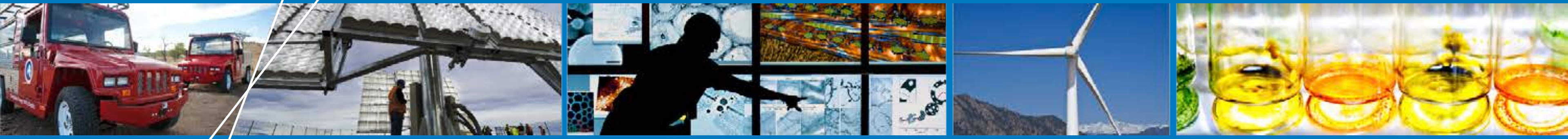
ST021

Weak Chemisorption Validation



2013 U.S. DOE HYDROGEN and FUEL CELLS PROGRAM ANNUAL MERIT REVIEW and PEER EVALUATION MEETING

Thomas Gennett

May 15, 2013

NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

Overview

Timeline

Start: October 2010
End: September 2013
% complete: ~95%

Budget

- Total project funding $995k
- Funding received in FY11: $765k ($220k)
- Funding for FY12: $210 (10k)
- Funding for FY13: $20k (15k)

1 subcontract continued in FY 13
Amount in parentheses

Barriers addressed

General: A. Cost, B. Weight and Volume,
C. Efficiency, E. Refueling Time
Reversible Solid-State Material:
M. Hydrogen Capacity and Reversibility
N. Understanding of Hydrogen Physi- and Chemisorption
O. Test Protocols and Evaluation Facilities

Partners (PI)

University of Hawaii - Craig M. Jensen (active)

University of New Mexico - Plamen Atanassov

Max Planck, Stuttgart, Germany - Michael Hirscher

Institut de Chimie et des Matériaux – Paris, France - Michel Latroche, Claudia Zlotea

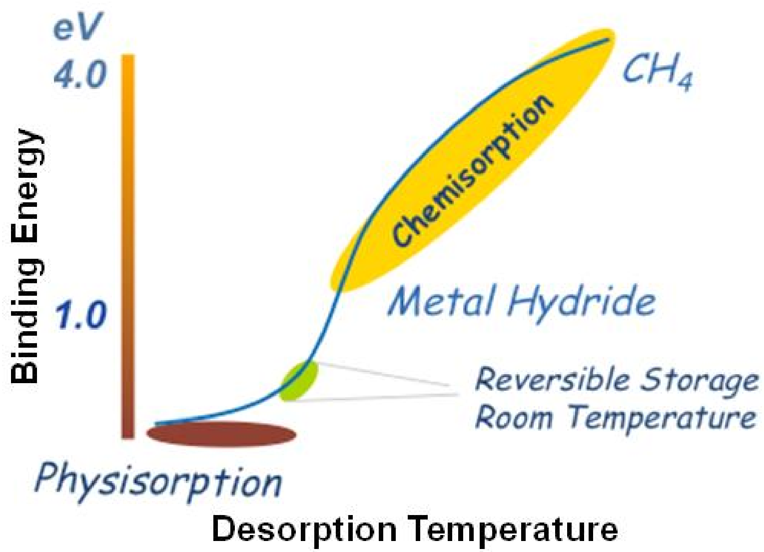
Collaborators: *Penn State - Angela Lueking; Griffith University - Evan Gray; Curtin University - Craig Buckley SWRI® - Mike Miller; Caltech – Channing Ahn; NIST – Craig Brown.*

Relevance:

•DOE Objective:

Evaluate the spillover process as a means to achieve DOE 2017 Hydrogen Storage goals.

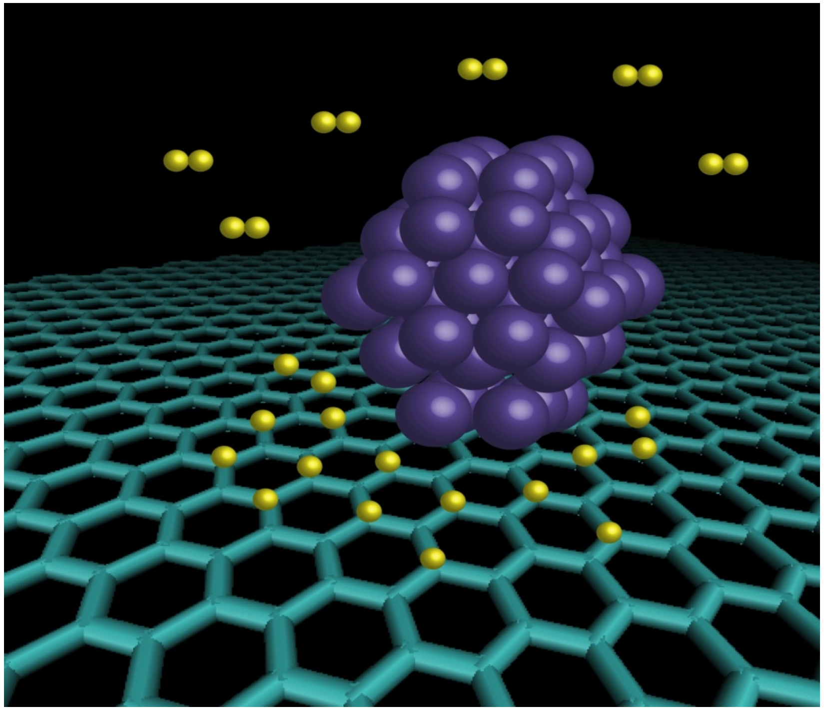
Binding Energy and Sorption-Desorption



•Project Goal:

- Validate measurement methods.
  - Reproducibility
  - Round-robin measurements of standards at several sites (ST014)
- Identify and synthesize several candidate sorbents for spillover.
- Determine hydrogen sorption capacity enhancement from spillover.
- Observe and characterize spillover hydrogen-substrate interactions with spectroscopic techniques.

RELEVANCE: Hydrogen Storage: Spillover Process



Hydrogen storage on metal-doped carbon materials, via **"spillover"** mechanism, involves a series of steps:

- Molecular H_2 dissociates on the metal catalyst particle.
- Atomic H migrates to the carbon support.
- Atomic H diffuses across the carbon surface.

ALL AT ROOM TEMPERATURE

Claims:

In literature anywhere from < 0 to > 400% enhancement associated with spillover (up to 4% w/w reversible sorption/desorption at 30 °C.

Reproducibility Issues:.

