ST021

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Weak Chemisorption Validation

2012 U.S. DOE HYDROGEN and FUEL CELLS PROGRAM ANNUAL MERIT REVIEW and PEER EVALUATION MEETING

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May 16, 2012

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Overview

Timeline

Start: October 2010
End: September 2012
% complete: ~85%

Budget

- Total project funding $975k
- Funding received in FY11: $765k ($220k)
- Funding for FY12: $210 (10k)

4 subcontracts continued in FY 12
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,

University of New Mexico - Plamen Atanassov

Max Planck, Stuttgart, Germany - Michael Hirscher

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

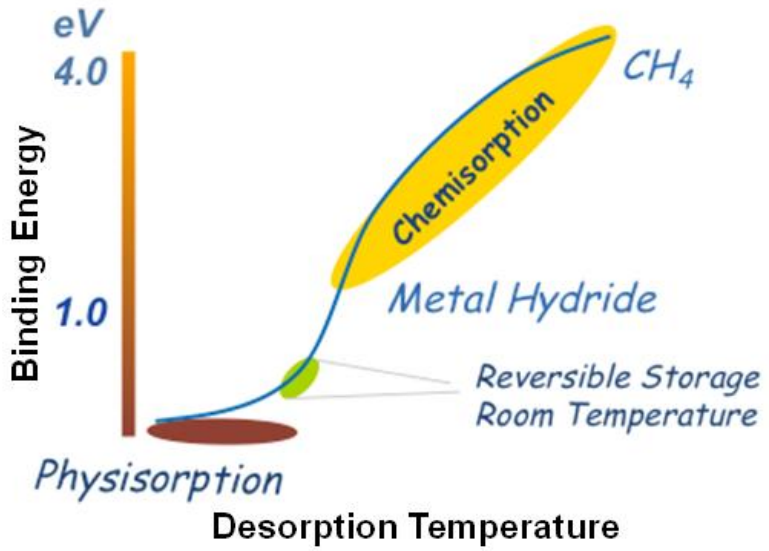
Collaborators: *Penn State - Angela Lueking; Griffith University - Evan Gray; Curtin University - Craig Buckley SWRI® - Mike Miller; Caltech – Channing Ahn; NIST – Craig Brown.*

Relevance:

•DOE Objective:

Evaluate the spillover process as a means to achieve DOE 2015 Hydrogen Storage goals.

Binding Energy and Sorption-Desorption



•Project Goal:

-Validate measurement methods.

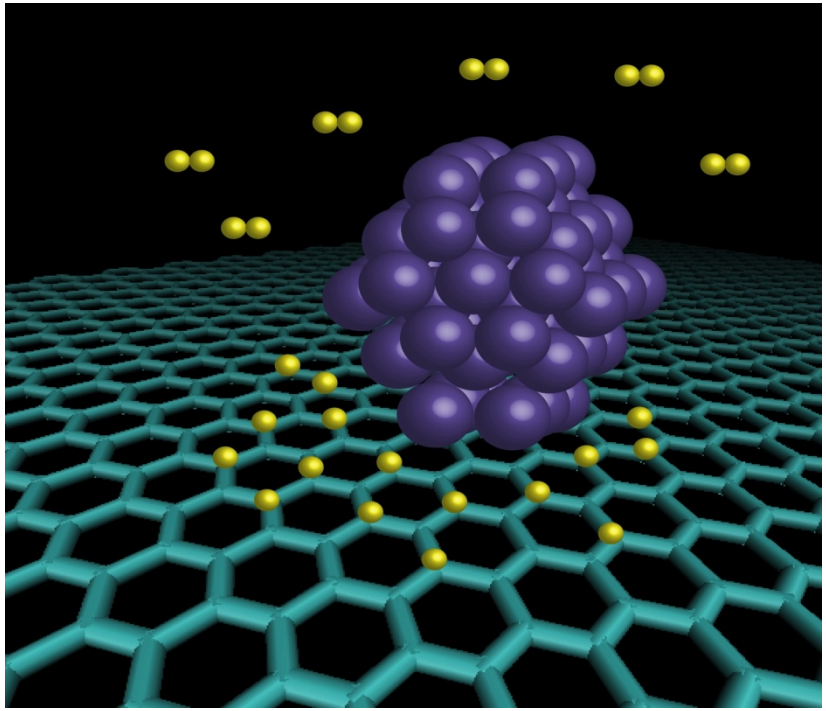
- Reproducibility
- Round-robin measurements of standards at several sites (ST014)

-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**	75% 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	75% complete
	6	Complete evaluation of the experimental results for weak chemisorption process exchange including the MOF and bridged MOF materials. [July 2012]	07/2012	60% 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	

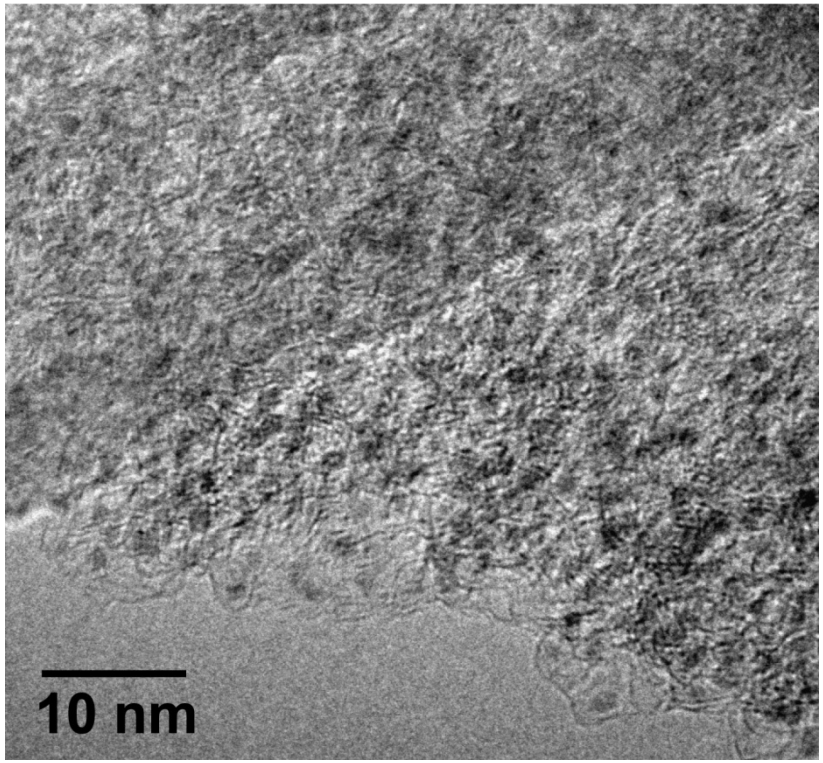
APPROACH: Spillover Collaboration

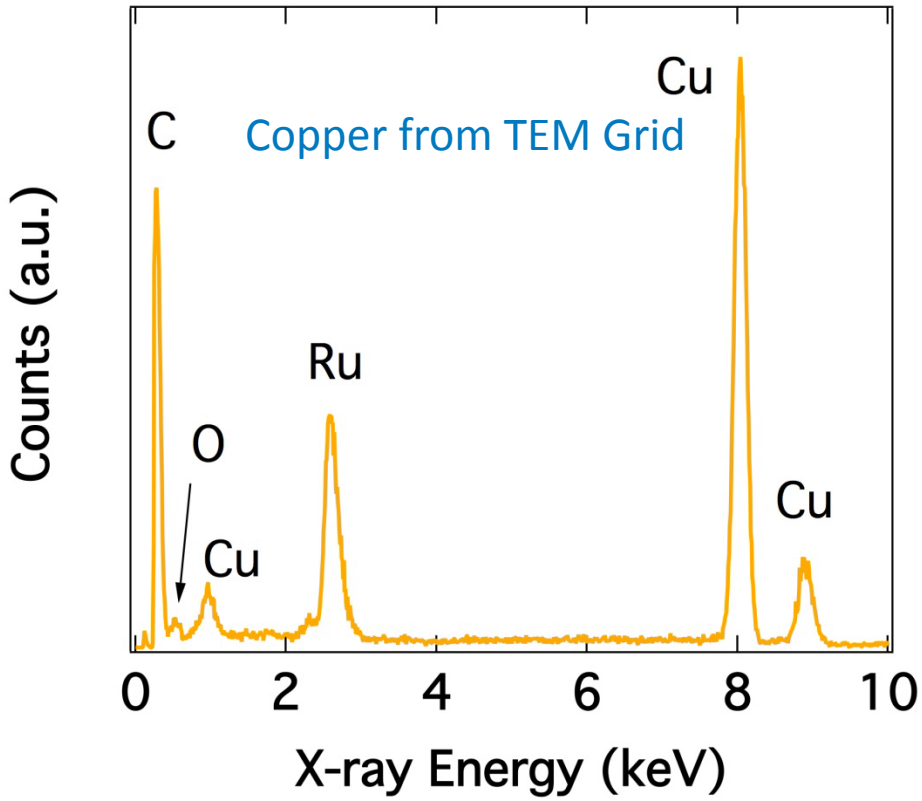
- **Objective:**
  - Demonstrate reproducibility of enhanced adsorption spillover effects.
  - Establish whether spillover is a viable process for hydrogen storage.
- **Approach:**
  - Validate observations for a narrow range of spillover material systems with at least 15% hydrogen sorption enhancement.
  - 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:

