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

P.I.: Angela D. Lueking, Ph.D.

The Pennsylvania State University

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ST024

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Overview

Timeline

- Project start date: Feb. 2009
- Project end date: Nov. 2013
- Percent complete: *66%*

Barriers

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

Budget

- Total project funding $2,166,895
  - DOE share: $1,614,000
  - Contractor share: $552,895
- Funding received in FY11: $276K
- Funding for FY12: $300K*

*$98,945 received, pending Go/No/Go

Partners

- Prof. Jing Li (Rutgers) Co-PI
- Prof. Milton W. Cole (Penn State)
- Institute of Nuclear Energy Research, Taiwan
- National Renewable Energy Laboratory
- Prof. John Badding (Penn State)
- Prof. Vin Crespi (Penn State)

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.

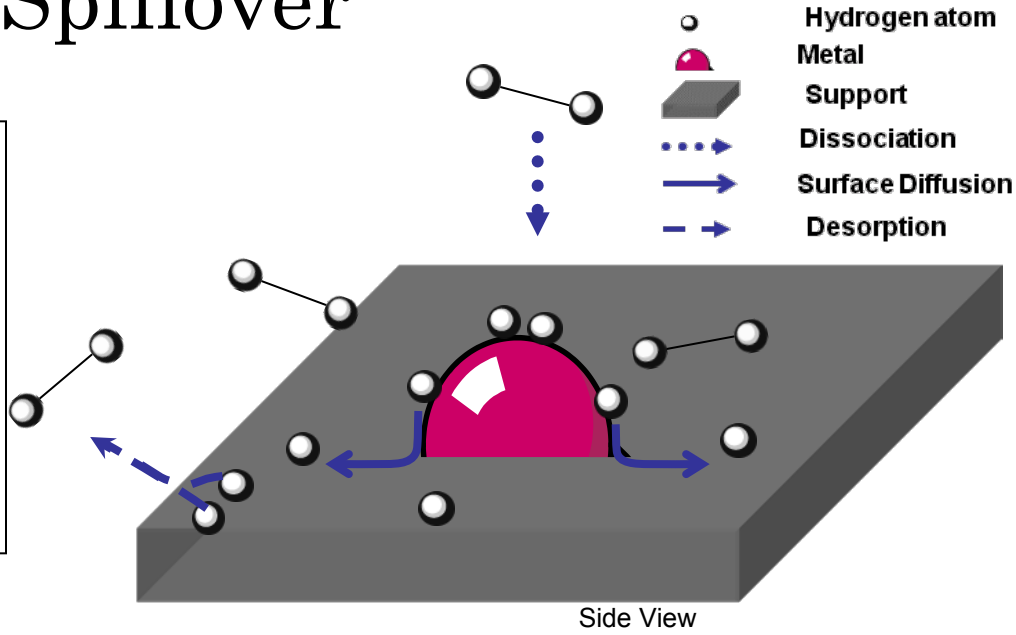
In the past year (March 2011 – March 2012), we have:

A. Published evidence for alteration of surface chemistry by trace water during *in situ* catalyst reduction that significantly increases subsequent spillover
B. Worked collaboratively to obtain in situ spectroscopic validation of spillover to carbon support (inelastic neutron scattering with INER; subsequent Raman with DOE-BES funding)
C. Published Ex Situ evidence of spillover and H chemisorption to CuBTC
D. Published evidence gate-opening in MOFs may be highly dependent upon kinetics
E. Worked with NREL in sample exchange and round robin testing
F. Tailored MOFs/ligands for direct doping studies to activate MOFs for spillover
G. Exploratory studies on direct-doping of MOFs for increased reliability/reproducibility of metal-doped MOFs

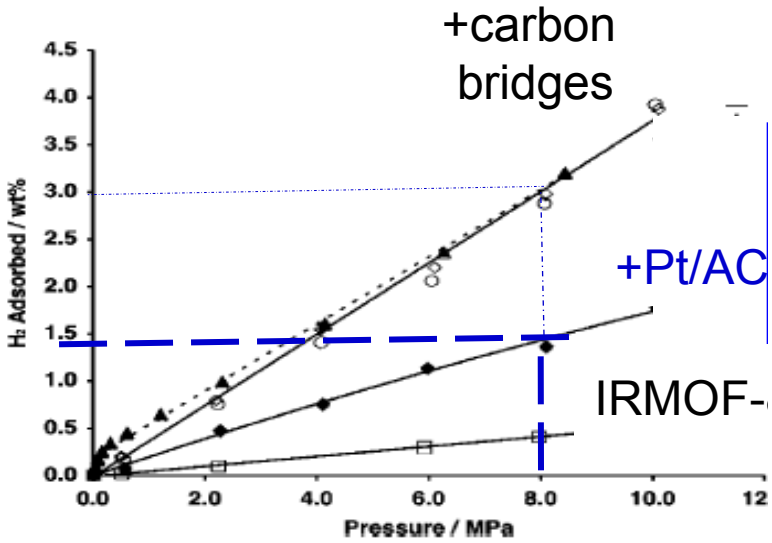
[1] d < 2nm (IUPAC)

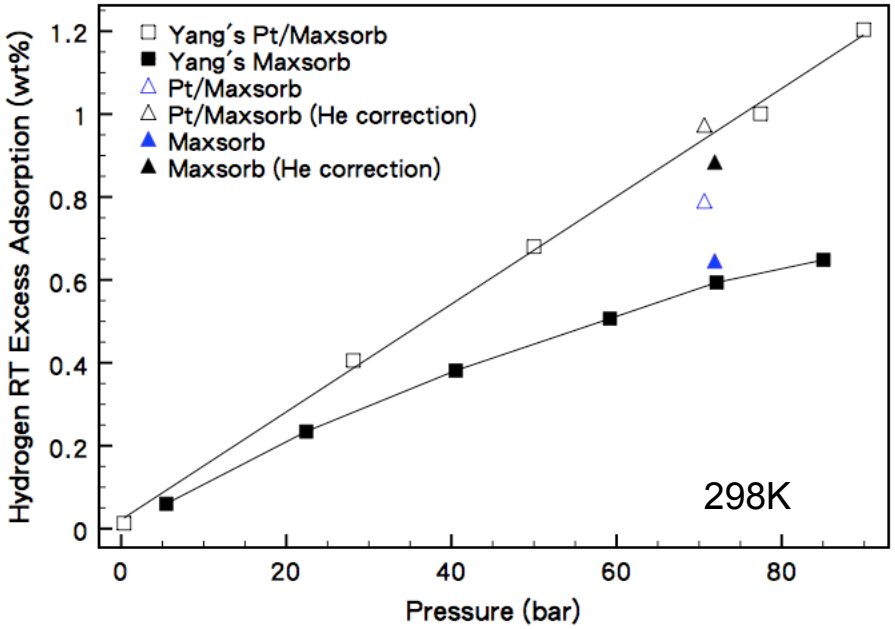
Approach: Hydrogen Spillover

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



Box 1: Reaction sequence for hydrogen spillover.





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

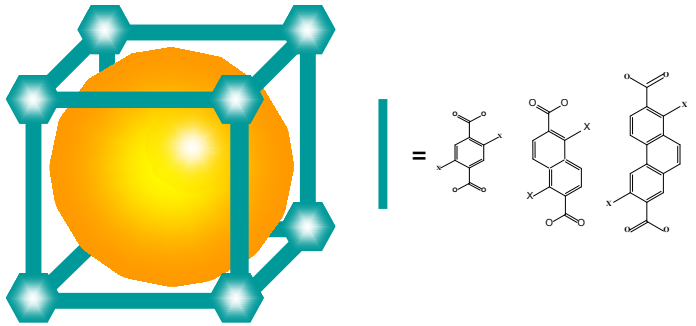
[Original] Approach: Material Design

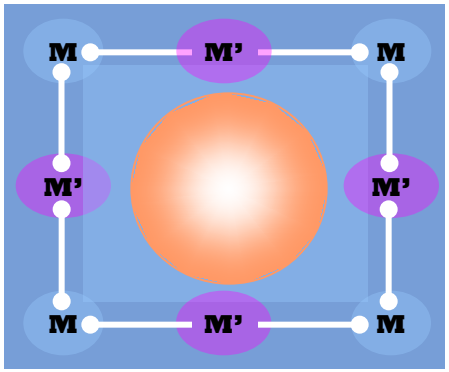
To increase uptake via Hydrogen Spillover Mechanism:

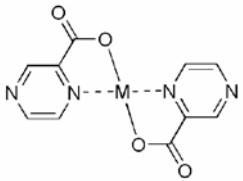
- Maximize metal dispersion
- Optimize hydrogen receptors to increase surface residence time → Surface Chemistry
- Change rate limiting step
  - Porosity?
  - Metal-Carbon Interface (Yang et al.)
- MMOFs provide systematic means to alter structure and porosity, however, direct doping is not trivial.

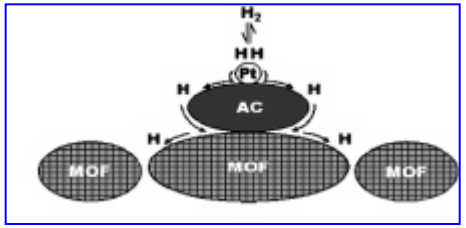
T vs. P switches:

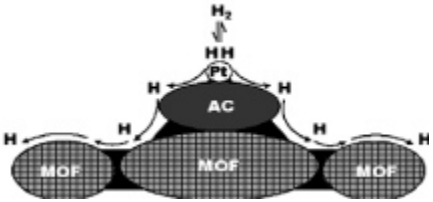
- Is it possible to use pressure to 'adsorb'; T to desorb…?
- Is it possible to use reverse spillover to 'trap' H in the material?











Li & Yang, JACS, 2006

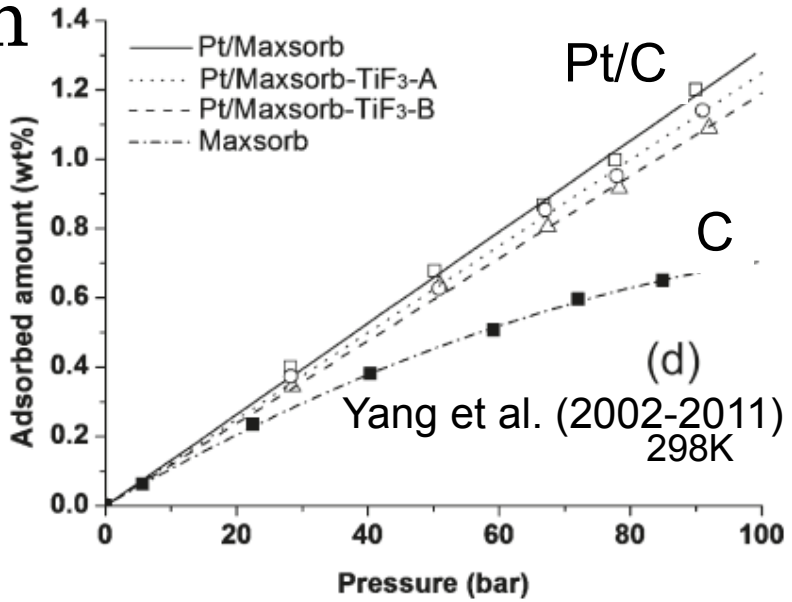
Modified Approach: Reproducibility, Verification, Mechanism

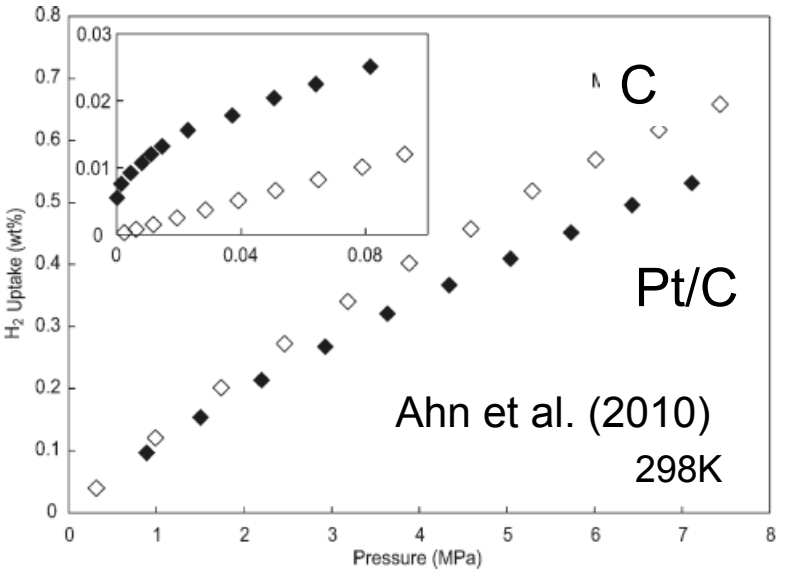
Reproducibility of spillover called into question in 2009/2010 (see figures, at right). Weak chemisorption workshop convened in August 2010.

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. Working synergistically with an on-going BES project, we have sought to add spectroscopic validation to our measurements.

In last year's AMR report, we concluded "grinding" method (originally used to mix MOF with catalyst) was more of an art than a science, and turned our attention to alternate ways to catalyze weak chemisorption to the MOFs.

