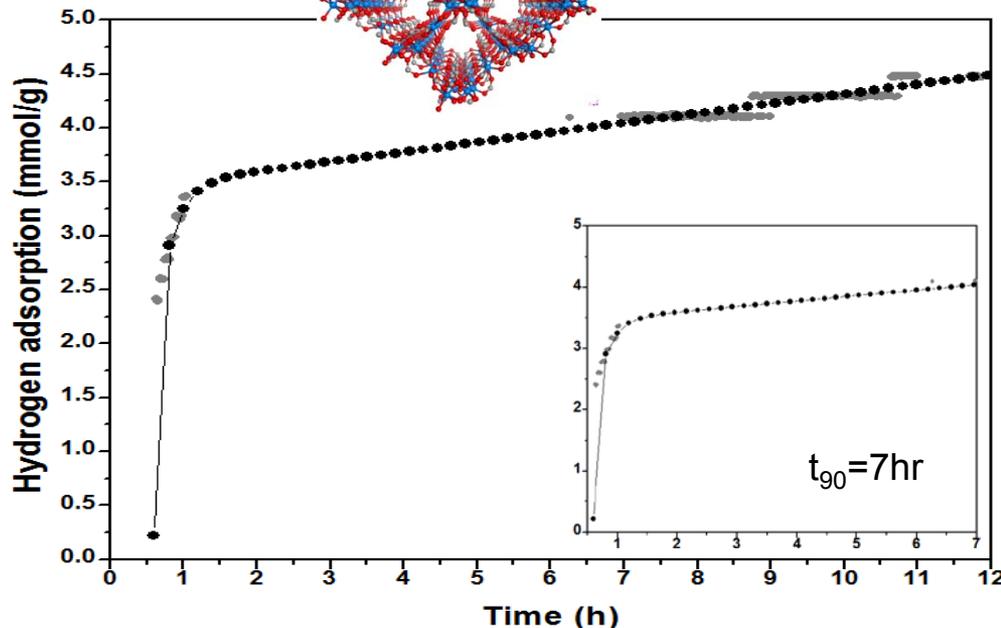
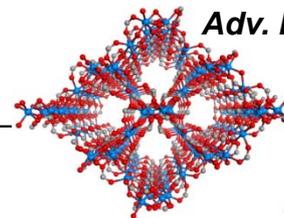
Ni(HCOO)₆

354 m²/g (L)

Ni-FA

304 m²/g (BET)

Adv. Func. Mater. 18, 2008, 2205



Benchmark data

Meets or exceeds benchmark

Technical Accomplishments

Screening with Pt/C catalyst

Mixed 9:1; $T_{\text{ads}}=298\text{ K}$;

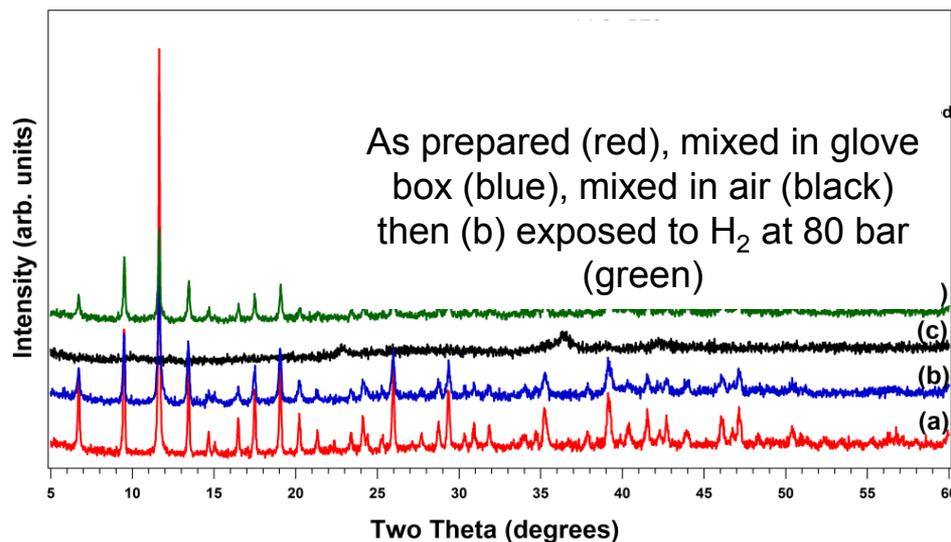
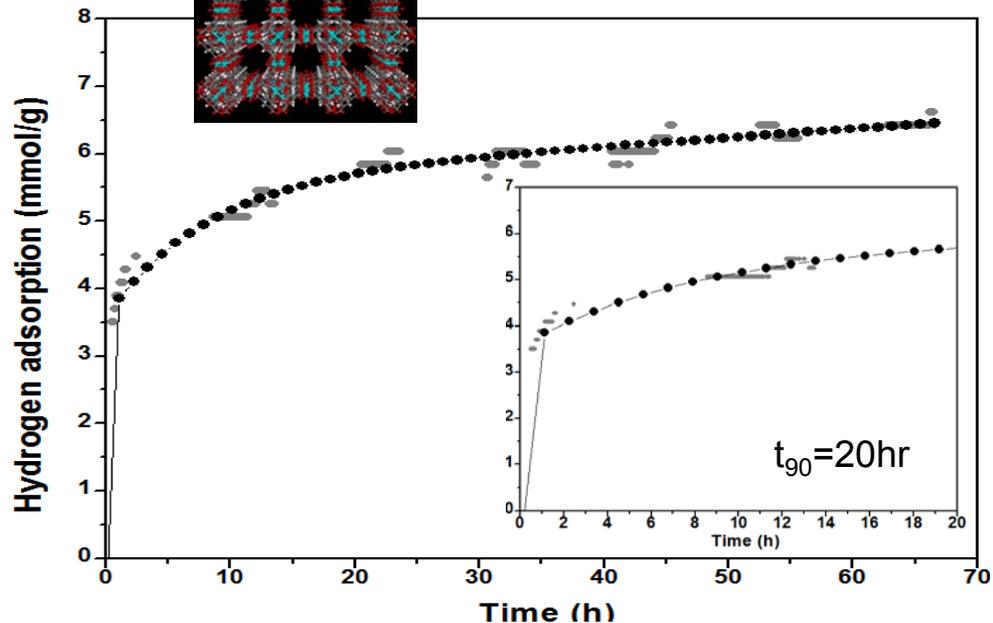
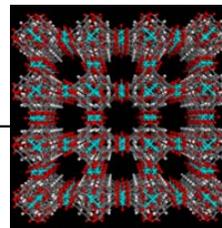
20: full isotherm IGA; 80: volumetric RST

Sample	Pressure (bar)	Wt.% of Hydrogen
+IRMOF-8	80	1.5
+Zn(NDC)(TED)	82	1.12
+Zn ₃ (bpdC) ₃ (bpy)	20 80	0.09 0.63
+Ni(HCOO) ₆ [+Ni-FA]	20 80	0.17 0.93
+CuBTC [+HKUST1]	20 80	0.61 1.32

Cu₃(BTC)

1874 m²/g (L)

1641 m²/g (BET)



Benchmark data

Meets or exceeds benchmark

Screening with Pt/C catalyst

Mixed 9:1; $T_{ads}=298\text{ K}$;