- **Ru/BC_x (NREL) (15% enhancement reported)**
- **Pd/Templated Carbon (ICPME) (50% enhancement reported in literature)**
- **Pt/Templated Carbon (UNM) (100 % enhancement reported)**

Technical Accomplishments and Progress: RuBCx

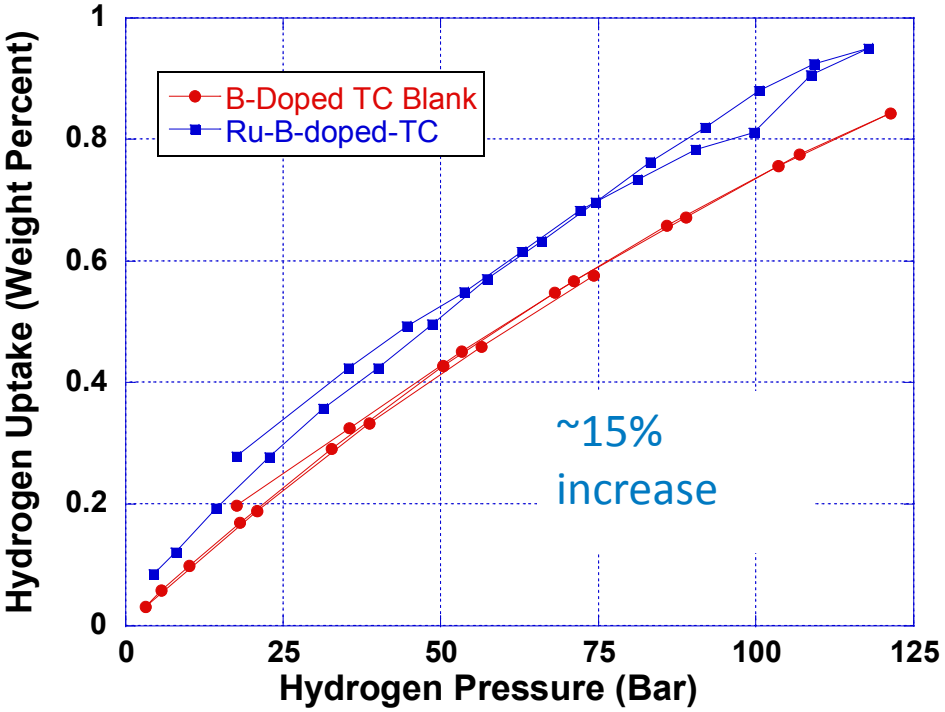


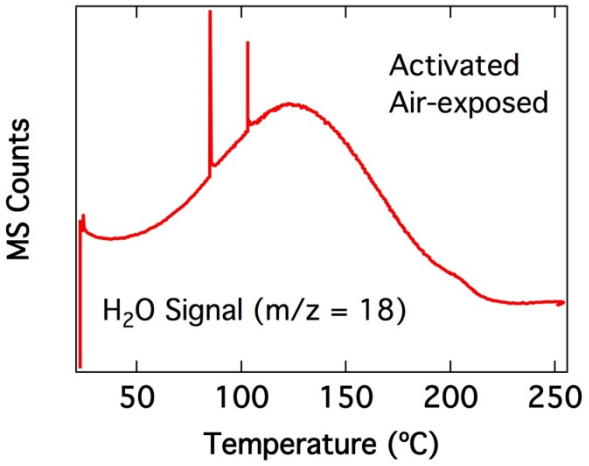


- Ru Nanoparticles ~ 2 nm via microwave deposition
- Oxygen seen in EDX analysis.
- Volumetric, DRIFTS, NMR and Neutron experiments all performed on same 5 gram synthesis batch
- Synthesized in multiple laboratories

Technical Accomplishments and Progress:

Materials Synthesis and Characterization: Ru-BC_x materials





Water formation can occur from Metal oxide reduction

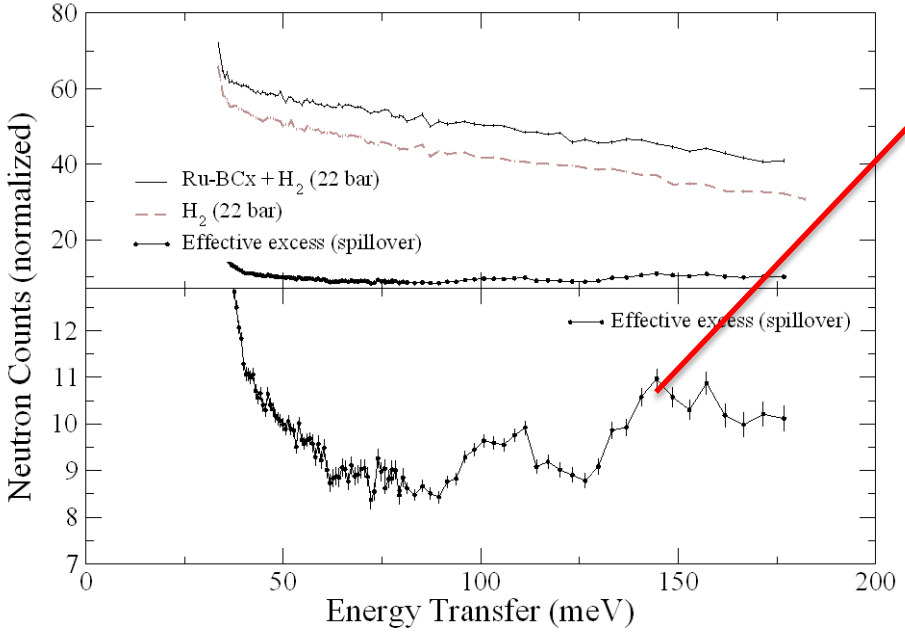
In-situ pre-reduction necessary before analysis

Boron substitutional materials via template (BC_x), substantially improves weak chemisorption kinetics

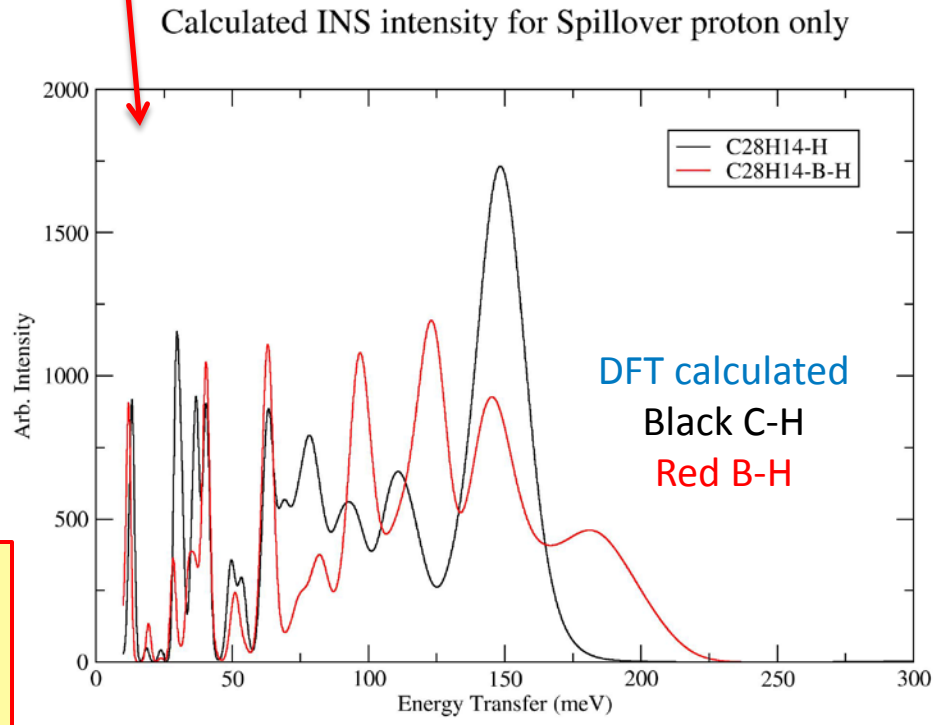
- **Rates substantially faster (10 minutes)**
- **Minimal irreversible component**
- **Stable in air**
- **Multiple cycles**