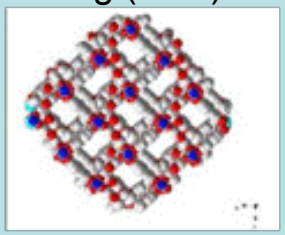




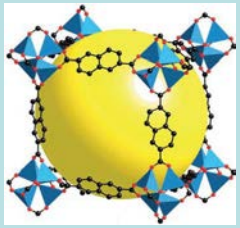
Previous (2009(left)-2010 (right) Results

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

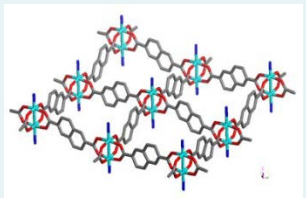
a: MMOF=O
230 m^2/g (BET)



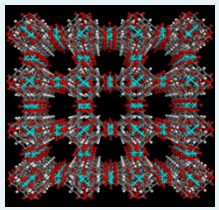
b: IRMOF8
1384 m2/g (BET)



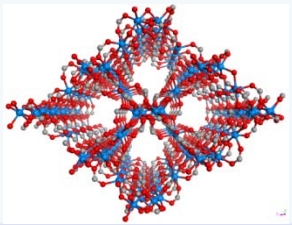
c: $Zn(NDC)(TED)_{0.5}$
2647 m^2/g (L)



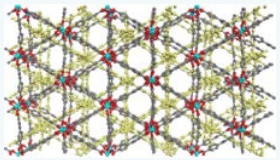
d: $Cu_3(BTC)_2(H_2O)_3$
1641 m^2/g (BET)



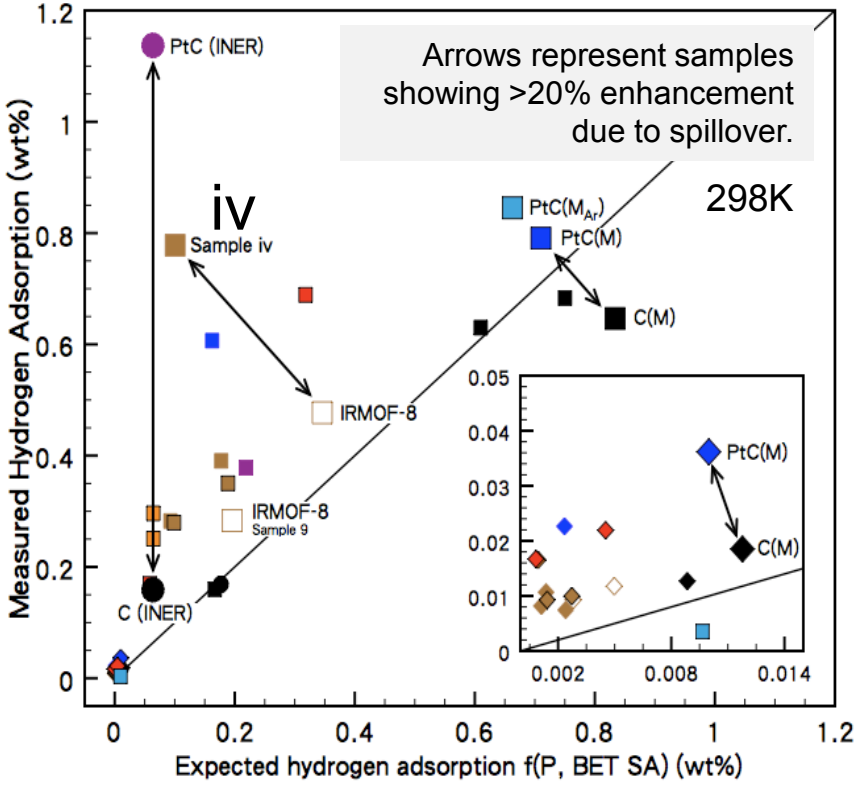
e: $Ni(HCOO)_6$
304 m^2/g (BET)

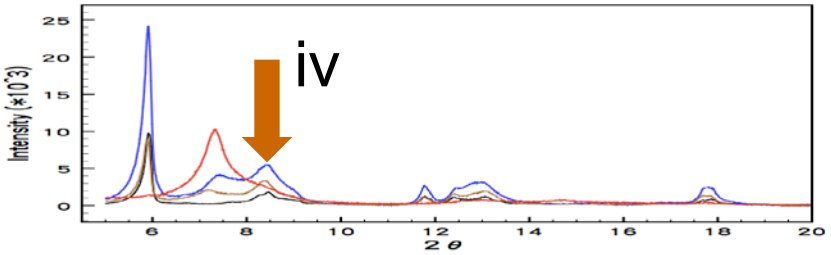


f: $Zn_3(bpdc)_3(bpy)$
792 m^2/g (BET)



Many MMOFs studied via 'grinding' method.
Select samples show enhancement via spillover; subtle changes in structure accompany 'good' uptake.





Approach: Upcoming Milestones and Go/No-Go

- Correlation between spillover and MMOF functional groups, leading to:
  - Correlation to surface chemistry of MOF ★
  - 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 leading to:
  - MMOF catalytic activity H-spillover (On-going)
  - Improved performance relative to Pt-C catalysts ★

Go/No-Go Decision Point (May 2012)

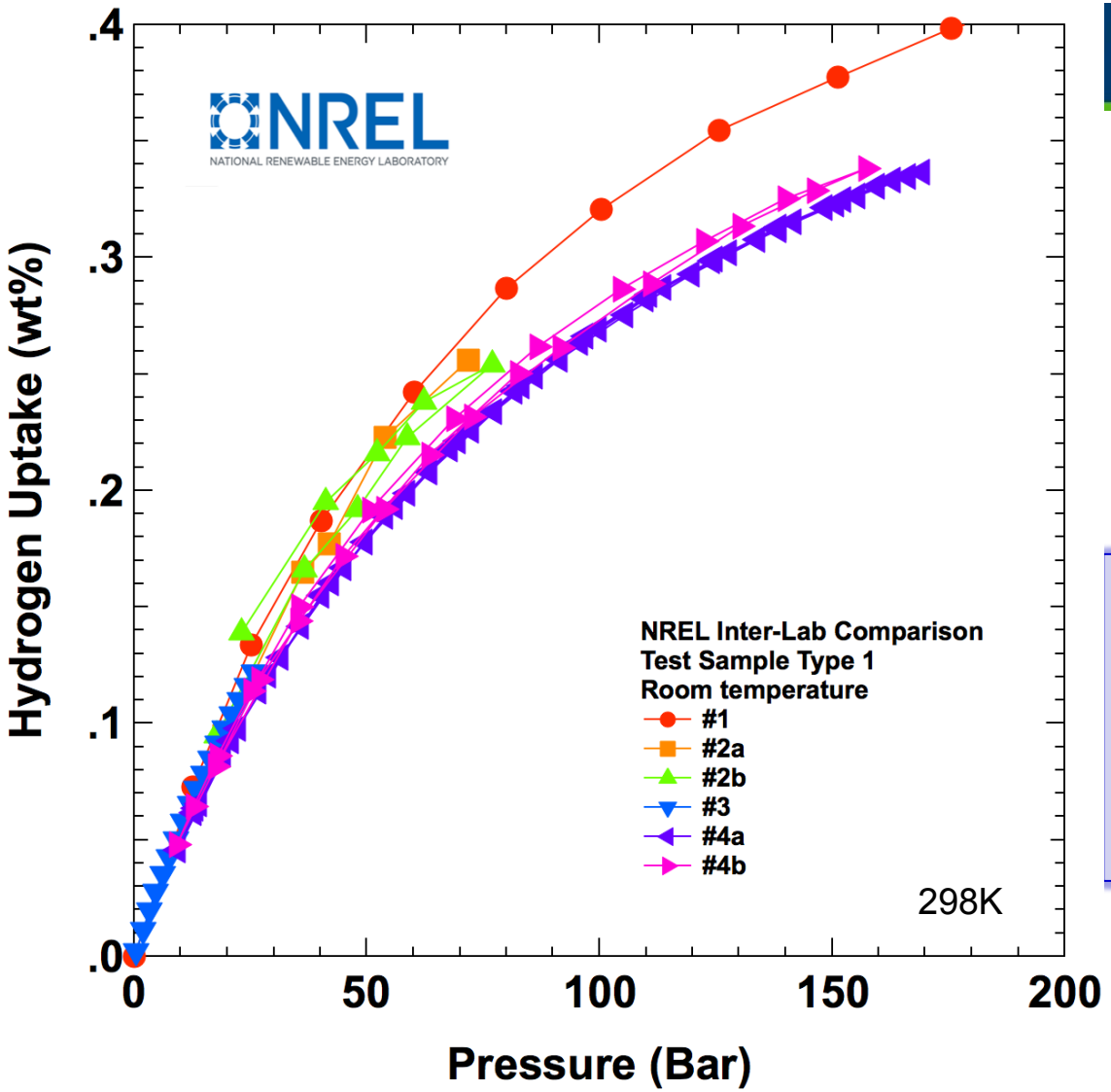
Exceed 5.5 wt% hydrogen storage through the use of the "hydrogen spillover" mechanism, MOF material, or a combination of the two as proposed at moderate temperatures (i.e. 300-400 K) and 100 bar with anticipated system penalties

Technical Barriers

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

Accomplishments and Progress

Worked Extensively with NREL for round robin testing, Pt/Maxsorb synthesis, and provided samples for DRIFTs



U.S. Department of Energy
Energy Efficiency and Renewable Energy

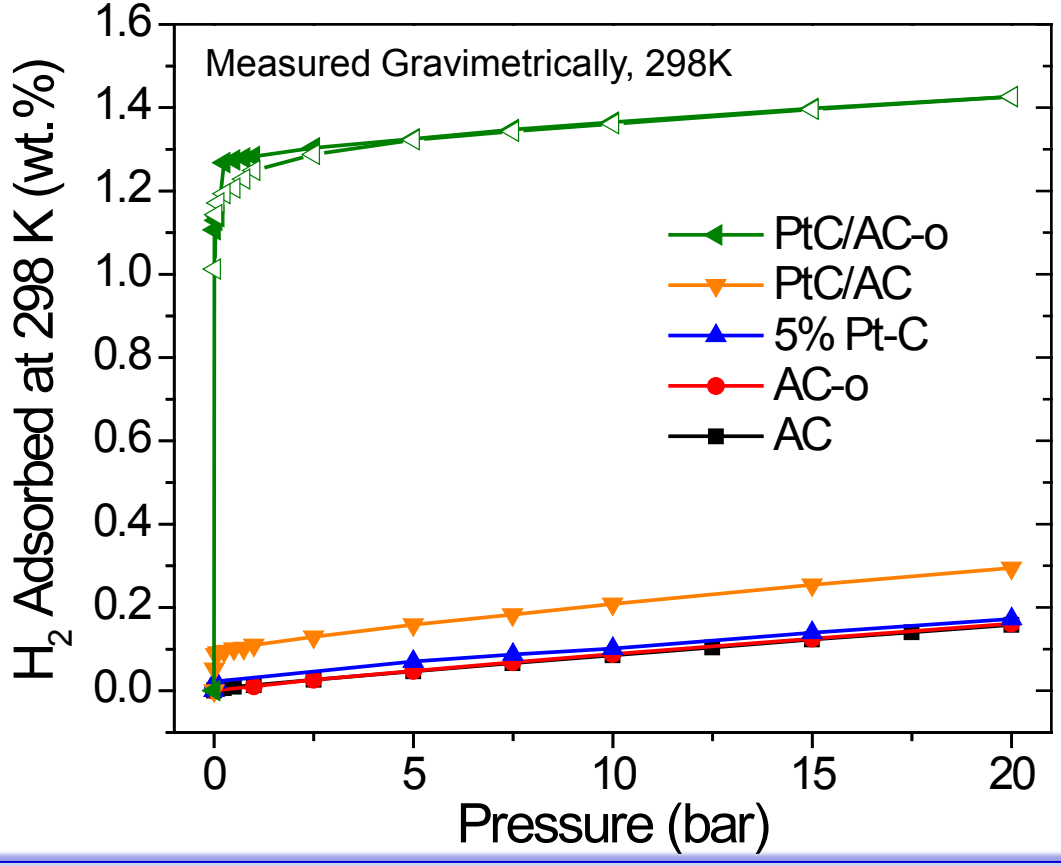
Spillover (Weak Chemisorption) Workshop

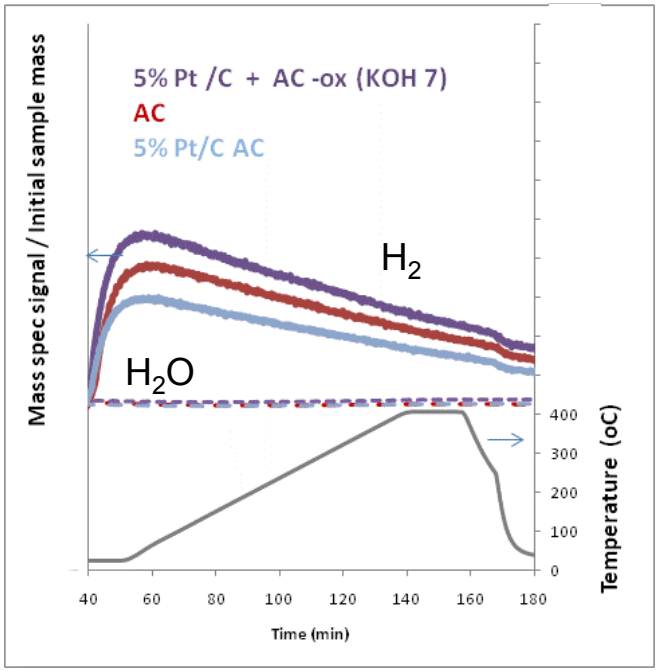
Contributors:
NREL: Thomas Gennett, Katherine Hurst, Philip Parilla, Lin Simpson.
Air Products: Alan Cooper
Univ of Toledo: Michael Heben
Penn State: Angela Lueking
NIST: Craig Brown
Institut de Chimie et des Materiaux de Paris Est: Michel Latroche
Max Planck-Institut für Metallforschung-Stuttgart: Michael Hirscher
Rice University: Boris Yakobson
Univ of Hawaii: Craig Jensen
LANL: Tony Burrell
SNL (ret) DOE Tech Team: George Thomas

Participated in Round Robin test (left). To be discussed by NREL.

Provided additional Pt/AC sample to NREL for validation of volumetric results and FTIR tests.

Effect of Surface O Groups and H_2O on Hydrogen Spillover in Pt/AC

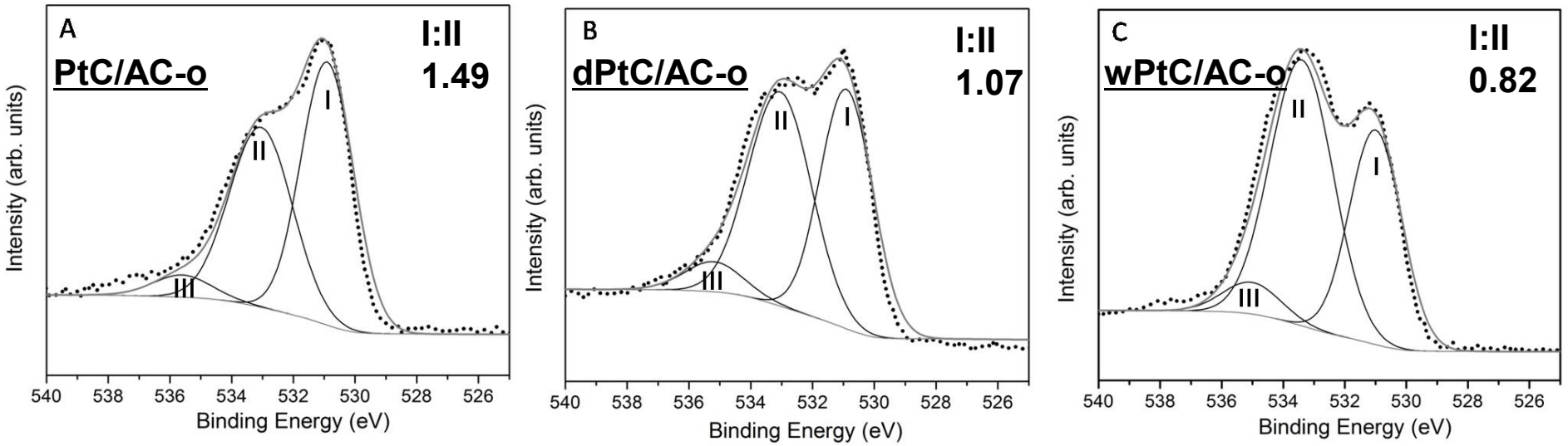




AC and Oxidized AC have same physisorption. No signficant change in pore structure.
Significant low-pressure increase when mixed with catalyst. H:M_T > 440.
(Catalyst is reduced in situ, so cannot be attributed to catalyst reduction.)
Incomplete desorption: 1 wt% after 40 minutes; 0.5 wt% at 8743 minutes.
No evidence for H_2O desorption found in TPD.
Uptake disappears when 6x9 H_2 purity used, reappears when water is added to pretreatment—Changes in surface chemistry in presence of H_2O seen in XPD.

