

# NREL Research as Part of the Hydrogen Sorption Center of Excellence

NREL Team: A.C. Dillon, J.L. Blackburn, J. Bult, C.J. Curtis, M. Davis, T. Elko-Hansen, C. Engtrakul, T. Gennett, A. Groves, M.J. Heben<sup>†</sup>, A. Herwadkar, K.M. Jones, Y-H. Kim, K.J. O'Neill, P.A. Parilla, J.D. Rocha, L.J. Simpson, E. Whitney, S.B. Zhang\*, Y. Zhao

National Renewable Energy Laboratory

<sup>†</sup> University of Toledo

\* Rensselaer Polytechnic Institute

DOE Annual Merit Review

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ST\_26\_Simpson

# Overview

## Timeline

- Center of Excellence start date: FY05
- Center of Excellence end date: FY10
- Percent complete: 80%

## Budget

- \$2.7 M in FY08
- \$3.0 M in FY09
  - ~6 full time equivalent
  - 3 full time post-docs
  - 1 full time intern/temporary

## Barriers

**General:** A. Cost, B. Weight and Volume, C. Efficiency, E. Refueling Time

**Reversible Solid-State Material:**

M. Hydrogen Capacity and Reversibility, N. Lack of Understanding of Hydrogen Physi- and Chemisorption, O. Test Protocols and Evaluation Facilities.

## Partners

Rice (J. Tour), Rice (B. Yakobson, R. Hauge), Air Products (A. Cooper), Duke (J. Liu), CalTech (C. Ahn), LLNL (J. Satcher), NIST (D. Neumann), ORNL (D. Geohegan), Penn State (V. Crespi), U. Michigan (R. Yang), University of Missouri (P. Pfeifer), University of North Carolina (Y. Wu), Texas A&M (J. Zhou), ANL (D.J. Liu). U. Chicago (L. Yu) + others outside of the COE

# Relevance: Objectives

NREL's research in the HSCoE is targeted at addressing key technical barriers in DOE's Hydrogen Program for On-Board Storage:

- **Weight and Volume:** System capacities approach material capacities as the tank operation moves toward ambient temperatures and pressures with materials that have optimum binding energies. In general, sorbents already meet the vast majority of DOE hydrogen storage targets and have minimal heat transport requirements. NREL **development efforts focus on** the remaining targets, e.g., **cost & capacity**.
  - Volumetric and gravimetric capacities are closely linked in sorbents
    - **Increase material density (i.e., >0.7 g/mL) to decrease size**
  - **Increase specific surface area & optimize pore sizes to decrease tank weight & size**
  - **Optimize binding energies to increase capacities and operating temperature**
    - Decrease heat transfer requirements to increase on-board refueling times
      - **Sorption materials typically meet DOE refueling and delivery rate targets**
- **Cost:** Typical high surface area light weight materials (e.g., activated carbon) are commercially manufactured in bulk at ~\$1/Kg with carbon costs only being a small fraction. Thus, **material costs for a system could be ~\$15/Kg-H<sub>2</sub>** (assume 7 wt%).
  - **Develop sorption materials using inexpensive materials and processes**
- **Impact:** NREL's H<sub>2</sub> storage material goals provides DOE with viable solutions that have the potential to **meet even the ultimate technical targets**. While this requires revolutionary materials, breakthrough technologies are being pursued.

# Approach: Focused Materials Development

**Increase Matrix Binding Energy:** Increase concentration of substitution atoms (e.g. B for C) in lattices to adsorb dihydrogen directly (via donation), stabilize active species (e.g. TMs) against agglomeration, and/or provide anchor points for building more complex sorbents.

- 11 KJ/mol H<sub>2</sub> binding energy from B-substitution provides near room temperature sorption

**Increase Storage Site Access:** Develop stable high surface area, sub-microporous (<1 nm), light matrix materials that can either stabilize large quantities of hydrogen directly or provide frameworks for incorporating/stabilizing other components for hydrogen storage.

- >2500 m<sup>2</sup>/g SSA with 0.7 to 1 nm pore sizes may provide >6 wt% cryocompression

**Form Multiple H<sub>2</sub> Binding Sites:** To exceed DOE 2015 and meet DOE ultimate storage targets, fundamentally new approaches must be developed to store >7.5 wt% and >70 g/L hydrogen.

- Require >1 H<sub>2</sub> adsorbed at each binding site and material densities >1g/ml.
- NREL pioneering development of materials with multiple dihydrogen molecules per binding site
  - Use inexpensive chemical and gas phase syntheses of organometallic materials and MOFs
  - Use viability in designs; theorists easily outpaced experiment, but use experiment
  - NREL identified >10 wt% and >100g/L dihydrogen storage materials

**Develop Near Ambient T Hydrogenation:** Develop detailed understanding using lightweight materials to reversibly store hydrogen via weak chemisorption processes. Investigate surface functionalization and catalyst integration to improve storage thermodynamics and kinetics.

- NREL observed C-H bonds on reversible charging/discharging hydrogenation
- Improve processing and measurements to make stable reproducible materials

NREL development efforts leverage each other and balance H<sub>2</sub> and material reactivity with the density and stability of the sorption sites. NREL's vast amount of material design, selection, synthesis, and testing is only partially summarized here.

# Approach: Integration

- **NREL Leads DOE Hydrogen Sorption Center of Excellence**
  - **Ensures all projects are highly integrated with other research within and outside the center**
    - See backup slides for NREL milestones and Deliverables
    - Organizes numerous HSCoE meetings at the group & center level to ensure optimum coordination
    - Publishes a newsletter that provides partners with important information and new results
    - Coordinates partner input for DOE Annual Merit and Tech Team Reviews, and Annual Report
    - NREL helps coordinate materials down-selection, roadmap development, and re-direction efforts
    - Work on Sorption Center Go/No-Go decision process
    - Part of DOE Hydrogen Storage Engineering CoE providing material properties
    - Works with SSWAG for storage tank analysis
    - Provide input to DOE's EERE Risk Analysis Assessment for Storage
    - Work to develop H-Prize Award Criteria
    - Provide technical information for management briefings and coordination efforts
- **NREL provides the hydrogen storage community with leadership and technical development**
  - Helps organize technical sessions at conferences around the world
    - 213th Meeting of the Electrochemical Society, May 18-23, 2008 in Phoenix, AZ
    - Nanoenergy Conference, October 2008, Paris France
    - The Materials Research Society, November 11/30-12/4, 2009, Boston, MA
    - The American Chemical Society, March 21-25, 2010, San Francisco, CA
  - NREL published numerous technical papers in prestigious journals (see Pub. List)
  - NREL made numerous presentations (see pres. list) at various conferences

NREL is fully versed in the technical and management issues for H<sub>2</sub> storage material development and has adjusted our R&D efforts to be fully integrated with HSCoE, DOE, and other efforts to maximize DOE funding and accelerate development.