Systematic/Measurement error(s)
Synthesis Issues
Cyclability
Catalyst/Matrix stability
Thermodynamics/kinetics issues

Approach – FY11-12 Milestones

2011	1	Complete standard sample(s) exchange and measurement validation	11/2010	100% complete
	2	Exchange initial set of spillover samples. Coordinate focus group efforts at IEA-HIA Task 22 Meeting (Australia) (subcontract/NDA delays of milestone)	01/2011	100% complete
	3	Complete Weak Chemisorption Focus Group meeting and report initial recommendations (at DOE Annual Merit Review)	05/2011	100%
	4	Establish type of C-H interaction from targeted materials.	07/2012	100% complete
	5	Complete evaluation of weak chemisorption process from exchanged materials.	07/2011	100%
	6	Complete meeting open to general public who may be interested, to report results on exchanged weak chemisorption samples. Was held at ACS meeting in Denver.	08/2011	100% complete

Approach – FY 11-12 Milestones

2012	1	Complete 2nd round of sample(s) exchange and measurement validation [Dec. 2011]	12/2011	100% complete
	2	Coordinate focus group efforts at NREL Workshop Meeting	01/2012	100% complete
	3	Complete round robin synthesis efforts and report results.	03/2012	100% complete
	4	Complete Weak Chemisorption Focus Group meeting and report recommendations at DOE Annual Merit Review	05/2012	100% complete
	5	Based on identified C-H interactions, determine ultimate potential for weak chemisorption based hydrogen storage	05/2012	100% complete
	6	Complete evaluation of the experimental results for weak chemisorption process exchange including the MOF and bridged MOF materials. [July 2012]	07/2012	100% complete
	7	Report results of exchanged weak chemisorption samples and synthesis processes with the different collaborators to quantitatively confirm the observed hydrogen adsorption/desorption behavior for MOFs. Provide to DOE Annual Report.	08/2012	100% complete

Approach: FY 13 Milestones:

2013	1	Conduct and correlate high pressure NMR spectroscopy results with NREL DRIFTS to determine the specific C-H interactions involved in weak chemisorption based hydrogen storage.	06/2013	90% complete
	2	Determine the upper limit of hydrogen uptake via wt% due to spillover in an optimized substrate matrix	09/2013	50% complete

APPROACH: Spillover Collaboration

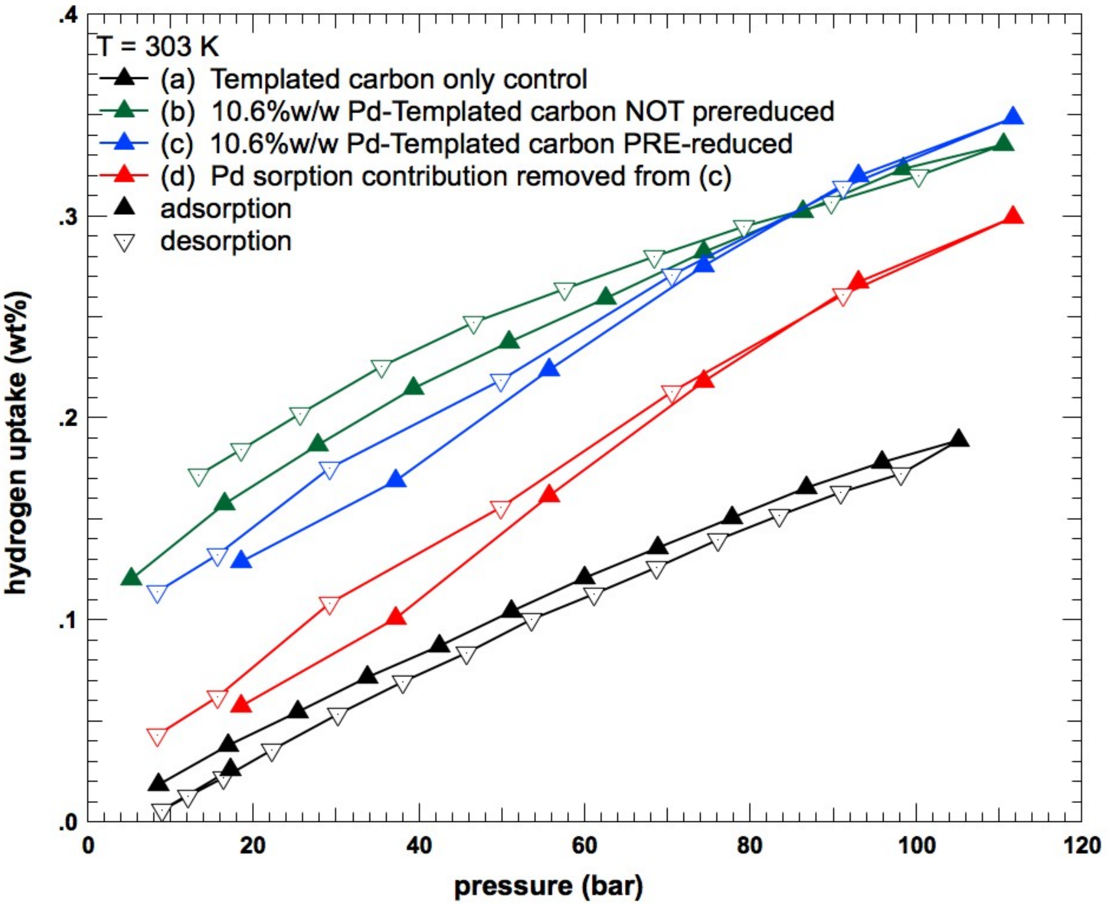
- **Objective:**
  - Demonstrate reproducibility of enhanced adsorption spillover effects.
  - Establish whether spillover is a viable process for hydrogen storage.
- **Approach:**
  - Validate observations for a narrow range of spillover material systems with at least 15% hydrogen sorption enhancement.
  - Synthesize and distribute targeted materials for group analysis.
  - Perform spectroscopic characterization using IR (DRIFTS), NMR, Neutron Scattering, *NEXAFS*.
  - Incorporate new information within mechanistic models.
- **Goals:**
  - Ascertain H/H_2-catalyst-substrate interactions and mechanisms.
  - Establish reproducibility of synthesis and validity of measurements.
  - Establish whether DOE targets can be reached.
  - Communicate validated results to community at large.