Li, Q.; Lueking, A.D., *J. Phys. Chem. C*, ***115,*** *4274,* 2011.

Effect of Surface O Groups and H_2O on Hydrogen Spillover in Pt/AC: Evolution of O Groups



High resolution O 1s XPS spectra. (a) as-synthesized PtC/AC-o, (b) after dry pretreatment and H_2 adsorption, dPtC/AC-o; and (c) after wet pretreatment and H_2 adsorption, wPtC/AC-o.

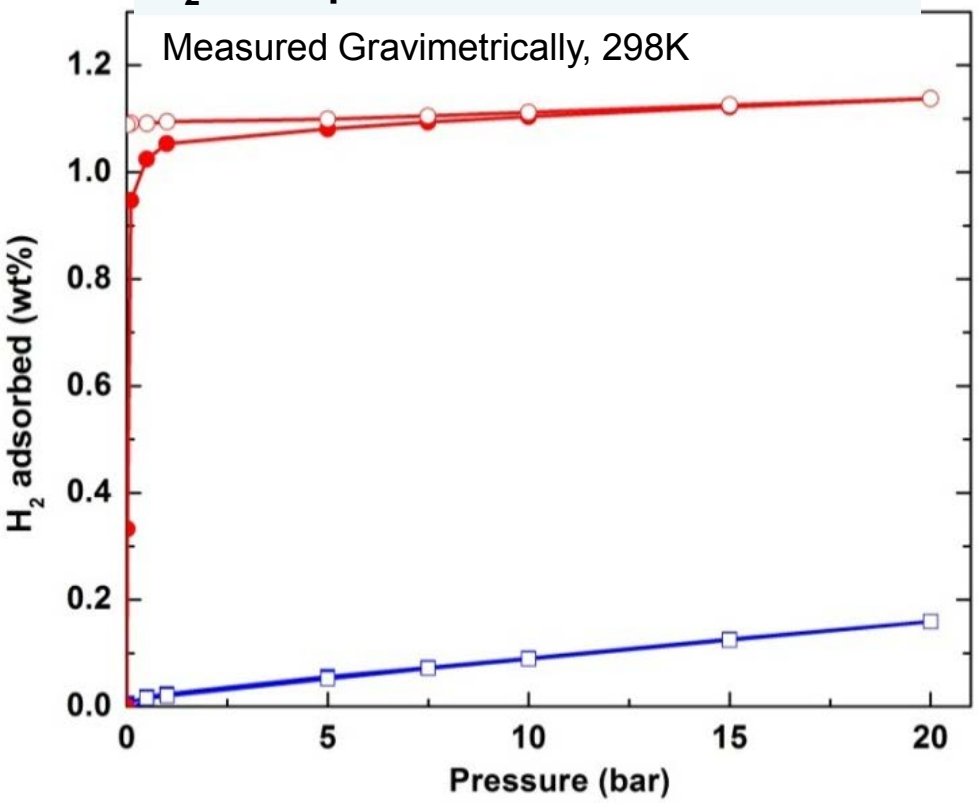
Sample code	C 1s (%)	O 1s (%)	K 2s (%)	Pt 4f (%)	O:C
PtC/AC	74.70	20.88	3.84	0.58	0.28
dPtC/AC-o	75.04	19.97	4.58	0.40	0.27
wPtC/AC-o	72.65	22.23	4.68	0.44	0.30

1) H_2O added more oxygen on the surface in the pretreatment, which facilitates spillover.
2) Carbonyl/quinone type groups bind with spilt-over hydrogen to form hydroxyl groups.

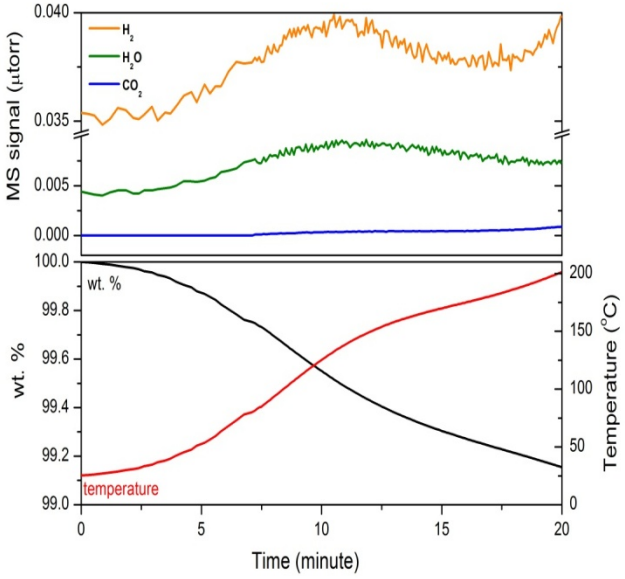
Li, Q.; Lueking, A.D., *J. Phys. Chem. C,* ***115,*** *4274,* 2011.

Unusual H_2 Uptake of Pt/C from INER

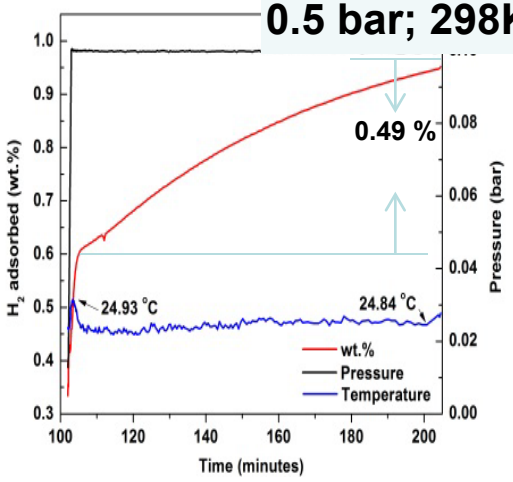
H_2 adsorption in static mode at 25 °C



TPD-MS after 'flow' 0.5 wt%



0.5 bar; 298K



Pt/C provided by INER had high low pressure uptake via gravimetric instrument in "6x 9s H2", similar to our oxidized Pt/AC.
Mass spec used (right) to test for water.
Uptake was slow ; Majority occurred at P<1 bar (right)
Uptake highly dependent upon activation and age.
Unusual dependence upon reactor configuration

Tsao, C.S.; Lueking, A.D., et al., *J. Phys. Chem. Lett.*, **2,** 2322, 2011.

Inelastic Neutron Scattering

A collaboration between INER, NIST, MIT.

PSU provided gravimetric data, guiding experimental conditions.

- Two Pt/AC samples
  - 1: 4.2 nm, 3.3 wt% Pt
  - 2: 1.6 nm, 0.79 wt% Pt
- INS with Filter-Analyzer Neutron Spectrometer
  - 4-45 meV
- H_2 loading:
  - 77K; (small loading to minimize background; compatible with isotherm); Sealed→ 4K (red triangles)
  - 298K, 6-10 hr, "spillover"→ 4K (black circles)
  - Loss of peak at 14.7 meV [and recoiling background] shows loss of H_2
  - Repeat (green) rules out leakage
- H:Pt estimated to be ~50-fold
- Results more pronounced for Pt/AC-2

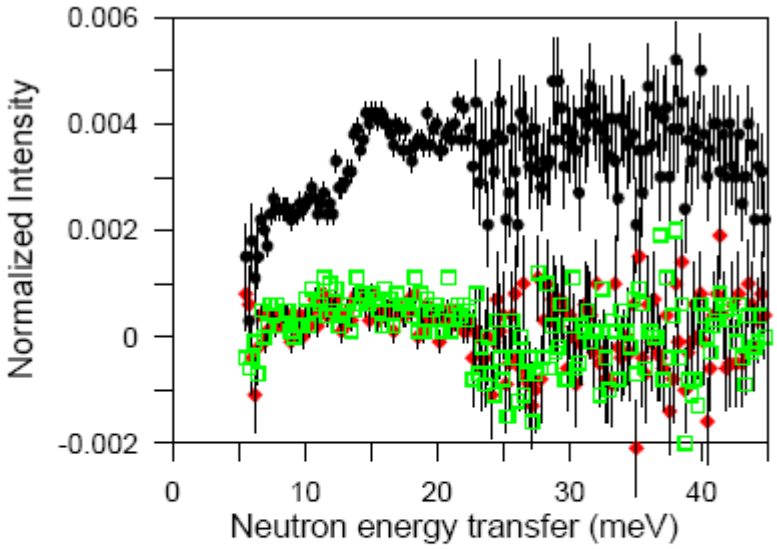


Figure 2. Rotational spectrum of the Pt/AC_2 sample (1) with preloaded hydrogen (black circle), (2) after the first temperature-cycling (red triangle), and (3) after the second temperature-cycling (empty green square). The sample weight is 0.4 gram.

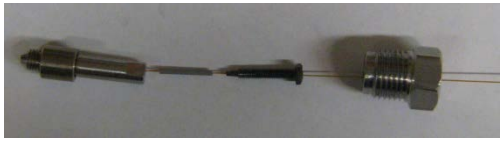
Tsao, C.S.; Lueking, A.D., et al., *J. Phys. Chem. Lett,* 2011, *2,* 2322-2325.

DOE-BES Study: New Raman mode in H_2 for Pt/C

Sample sealed within fiber, degassed within the capillary at 498K for 72 hours
Subsequent gas exposures have intermediate degas at 298K for 72 hr

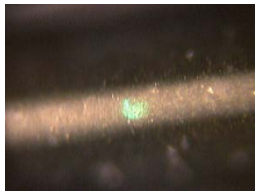
New REVERSIBLE mode at 1180 cm^{-1} seen upon H_2 exposure. Isotopic shift seen for D_2.

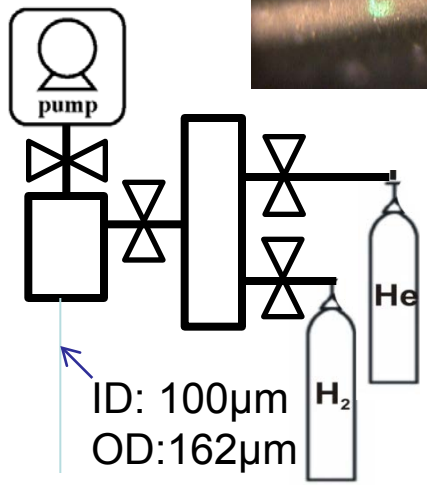
Please come to my BES poster later today for further information.