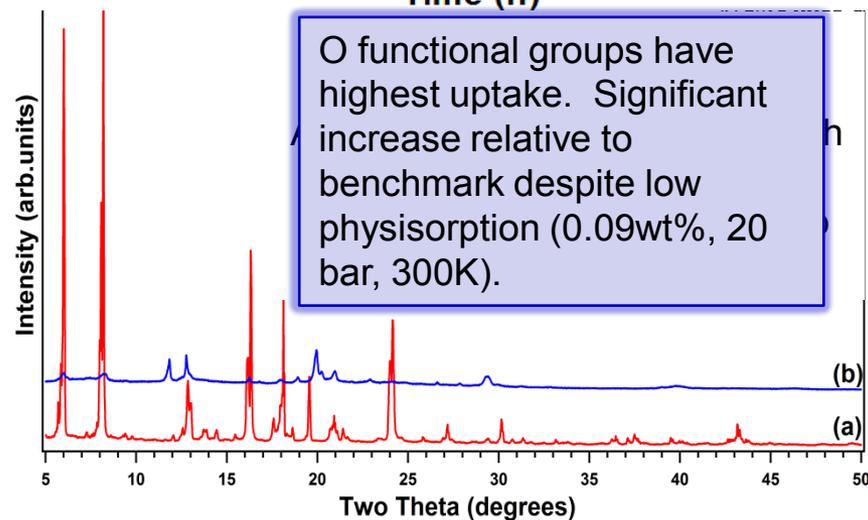
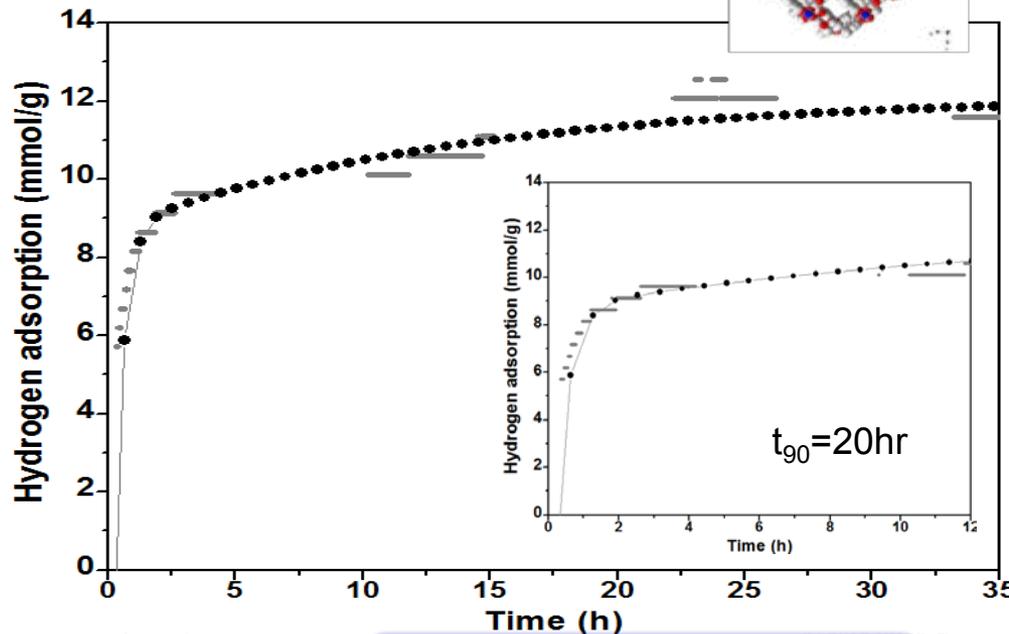
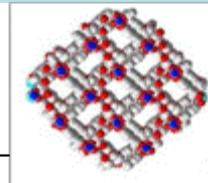
20: full isotherm IGA; 80: volumetric RST

Sample	Pressure (bar)	Wt.% of Hydrogen
+IRMOF-8	80	1.5
+Zn(NDC)(TED)	82	1.12
+Zn ₃ (bpdC) ₃ (bpy)	20	0.09
	80	0.63
+Ni(HCOO) ₆ [+Ni-FA]	20	0.17
	80	0.93
+CuBTC [+HKUST1]	20	0.61
	80	1.32
+MMOF=O	80	2.4

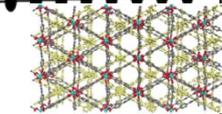
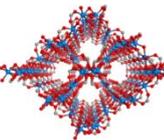
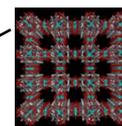
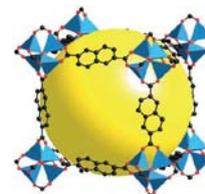
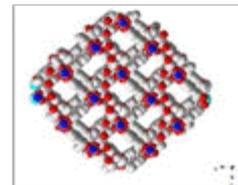
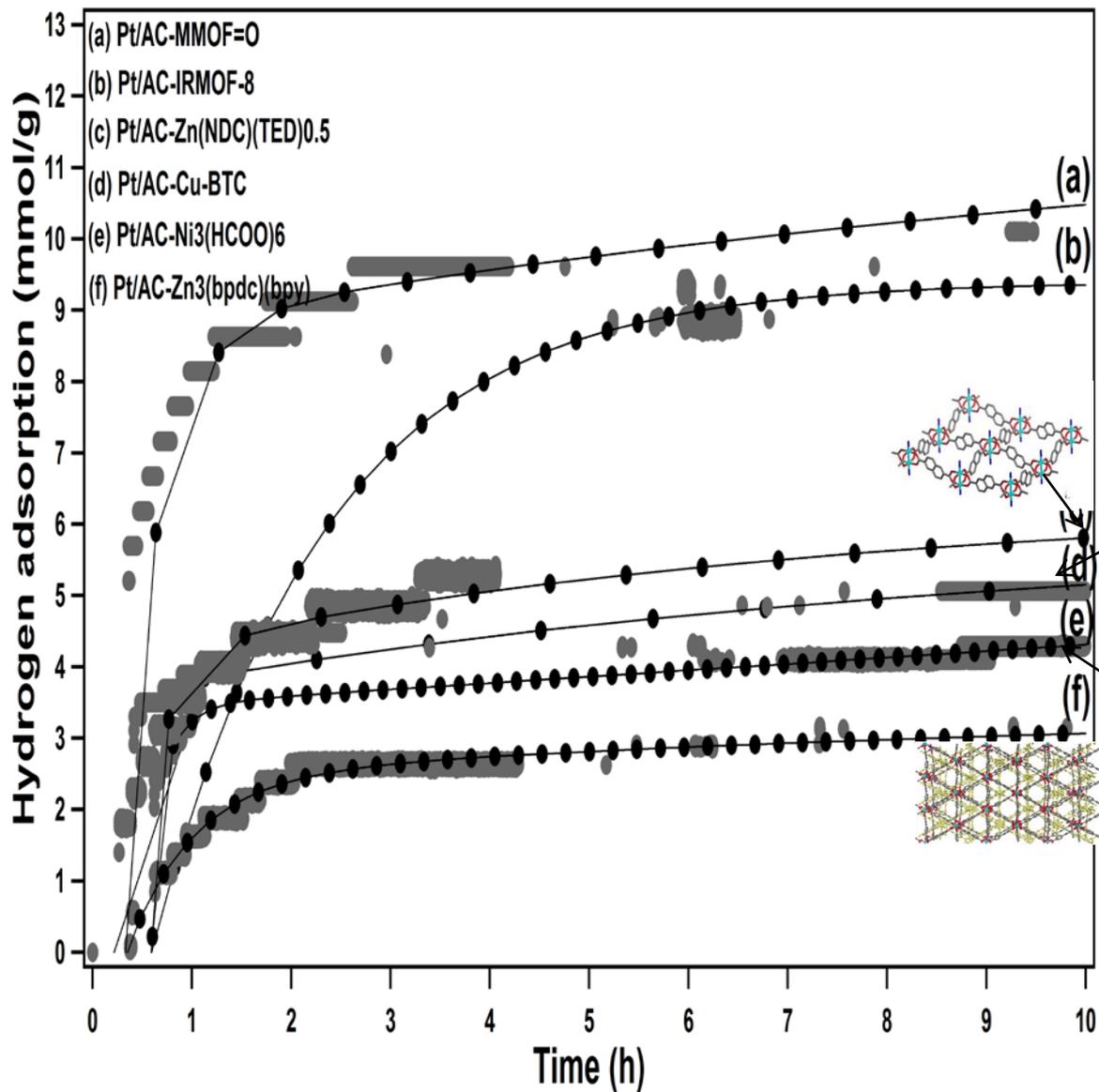
Benchmark data