Materials systems chosen for DRIFTS-NMR Study:

- **Pd/Templated Carbon (ICPME/NREL) (FY13)**
- **Pd/BC_x (NREL)**
- **Ru/BC_x(NREL)**

Technical Accomplishments and Progress:

Pd-TC Reversible Room Temperature Sorption (Previously Reported)



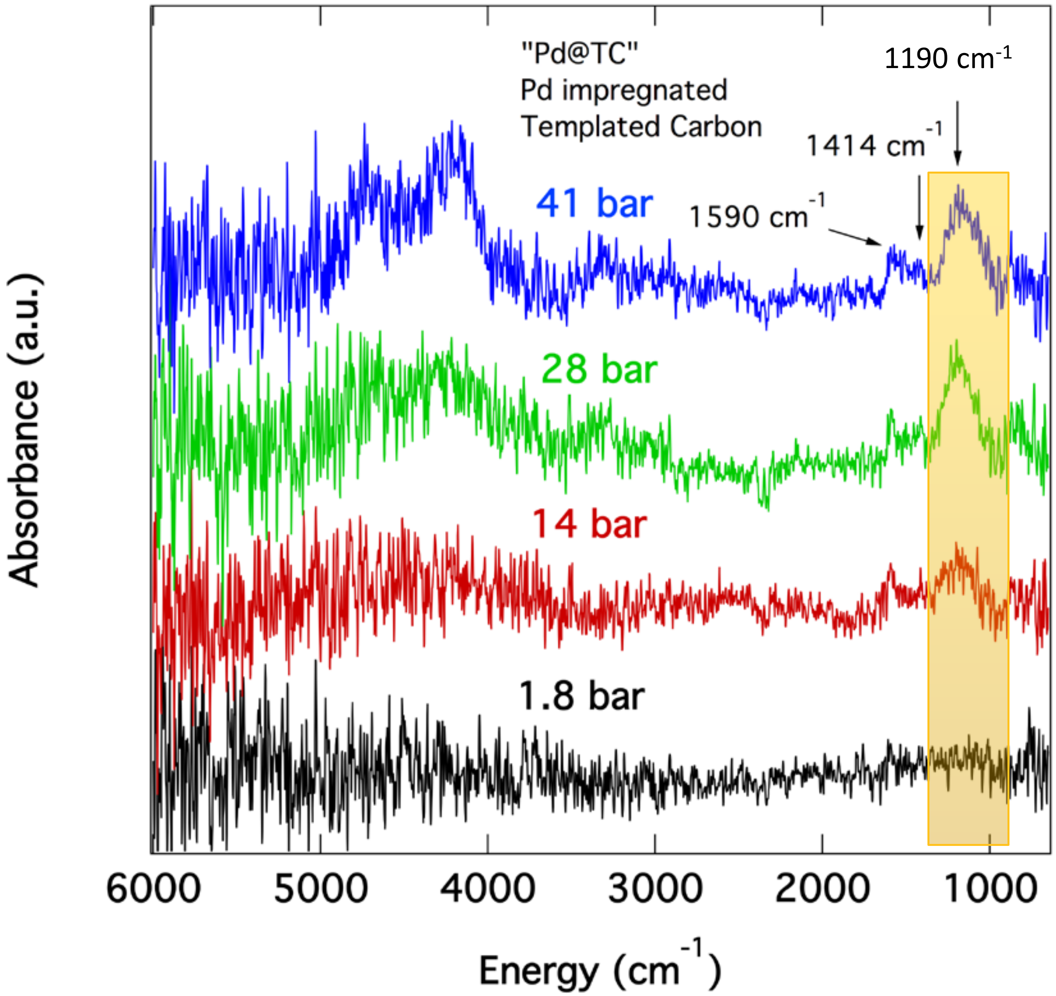
Volumetric adsorption isotherms for hydrogen sorption on a Pd-TC sample.

(a) templated carbon blank control sample for baseline adsorption;
(b) as-received, degassed Pd-TC not pre-reduced;
(c) degassed, hydrogen reduced, degassed Pd-TC sample;
(d) the red curve is the data from (c) with the Pd hydrogen storage contribution removed.

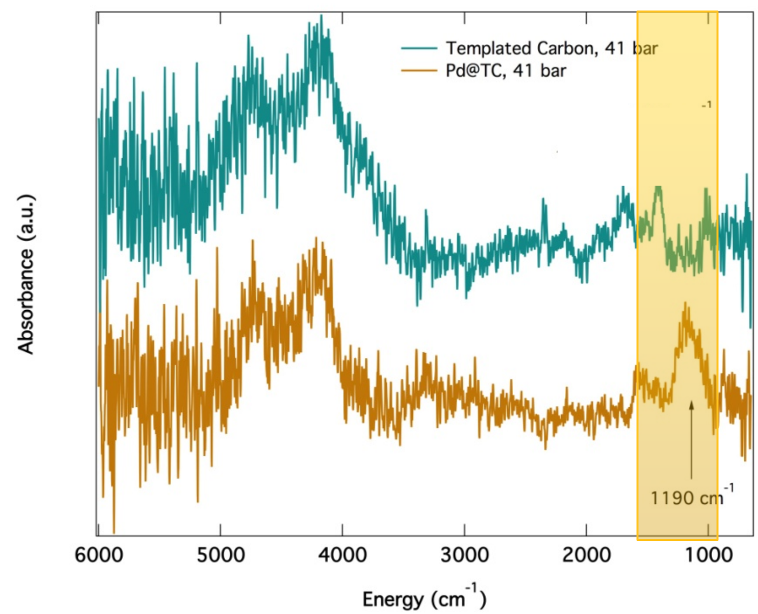
Lack of metal-oxide pre-reduction can lead to erroneous sorption measurements Significant enhancement of sorption observed after metal contribution is removed for Pd-TC materials. A multi-laboratory verification of a reversible enhanced hydrogen sorption via spillover at room temperature