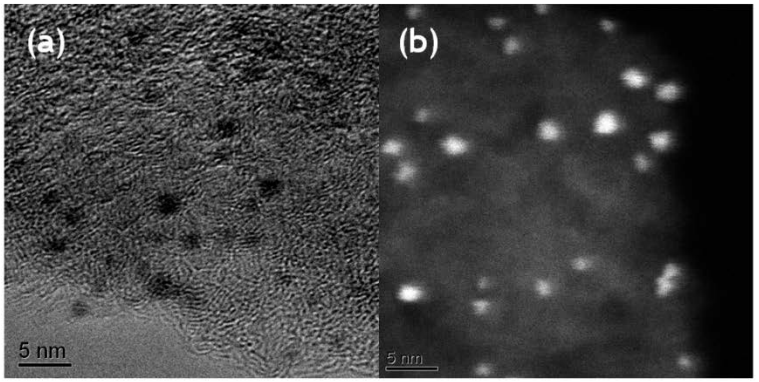


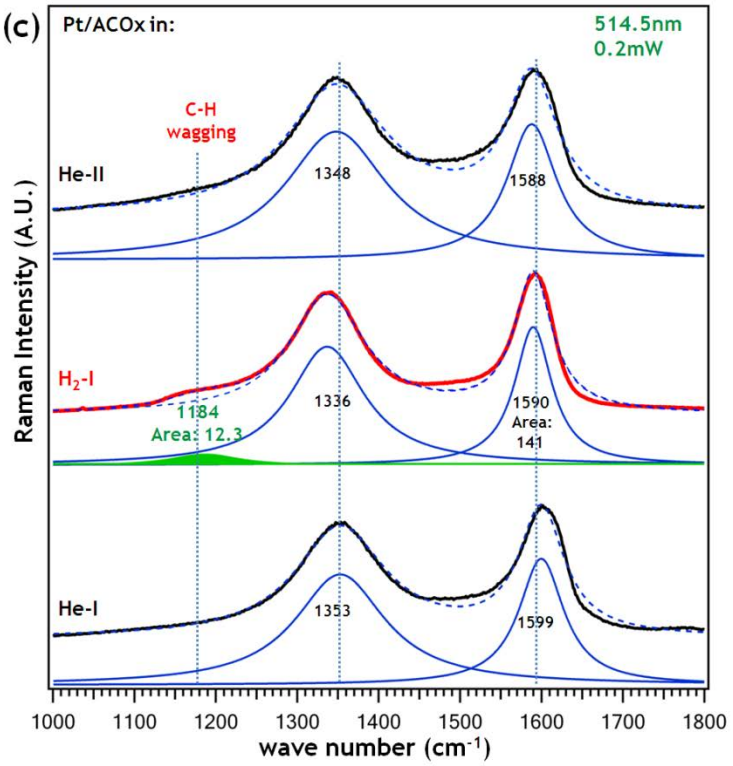
ID: 102μm OD: 162 μm

100μm



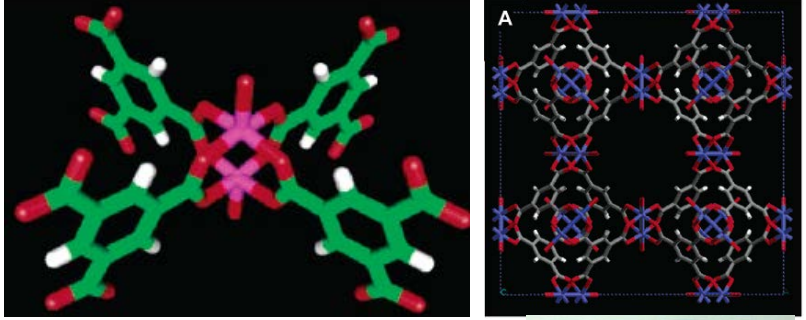


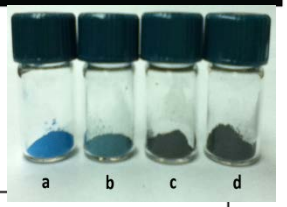




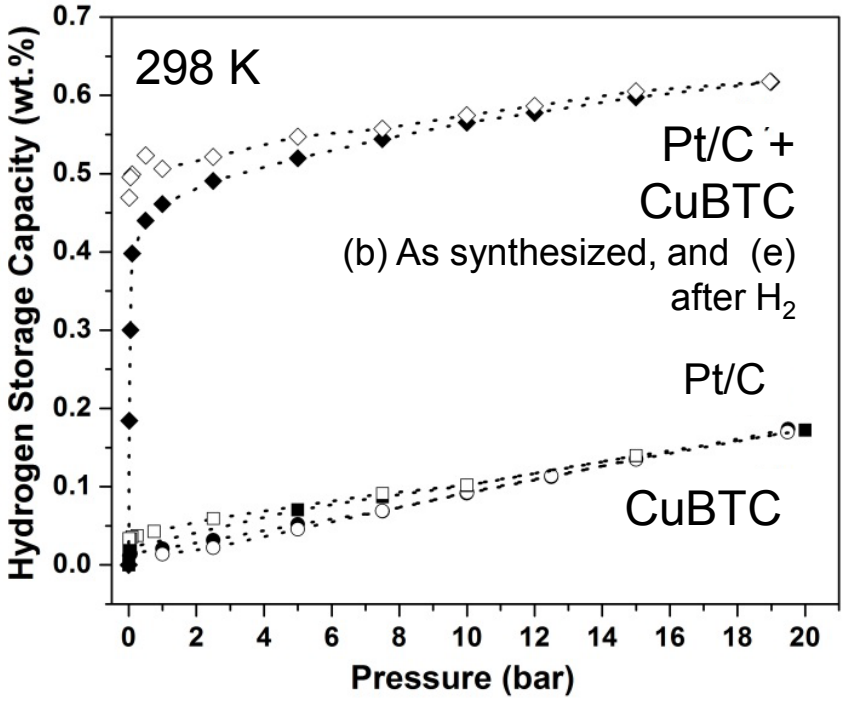
(6) Liu, X.M.; Lueking, A.D., Badding, J.V., Crespi, V., Tsao C.S., et al., In Progress

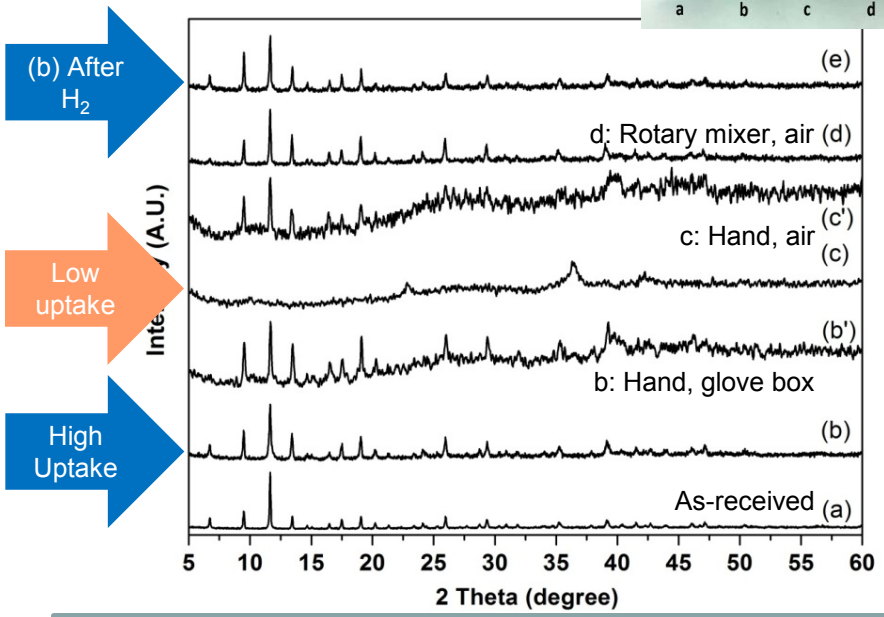
Ex Situ Evidence for Spillover to CuBTC





Previously: chemisorption of CuBTC via spillover from PtC





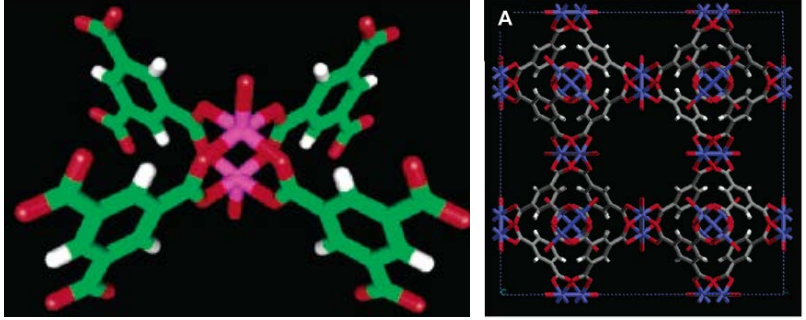
Sample with intact structure (b, multiple measurements), had high uptake at low P, 298 K

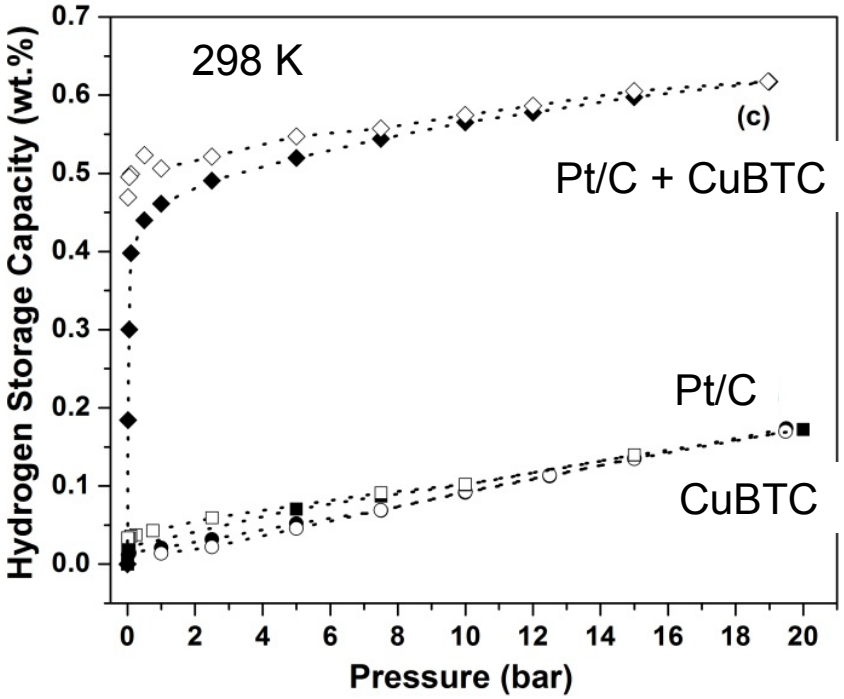
Irreversible binding of ~0.5 wt%

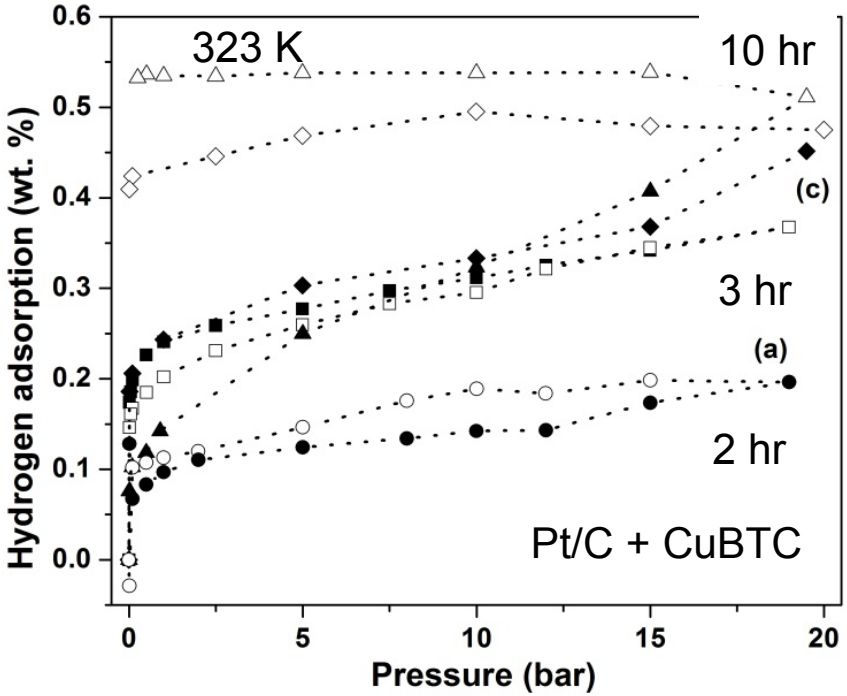
Stability correlates with mixing intensity, not atmosphere

Lueking et al., *J Phys. Chem. C,* 116 (5), 3477–3485, 2012.

Evidence for chemisorption of CuBTC via spillover from PtC





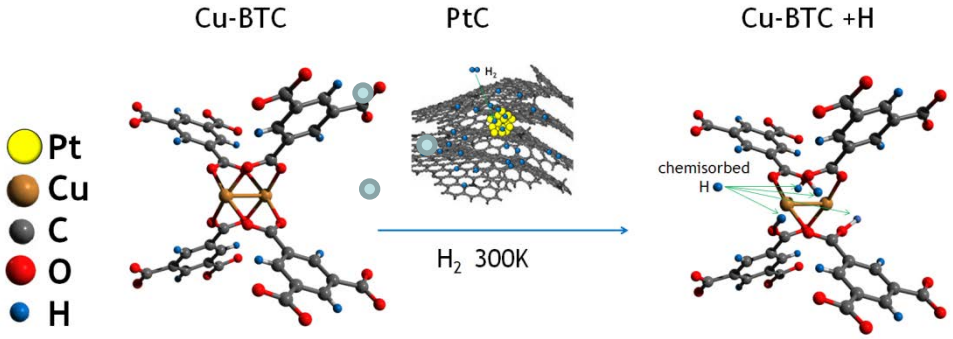


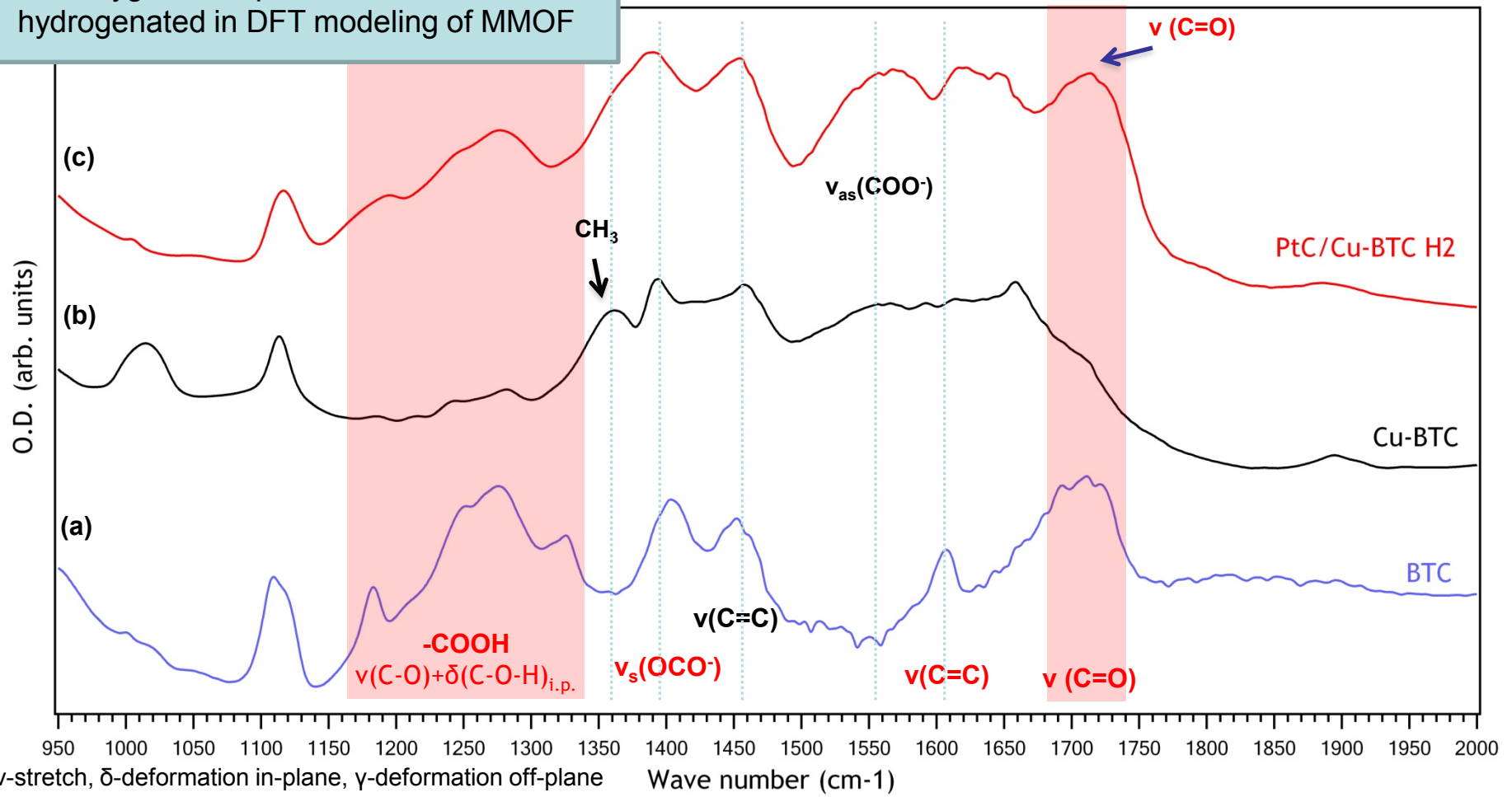
Increased Temperature Led to Slow, P-independent Uptake;
Irreversible binding of ~0.5 wt%

Lueking et al., *J Phys. Chem. C,* 116 (5), 3477–3485, 2012.