Technical Accomplishments and Progress:

Inelastic Neutron Scattering (INS) RuBCx NREL/NIST



- Fine structure at ~90 to 160 meV
- Matches expected peaks from first principles calculations for C-H

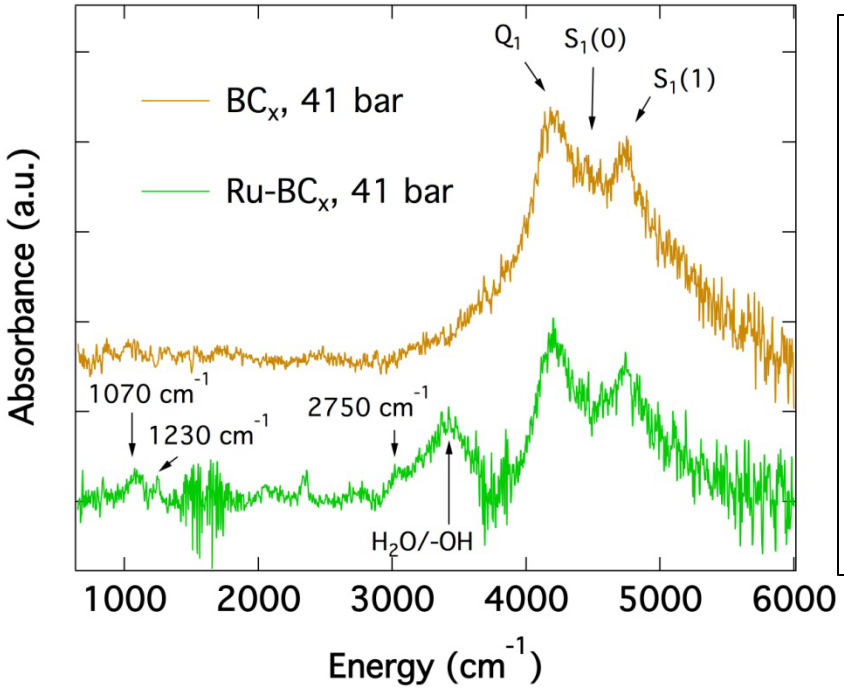


As we move to DRIFTS analysis, the approximate infrared adsorption energies would be in regions of:
800 – 1000 cm^{-1} and 1050 - 1290 cm^{-1}.

Predicted INS spectra for C-H and B-H on model graphene patches (NREL) (Technical back-up slide)

Technical Accomplishments and Progress:

DRIFTS - RT H_2 Charging of boron-doped carbon ~2 nm Ru nanocatalyst

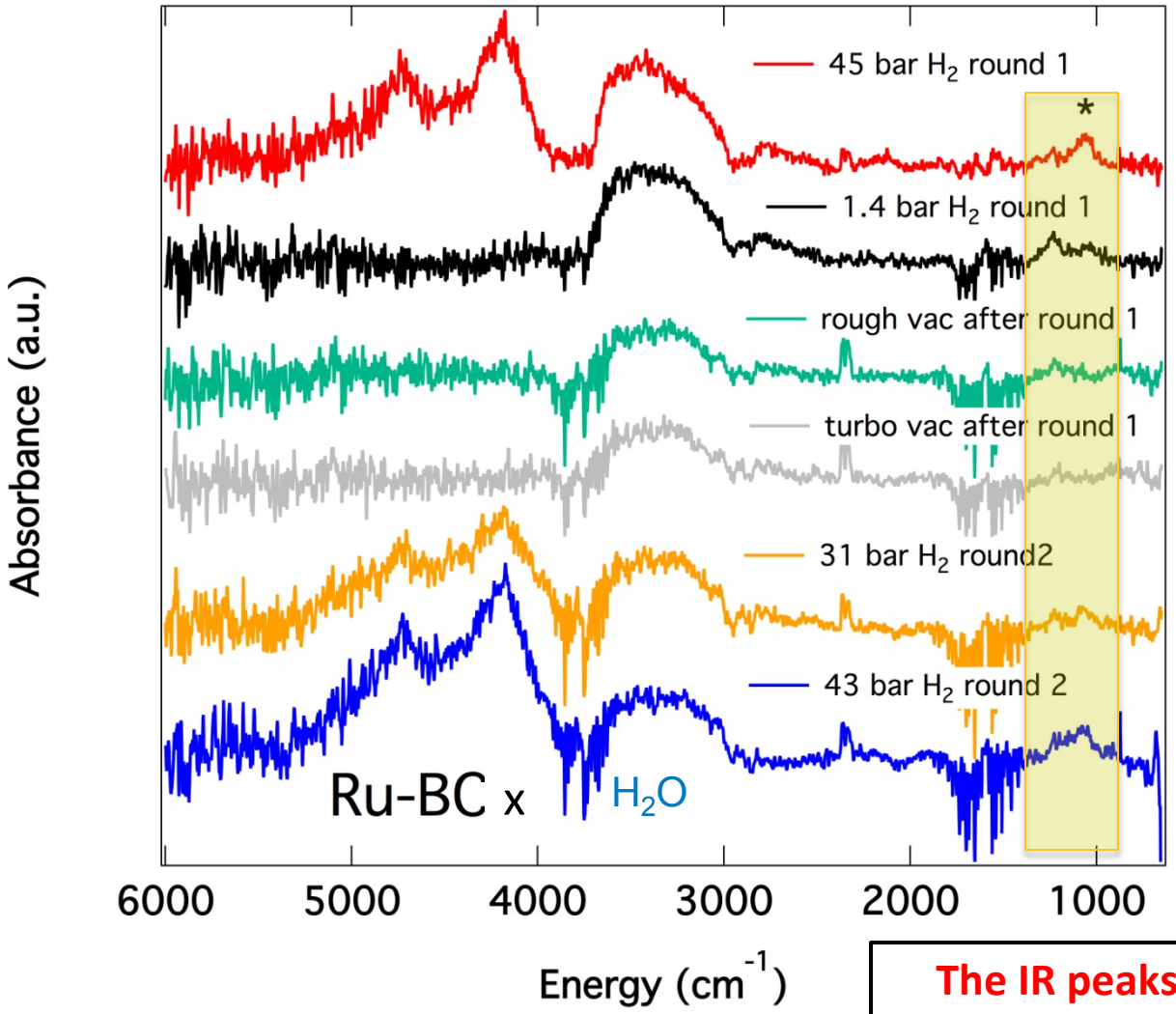


- Physisorbed vibration/rotation peaks between ~4000 – 6000 cm^{-1} - Q_1, $S_1(0)$, $S_1(1)$
- H_2O/-OH peak ~3400 cm^{-1}, only on Ru-BC_x sample
- New peaks on Ru-BC_x sample at 2750, 1230, and 1070 cm^{-1}
- Similar to peaks observed in INS spectra:
  - 1070 cm^{-1} = 132 meV
  - 1230 cm^{-1} = 153 meV

- **These peaks are all ~10% lower in energy than pure theoretical C-H modes, but would still be too strong for diffusion away from catalyst**
- **All show expected isotope exchange dependence for D_2 charging (Technical back-up slide)**
- **All are reversible with hydrogen sorption/desorption at room temperature**
- **OH peaks are only observed when metal present**