Technical Accomplishments and Progress

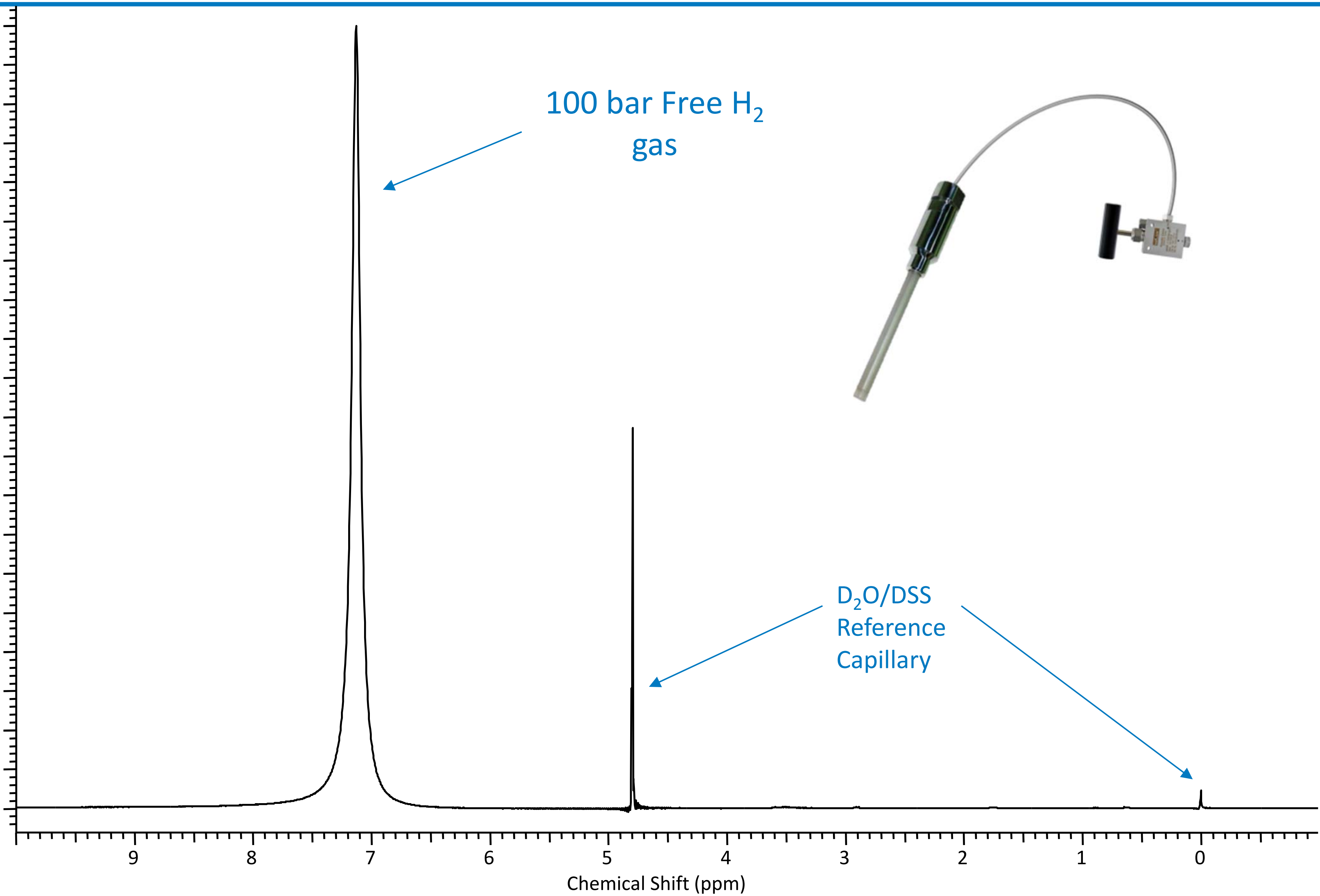
DRIFTS of Pd-TC material



- PdH_2 <1000 cm^{-1}
- Stretches from 1400 - 1600 cm^{-1} on both TC and Pd/TC
- **Reversible C-H stretch at 1190 cm^{-1} for Pd-TC.**
- Results are the same for samples synthesized at NREL and ICPME.