Spectroscopic (ex situ) validation of hydrogenation

Ex situ FTIR suggests hydrogenation of C-OO-Cu to form C-OH-O-Cu complex Oxygen Group never found to be hydrogenated in DFT modeling of MMOF





*Additional Data: XRD, Raman, Preliminary DFT

Lueking et al., *J Phys. Chem. C,* 116 (5), 3477–3485, 2012.

Accomplishments and Progress

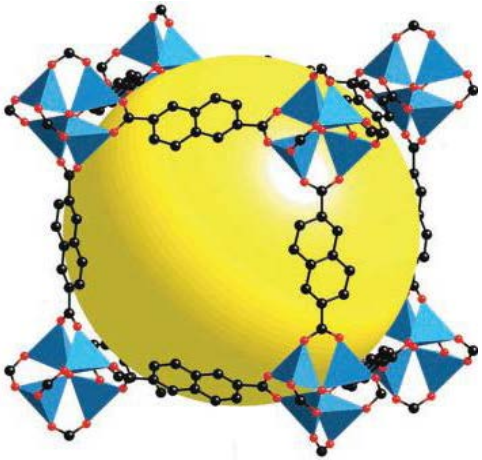
Direct-Doping of MOFs

Grinding "Method 0" produces inconsistent results. Exploring methods to 'direct dope' MOFs with specifically tailored structures.

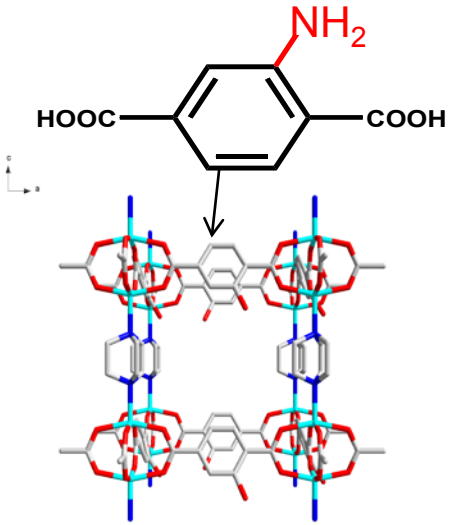
0. Original Grinding Method (Yang et al.)

1."Pre-bridge" with Pt/C in MMOF synthesis (Bandosz, *Adv. Mater.* 2009; Park, *Int.J. H_2 Energ.* 2010)

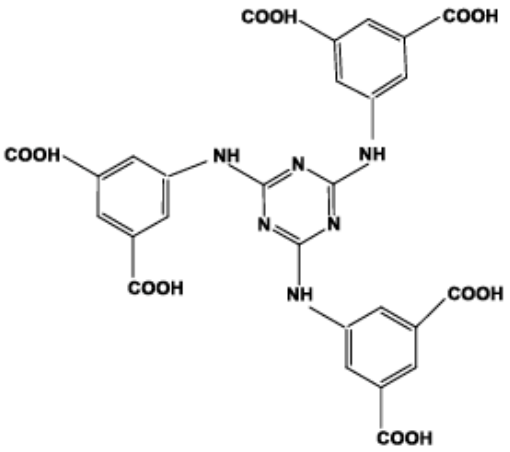
2.Direct doping with Tailored MOFs to anchor catalysts: 2a--Organic (Sabo et al., *J. Mater. Chem.* 2007) vs. 2b--Aqueous



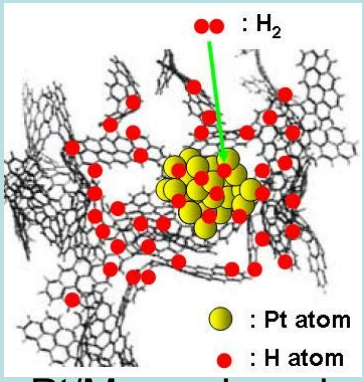
IRMOF8



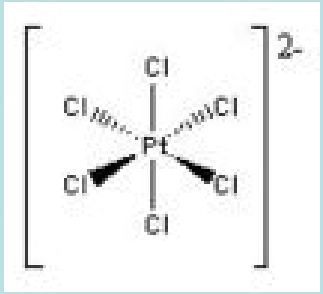
$[Zn(BDC\text{-}NH_2)(TED)_{0.5}]$



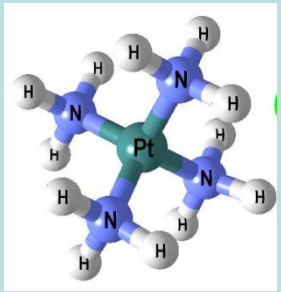
TDPAT



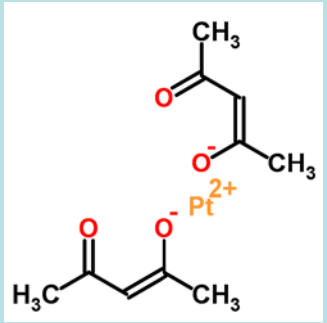
Pt/Maxsorb and Pt/Carbon Aerogel



$PtCl_6^{2-}$



$Pt(NH_3)_4^{2+}$



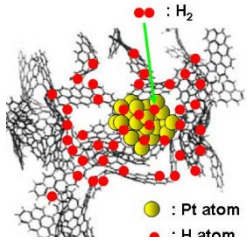
$Pt(acac)_2$

Accomplishments and Progress

MOF Direct-Doping:

1. "Pre-bridge"

Pt-doped Maxsorb AC had better properties than Pt-doped Carbon Aerogel. Oxidation of carbon aerogel led to decrease of uptake.

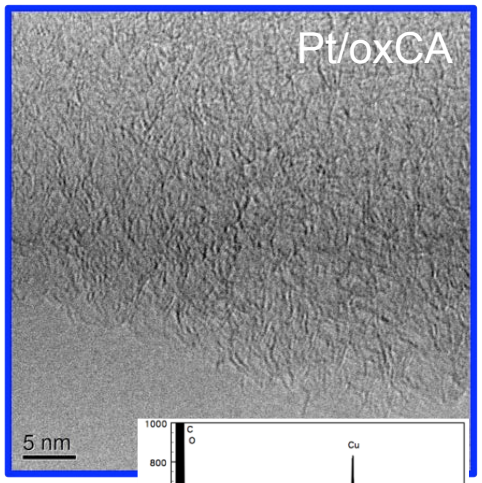


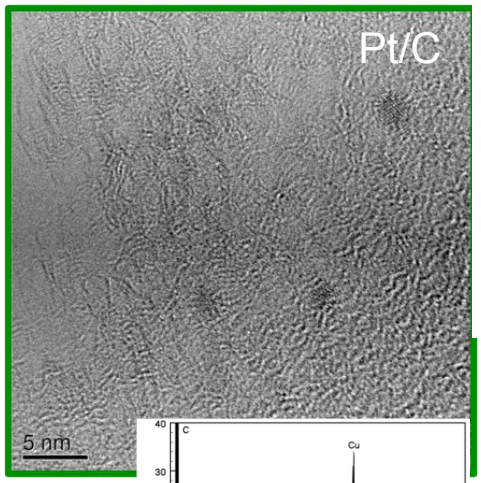
CA (Carbon Aerogel) → oxCA → (5 wt%) PtoxCA

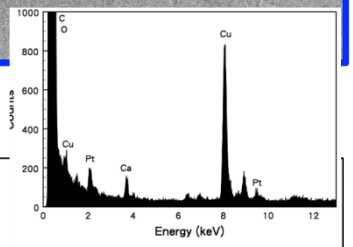
Oxidation

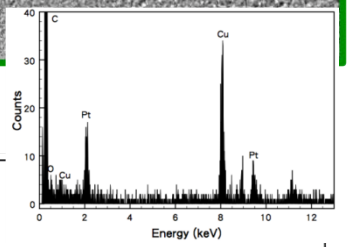
Maxsorb "C" → (5 wt%) PtC

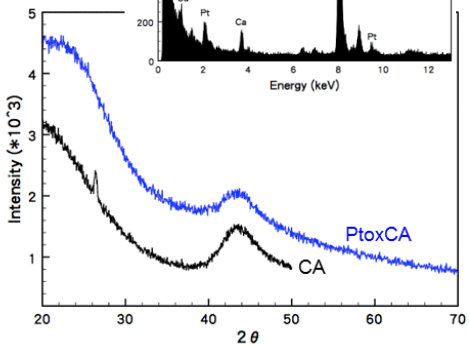
$Pt(acac)_2$ doping

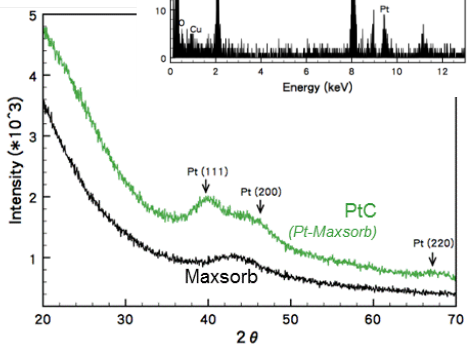


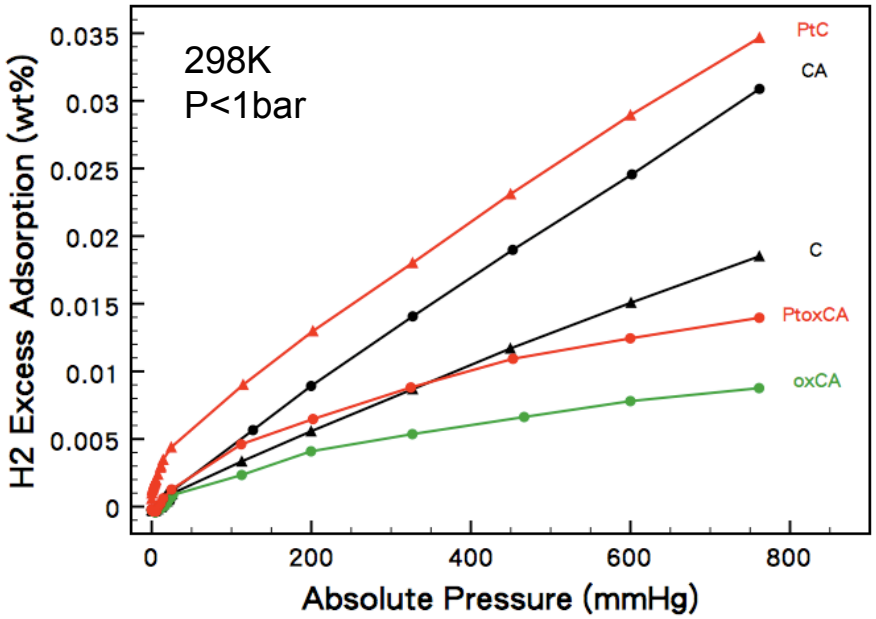


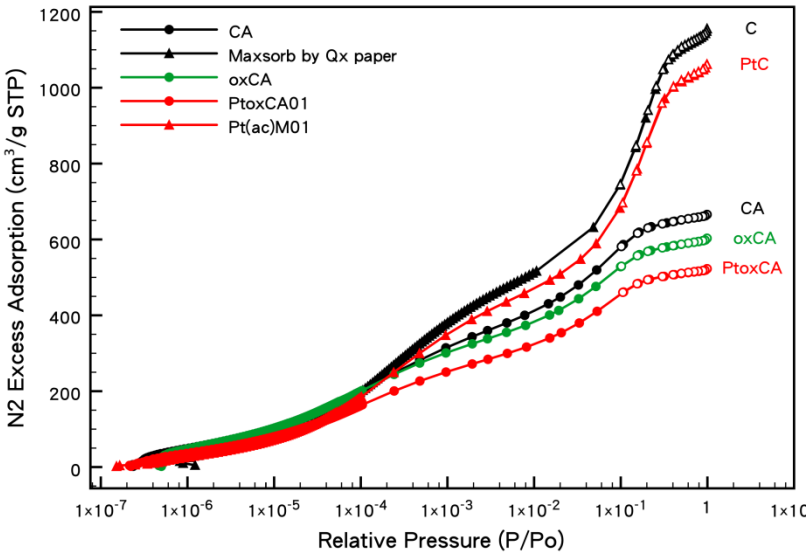








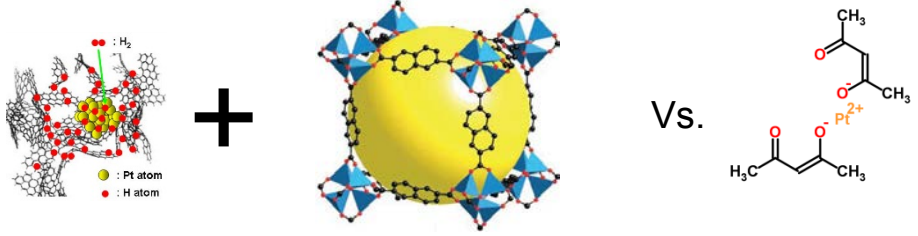




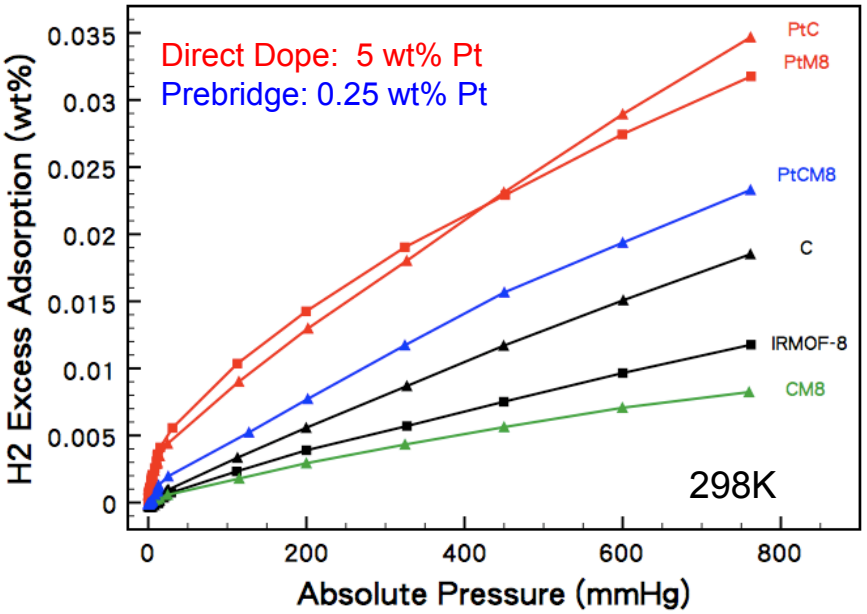
MOF Direct-Doping:

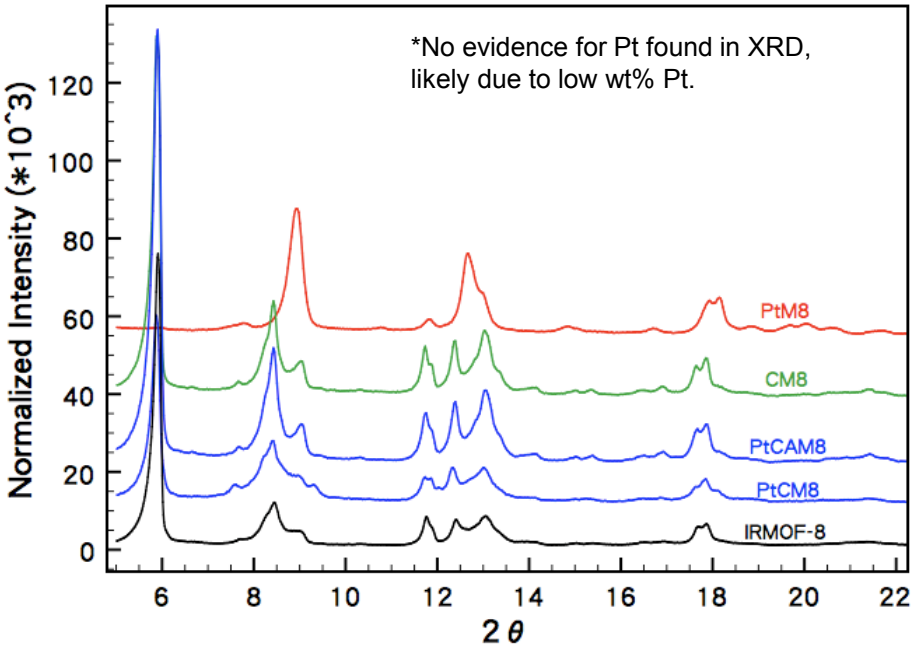
1."Pre-bridge" (PtC+IRMOF8) vs.