Meets or exceeds benchmark

MMOF=O



Comparative Study and Correlations



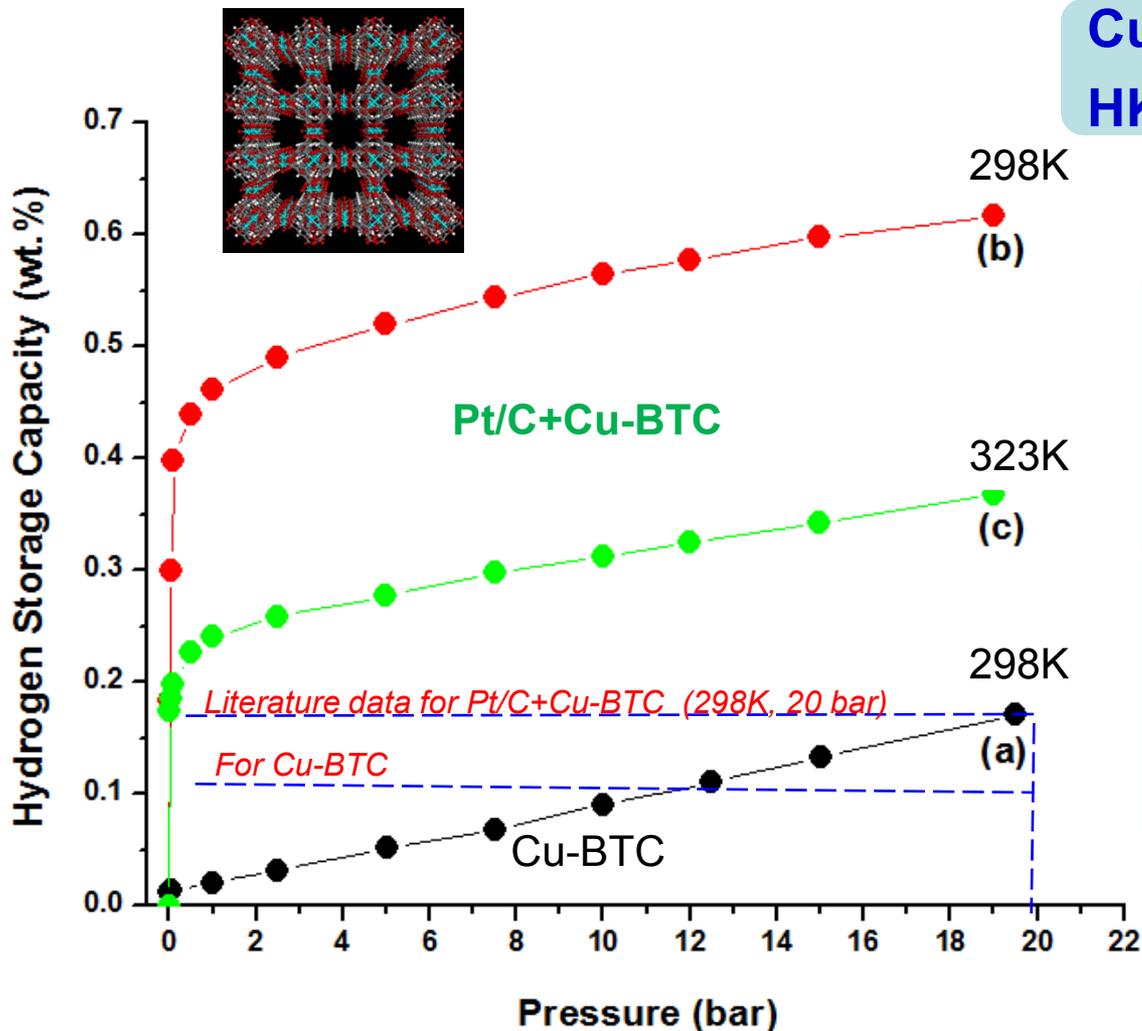
O functional groups have highest uptake and kinetics are improved.

Possible effect of channel size on rate of uptake.

Other trends are unclear, but more detailed analysis needed with characterization details after catalyst mixing.

Technical Accomplishments

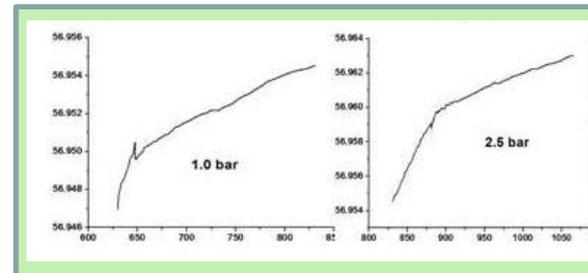
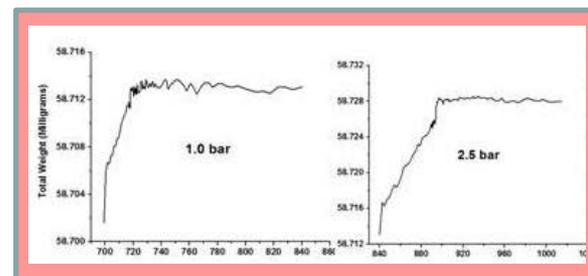
Importance of handling and pretreatment: 3-fold increase relative to literature



**Cu-BTC/
HKUST-1**

1874 m²/g (L)

1641 m²/g (BET)



Uptake needs to be revisited with preparation in inert environment. Rate temperature dependence may serve as T-switch.

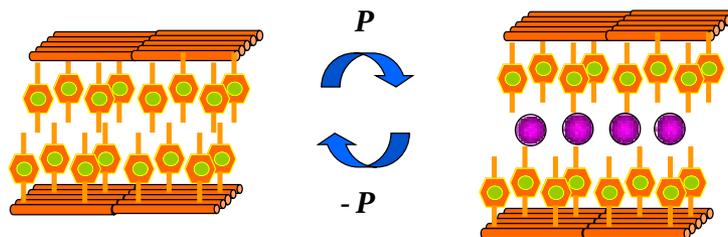
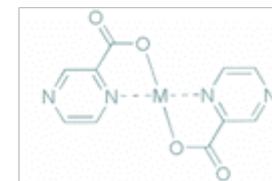
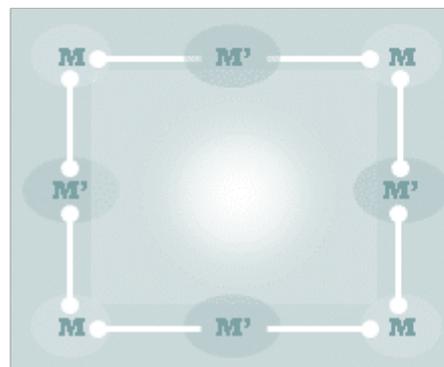
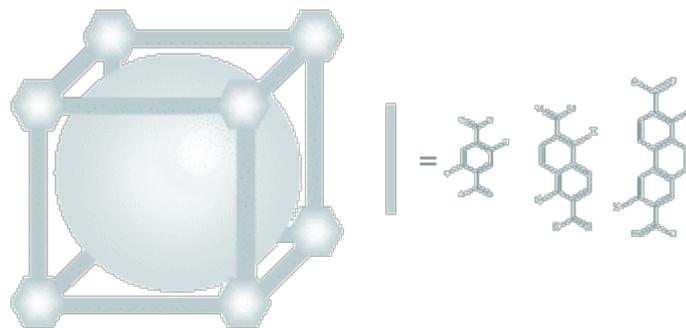
Material Design

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.)

To enable P savings:

- Build in T- and P- switches into material to separately optimize adsorption vs. desorption



Strategies/Approach (II): Material Design

Exploring H Trapping via Hysteretic Sorption, or P-switches

Types of hysteretic adsorption-desorption in MMOFs

1. “Gated / Butterfly”

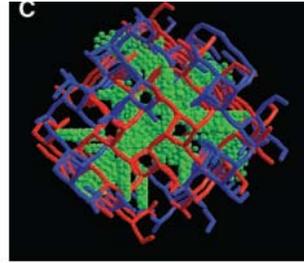
Mass transfer limitations into extremely small pores.