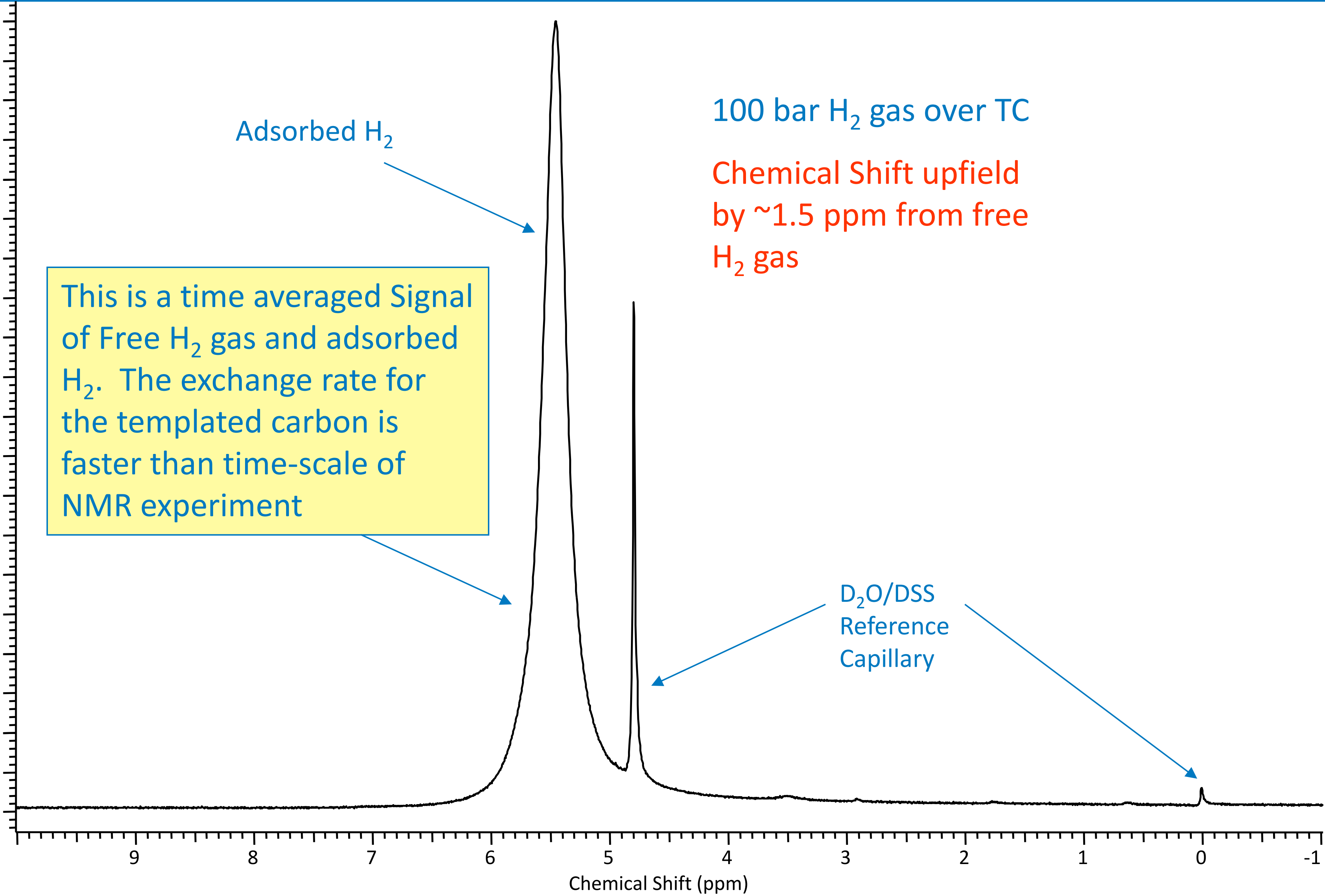


Technical Accomplishments and Progress: High Pressure NMR: Empty Vessel

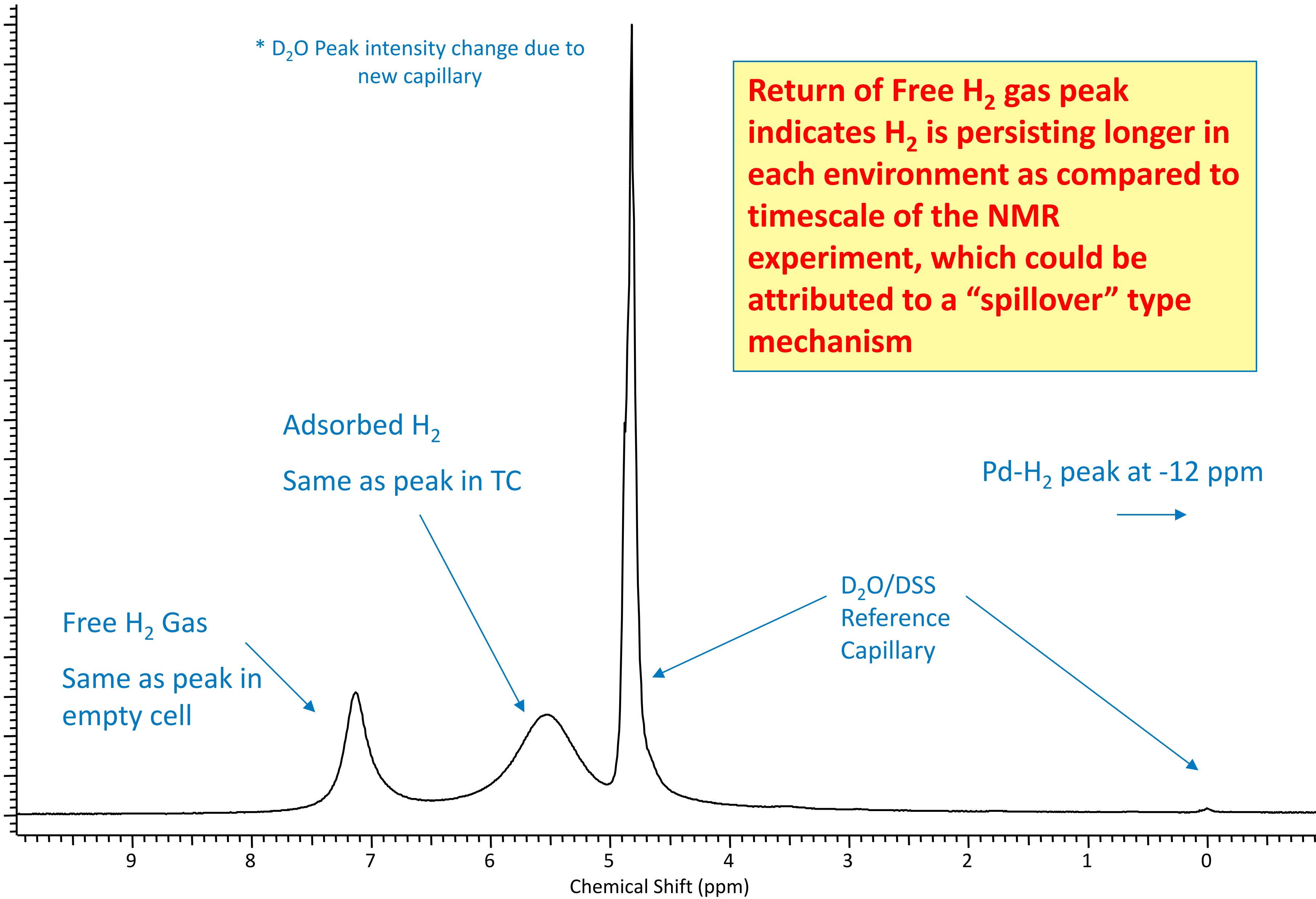


Technical Accomplishments and Progress:

High Pressure NMR Results, Templated Carbon (TC) no metal

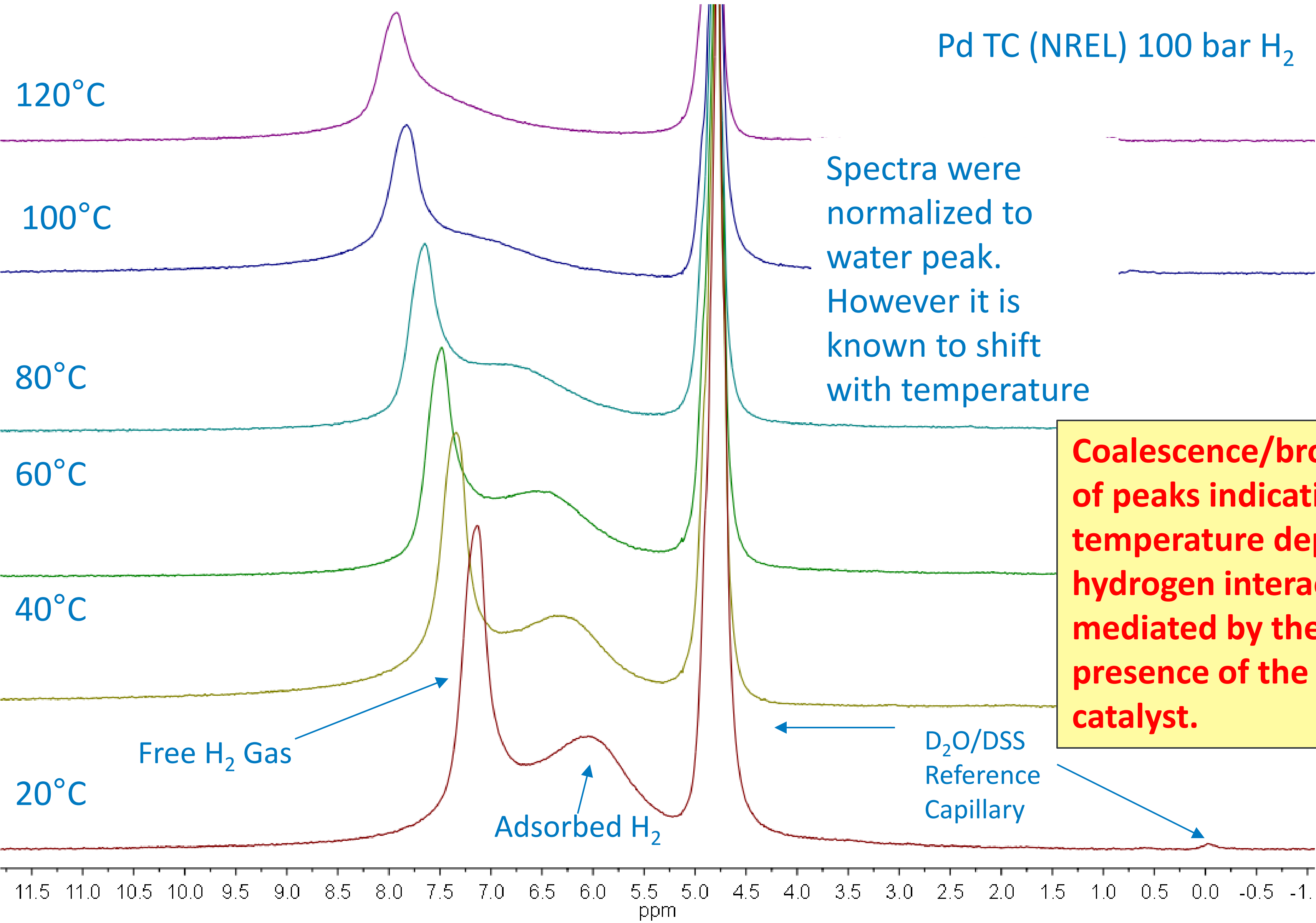


Technical Accomplishments and Progress: High Pressure NMR Experiments: 100 bar H_2 gas over Pd-Templated Carbon



Return of Free H_2 gas peak indicates H_2 is persisting longer in each environment as compared to timescale of the NMR experiment, which could be attributed to a "spillover" type mechanism

Technical Accomplishments and Progress: Variable Temperature NMR



Coalescence/broadening of peaks indicative of temperature dependent hydrogen interaction mediated by the presence of the metal catalyst.

Summary and Conclusions

Pd-TC DRIFTS data similar to RuBCx DRIFTS results

Ru-BCx NMR no-go because of paramagnetic nature of Ru(III) in complex

Pd-BCx material undergoing variable temperature NMR experiments

Pd-TC variable temperature NMR

- **Free H_2 (7.2 ppm) and carbon substrate (6 ppm) hydrogen gas peaks indicates H_2 is persisting longer in each environment.**
  - **(Pd-H_2 peak is about -12 ppm)**
- **Coalescence of peaks indicates temperature dependence.**
  - **Low temperature experiments planned to completely resolve peaks.(probe temperature limits ill-defined)**
  - **Approximate ΔH* will be calculated from line fitting analysis of peak**

Summary of Experimental observations/limitations of current spillover-sorbent materials

- **Activated Carbon**
  - Condensation reactions dominate
  - Solvent contamination
  - Metal oxidation state
- **Bridged Frameworks**
  - Incomplete pyrolysis of sucrose
  - Condensation reactions
  - Framework reactions

Weak Chemisorption Collaborators

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Philip Parilla	Jeffrey Blackburn
Katherine Hurst	Chaiwat Engtrakul
Kevin O'Neill	Justin Bult
Steve Christensen	Lin Simpson
Justin Lee	Yufeng Zhao

Materials Synthesis, Volumetric Analysis, DRIFTs, NMR, Modeling, project coordination

Contributors: *ANL - Tony Burrell; Penn State - Angela Lueking; Griffith University - Evan Gray; Curtin University - Craig Buckley; SWRI® - Mike Miller; Caltech – Channing Ahn; NIST – Craig Brown.*

University of Hawaii - Craig M. Jensen, Derek S Birkmire *NMR*

University of New Mexico - Plamen Atanassov, *Materials Synthesis*

Max Planck, Stuttgart, Germany - Michael Hirscher, *Volumetric analysis and verification, synthesis*

Institut de Chimie et des Matériaux – Paris, France - Michel Latroche, Claudia Zlotea, Materials *Synthesis, volumetric analysis, verification.*

Future Work

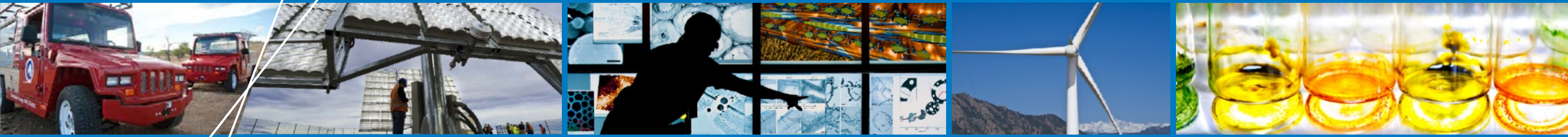
- **Reconcile spillover propagation mechanisms**
  - Reconcile mechanism with metal mediated processes with different substrate matrices.
    - Investigate new weak bond or localized catalytically activated interaction.
    - Use metal dispersion effects to establish whether current enhancements are localized or if there is evidence of long-range interactions.
- **Determine ultimate spillover capacity possible with optimized interactions and substrate chemistry**
  - Investigate pore structure.
  - Design materials to enhance diffusion across substrate surface away from metal sites.
  - Establish whether PdBCx shows comparable enhancement to PdTC.
- **Establish ability to quantify hydrogen adsorption via DRIFTS and/or NMR spectroscopic techniques**
  - Investigate whether or not volumetric enhancements match new spectroscopic data.
  - Analyze Pd-TC and Pd-BCx materials via DRIFTS and NMR.
  - Utilize Spectroscopic techniques to calculate Isosteric Heats of adsorption