# Background: Produce High SSA High B Substituted C

## • Templating

- Use chemical vapor deposition to form film on surface
  - Remove template via chemical or vapor processing
- Light single layer film remains with template structure
  - Technology directly amenable to forming high surface area materials with the desired pore structure and composition with  $>3000 \text{ m}^2/\text{g}$  to deliver  $>6 \text{ wt}\%$ , and  $>60 \text{ g/L}$  capacities
    - Yang et. al., JACS 129, 1673 (2007); Wang et. al., J. Phys. Chem. C. 112, 12486 (2008)
- Applicable to all research clusters
  - Optimized pore size for maximum **physisorption**
    - » See Duke presentation and others demonstrate  $>8 \text{ kJ/mol}$
  - Boron **substitution** to increase dihydrogen binding (see back up slide)
    - » Previously demonstrated  $\sim 11 \text{ kJ/mol}$  (theory and experiment)
  - B and N substitution **stabilizes metal atoms** for multiple  $\text{H}_2$  sorption
    - » Y-H Kim et. al., PRL 96, 16102 (2006), also see Rice (Yakobson's) AMR Presentation
  - B and other atom substitution may **enhance spillover**
    - » See APCI's AMR Presentation

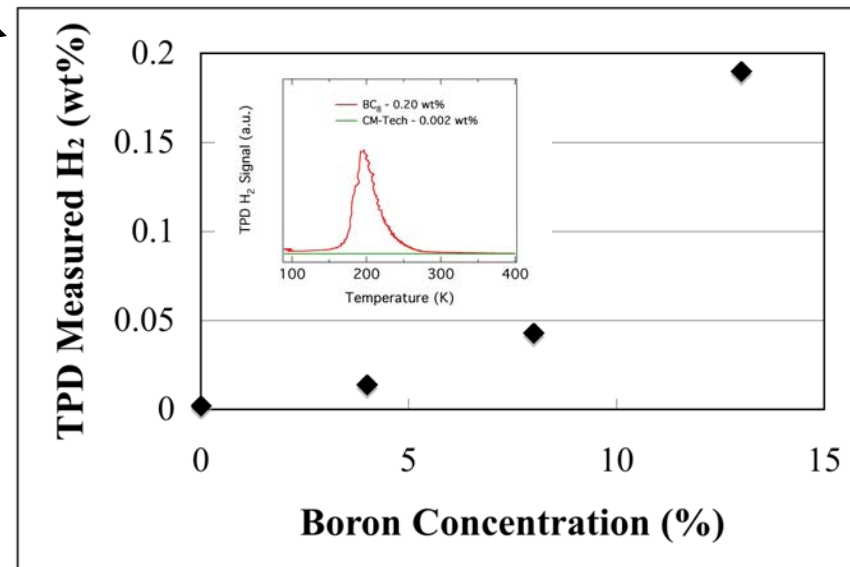
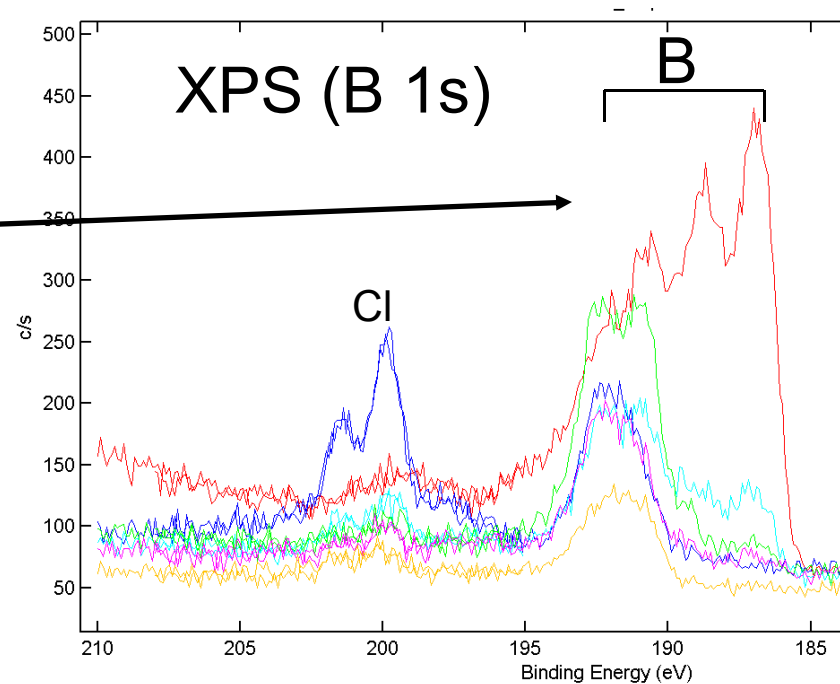
Templating process development enables lightweight materials to be easily produced with the appropriate pore structure and composition. This technique accelerates development by increasing the synthesis rate of appropriate materials where all the higher hydrogen binding sites are accessible.

# Accomplishment: Templating with $\text{BC}_3$

Known process to form high B substituted C

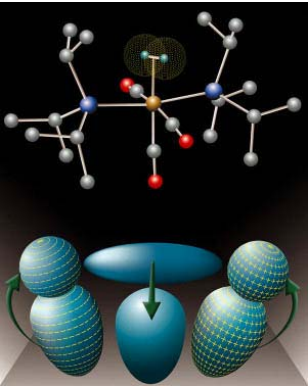
- e.g.  $2\text{BCl}_3 + \text{C}_6\text{H}_6 \rightarrow 2\text{BC}_3 + 6\text{HCl}$   
e.g. Kouvetakis, J. Chem. Soc. Chem. Comm. 1758, (1986)
  - XPS: overall B content and binding environment
    - Multiple peaks means multiple bonding
    - Will perform other characterization (neutron, IR, NMR)
  - Will investigate other hydrocarbons and  $\text{B}_2\text{H}_6$ 
    - More reactive B with no Cl
  - Demonstrated materials with ~15% B
- **$\text{BC}_x$ : enhanced  $\text{H}_2$  capacity & binding**
  - TPD: desorb @ ~ 200 K, capacity 100X > AX-21
    - @240  $\text{m}^2/\text{g}$  compared to 3300  $\text{m}^2/\text{g}$
    - Capacity increases with B concentration
  - 2 bar, 77 K Sieverts: 1.35 wt%
    - AC with similar SSA ~0.2 wt% (5 X lower)
- Optimize zeolite templating procedure
  - SSA (>3000  $\text{m}^2/\text{g}$ ), <1 nm pores & >25% B
  - May net >5 wt%, >50 g/L at 220 K & 100 bar

**B substitution in C increases capacity and binding energy. Binding energy sufficient to store substantial hydrogen within DOE target temperature range of ~220 to 350 K; in good agreement with theoretical models.**

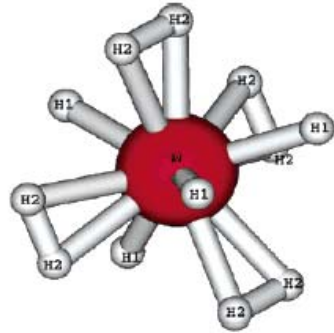




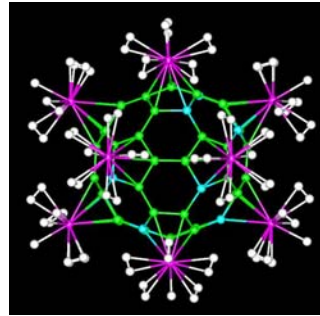
# Background: Kubas Materials Discovery



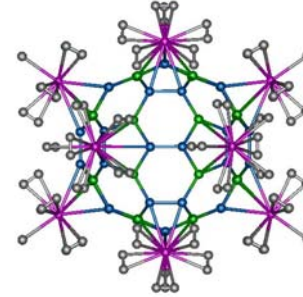
Kubas (JACS 106, 1984)  
exp. 80, theory 70 KJ/mol  
 $H_2 - W(CO)_3(P-i-Pr_3)_2$ .  
 $W-(H_2)_4$  shown