2. “Gate-opening” - Rigid

Adsorption (or gas)-induced structural changes in semi-rigid structures

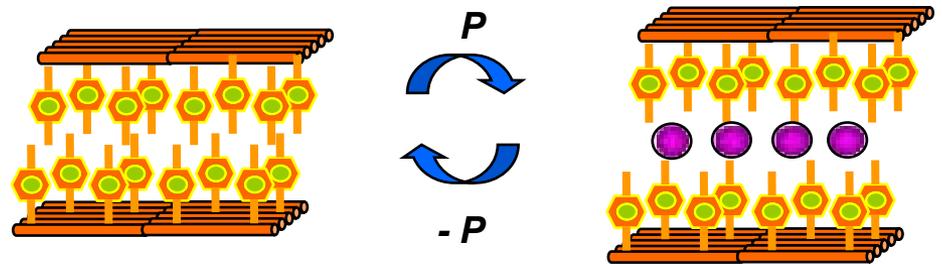
3. Gate-opening - Flexible

*Adsorption-induced structural changes in flexible structures**

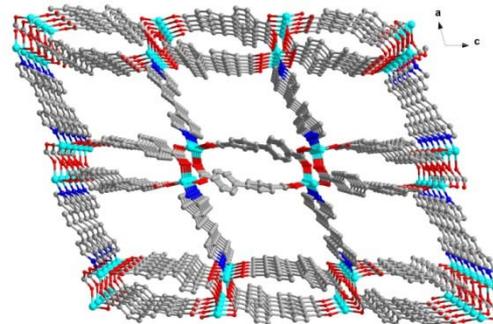


e.g., $\text{Ni}_2(\text{bipy})_3(\text{NO}_3)_4$
(bipy is 4,4-bipyridyl)

Zhao et al., Science 2004
Simmons & Yildirim, 2009



Li & Kaneko CPL, 2001
Kitagawa et al., 2002, 2003
MIL-53; NIST

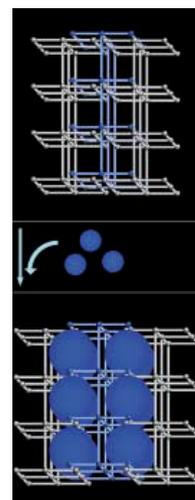


****Note:** *Effect of gas-solid interactions on structural changes is not well understood.*

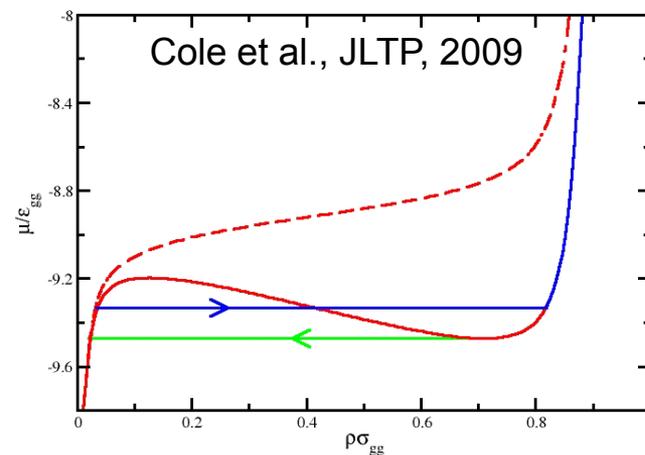
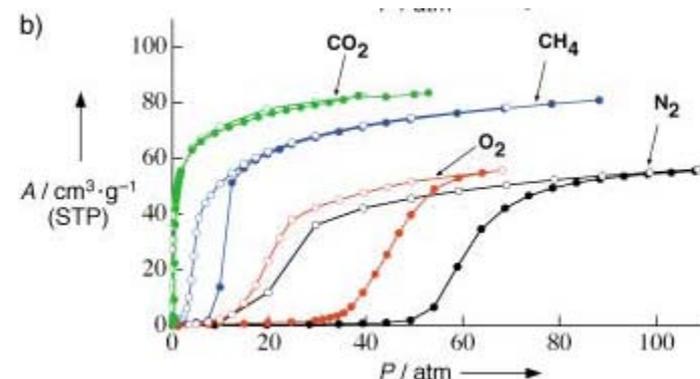
Technical Accomplishments

Theoretical Considerations: Initial model with Semi-rigid MOFs with simple parametric model of 1-D distortion

- Simple treatment of the Cu-dhbc-bpy structure with statistical mechanics predicts a gate-opening P for H_2 of 86 atm.
 - Experimental validation to start Summer 2010.
- Width of hysteresis loop analogous to general behavior for substrate relaxation on adsorption in pores by Cole et al. (JLTP, 2009).
 - Rough agreement for $\Delta\mu/\varepsilon_{gg}$: CH_4 (1.03) O_2 (1.03), N_2 (1.10)
 - Theory: $\Delta\mu/\varepsilon_{gg} = 0.45$, difference may be due to screening of Lennard Jones interatomic potential



Cu-dhbc-bpy from Kitagawa et al.,
Angew. Chem. Int. Ed. 42, (2003) 428



Technical Accomplishments

Hydrogen Trapping: Baseline Hysteretic Adsorption Models and Experimental Validation

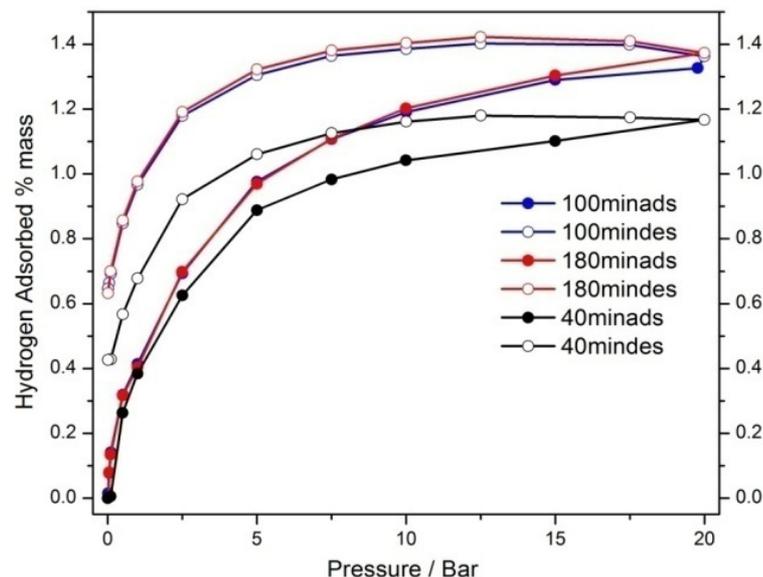
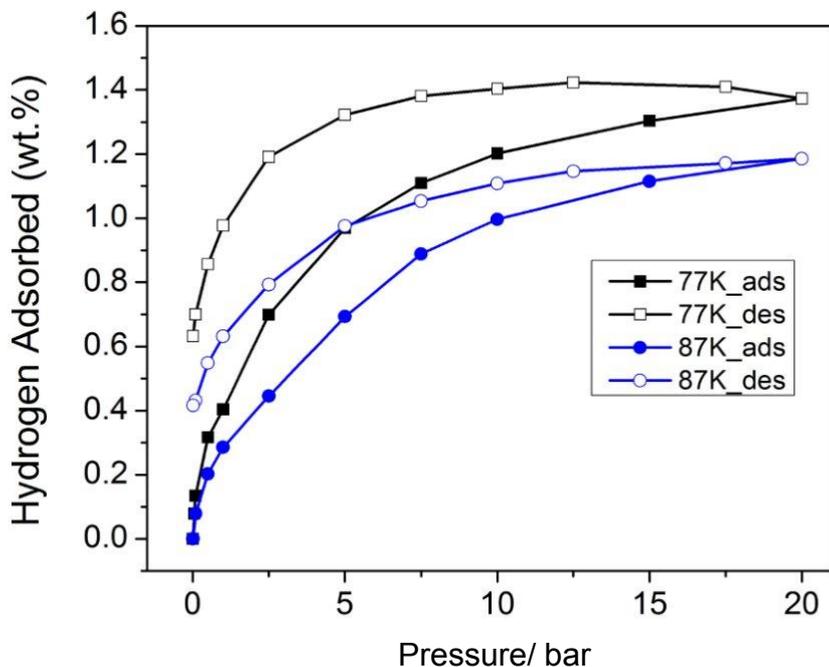
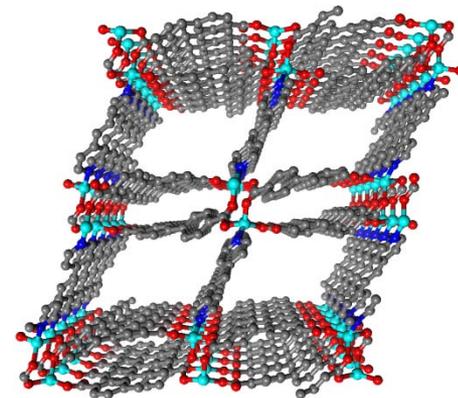
$\text{Zn}_2(\text{bpdc})_2(\text{bpee})$

483 m^2/g (L)

328 m^2/g (BET)

H_2 adsorption shows hysteresis and trapping:

- At 87 K: 35% trapping from 20 to 0 bar.
- At 77 K: 45% trapping from 20 bar to 0 bar.