Suggest BES/NSF fundamental level work:

- **Hydrogen Spillover mechanism on sorbents needs to be established to better define substrate chemistries needed to optimize sorption capacities.**

Summary

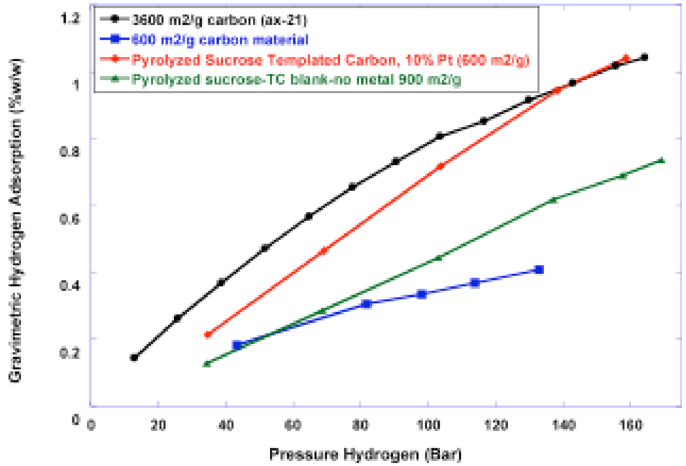
- **Relevance:**
  - Evaluation the spillover process as a means to achieve DOE 2015 Hydrogen Storage goals.
  - Validation of measurement methods.
  - Determination of hydrogen sorption capacity enhancement from spillover.
- **Approach**
  - Validate observations for a narrow range of spillover material systems with at least 15% hydrogen sorption enhancement in multiple laboratories.
  - Synthesized and distributed targeted materials for group analysis.
  - Spectroscopic characterization, IR (DRIFTS), NMR
- **Accomplishments & Progress**
  - First **DIRECT** spectroscopic evidence of a reversible room temperature sorption/desorption apparently from a unique C-H interaction via DRIFTS, NMR and Neutron Scattering spectroscopy techniques.
  - Variable temperature NMR illustrated the rate of hydrogen exchange on substrate metal dependent
  - Multi-laboratory observation of effect that metal oxide can have on hydrogen capacity measurements in metal-mediated sorption process.
- **Collaborations**
  - 4 groups worked on verification of "spillover".
  - 11 groups focused on measurement techniques and procedures.
- **Proposed Future Work**
  - Reconciliation of spillover propagation mechanisms to theoretical models
  - Determination of ultimate spillover capacity possible once completely establish/optimize interactions and substrate chemistry.
  - Quantification of hydrogen sorption with the high pressure spectroscopic techniques. (DRIFTS, NMR)