Saillard & Hoffmann  
JACS 106 (1984)  $H_2 - Cr(CO)_5$  ~75 KJ/mol  
theory and ~65 KJ/mol measured



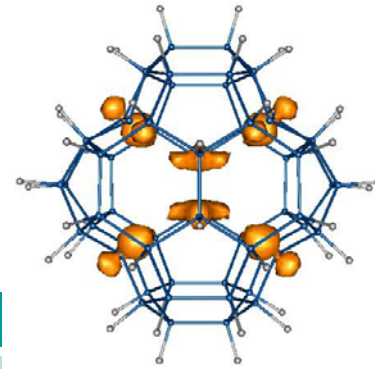
~9 wt%, 43 g/L  
Y. Zhao et al. PRL  
**94**, 15504 (2005)  
MD simulation: no  
sign of Sc clustering or  
disintegration of B-  $C_{60}$   
to 1000K



50 g/L, 10.5 wt%  $C_3B_2ScH_{12}$

Zhao ..., Nano Lett. 2008

All capacity estimates  
for multiple  $H_2$  binding  
are reversible net  
capacities for tank  
operation within  
DOE's Temp. targets



50 g/L, 6.1 wt%  
 $Ca_2@C_{60}H_{52}$

Endohedral  
Metallofullerenes  
Zhao et al. JPC C 111,  
13275 (2007)  
These materials are  
available. (e.g. H. Dorn,  
VaTech)

**C-M and C-M-H theory & experiment agreed from outset**

## M- $H_2$ theory & experiment agree i.e. binding energy and # of $H_2$

G.J. Kubas, J. Organometallic Chem. 635 37, (2001)

## NREL models agree with all known 3d M- $H_2$

Bowers, AC, **27**, 324 (1994); (see back up slides)

### Note:

- While single metal atom decoration of pure element matrices is possible without metal agglomeration, typically **metal atoms are stabilized further at dopant sites** (e.g., Boron in Carbon), and/or **with H**
- **Durability and contamination issues should be similar to metal and chemical hydrides**

## Theory and experiment iteratively interact to design feasible materials:

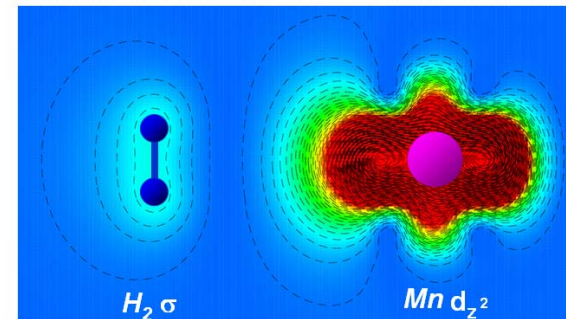
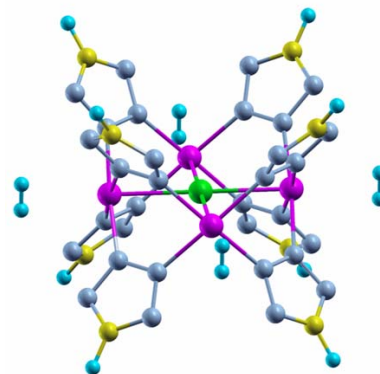
- From outset, ability to synthesize, stability, and DOE targets have always been selection criteria for the design of new materials
- Theory always works closely with experiment to find viable synthetic paths



# Accomplishments: Multiple H<sub>2</sub> Storage

MOF with Open Mn Sites (Jeff Long)

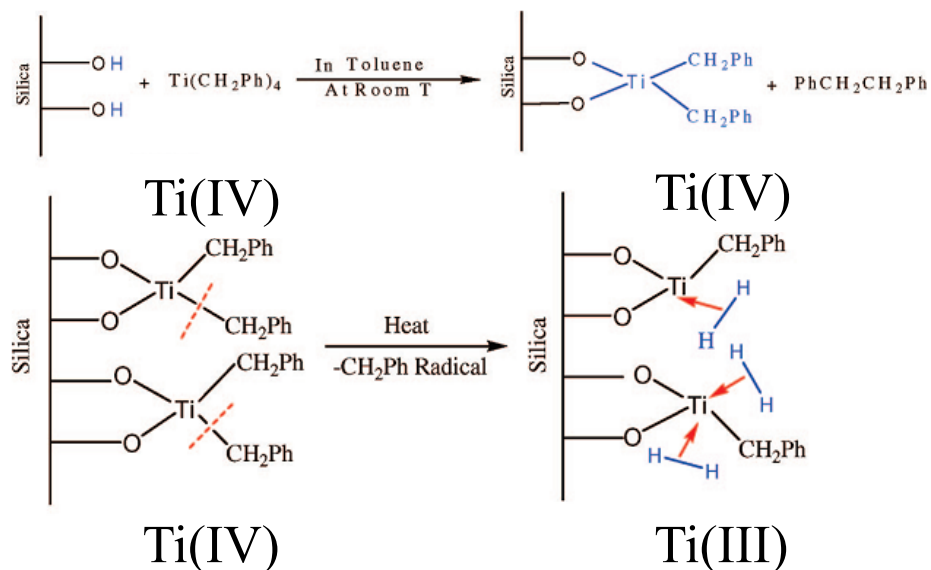
- Experiment 1 H<sub>2</sub> / Mn; theory 1 H<sub>2</sub> / Mn
- Experiment maximum binding energy = 10 kJ/mol; NREL theory 8.4 kJ/mol
- Binding mechanism is same as M-C<sub>60</sub>



NREL: Sun, Kim, Zhang, *JACS*129, 12606 (2007)

Ti-Porous Silica: U. Windsor, Hamaed... 130 6992 JACS 08

- Ti experimentally dispersed on amor- **silica** internal surface w/ strong **Ti-silanol bonds**.
  - On average **2.7 H<sub>2</sub>** were stored on each Ti atom with **22 kJ/mol-H<sub>2</sub>** binding energy
- **NREL Modeling agrees with experiment**
  - <Binding>: **31.5 kJ/mol-H<sub>2</sub>** with **2.4 H<sub>2</sub>/Ti**
  - In all cases, Ti forms strong bonds to O on silica surfaces (~400 kJ/mol)
  - **Exact same processes identified in 2005**
    - **Validates original NREL predictions of multiple (>2) H<sub>2</sub> storage on a single 3d metal atom**
    - **Binding good for ambient storage**



NREL: Ni(BF<sub>4</sub>)<sub>2</sub> (PPh<sub>2</sub>)<sub>2</sub> - SiO<sub>2</sub> aerogel

- Observed 1 H<sub>2</sub> / Ni at ~25 kJ/mol
  - See LLNL pres. & back up slides for more info.

**Experiment validated the original NREL predictions that single metal atoms dispersed and stably supported on a matrix can reversibly hold more than 2 H<sub>2</sub>. Thus, we have routes to meeting DOE's ultimate storage targets.**

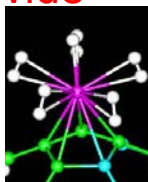
# Accomplishment: RT H<sub>2</sub> Storage with New Kubas Sites

- Identified and systematically developed processes to **form metal atoms on supports** that provide reversible dihydrogen storage

- Processes amenable for most metals

- e.g. Li, Na, Mg, Ca, Sc, Ti, V, Mn, Co, ...

e.g.