Technical Accomplishments and Progress:

Hydrogen Sorption/Desorption multi-cycle Experiment RuBCx



Sample degassed To 250 C

First dose shows water formation similar to observed with TPD

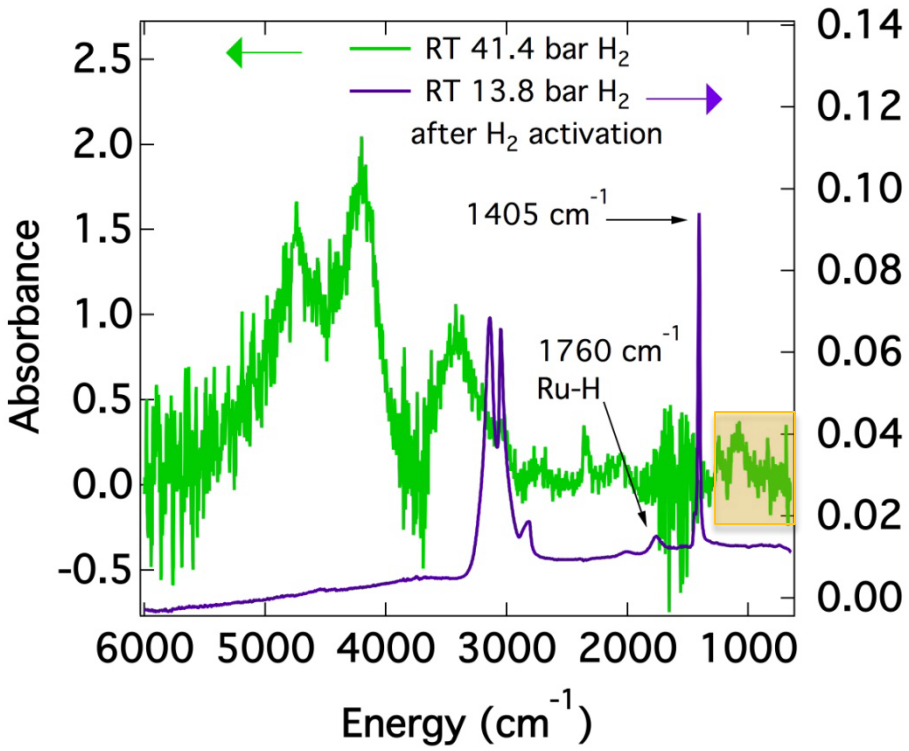
Upon evacuation, peaks at 1070 and 1230 cm^{-1} "disappear"

No degas prior to second dose.

Peaks reappear at 1070 and 1230 cm^{-1}

The IR peaks, apparently from spillover process, are reversible

Technical Accomplishments and Progress: High Temperature Hydrogen Activation

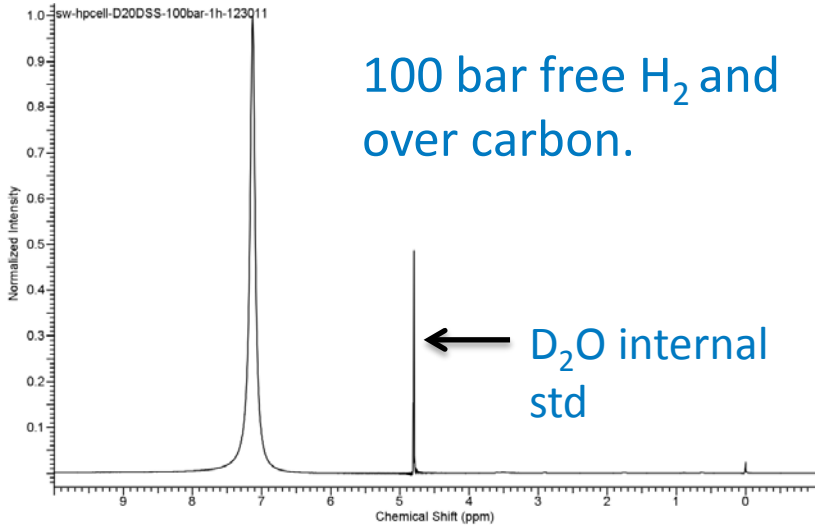


- 14 bar H_2, 2 hours to 200 °C (purple)
- Attempt to hydrogenate sample, and form chemisorbed hydrogen in form of M-H and C-H
- Note spectral intensity is ~40 times higher than a 30 °C charge
- **Ru-H "on-top" site at 1760 cm^{-1}**
- **C-H/OH peaks between 2700 and 3100 cm^{-1}**
  - **3140 cm^{-1} – surface hydroxyl**
  - **3047/2808 cm^{-1} – C-H stretching**
- **C-H bend / OH at 1400 cm^{-1}**

- **Must degas to 250 °C to observe reversible peaks at 1070 and 1230 cm^{-1}**
- **Reversible spillover peaks in different IR region than *chemisorbed* hydrogen**

Technical Accomplishments and Progress:

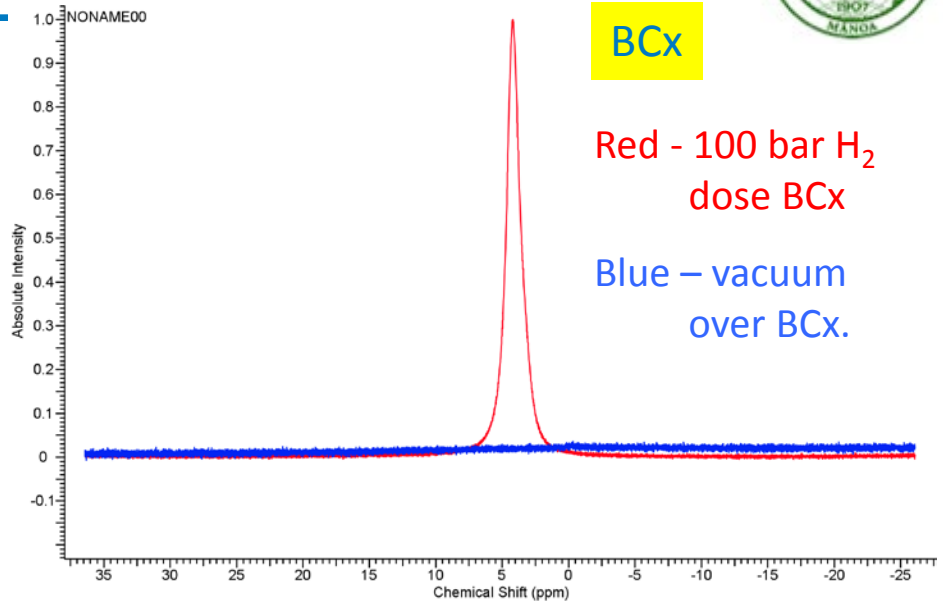
RuBCx, Solid State ^{1}H NMR



100 bar free H_2 and over carbon.

D_2O internal std

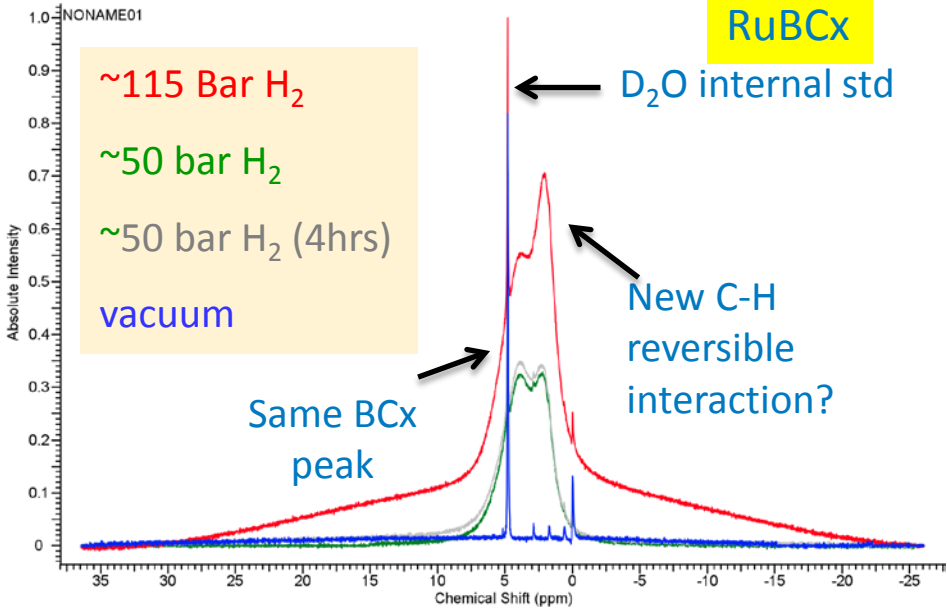
Signal shifted upfield 2.2 ppm (from 7.1 to 4.9ppm) Chemical shift and broadening indicate physisorbed H_2 interacting with BCx.