Unexpected time behavior:
Hysteresis is the same for 100 and 180 minutes adsorption. Closed adsorption; open desorption.

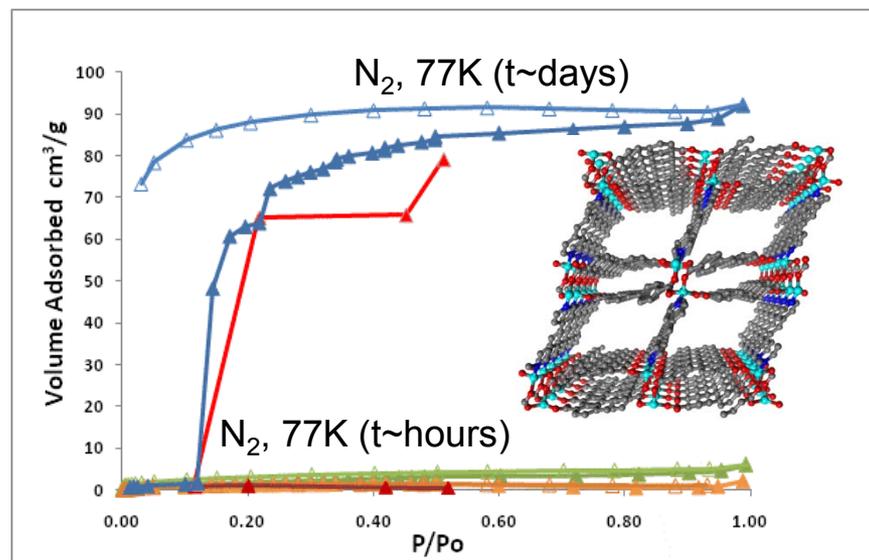
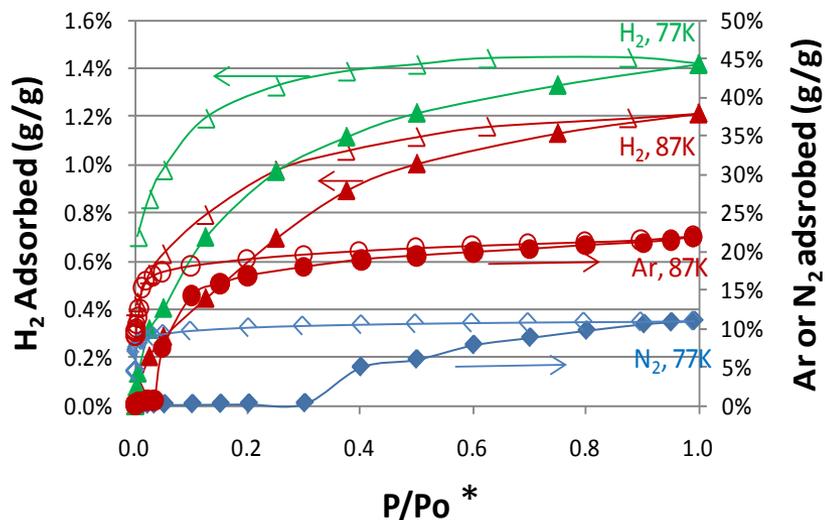
Technical Accomplishments

Hydrogen Trapping: Baseline Hysteretic Adsorption Models and Experimental Validation

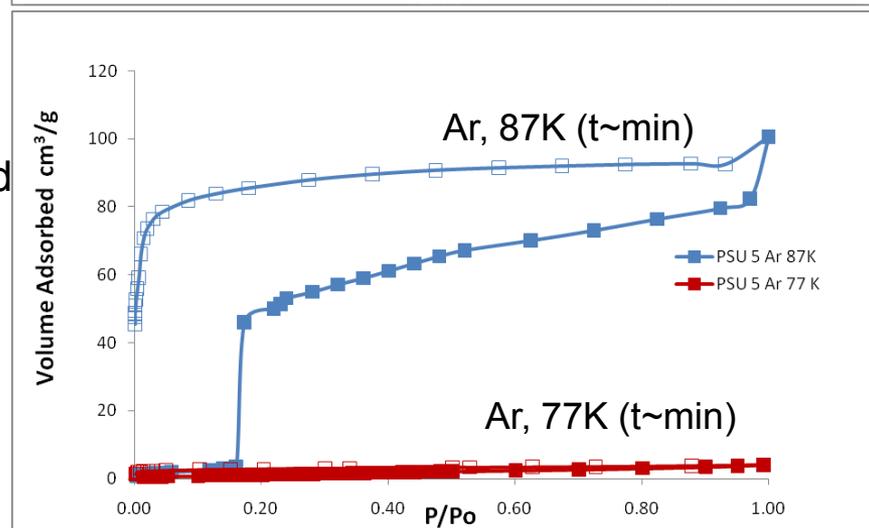
$\text{Zn}_2(\text{bpdc})_2(\text{bpee})$

483 m^2/g (L)

328 m^2/g (BET)



Hysteresis is observed for both super-critical (H_2) and sub-critical gases (N_2 , Ar). We are hoping to develop predictive models for hysteresis, validated by experimental data, similar to our previous studies (Lueking & Cole, *Molec. Phys.* 2008) in mapping universal adsorption behavior. Interesting time, Temperature effect (at right)



* P_o for N_2 is saturation; P_o for H_2 is set at 20 bar.

Summary

I: Summary of Mechanistic Studies

- A total number of eight MMOFs synthesized, with variations in surface chemistry and porosity
- Six MMOFs mixed with Pt/C and screened at high pressure (as of 4/9/2010)
- IRMOF-8 with Pt/C confirms literature data
- Cu-BTC +Pt/C showed importance of preparation conditions
- Pretreatment, Handling, Mixing, Gas exposure key parameters to ensure reproducibility
- Oxygenated ligand exceeds uptake of IRMOF-8 benchmark with rapid initial uptake.

II. Summary of H₂ uptake, versus corresponding 'benchmark' data

	Pressure (bar)	Wt.% of H ₂ (298K)
IRMOF-8 ¹ +5%Pt/AC ¹ +Bridge ¹	20,70, & 100 20,80, & 100 20,70, & 100	0.09,0.37,0.52 0.38,1.4,1.80 0.74,2.68,3.94
+IRMOF-8	80	1.5
HKUST-1 +5% Pt/AC ² +5% Pt/AC	20 20 20 80	0.1 0.165 0.6 1.32
MMOF=O	80	2.4
AC*+Pt/AC ³	1, 20	1.2, 1.4

Benchmark data

Meets or exceeds benchmark

(1) Yang et al. JACS. 2006,128,8136

(2) AIChE, 2008,54,269

(3) Lueking et al., *Submitted*—UCR funding

Future Work

- Repeat RST measurements with different mixing technique
- Detailed study of ligands with modified surface chemistry
- Introduce pore modification in synthesis of like compounds
- Validate theoretical imbibition study with experiment; Evaluate P-trapping of MMOF structures at ambient conditions; Assess opening via spilled over H
- Evaluate potential for T trapping
- Develop MMOFs containing built-in catalytic functionality using metalloligands.
- Characterize porosity and surface area of MMOFs after Pt/C mixing and H₂ adsorption to analyze possible correlations between uptake, kinetics and structure

Related Collaborative Work

- Independent measurement of Tsao et al. sample
- Multi-scale modeling of spillover
- Validate Pt/C/AC* with RST and NIST collaboration

Collaborations

University:

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

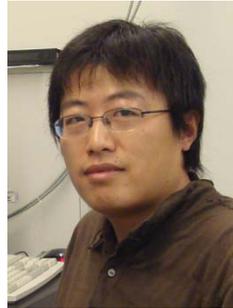
Pending Collaborations / On-going discussions

- Prof. Adri Van Dunn, Penn State (Multi-scale modeling)
- Prof. Silvina Gatica, Howard University (Modeling)
- Prof. Hye-Young Kim, SELUniveristy (Modeling)
- NIST, (Federal Laboratory)
- Tsao, INER (Taiwan Federal Laboratory)

Acknowledgements



Prof. Jing Li



*Yonggang
Zhao*



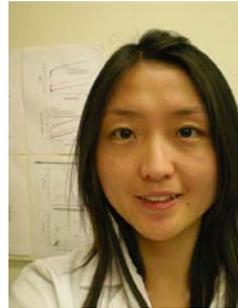
Anjian Lan



Haohan Wu



Prof. Milton Cole



Qixiu Li



*Dr. Sami-
Ullah Rather*



*Sarmi
Sircar*



*Cheng-Yu
Wang*

Funding Provided by:
Department of Energy: Energy Efficiency and Renewable Energy

Contact Information:

Angela D. Lueking, Ph.D.; Dept. of Energy & Mineral Engineering; Pennsylvania State University;
University Park, PA 16802; lueking@psu.edu; (814) 863-6256

Supplemental Slides

(Note: please include this “separator” slide between those to be presented and the “Supplemental” slides.