- Demonstrated that in agreement with theoretical predictions, the H<sub>2</sub> desorption temperature (i.e. H<sub>2</sub> binding) changed with different metals and B-doping, and that **B stabilizes metal atoms**

- See backup slide for binding for different metals

- Reversible loading H<sub>2</sub> at ambient conditions results in H<sub>2</sub> desorption at **different T's based on metal**

- M-C and M-BC changes H<sub>2</sub> binding**

- Different processing and the use of boron substituted materials changes desorption temperatures

- BC stabilizes Li, H<sub>2</sub> on Li-BC > 10X AC (at RT) with ~5 m<sup>2</sup>/g**

- BC may be needed for all solution phases processes

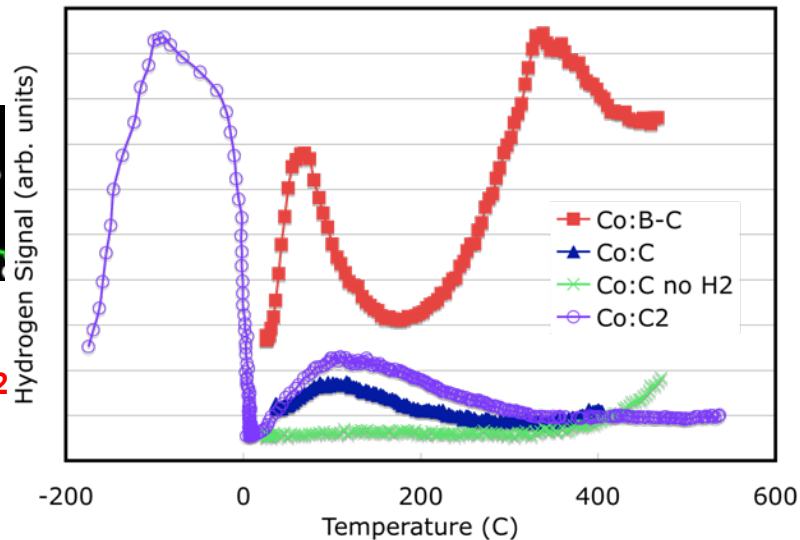
- Next: Increase site density with B-C and correct M

- Optimize processing & surface preparation

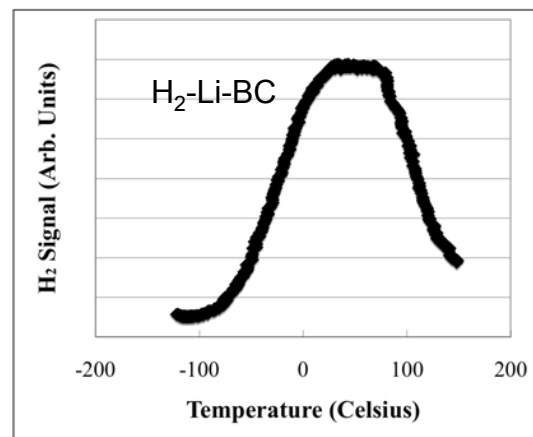
- Fully Characterize materials

- Determine M-BC attachment, M-H<sub>2</sub> binding & proximity

- Make enough material for neutron, IR, Raman, NMR ...



H<sub>2</sub> desorption from M on C and B-C indicates matrix affects H<sub>2</sub> storage; as predicted. Also, different M (e.g. Li, Co or Fe) affects storage. No H<sub>2</sub>-Li observed with pure C materials



Created new M-xH<sub>2</sub> materials that validate theoretical predictions for multiple H<sub>2</sub> binding. This work provides viable synthetic pathways to produce materials that can meet DOE's ultimate storage targets.

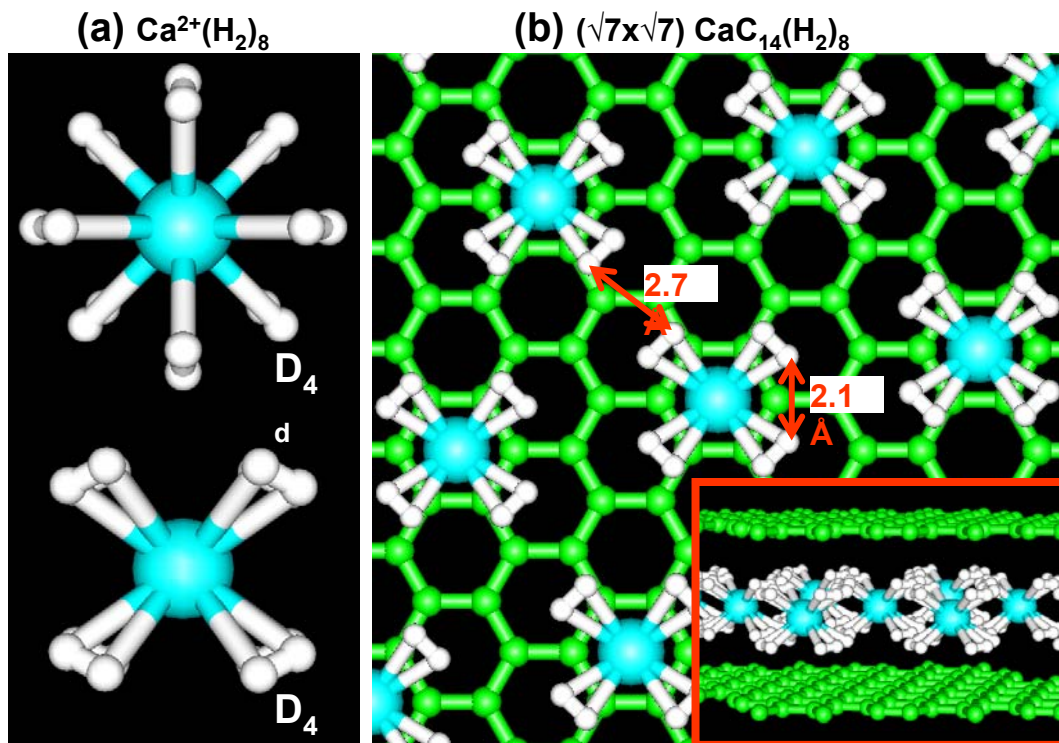
# Accomplishment: Exceeding 100 g/L & LH<sub>2</sub> Density

NREL first to submit paper identifying special properties of inexpensive Ca; act like TM, low clustering

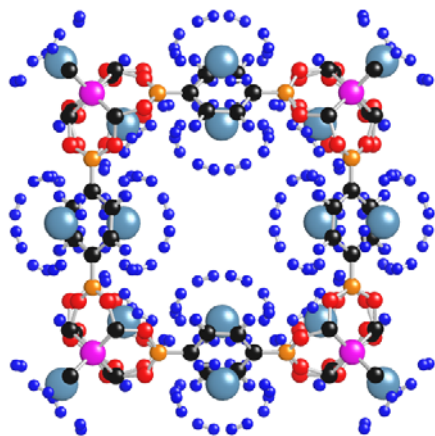
- Li, Na, Mg not like TM
- e.g. Ca intercalated graphene net capacity >100 g/L, 10 wt%
  - H<sub>2</sub>-Ca 20-40, Ca-C 50-90 KJ/mol
  - Graphene stabilizes Ca w/ +1.3
  - Graphitic B-C material could have improved Ca binding

## Ca-COF for H<sub>2</sub> storage

- Ca-COF binding ~120 kJ/mol
  - 2 Ca per benzene linker
- 4H<sub>2</sub>/Ca (<binding>~15 kJ/mol)
  - Net reversible 44 g/L, 5.6 wt%