BCx

Red - 100 bar H_2 dose BCx

Blue – vacuum over BCx.



RuBCx

~115 Bar H_2

~50 bar H_2

~50 bar H_2 (4hrs)

vacuum

D_2O internal std

New C-H reversible interaction?

Same BCx peak

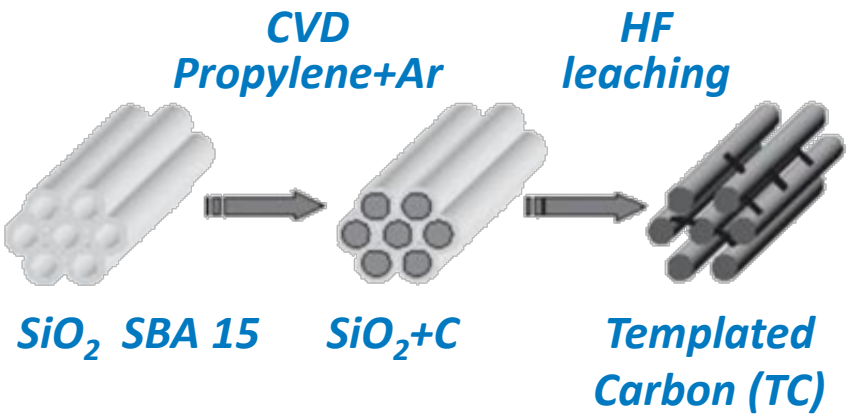
NMR Signal is reversibly split on RuBCx with hydrogen dose as compared to BCx blanks

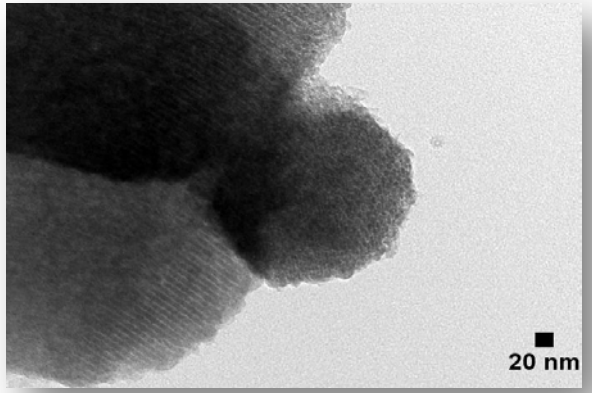
No new signals observed for ^{11}B NMR.

Possible new reversible C-H interaction observed

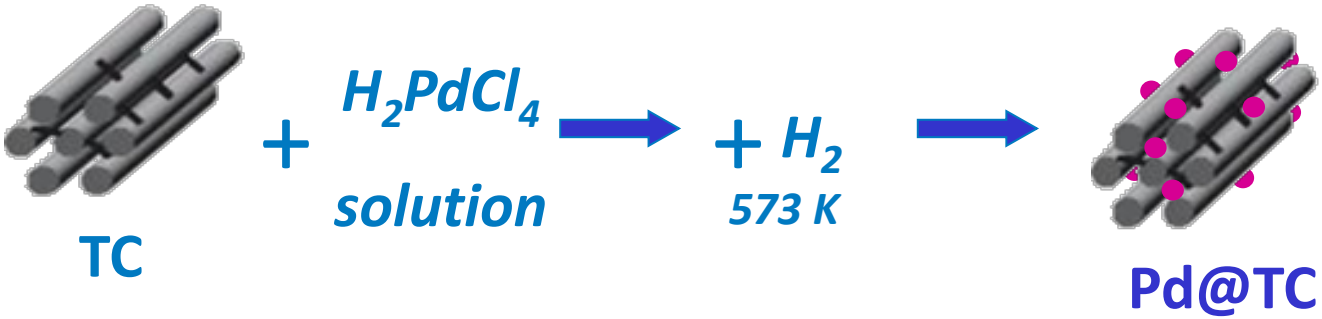
Technical Accomplishments and Progress: Pd@TC

Synthesis of templated mesoporous carbon – SBA 15





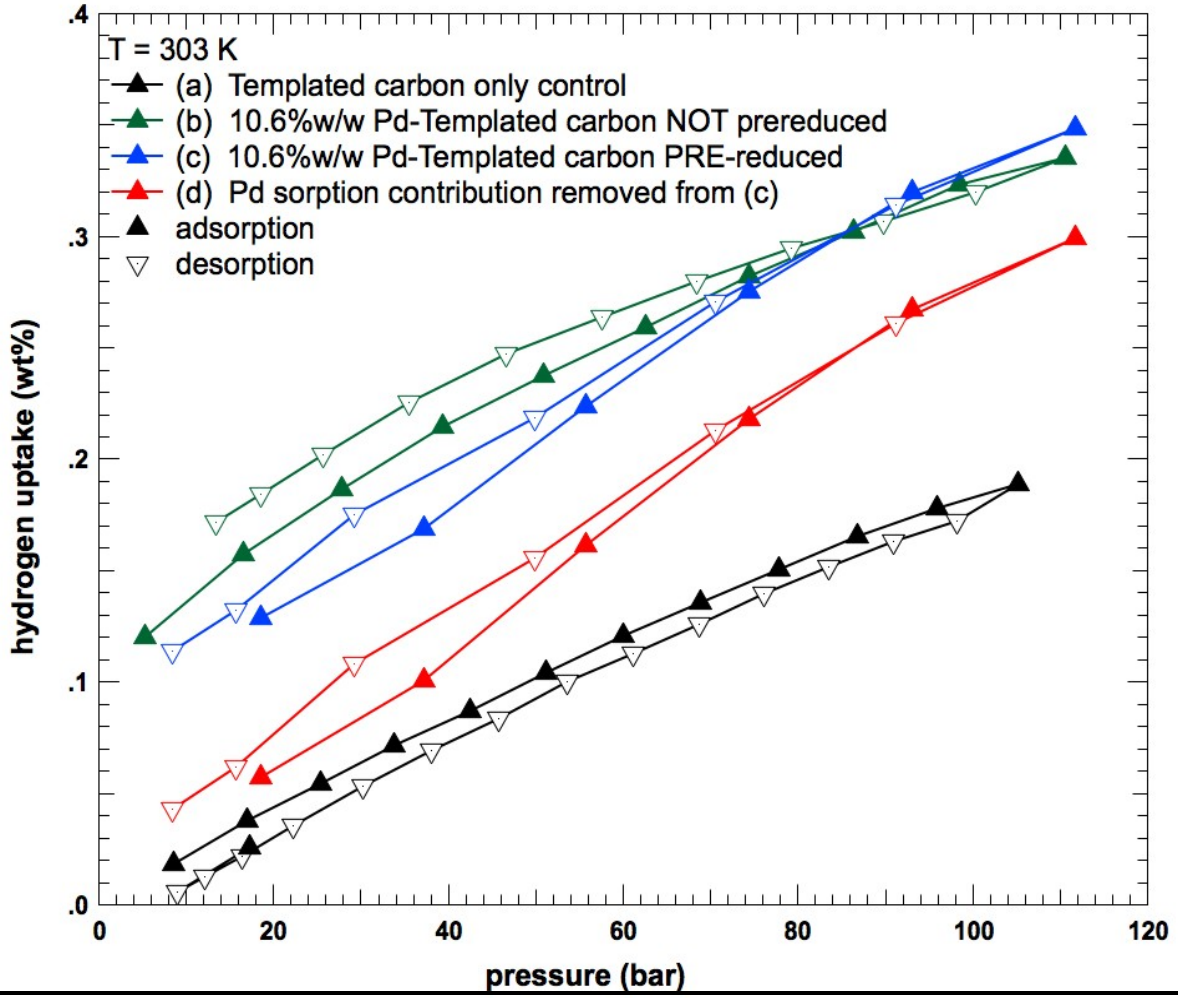
1. Liquid impregnation of carbon with a salt precursor solution (H_2PdCl_4)
2. Reduction under Ar/H_2 flow at 573 K (0.1 MPa)