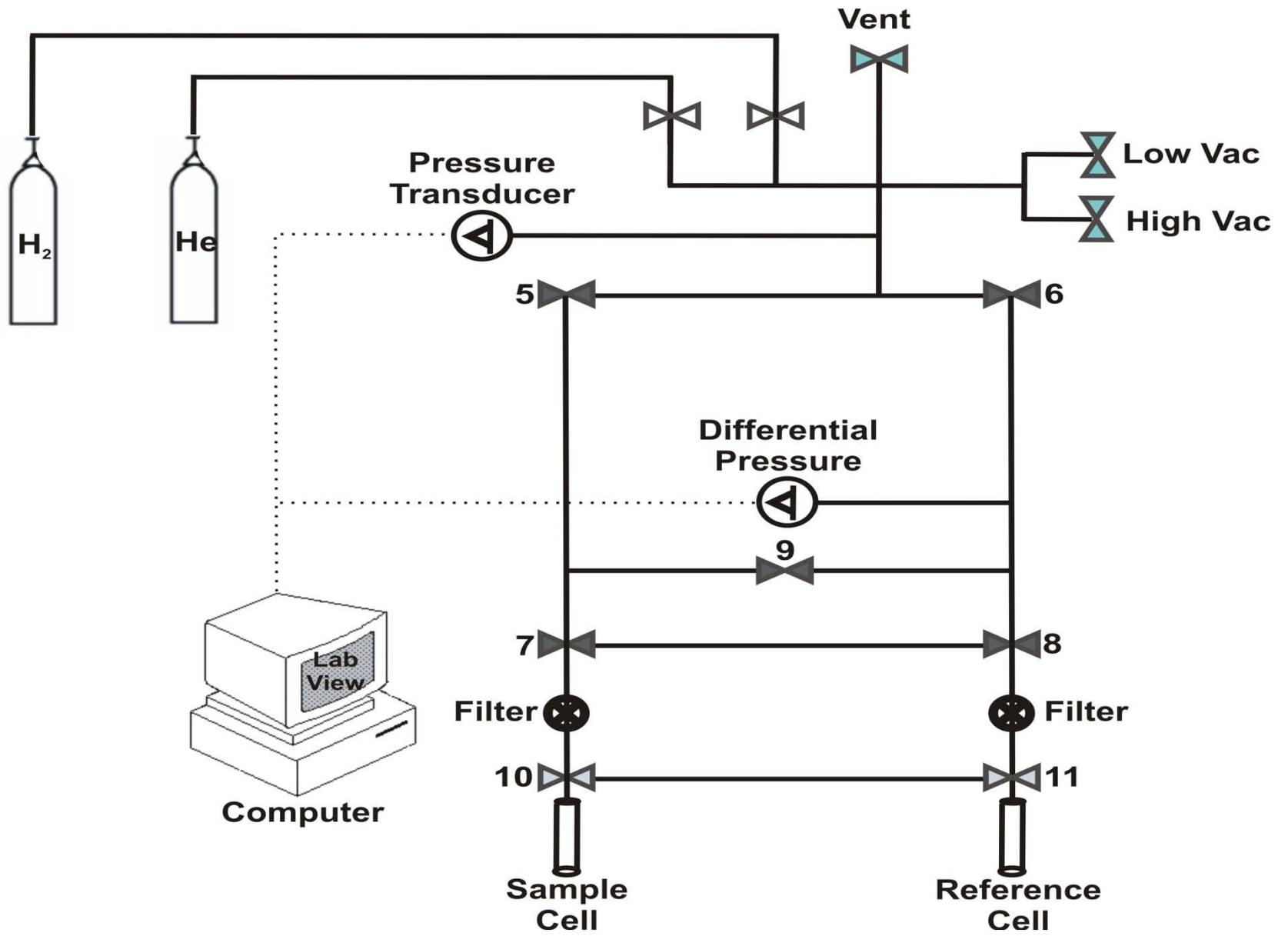
- ❖ **5%Pt/AC-[Zn₄(NDC)₃·(DEF)₆]-IRMOF-8**
- ❖ **5%Pt/AC-MMOF-O**
- ❖ **5%Pt/AC-[Zn(NDC)(TED)_{0.5}]-3DMF**
- ❖ **5%Pt/AC-[Zn₃(bpdc)₃(bpy)]·4DMF·H₂O**
- ❖ **5%Pt/AC-[Ni₃(HCOO)₆·DMF**
- ❖ **5%Pt/AC-[Cu₃(BTC)₂(H₂O)₃·(H₂O)₁₂**
- ❖ **5%Pt/AC-MMOF=O**
- ❖ **Zn₂(bpdc)₂(bpee)**



S.No	Molecular Formula	Short Formula	Pretreatment Conditions
1	$[Zn_4(NDC)_3 \cdot (DEF)_6]$ 5%Pt/AC- $[Zn_4(NDC)_3 \cdot (DEF)_6]$	IRMOF-8	200°C, Vac, 24h
2	$[MMOF-O] \cdot 2DMF$ 5%Pt/AC- $[MMOF-O] \cdot 2DMF$	MMOF-O	170°C, Vac 6-8 h
3	$[Zn(NDC)(TED)_{0.5}] \cdot 3DMF \cdot H_2O$ 5%Pt/AC- $[Zn(NDC)(TED)_{0.5}] \cdot 3DMF$	Zn(NDC)(TED)	100°C, Vac, 8-10h
4	$[Zn_3(bpdc)_3(bpy)] \cdot 4DMF \cdot H_2O$ 5%Pt/AC- $[Zn_3(bpdc)_3(bpy)] \cdot 4DMF \cdot H_2O$	[Zn(bpdc)(bpy)]	100°C, Vac, 6-8h
5	$[Ni_3(HCOO)_6 \cdot DMF]$ 5%Pt/AC- $[Ni_3(HCOO)_6 \cdot DMF]$	Ni(HCOO) ₆	150°C, Vac, 6-8h
6	$[Cu_3(BTC)_2(H_2O)_3] \cdot (H_2O)_{12}$ 5%Pt/AC- $[Cu_3(BTC)_2(H_2O)_3] \cdot (H_2O)_{12}$	Cu-BTC or HKUST-1	180°C, Vac-12h
7	MMOF=O 5%Pt/AC-MMOF=O	MMOF=O	100°C, vac, 3 h

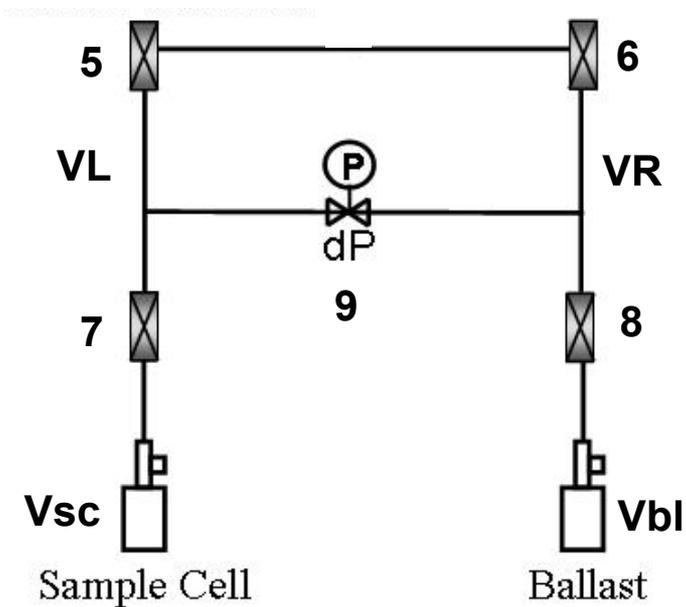


Sievert's Volumetric Apparatus-Nellie



Methods: Upgrades and Validation

High-P Differential Volumetric Measurements and Training



The following procedure is followed:

A. At time 0:

a. Valves 7,8 are closed.

i. P_{Sc}^o is known; P_{Bl}^o is known. Define: $dPo = P_{Bl}^o - P_{Sc}^o$

b. Valve 9 is open. $P_L^o = P_R^o$

c. Valve 9 is closed. Assume symmetrical closure $P_L^o = P_R^o$

B. At time t:

a. Valve 9 is closed; Valve 7,8 are open.

i. $P_L = P_{Sc}$

ii. $P_R = P_{Bl}$

iii. $dP = P_R - P_L$

The right hand, ballast, side does not adsorb. Moles are conserved:

$$N_2(t) = N_2^o = N_R + N_{Bl} = N_R^o + N_{Bl}^o$$

Adsorption may occur on the left hand side:

$$N_1(t) + dN_{ads}(t) = N_1^o = N_L^o + N_{Sc}^o + N_{ads}^{previous}$$

$$P_1 \gamma_1 + dN_{ads}(t) = N_L^o + N_{Sc}^o + N_{ads}^{previous}$$

Combining above equations:

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

Rearranging:

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

Technical accomplishments

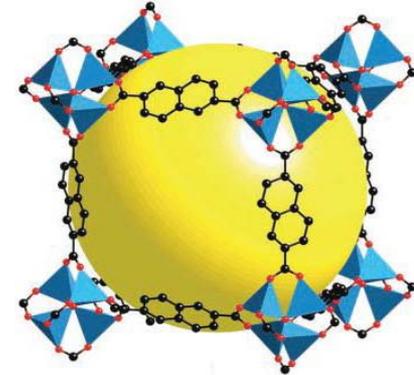
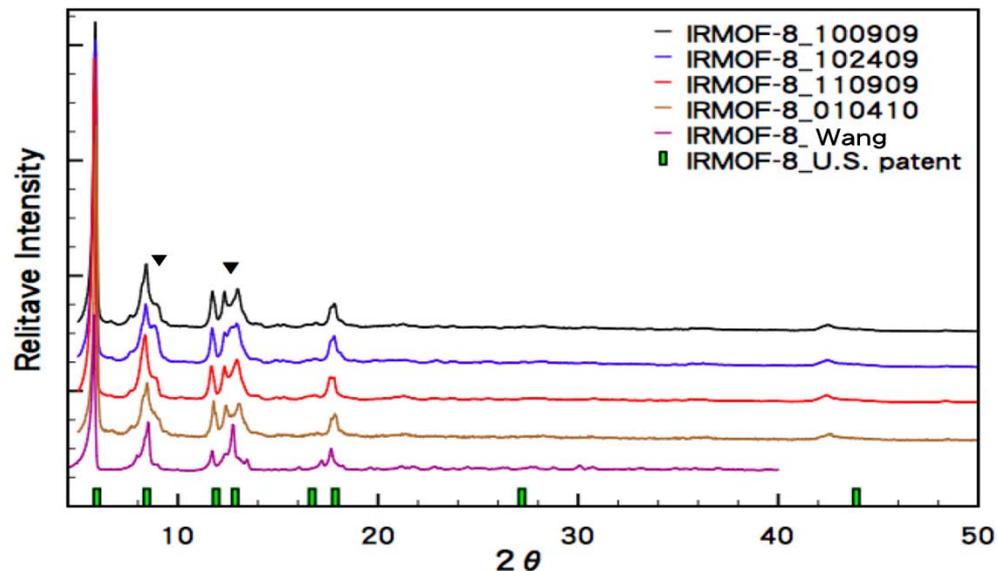
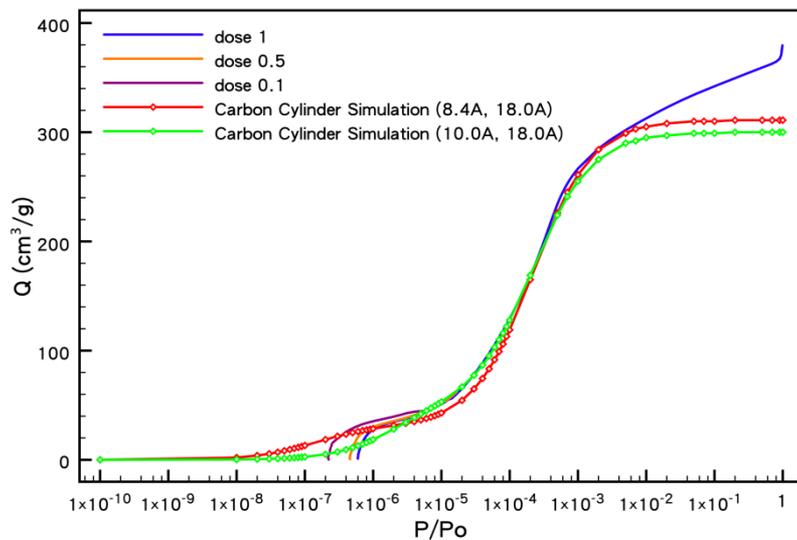
A2: Mechanistic Studies--Porosity

IRMOF-8

$[\text{Zn}_4(\text{NDC})_3 \cdot (\text{DEF})_6]$

1527 m^2/g (L)

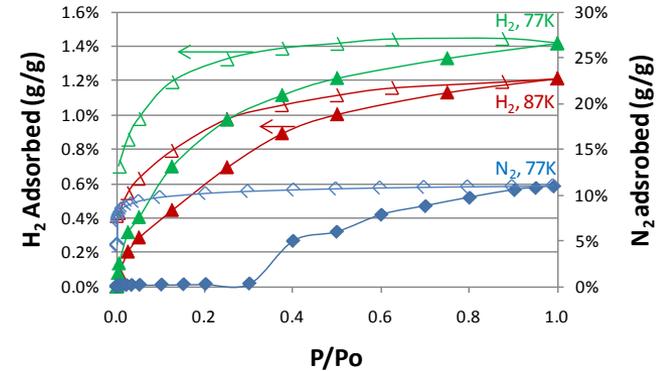
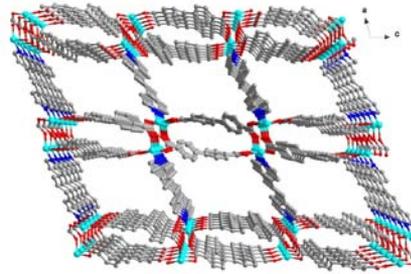
1384 m^2/g (BET)



XRD indicates slight structure changes,
dependent on synthesis conditions;
Consistent with Tsao et al., -2010

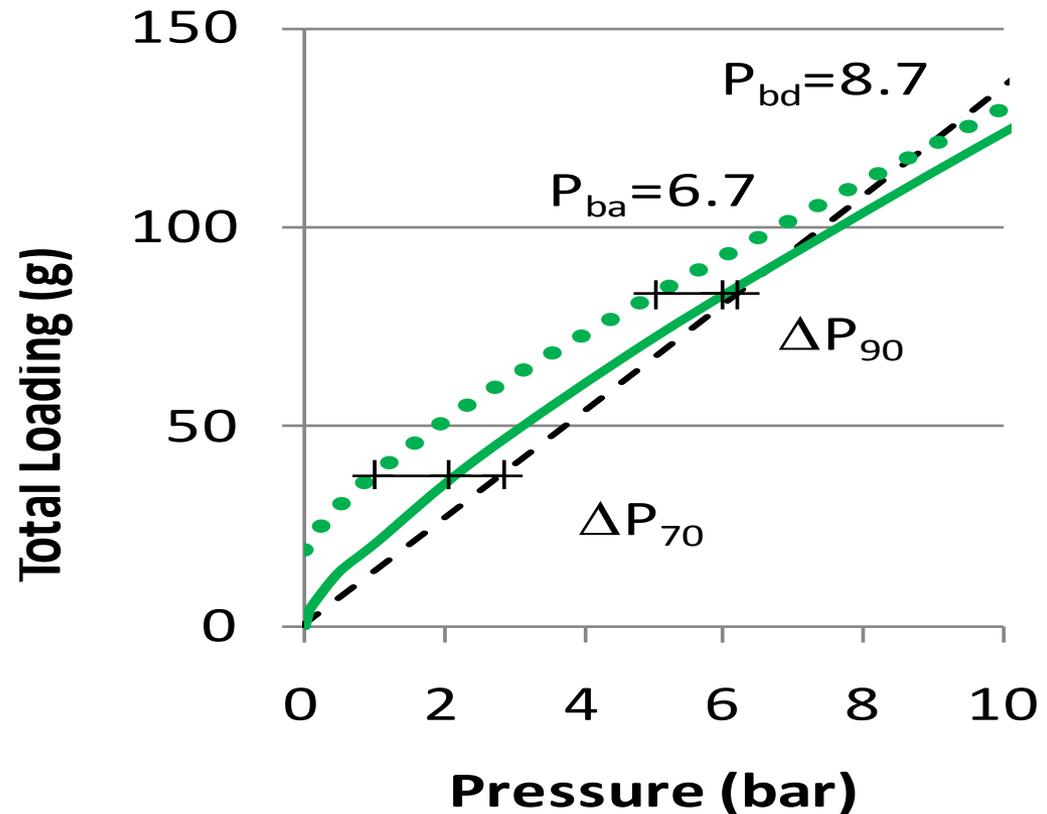
Also, intentional pore blocking will be
introduced.