*Kim, et al., PRB79, 115424 (2009), submitted in 2007*

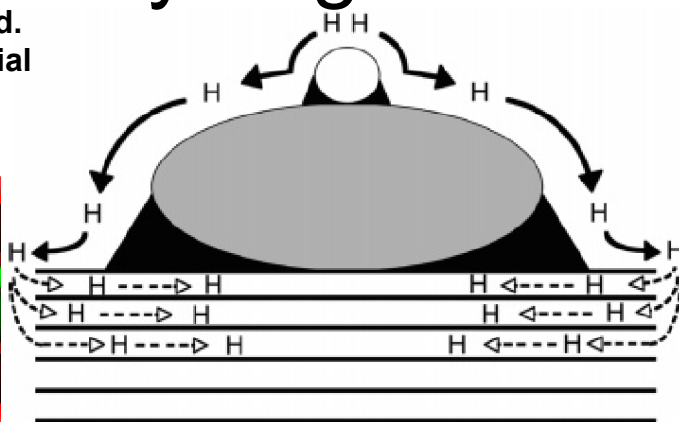
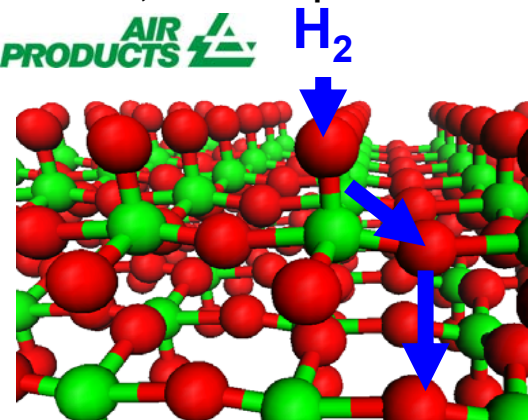


Fully loaded H<sub>2</sub>-Ca-COF

- Identified new **inexpensive** materials that use unique properties of Ca with viable synthetic routes to store H<sub>2</sub> at >100 g/L and >10 wt%.
- Exceeds LH<sub>2</sub> & DOE's ultimate targets including cost and capacities.
- Ca stabilized by matrix with no H<sub>2</sub>, and uniquely stabilizes multiple H<sub>2</sub>.

# Background: Hydrogen Storage via Spillover

APCI models validated using “hyd. bronze”, a known spillover material

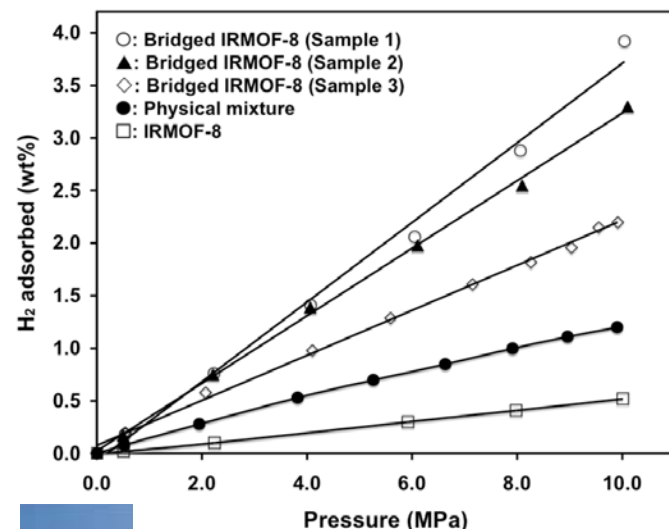


UM developed phenomenological model of spillover. Diffusion on carbon matrix is the limiting factor, not dissociation.

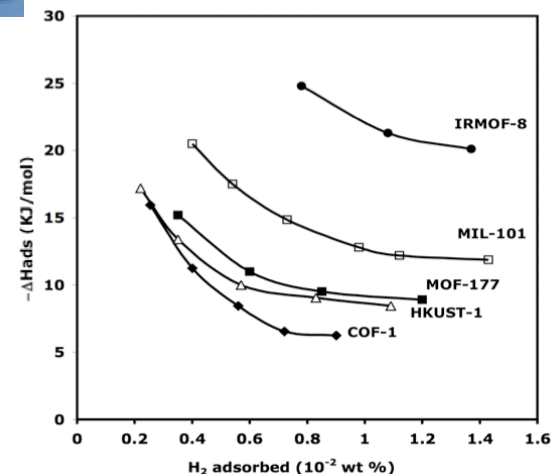
Phenomenological spillover schematics

R. T. Yang et al, *Langmuir* 2005, 21, 11418.

Isotherms at 298K from Pt/AC (10%) & receptor



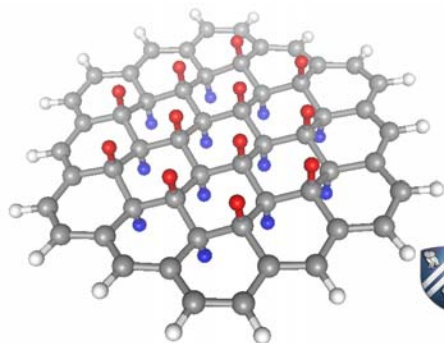
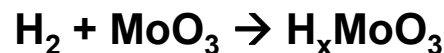
Li et al. *JACS* 128, 8136 (2006)



Spillover demonstrated experimentally and proven thermodynamically

- Issues:
  - Calculations by Rice and others did not identify kinetics for H to move on surfaces
  - Loss of spillover activation
  - Stability of MOFs in spillover

For spillover to be a viable H storage process, we must develop a better understanding of experimental processes and theoretical foundation. **SSWAG showed spillover system capacity ~75% of material capacity.**



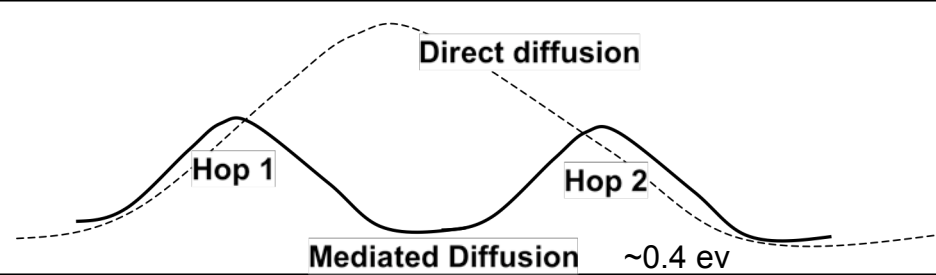
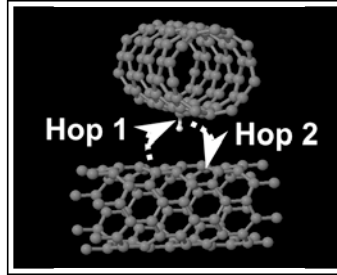
Rice calculations indicate that propagation front of H requires as little as 5 kJ/mol per H atom, compared to ~70 kJ/mol for an isolated H atom.