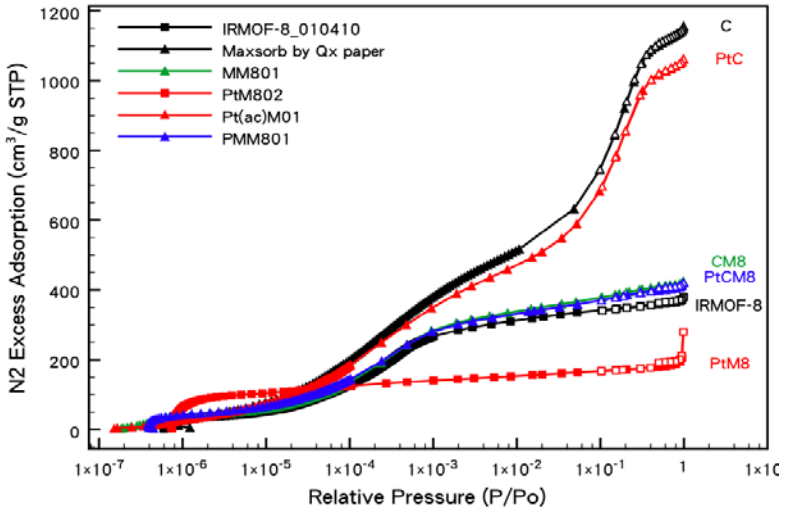
2a. Direct Doping (Pt/M8=IRMOF8)



- Pt/C and Pt/CA catalyst added to IRMOF8, *increasing* porosity, and not altering XRD.
- H_2 uptake was not as high as direct-doped MOF, but less Pt used
- Direct-doping led to increase in microporosity, decrease in mesoporosity and change in XRD





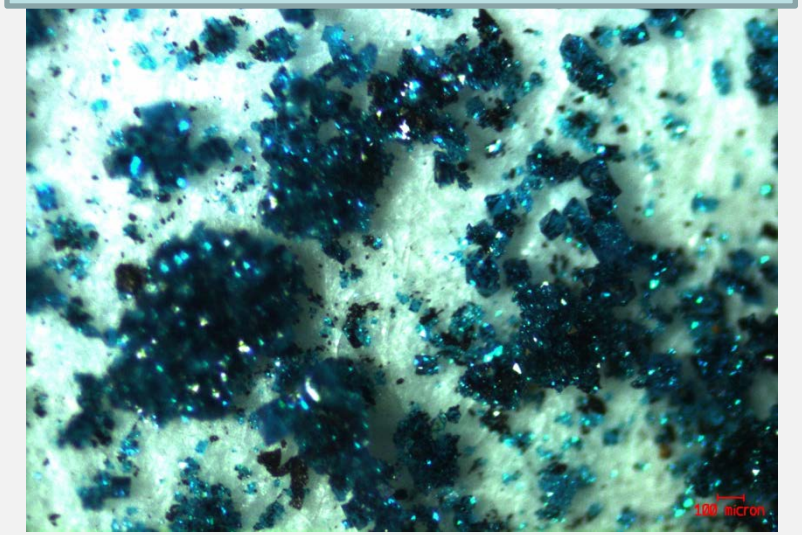


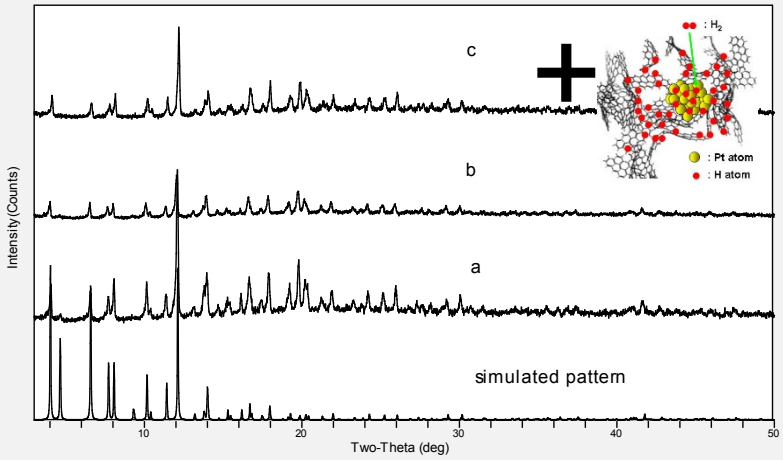
Accomplishments and Progress

MOF Direct-Doping:

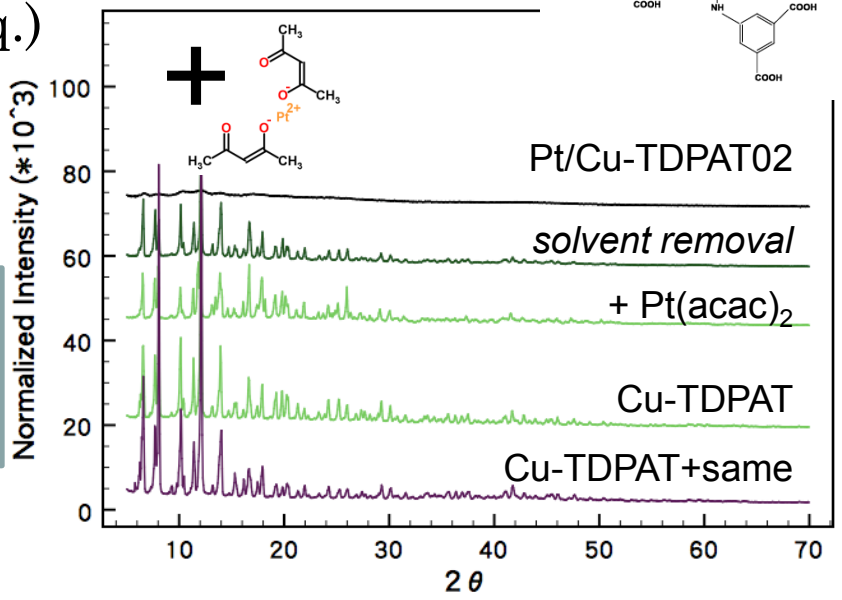
2b. Direct Doping with tailored MOF (aq.)

Phase separation seen with ‘pre-bridge’; XRD intact.

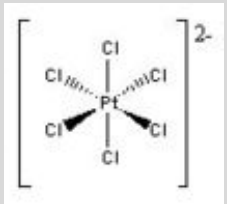




Instability with organic doping. →

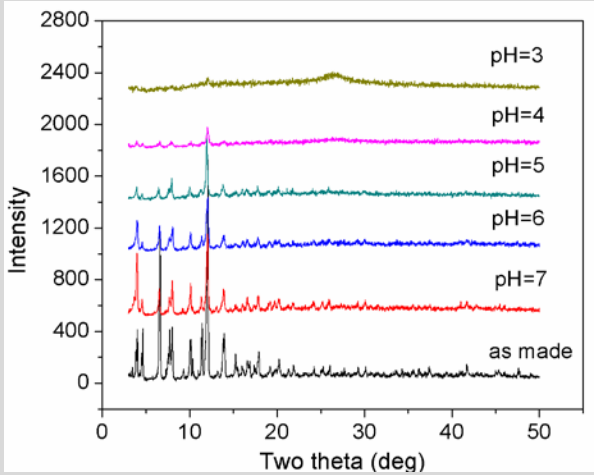


	pH				
before	7	6	5	4	**3**
after	**7**	**6**	**5-5.5**	**4.5-5.0**	**4-4.5**

+ 

$PtCl_6^{2-}$

Aqueous doping in progress. MOF is stable at pH>~4, allowing for charge of NH groups.



Collaborations

University:

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

Collaborations in 2011

- Tsao, Taiwan Federal Laboratory (sample exchange, INS)
- National Renewable Energy Laboratory (spillover, blind tests, and measurements)
- Ted Baumann (LLNL, provided carbon aerogel for Pt/CA)
- Badding and Crespi (PSU, application of in situ characterization methodology developed under BES project to CuBTC)

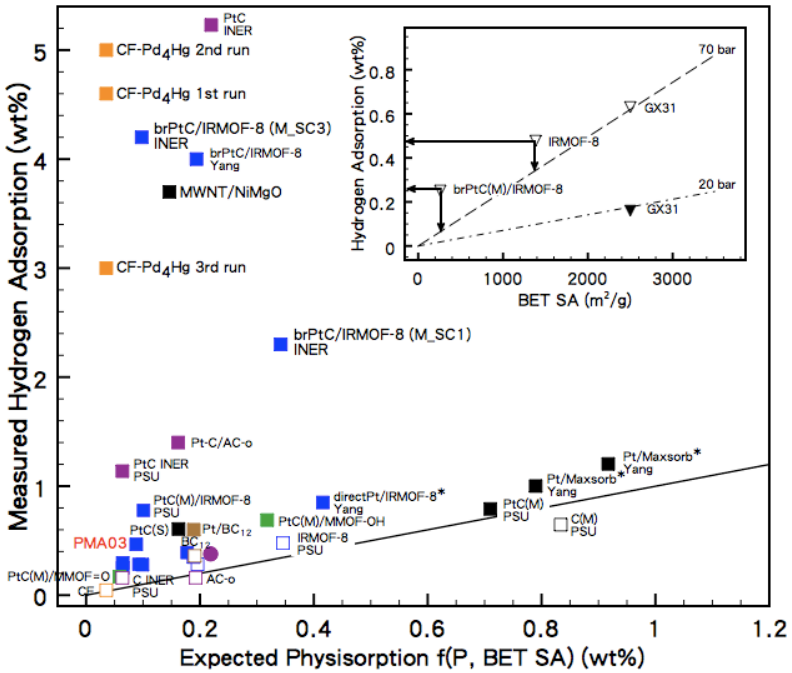
Upcoming Collaboration

- George Froudakis, University of Crete (modeling)

Outside and Inside DOE H_2 and FC Program

Summary

- Spectroscopic evidence for spillover
  - Inelastic neutron scattering (with INER)
  - Ex Situ IR of PtC/CuBTC shows evidence carboxylate converts to carboylic acid
  - Reversible C-H mode seen for INER Pt/C (To be discussed at BES poster)
- Anomolous low-P uptake for Pt/Cs can now be explored with spectroscopy
  - Pt/Cs have low P Uptake >1 wt%
  - Samples are pre-reduced, so cannot be catalyst reduction.
  - Configuration dependent, exploring 'energy window'
- Mixed results for direct-doping of MMOFs
  - Additional studies on-going for reproducibility measurements
  - Plan to resolve with aqueous doping and in situ spectroscopy



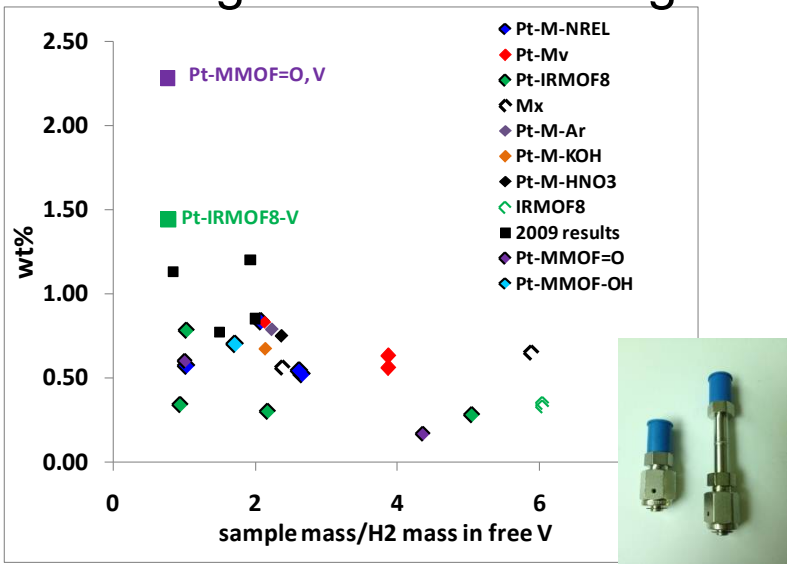
- Fundamental studies are needed to realize key to 'activate' spillover