Chemical composition: 10-11 wt.% Pd (ICP-OES)

R. Campesi, F. Cuevas, R. Gadiou, E. Leroy, M. Hirscher, C. Vix-Guterl, M. Latroche, ***Carbon*** *46 (2008) 206*
C. Zlotea, F. Cuevas, V. Paul-Boncour, E. Leroy, P. Dibandjo, R. Gadiou, C. Vix-Guterl, M. Latroche, ***JACS****, 132 (2010) 7720*

Technical Accomplishments and Progress:
Pd-TC Reversible Room Temperature Sorption



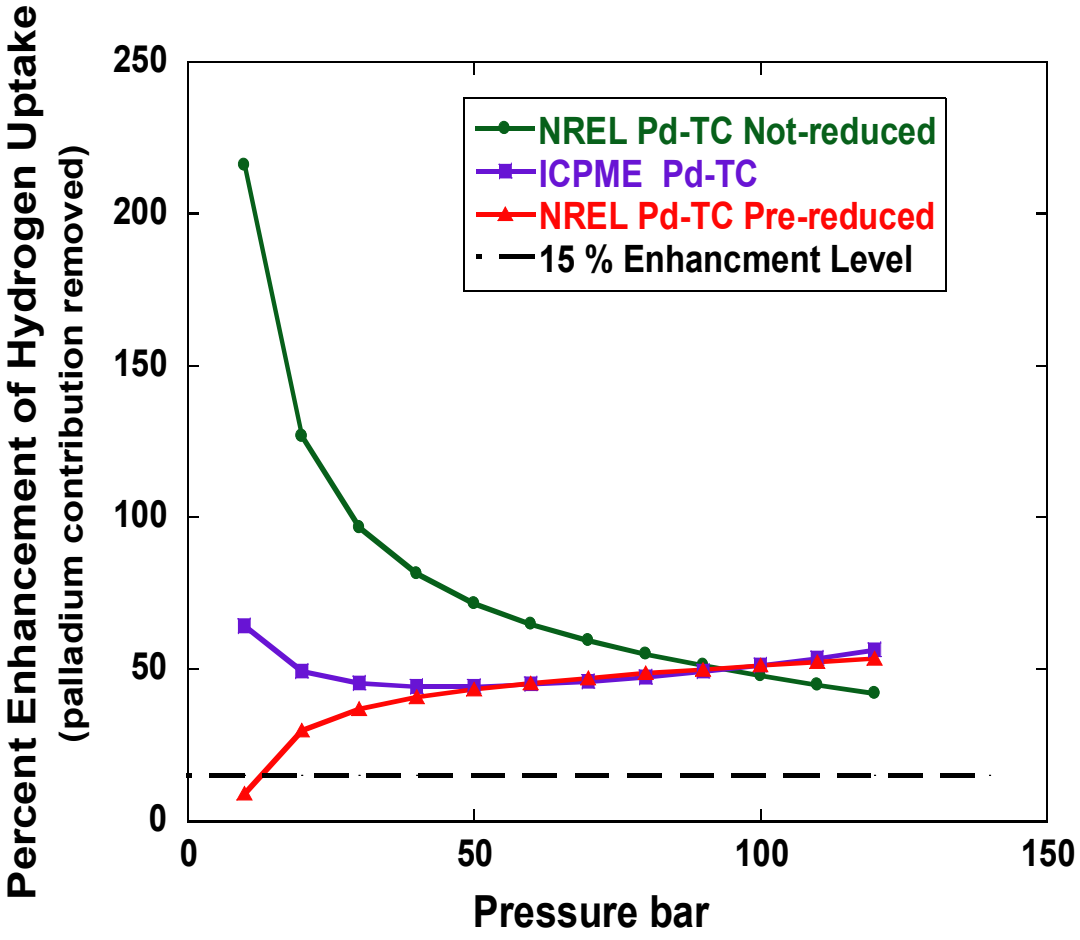
Volumetric adsorption isotherms for hydrogen sorption on a Pd-TC sample.

(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.

Technical Accomplishments and Progress:

Verification of >15% Enhancement of Reversible Room Temperature Hydrogen Sorption

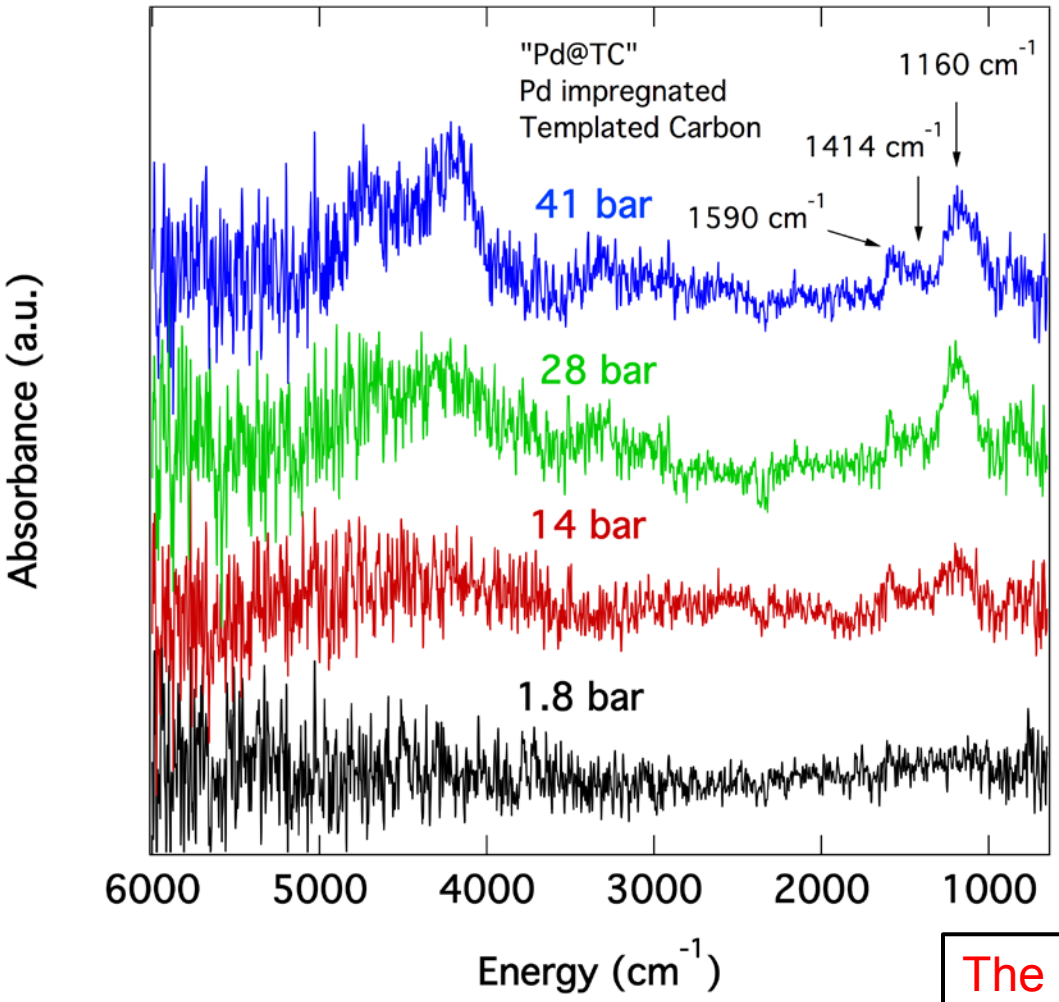


- A greater than 15 percent increase in hydrogen uptake over baseline sorbent material at room temperature conditions is demonstrated.
- Data from two separate laboratories (purple and red traces) are shown.
- A false enhancement is observed when the metal oxide is initially present in the Pd-TC materials (green isotherm).