**Spillover enables substantial RT hydrogen storage**



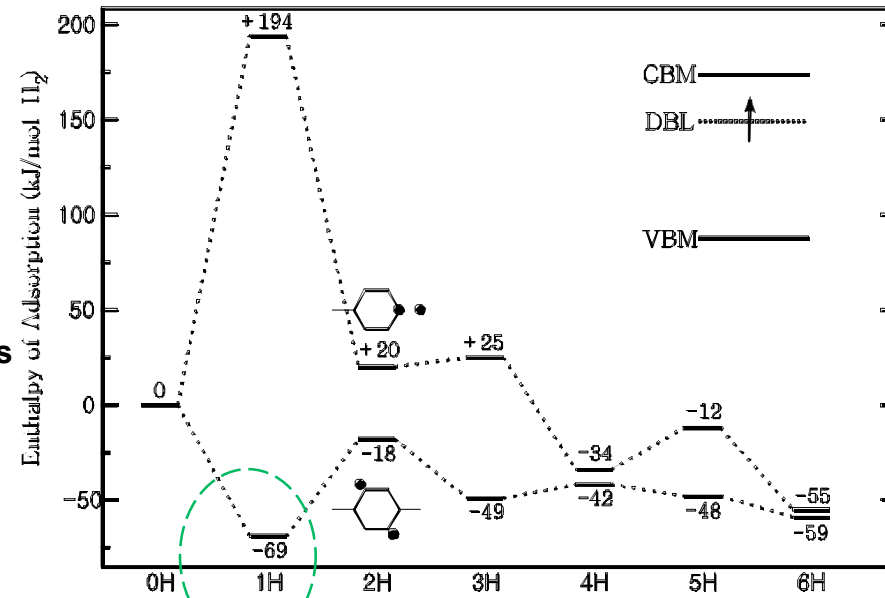
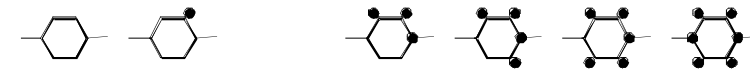
# Accomplishment: Kinetically Allowed H Migration Mechanisms

**Hopping between surfaces (@ ~ 3.4 Å) much faster than H diffusion on a single surface. H migration mediated by neighbors.**



NREL discovered several mechanisms that affect H diffusion

- **H migration increased substantially via hopping between surfaces that are closely spaced**
  - Perhaps layered or corner structures will have hopping
- **H mobile at RT & spillover takes place w/ free-holes**
  - *Benzene*: Holes lower energy of inaccessible high-energy 1H state due to the H strong negative-potential behavior
  - *Graphene*: barrier drops 1.04 eV H<sup>0</sup> to **0.60 eV** for H<sup>+</sup>
  - *MOF linker*: barrier drops 1.52 eV H<sup>0</sup> to **0.52 eV** for H<sup>+</sup>
  - **Try doping, defects, or functionalization to form holes**
- **RT quantum tunneling lowers energy**
  - H diffuse/tunnel (e.g. graphene) before desorb



Lee, et al. (to be submitted)

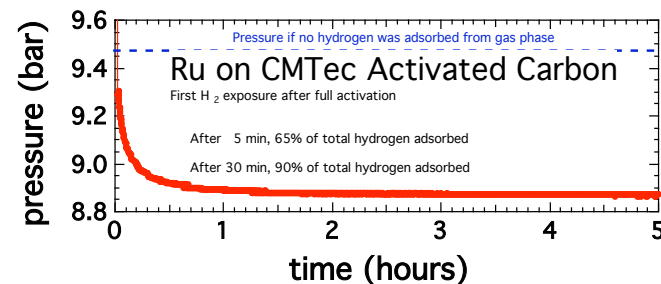
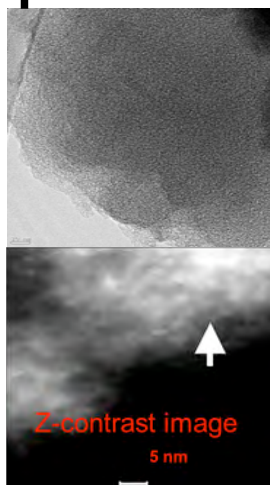
**NREL first to identify that barriers to migration are lowered sufficiently to enable spillover via structural & electronic features, and/or QM tunneling where H will diffuse before it desorbs. These results provide development paths to create high capacity, high rate H storage spillover materials that meet DOE targets**

**2. Free hole** lowers the energy of the 1H state by eliminating the unpaired electron from its dangling bond level.

# Accomplishment: Improved Spillover Catalyst

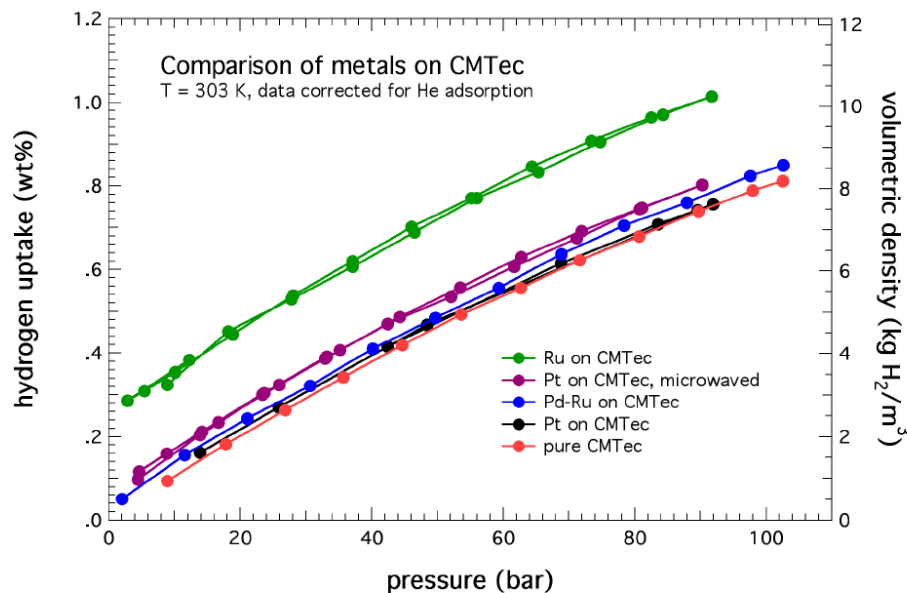
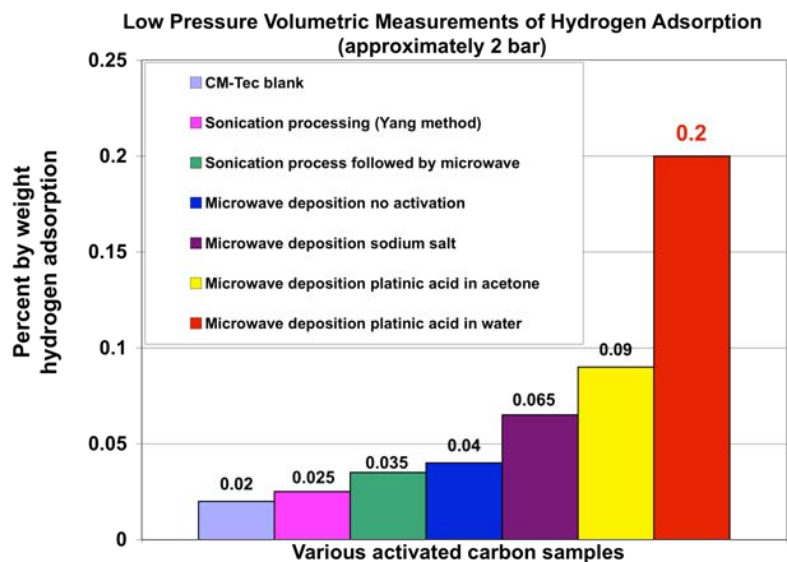
## Developed improved catalyst process

- Reduced catalyst particle sizes to >1nm
- Improved low pressure uptake by 5X
- Achieved enhanced H sorption with Pt, Pd, or Ru (~5 %) on CM-Tec and AX-21
  - Stable for several cycles; need more tests
  - May enable less catalyst to be used
  - Binding Energies estimated at ~20 KJ/mol region for these samples
- Reduced catalyst deposition to 3 min
  - Decrease sample prep. time 25-50%
  - Process is scalable to large quantities