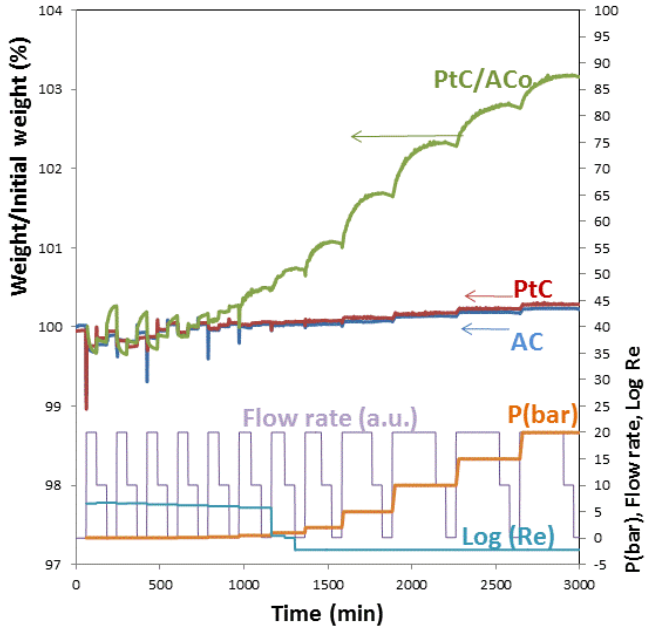
Future Work

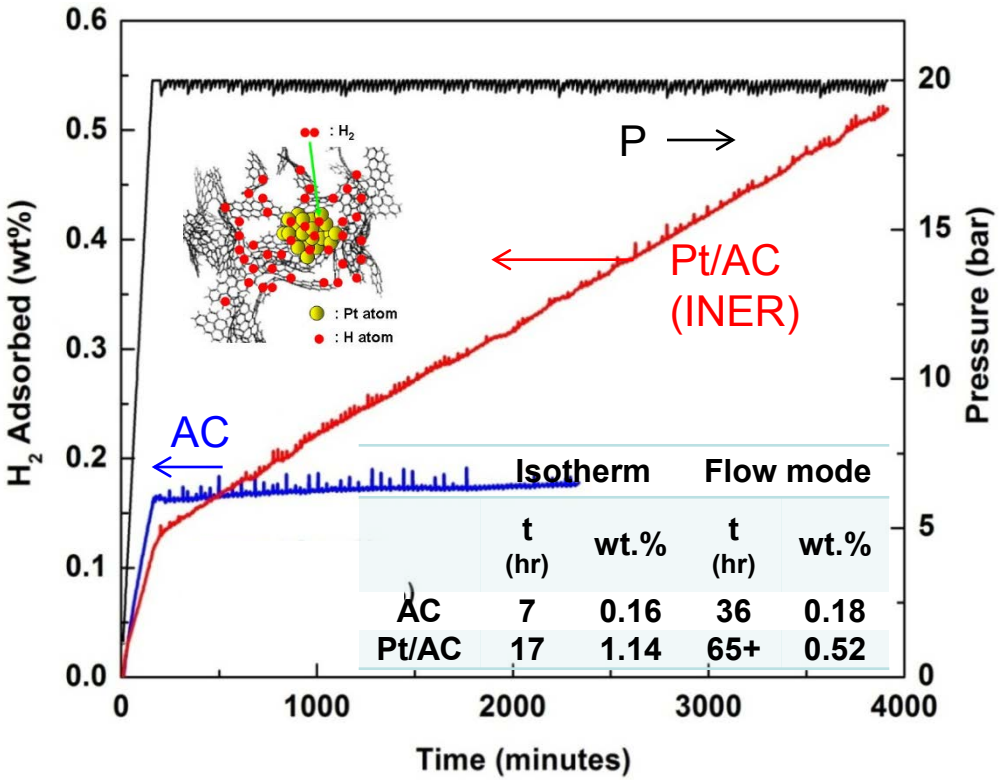
- Finalize MOF Doping Studies
- "Energy Window" to Account for Reactor Configuration
- Simultaneous, In situ, Adsorption + Spectroscopy
- Controlled metal adsorption during doping in aqueous environment

Related Collaborative Work

- Raman test of "Good" vs. "Bad" Samples
- Modeling for Material Design







Technical Back-Up Slides

Effect of Surface O Groups and H_2O in Pt/AC

Change in Pore Structure

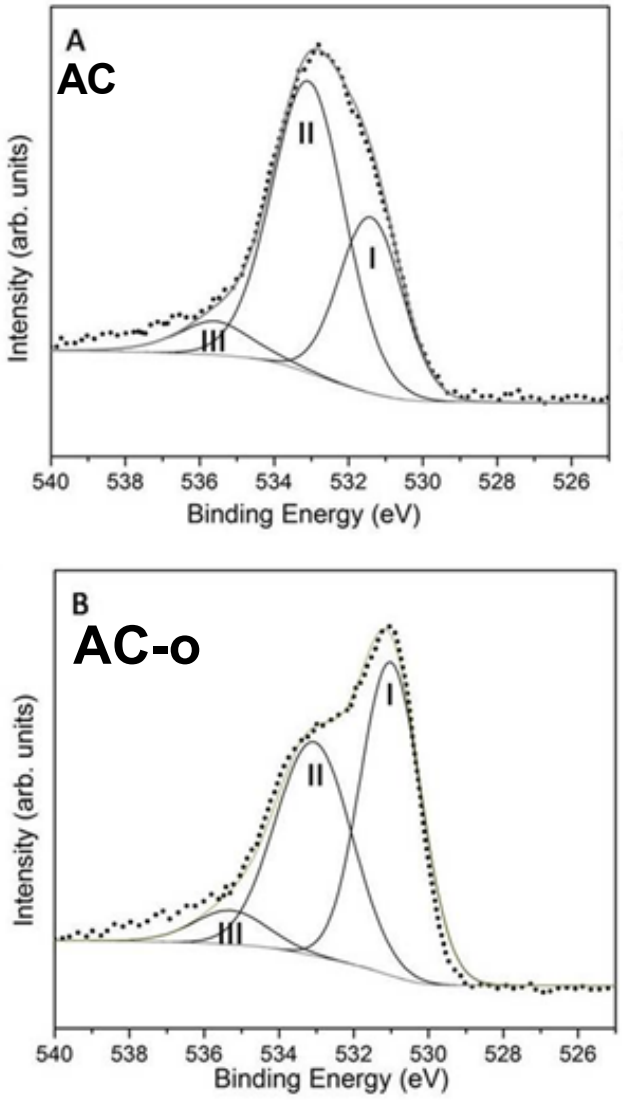
Sample code	S_{BET}[a] (m^2/g)	V_{N2}[b] (cm^3/g)	S_{micro}[c] (m^2/g)	V_{micro}[d] (cm^3/g)	W_{ave}[e] (nm)
AC	3145	1.35	512	0.14	0.56
AC-o	2720	1.13	486	0.13	0.52
5% Pt-C	651	0.18	380	0.10	0.54
PtC/AC-o	2286	0.97	445	0.12	0.52

I: C=O
II: C-OH, C-O-C, COOH
III: Adsorbed water or oxygen

Change in Surface Chemistry

Sample code	C 1s (%)	O 1s (%)	K 2s (%)	Pt 4f (%)	O:C[c]
AC	81.15	18.85	0	0	0.23
AC-o	72.94	20.48	6.58	0	0.28

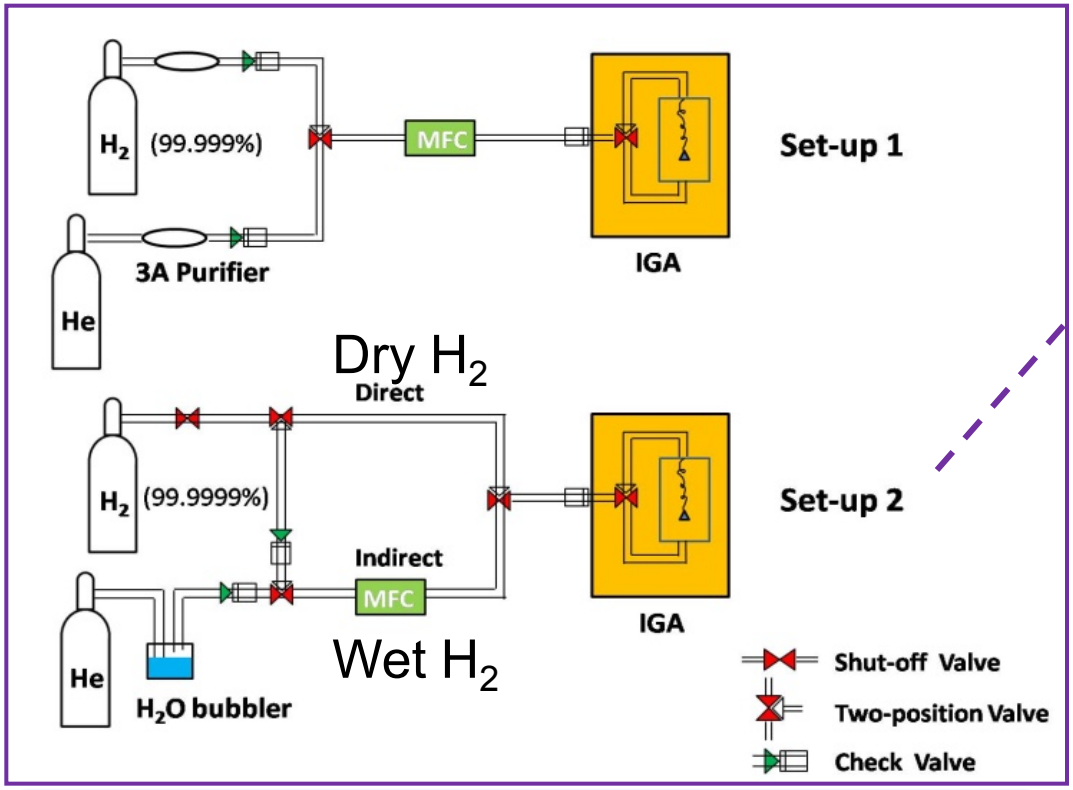
XPS O 1s

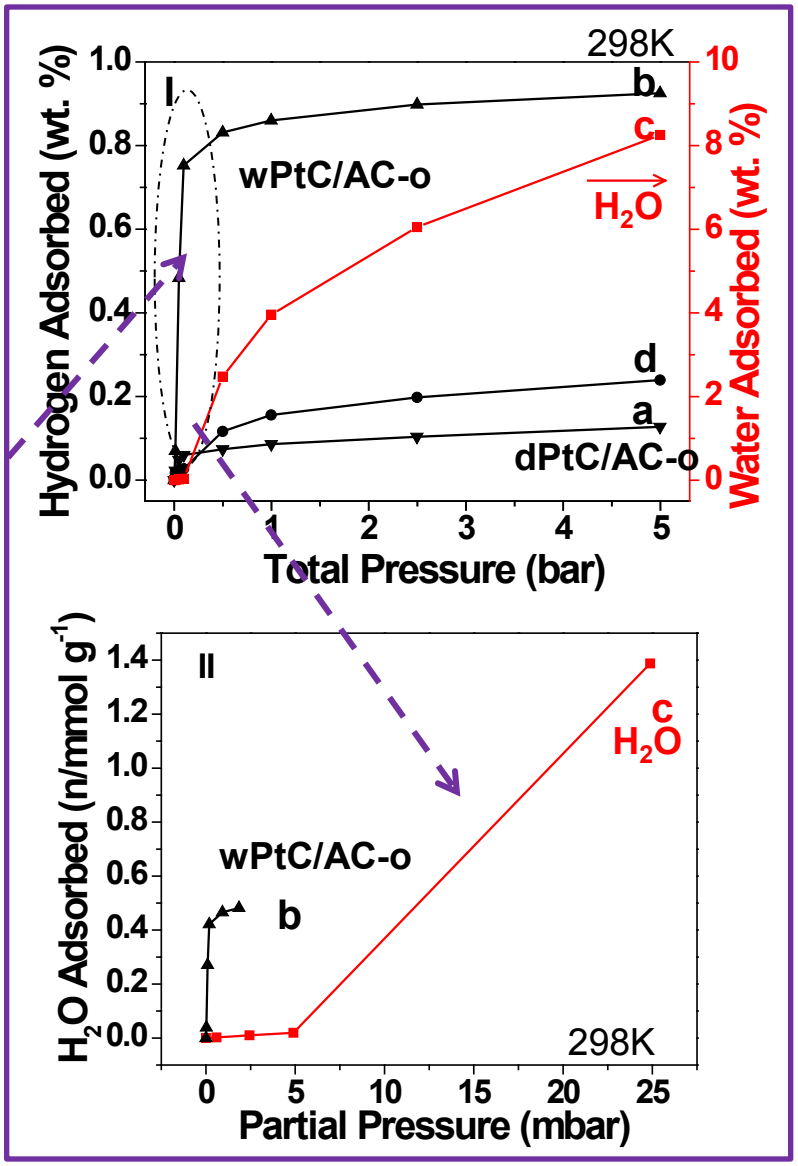


Li, Q.; Lueking, A.D., *J. Phys. Chem. C,* ***115,*** *4274,* 2011.

Effect of Surface O Groups and H_2O on Hydrogen Spillover in Pt/AC

Gas line for Set-up 1 vs. 2 from gas cylinders to gas adsorption instrument IGA





Trace water in pretreatment line implicated in changing surface chemistry and/or doping carbon surface.

Water adsorption cannot account for observed behavior. No H_2O desorption seen in TPD (previous slide).

Li, Q.; Lueking, A.D., *J. Phys. Chem. C*, ***115,*** *4274,* 2011.

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.