A multi-laboratory verification of a reversible enhanced hydrogen sorption via spillover at room temperature

Technical Accomplishments and Progress

DRIFTS of Pd-TC material, preliminary results



- PdH_2 <1000 cm^{-1}
- Reversible C-H stretch?
- Isotope, palladium controls underway.

The reversible peaks are in a similar region to those observed for the RuBCx material.

Weak Chemisorption Collaborators

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

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

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

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.*

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.*

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.
  - Investigate NEXAFS.
    - Determine specifics of new C-H interaction on RuBCx material through SLAC investigation.
- **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.
- **Expand NMR work**
  - Deconvolute the observed features.
  - Perform variable temperature analysis of the BCx samples to verify the dynamic behavior.
  - Characterize the features in the RuBCx spectrum:
    - Quantification by line fitting
    - Characterization by T_1 analysis
    - Further analysis by study of ^{13}C labeled materials
    - Coupling constant and off resonance analysis.

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 distribute targeted materials for group analysis.
  - Spectroscopic characterization, IR (DRIFTS), NMR, Neutron Scattering
- **Accomplishments & Progress**
  - Multi-laboratory verification of enhancement of room temperature hydrogen sorption by a catalyst-mediated process for multiple samples.
  - 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.
  - 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”. All participants attended and presented their work summaries at Spillover Workshop, Denver , CO February 1-2, 2012.
  - 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)

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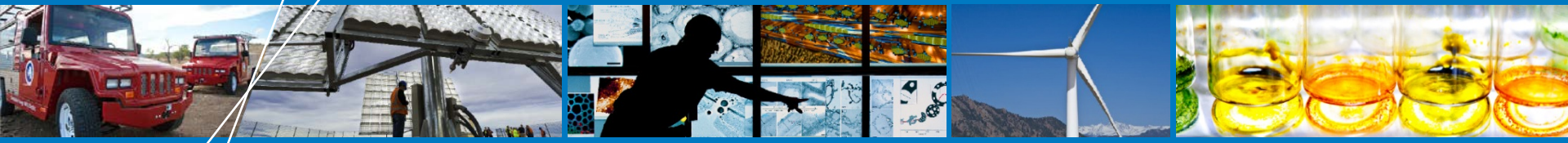


Technical Back-Up Slides

Technical Accomplishments and Progress:

Synthesis and Characterization of Ru-BC_x

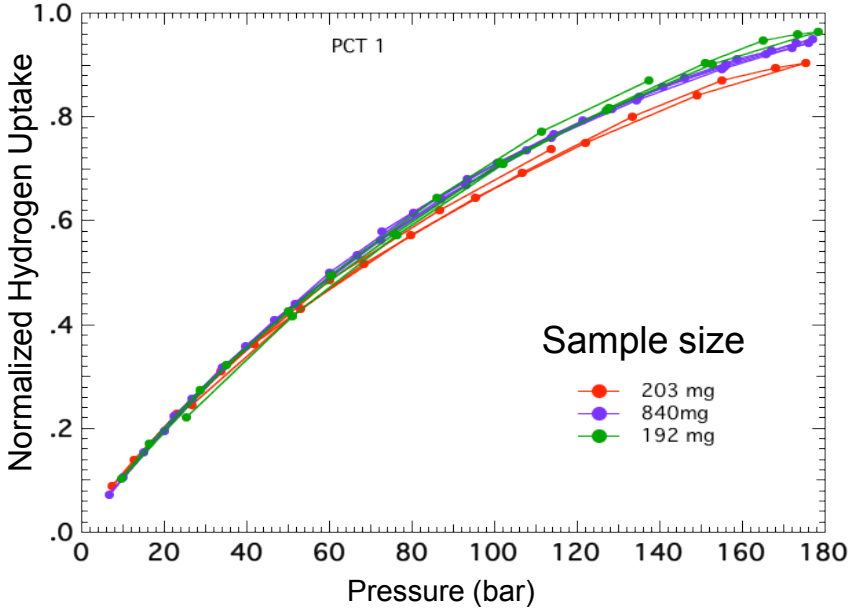
- **Thermal decomposition of triethylborane (TEB) onto MSC-30 at 800 °C**
  - XPS indicates BC_{12} templated growth on MSC-30
  - BET SSA = 1800 m^2/g
- **Ru (2 nm) deposited by microwave assisted deposition from a BC_x with $RuCl_3$/acetone dispersion.**
  - BET SSA = 1400 -1600 m^2/g
  - 4-8%w/w metal deposited. Gram quantities synthesized.

NOTE:

Pure TEB is BC_6, but decomposition of pure TEB gave BC_{12}

Theory predicted puckering of graphene plane would increase reactivity of carbon to hydrogen sorption

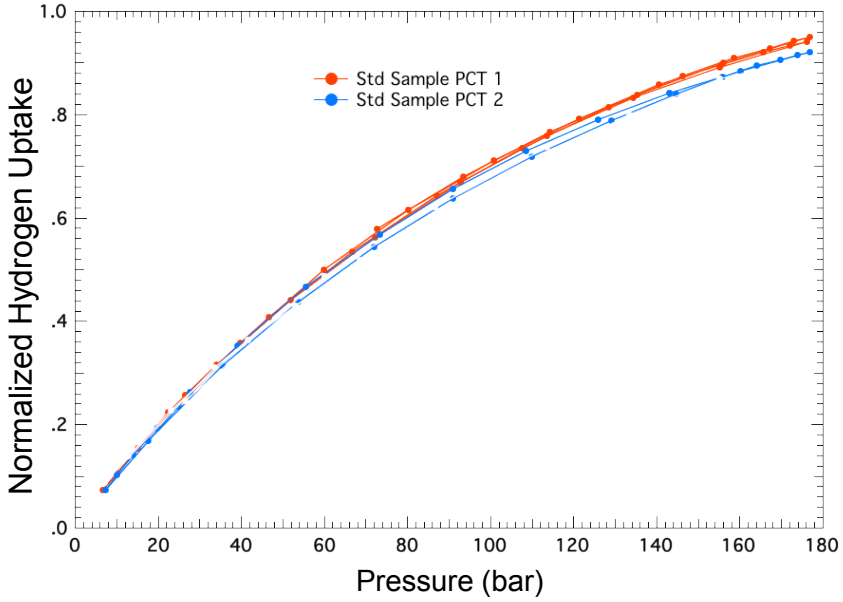
Technical Accomplishments and Progress: (FY 11 Milestone)
Volumetric Measurement Validation



Representative data of multiple samples.

- Different aliquots of one sample
- Error bars are +/- 5%.
  - Sample size 150 mg – 1 gram.

- Improved with corrections for temperature fluctuations between measurements.