Current adsorption rates single pressure step:

- 10 bar: 5 minutes, 65%; 30 minutes 90%
- 42 bar: 5 minutes, 83%; 12 minutes 90%
- Suggests loading with single higher P (e.g. 100-150 bar)
- Spillover may meet DOE delivery rate targets



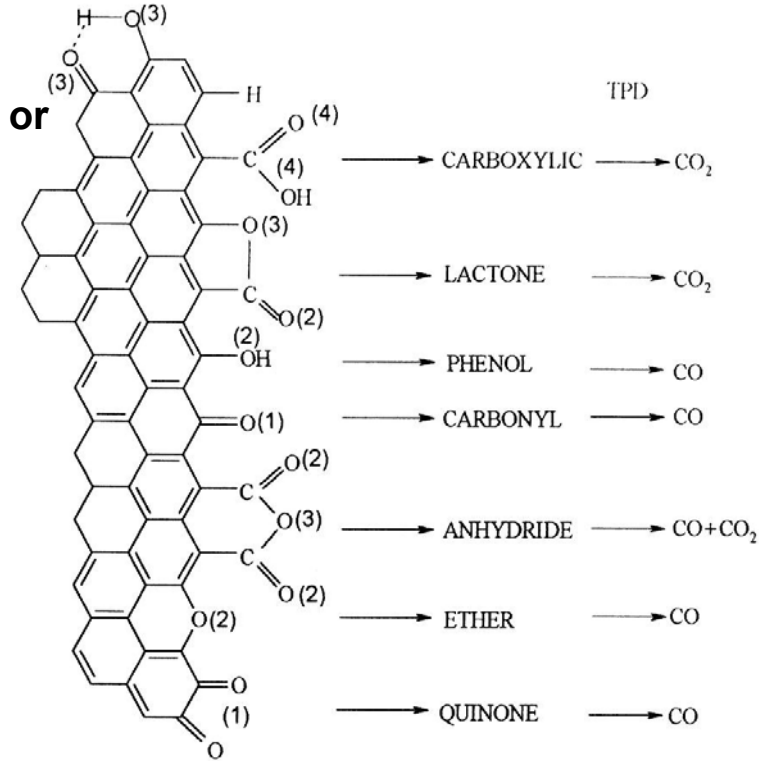
High Pressure H Sorption on AC Materials have >1.0 wt%

NREL developed new catalyst processing that improves spillover capacity and charging rates. The decreased processing time, scalability, and improved performance will accelerate spillover materials development to meet DOE targets.

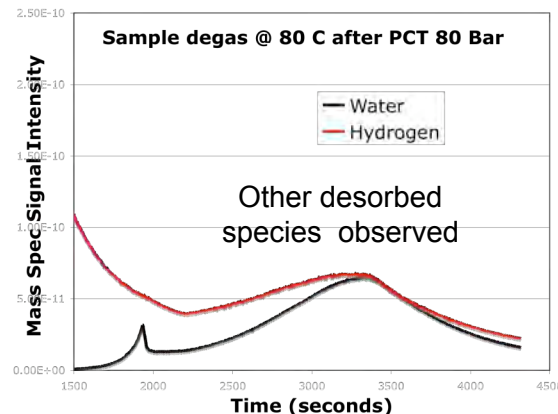
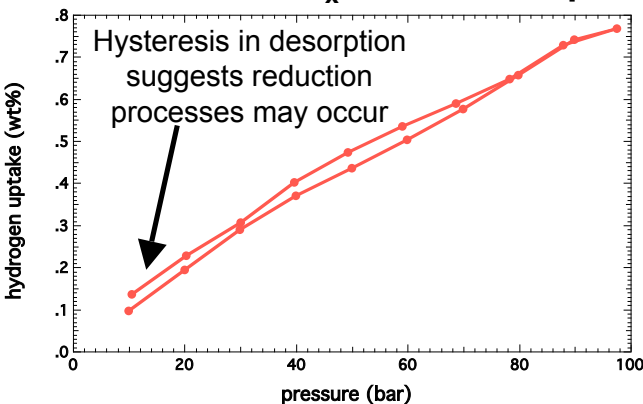
# Accomplishment: Spillover Affected by Surface Functional Groups

## Surface composition important for H diffusion

- Reactions with oxygen surface moieties can inhibit or promote spillover mechanism
- TPD analysis of desorbed gases from spillover samples indicate that reductions occur
  - Water, CO<sub>2</sub>, CO, CH<sub>4</sub>, and other hydro-carbons found
  - Suggests some functional groups reacting with H
    - Produces some irreversibility, i.e. hysteresis in desorption
    - Removed by higher temperature degassing
    - Typically the higher the O the more water produced
- Systematically performing research with model systems in conjunction with calculations and species specific characterization, e.g.
  - TPD, IR, Raman, neutron scattering, and NMR
  - Define surface species that enhance H diffusion
  - Produced 2 wt% reversible RT H spillover with chemical alteration of carbon surfaces
  - BC<sub>x</sub> materials improve spillover



J.L. Figueiredo et al., *Modification of the surface chemistry of activated carbons* Carbon 37 (1999) 1379–1389  
 Jing-Hong Zhou et al, *Characterization of surface oxygen complexes on carbon nanofibers by TPD, XPS and FT-IR* Carbon, 45, (2007), 785-796

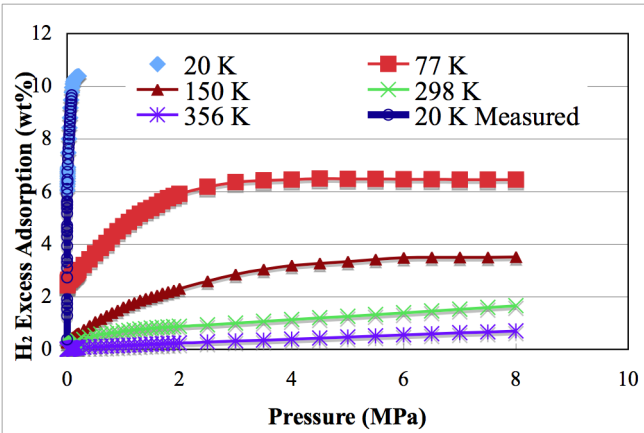


NREL identified potential issues that produce irreversibilities and cause irreproducible hydrogen sorption measurements. Improved understanding of surface functionalization will enhance spillover capacity and sorption rates.



# Accomplishment: Rapid Throughput Screening Measurements

- Methods used include: BET, TPD, TGA, low & high pressure Sieverts
- Fully characterize hydrogen storage properties with milligram samples.
- NREL developed transfer procedures & equipment for **airless sample transport from synthesis systems & external labs**
  - Uniquely create air sensitive H<sub>2</sub> storage materials
- Work with Karl Gross to ensure measurements best practices.



Isotherm models accelerate materials development by providing accurate T&P behavior even from a small (mg) sample. Model indicates that PEEK material from Duke has outstanding higher T performance. Thus, larger quantities should be made for higher T and P measurements.