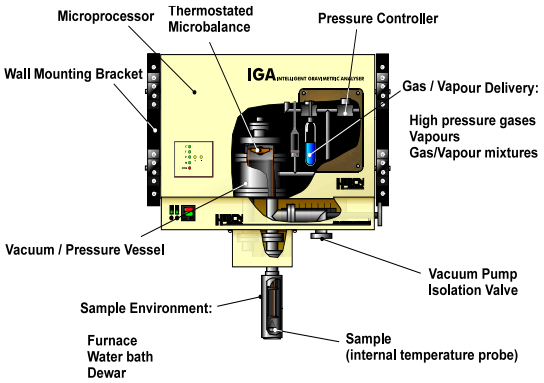
Change in 2011- increased accuracy

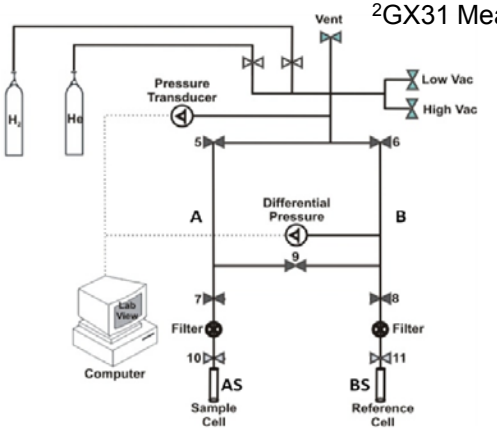
Increased Pressure & Uptake: Used for Rapid-Screening for Go / No-Go

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)**

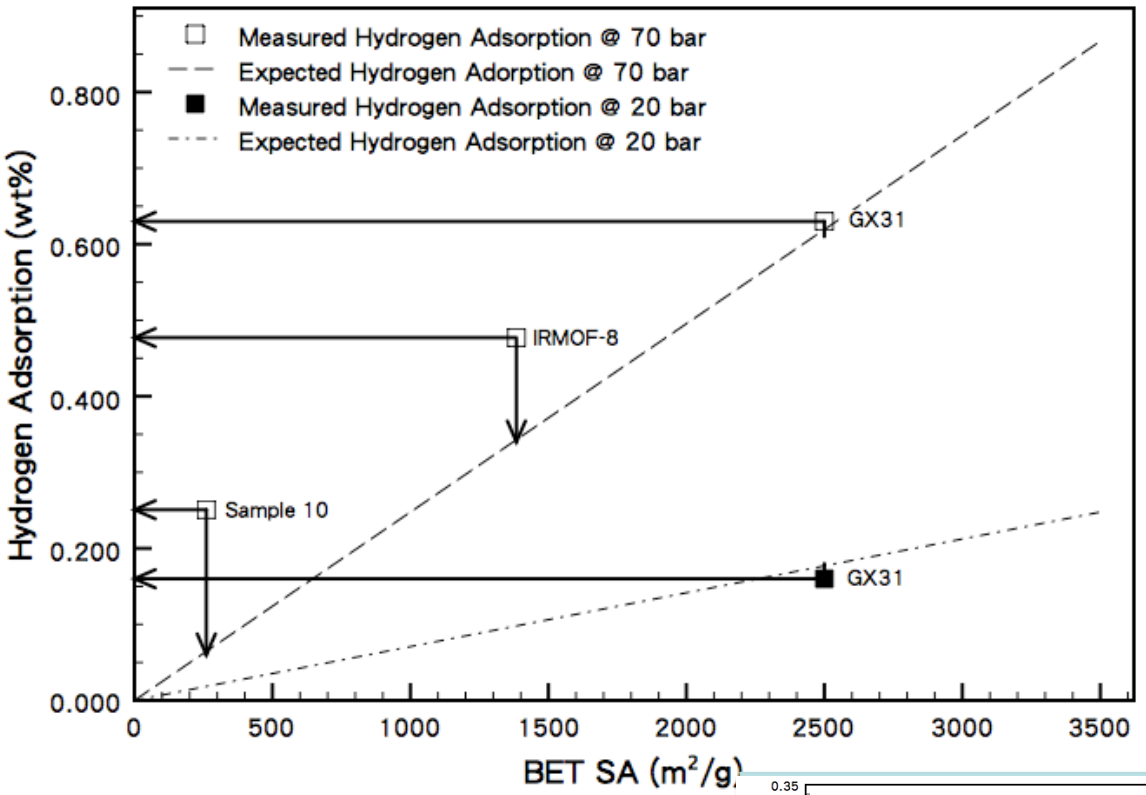
Quality Check

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)**

(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).

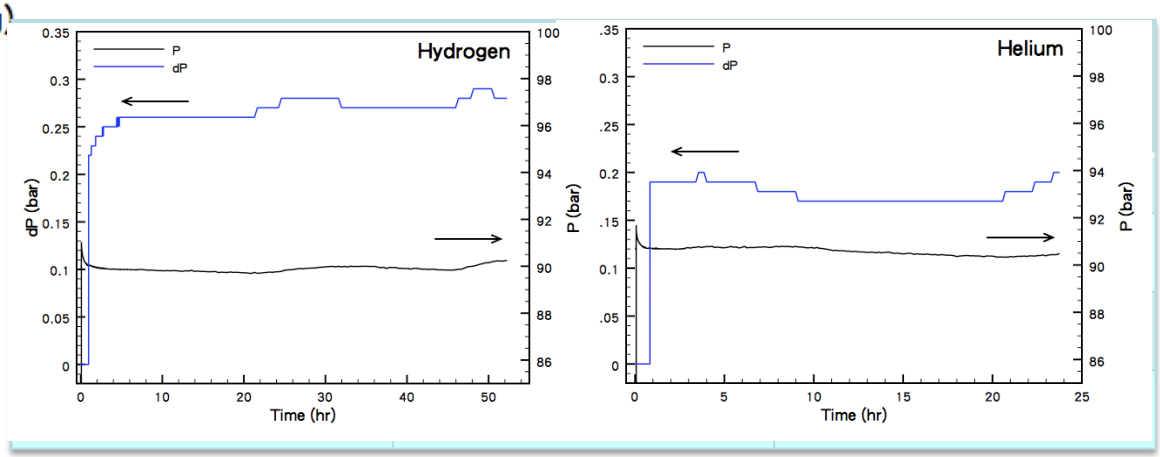
Deviations above the line can be attributed to enhancement due to hydrogen spillover.

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

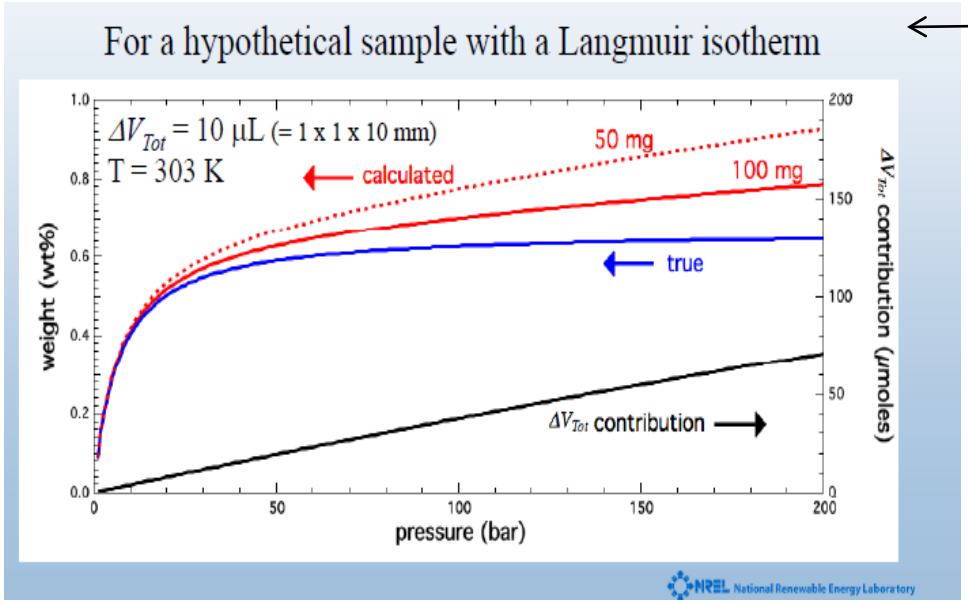
Kinetic data tracked for >=24 hours. Slow uptake is.not seen unless otherwise specified.

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

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

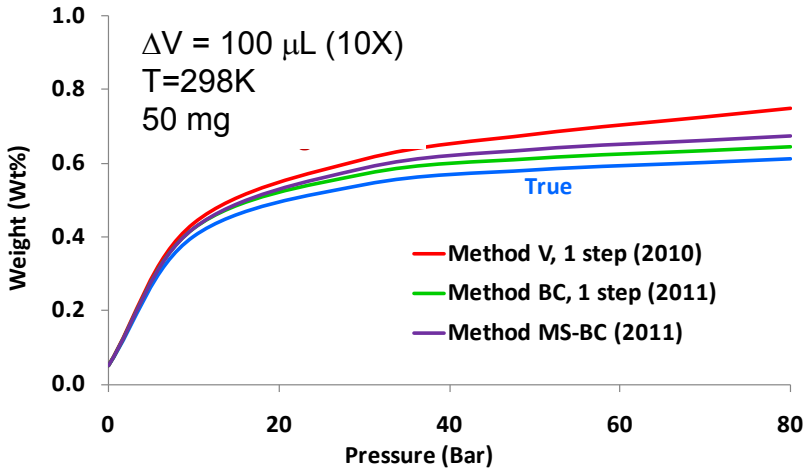


Significant increase in volumetric accuracy
Minimization of Effect of Volume Errors; Valve volume



NREL's analysis; Courtesy of Parilla

Similar analysis for differential

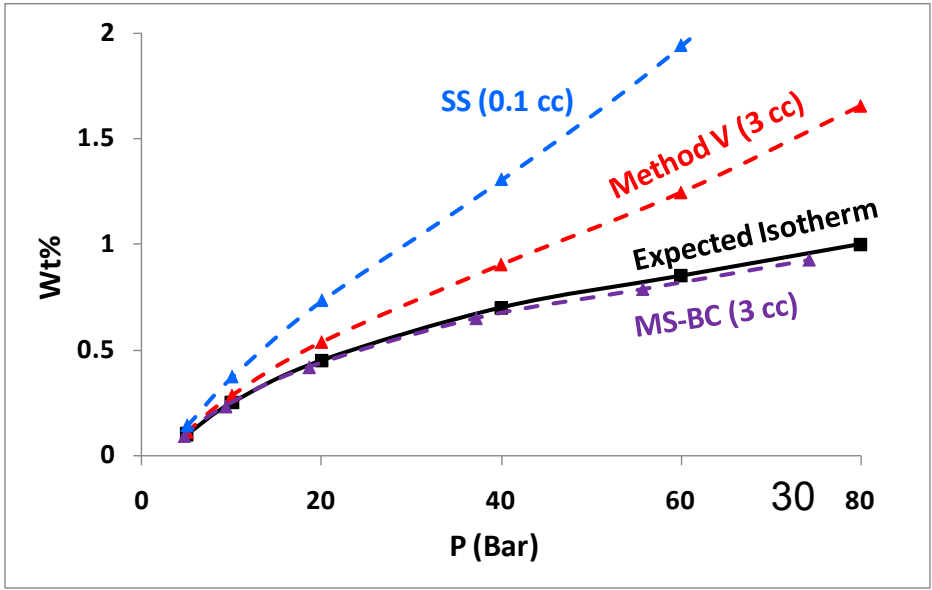


Although Differential provides improvements over single-sided, Method "V" used in 2009 is still fairly sensitive to volume calibrations.

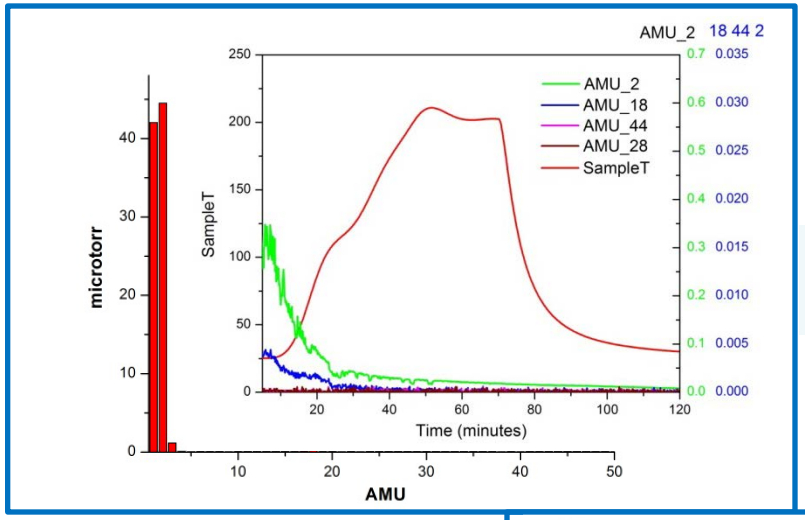
Methods "BC" and "MS-BC" developed in 2010 are insensitive to volume calibrations. Even with a 10-fold increase in volume error , error is less than single-sided.

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

Full details in supplementary information.



H_2O & gravimetric measurement (IGA)

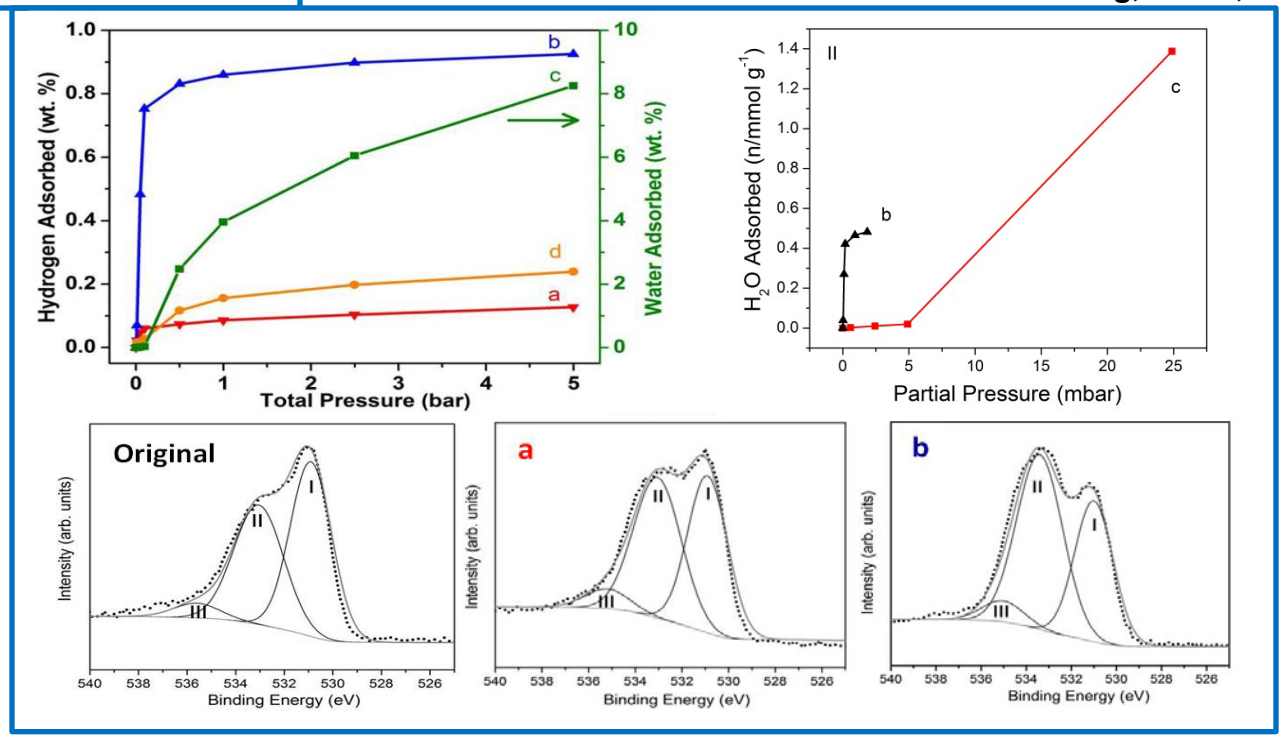


1. 99.9999 purity H_2 and T-purge valve

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