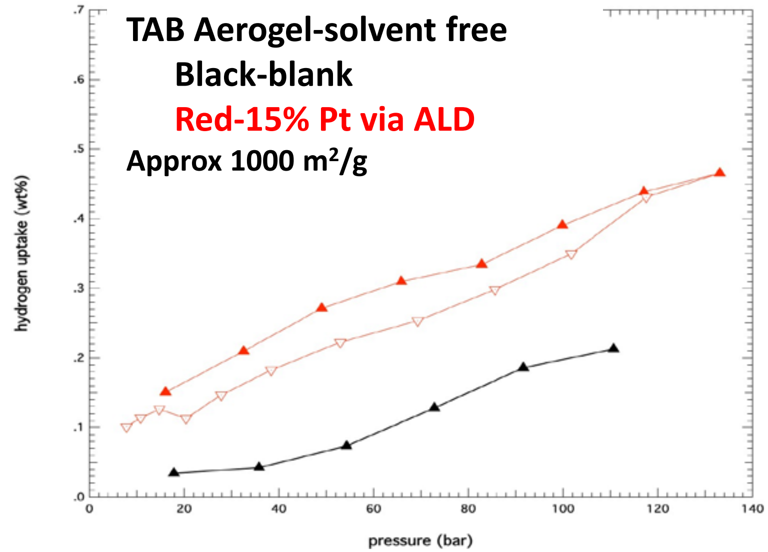


Technical Back-Up Slides

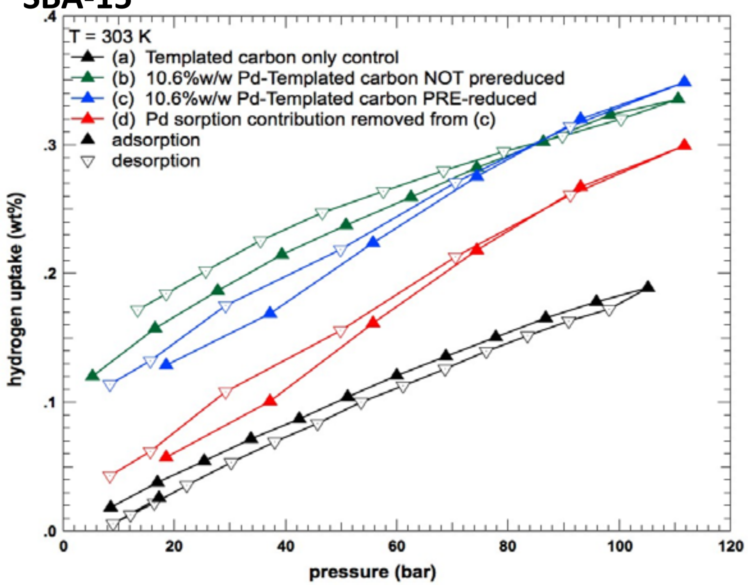
Hierarchal Carbon Materials with Pt/Pd

UNM: Silica-sphere templated-carbon with defined pore structures





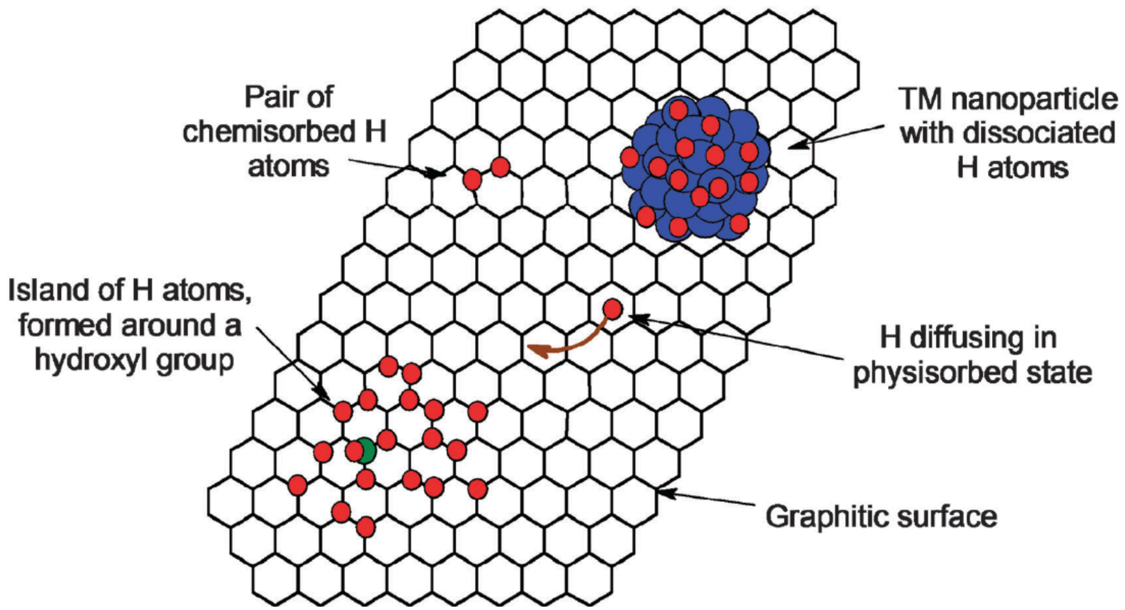
ICPME and NREL templated carbon from SBA-15



Have observed 10 to 100% increase in hydrogen sorption properties of well defined materials low capacity materials. DRIFTS, NMR, Neutron studies confirm reversible adsorption/desorption behavior.

BES level work, mechanism needs to be established to better define substrate chemistries needed to optimize sorption capacities.

Future Work: Must Define phenomenon, fundamental basis for new interaction(s)



•The illustration shows the proposed mechanism for hydrogen spillover on metal-doped graphitic materials with adsorbed oxygen functionalities.

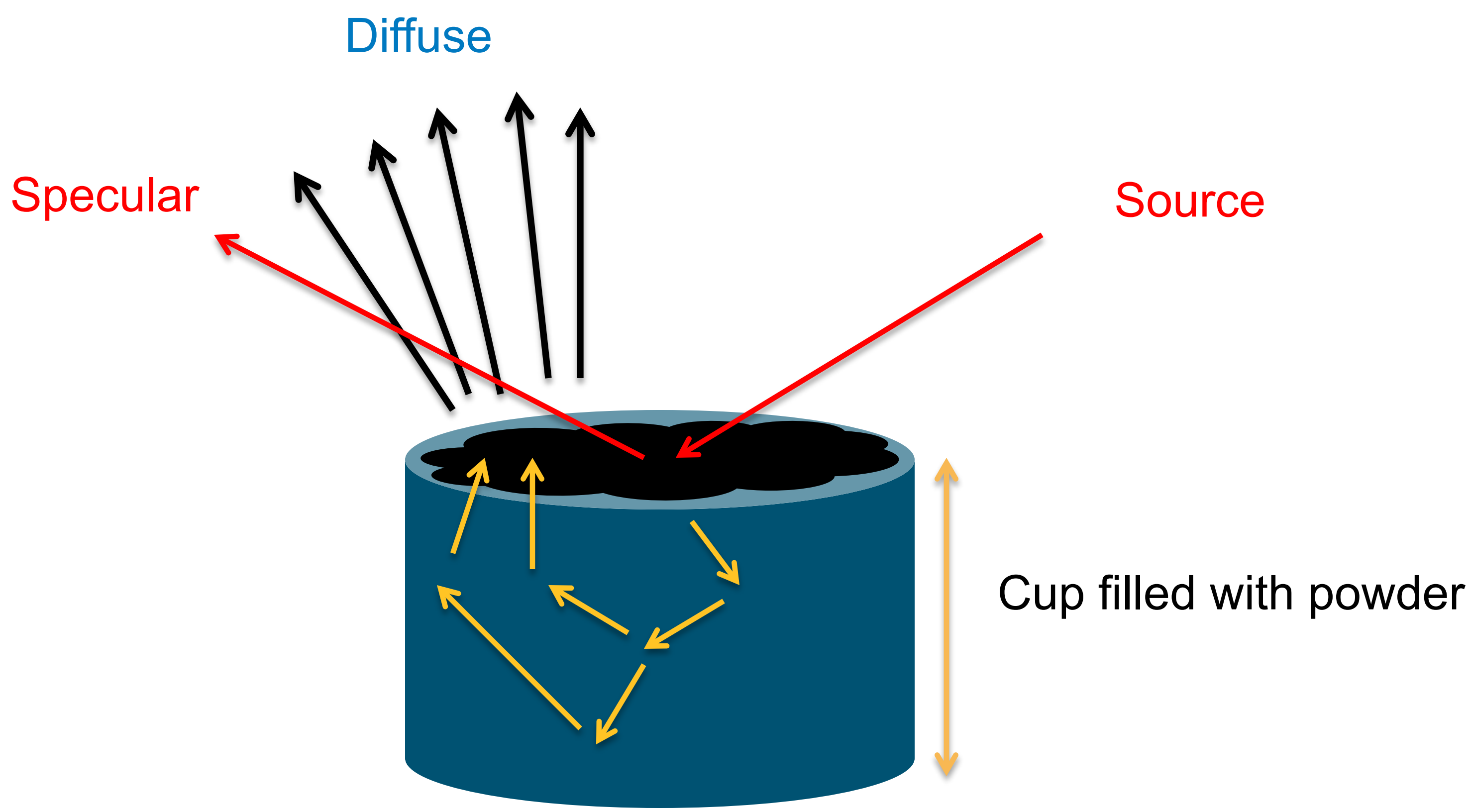
-Mobile H atoms are generated on the metal nanoparticles and migrate in physisorbed atomic state on graphite.

• The H atoms **chemisorb** preferentially around surface oxygen groups or other surface irregularities.

• Small amounts of chemisorbed hydrogen (>200 ^{o}C desorption) is observed even when no metals are present

Froudakis, Chem. Commun., 2011, 47, 7933–7943

Approach: Principles of DRIFTS



- Align with known organic material – e.g. carboxymethyl cellulose
- Align such that specular reflection is not collected, but diffuse reflectance is
- All spectra are taken relative to background
- Background taken on sample under ~0.5 bar H_2

Spectra were normalized to organic DSS standard set to 0.00 ppm