Significance



Pressure savings analysis (ΔP) for hysteretic adsorption (solid line)-desorption (dotted) of MMOF-1-Zn at 77K relative to the empty tank (dashed).

P_{ba} , and P_{bd} are the pressures where the adsorbent offers an advantage for adsorption and desorption, respectively.



Extending the GX31 analysis above to a hypothetical adsorbent with adsorption-desorption hysteresis comparable to that seen in Fig. 5 for Cu(hfipbb) (i.e. 90%) leads to a pressure savings of 78% (relative to 2000 psi empty vessel). Of course, the hysteresis seen at 77K may not extend to 300K--at least 37.5% trapping at 294K must be achieved for hysteresis to realize a pressure savings relative to the 2000 psi empty tank.

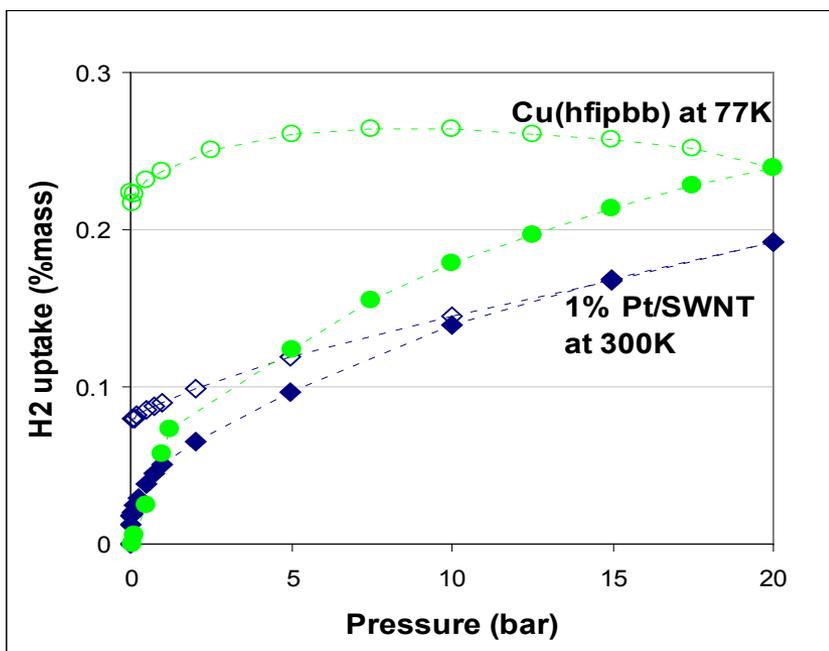


Fig. 5: Examples for hysteretic adsorption (closed symbols) –desorption (open). 300K is indicative of strong C-H; 77K is indicative of trapping.

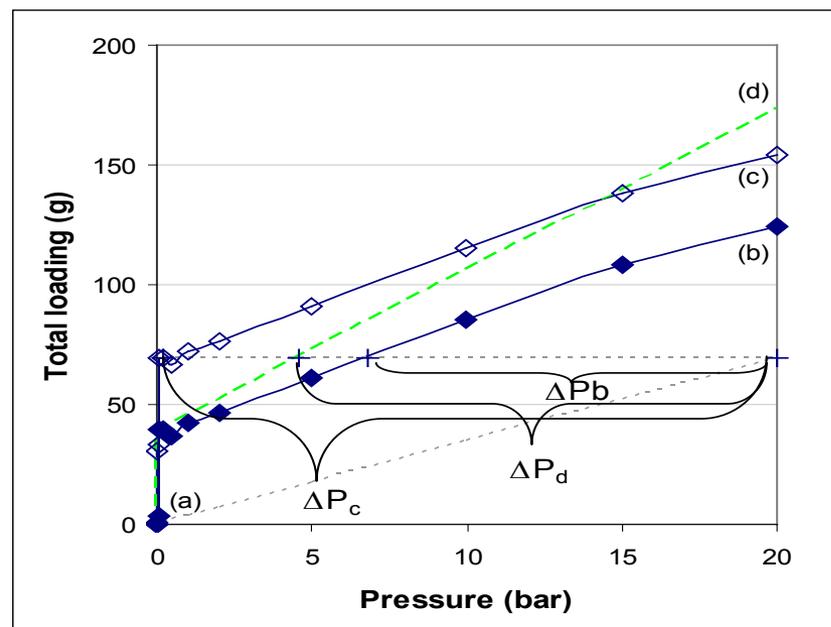


Fig. 6: Pressure savings (ΔP) relative to an (a) empty vessel at 294 K, for (b) 1:9 PtC + Zn(bdc)(ted)_{0.5}, after (c) enhancing spillover, and (d) enhancing porosity (see text).

Summary

I: Summary of Mechanistic Studies

II. Summary of H₂ uptake, versus corresponding ‘benchmark’ data

Sample	H ₂ uptake (wt.%) at 298 K & 20 bar	Reference
5%Pt/AC- Cu-BTC	0.180 [Physical mixture 9:1-outside glove box]	Previous report
5%Pd/AC- Cu-BTC	0.220 [Physical mixture 9:1-outside g box]	Previous report
5%Pt/AC- Cu-BTC	0.610 [Physical mixture 9:1-inside g box]	This report
5%Pt/AC-HKUST-1	0.165 [Physical mixture-9:1]	AICHE, 2008,54,269
Bridged- HKUST-1	0.254 [Physical mixture-carbonization-8:1:1]	
5%Pt/AC-COF-1	0.090 [Physical mixture-9:1]	AICHE, 2008,54,269
Bridged-COF-1	0.142 [Physical mixture-carbonization-8:1:1]	
5%Pt/AC-MIL-101	0.217 [Physical mixture-9:1]	AICHE, 2008,54,269
Bridged-MIL-101	0.340 [Physical mixture-carbonization-8:1:1]	
5%Pt/AC-MOF-5	0.320 [Physical mixture-9:1]	JACS,2006,128,726
5%Pt/AC-IRMOF-8	0.365 [Physical mixture-9:1]	JACS,2006,128,726
5%Pt/AC-IRMOF-1	0.334 [Physical mixture-9:1]	JACS,2006,128,8136
Bridged-IRMOF-1	0.500 [Physical mixture-carbonization-8:1:1]	
5%Pt/AC-IRMOF-8	0.365 [Physical mixture-9:1]	JACS,2006,128,8136
Bridged-IRMOF-8	0.700 [Physical mixture-carbonization-8:1:1]	
20%Pt/AC-MIL-53	0.170 [Ball milling (inside g box)]	IJHE,2007,32,4005
Bridged-MIL-53	0.248 [Ball milling-Carbonization]	
20%Pt/AC-MIL-101	0.295 [Ball milling (inside g box)]	IJHE,2007,32,4005
Bridged-MIL-101	0.470 [Ball milling-carbonization]	
5%Pt/AC-MOF-177	0.185 [Physical mixture-9:1]	Langmuir,2007,12937
Bridged-MOF-177	0.395 [Physical mixture-carbonization-8:1:1]	