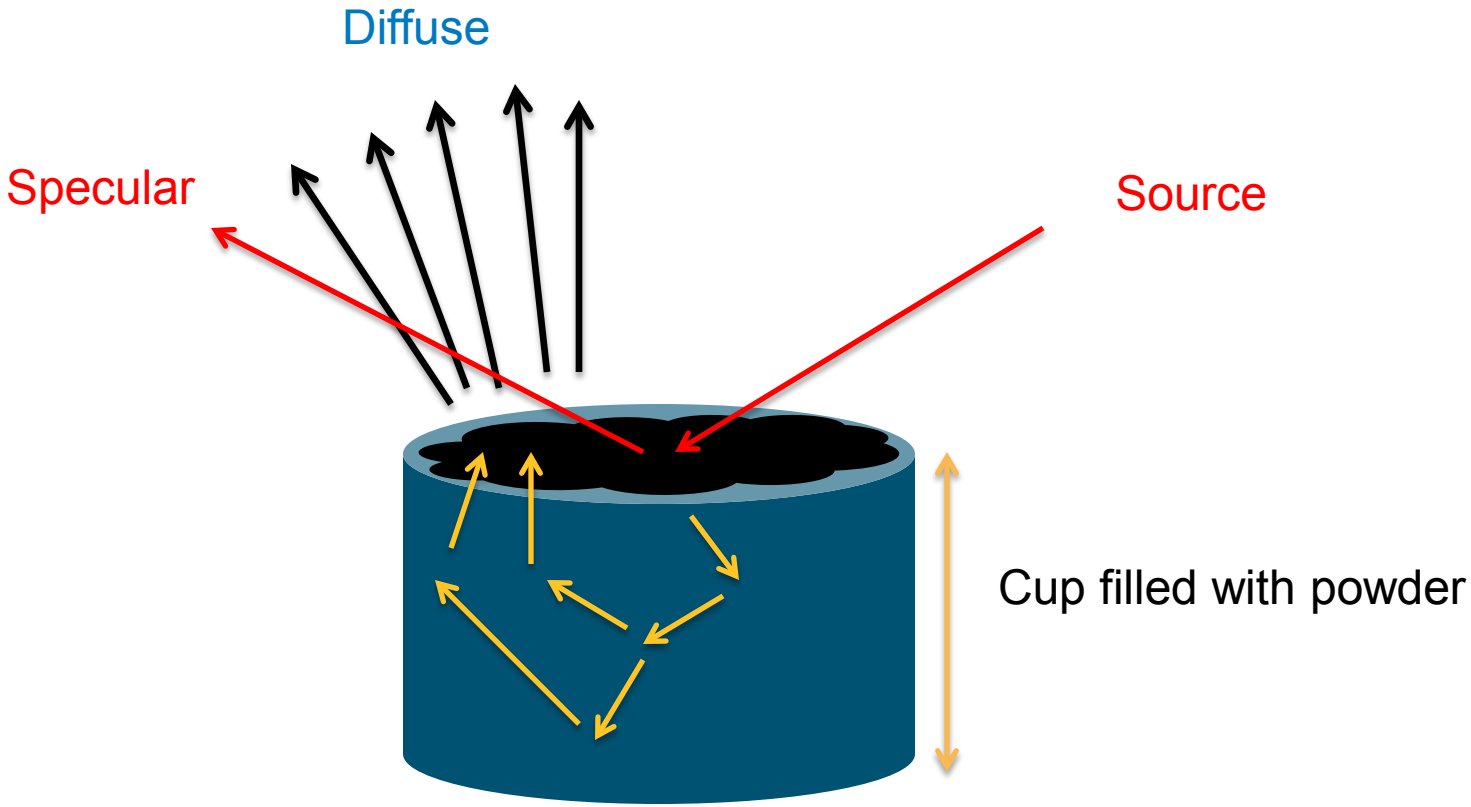


2 instruments
2 scientists
Same sample (≈500 mg)

Reproducible with error < 2 % for two different instruments.

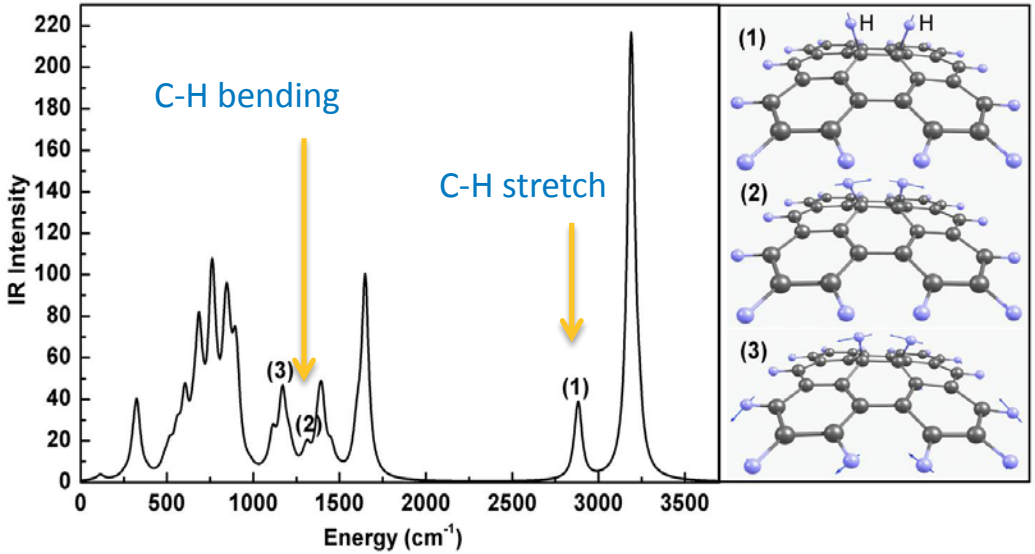
NREL established accuracy and precision limits of our volumetric instrumentation.

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

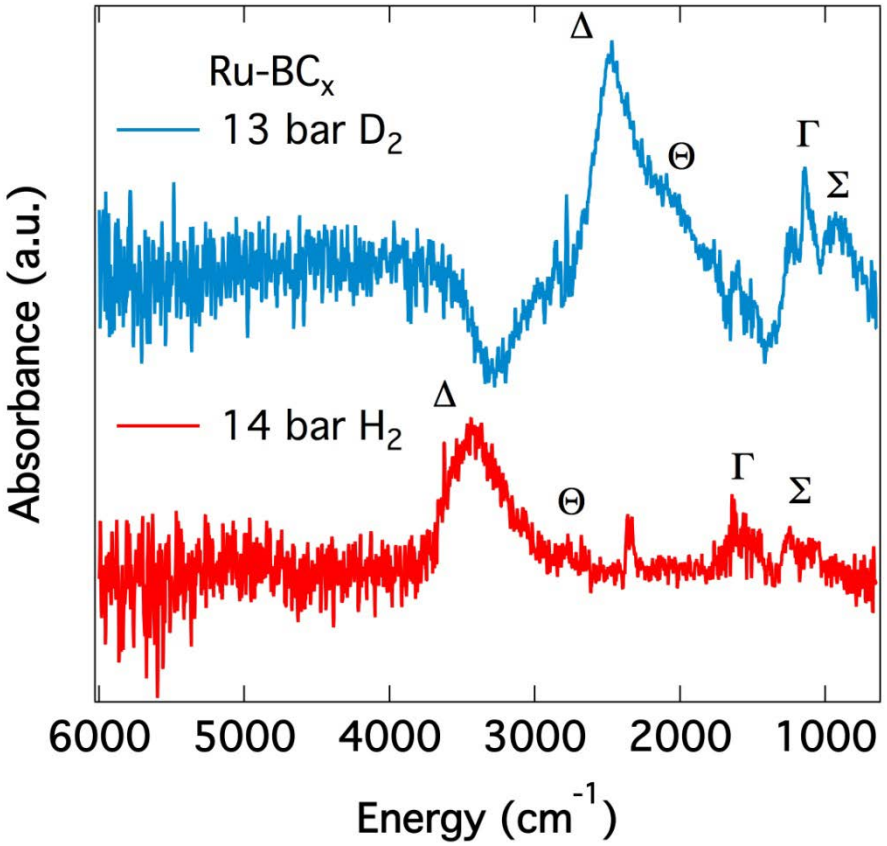
Technical Accomplishments and Progress: DFT Calculations



We performed first principles calculations to help identify the peaks observed in DRIFTS and neutron scattering experiments. To mimic the experimentally synthesized materials, we model a graphene fragments with 28 carbon atoms with each of the 14 edge C atoms terminated by an H atom, i.e., $C_{28}H_{14}$. Boron doping was studied by replacing a C atom in the middle of the fragment with a boron atom, i.e., $C_{27}BH_{14}$. Then, in both materials one weakly chemisorbed H atom is added to the C atom in the middle of the sheet fragment. Employing the DFT method with B3LYP[10] exchange-correlation potential and the 3-21G basis set as implemented in Gaussian 09 package (Gaussian 09, Revision A.1, M. J. Frisch et. al, Gaussian, Inc., Wallingford CT, 2009), we optimize the atomic structures of the undoped and boron-doped graphene fragments. Vibration frequencies are calculated with the Hessian matrix method. The neutron scattering spectra are generated within the DAVE method with the components of vibrational motion identified from the atomic structure analysis.

Technical Accomplishments and Progress:

DRIFTS Comparison of D_2 to H_2 Load



- D_2 charge performed after H_2 charge
- R-D peaks (ω_{RD}) should shift lower in energy according to $\sqrt{1/2}(\omega_{RH})$

Peak Assignments

- $\Delta = H_2O/OH$ stretching
- Θ = CH stretching
- $\Gamma = H_2O/OH$ bending
- Σ = CH bending (merges to one broad peak for D_2)