## Rapid Throughput Screening

- **Measure mg H<sub>2</sub> storage material**
  - Enables full characterization of laboratory scale samples
    - Minimize time synthesizing larger batches
    - Minimize materials used
  - Scale up only good materials
- Adjust measurements to minimize time while measuring the needed characteristics for rapid feedback

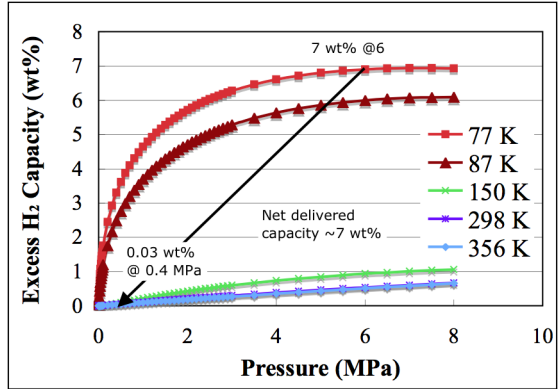
## – Model to accurately predict T & P dependence of sorbents

Modified Dubinin-Astakhov Model, Richard, Benard, Chahine, Adsorption (2009)

- **Minimizes measurements & samples to accelerate R&D**
  - e.g. Measure full isotherms more accurately at lower T & P with mg samples and then provide higher T (e.g. 20 to 400K) and P (0.1 to 700 bar) isotherms
- Chahine’s group developed model that is accurate for T & P used for typical sorbents.

NREL worked with dozens of institutes to provide measurements. In last year:

- Performed ~200 sample measurements to assist partners and collaborators
- Performed nearly **1000 measurements** on external and internal samples.



Model (Dubinin-Astakhov) fit of MOF-177 isotherm. Enables rapid assessment of delivered capacity. e.g. **>95% of stored H<sub>2</sub> will be delivered at 4 bar** or higher from the tank if the initial system is filled at ~80 K and the system is heated up to ~room temperature during delivery.

**NREL improved measurement capabilities to provide more accurate and unique hydrogen storage materials characterization at high throughput.** 16

# Collaborations

As HSCoE lead & leader in H<sub>2</sub> storage materials development & measurements, **NREL collaborates with a large number of groups/institutions around the world.** e.g.

- Works closely with all **HSCoE partners** on a technical and management level
- Works with many **DOE BES projects** on technical and measurement issues, e.g.
  - RPI on development of a more fundamental understanding of physisorption
  - North Dakota State University providing measurements for novel sorption materials
- As part of **HSECoE**, work with several institutions for engineering storage systems
  - Savannah River National Laboratory: Center Lead
  - University of Quebec (Trois-Rivieres), Sorption Task Lead
  - Sorption storage tank analysis and design groups
  - Storage System Working Analysis Group
- **Individual research groups**
  - Work with Karl Gross to develop hydrogen storage measurements best practices
  - Thanos Stubos: Reproduce and validate Demokritos' spillover results using Pd/Hg carbon foam materials for hydrogen storage and assist in improving spillover on these materials
  - Seung-Hoon Jhi, POSTECH, Korea; Hydrogen Storage Materials Modeling
  - CRADA with HSM Systems and the University of New Brunswick to measure light metal hydrides
  - University of Trento, Italy: Develop joint funded effort to produce novel OxyCarbide Derived Carbon (OCDC) porous materials for H<sub>2</sub> storage
  - University of Liverpool: Create joint effort to develop clathrate and other H<sub>2</sub> storage materials leveraging Liverpool's unique combinatorial chemistry systems and NREL's unique measurements capabilities,
  - University of Nottingham: Develop novel templated carbon materials for hydrogen storage,
  - Others include: University of Windsor, Stanford University, Colorado School of Mines, University of Colorado, Virginia Tech, Rochester Institute of Technology, Southwest Research Institute®, University of Delaware. National Aeronautics and Space Administration, Stanford University, University of Quebec (Trois-Rivieres), and other researchers involved in the International Energy Agency and the International Partnership for the Hydrogen Energy.

# Future Work/Recommendations

## FY09: Materials Development and Center Go/No-Go Activities

- **Develop and optimize H<sub>2</sub> storage materials**
  - **Optimize templating processes to synthesize high surface area materials with >2500 m<sup>2</sup>/g, <1 nm pore diameters, and/or boron concentrations >20%.**
    - Develop/improve gas phase synthesis of targeted carbon and non-carbon sorbents
  - **Create stable coordinated unsaturated metal centers** with higher site density that have substantial hydrogen storage using inexpensive materials including Li, Na, Ca, TM, and BC<sub>x</sub>
    - Vapor and chemical deposition of single metal atoms on materials with sites that stabilize the metal atoms.
  - Perform systematic experiments to determine surface/material processing that **increases spillover capacity and sorption rates**, including substitution, functional groups, and post-treatments
    - Use model systems and processing to construct specific surface features to test designs for improving spillover
    - Perform appropriate characterization (IR, Raman, TPD, Neutron scattering, NMR) to determine H state on receptor
      - Send grams of material to NIST and UNC with and without air exposure to determine site poisoning
  - **Accelerate theoretical efforts to design viable materials and synthetic routes**
- Continue to develop state-of-the-art measurement techniques and to provide high-throughput measurement for partners
- **Down-select materials and help with center go/no-go based on material/system potentials**

## FY10: Wrap-up Materials Development and Characterization and Recommend Materials

- **Scale-up synthesis of most promising materials for round-robin verification of samples**
- **Provide materials/systems recommendations for DOE & HSECoE**
  - Determine viability of high surface area materials to meet DOE 2010, 2015 and ultimate targets
    - Determine whether high surface area materials with optimum pore size substantially improves volumetric capacity
    - Quantify the enhancements produced by substitutions for dihydrogen binding and metal stabilization
    - Demonstrate the ability to form and quantify the H<sub>2</sub> binding of metal centers and their ultimate storage potential
    - Quantify the potential of weak-chemisorption along with the affects of intrinsic and functionalized material properties
- **Complete and submit a final report and/or publication for the center**

# Summary

- Develop novel scalable synthetic processes, like templating, to form high surface area lightweight materials with optimum pore structure and composition for H<sub>2</sub> storage. These technique accelerates development by increasing appropriatematerial synthesis rates where all the higher H<sub>2</sub> binding energy sites are accessible.
- Demonstrated that B substitution in C increases capacity and binding energy. The enhanced binding energy is sufficient to store substantial hydrogen within the DOE target temperature range of ~220 to 350 K; in good agreement with theoretical models.
- Theory and experiment continued to iteratively interact to design feasible H<sub>2</sub> storage materials. From the outset 5 years ago, the ability to synthesize, stability, and DOE targets have been selection criteria for the design of new materials. Also, theory always works closely with experiment to find viable synthetic paths.
- Validated the initial theoretically prediction of single metal atoms dispersed and stably supported on a matrix being able to reversibly hold more than 2 H<sub>2</sub>. This was done by demonstrating that the same models accurately predict the number of H<sub>2</sub> molecules adsorbed and the binding for the Ti-Silica system. This removes all doubt to the validity of the predictions and indicates that we have routes to meeting DOE's ultimate storage targets.
- Identified new inexpensive materials that use unique properties of Ca with very viable synthetic routes. These revolutionary new materials could store H<sub>2</sub> at > 100 g/L and > 10 wt%, exceeding all of DOE's ultimate targets including cost, and volumetric and gravimetric capacities.
- NREL identified that barriers to migration are lowered sufficiently to enable spillover via structural & electronic features, and/or QM tunneling where H will diffuse before it desorbs. These result provide development paths to create high capacity, high rate H storage spillover materials that meet DOE targets
- NREL developed new catalyst processing that improved spillover capacity and charging rates. The decreased processing time, scalability, and improved performance will accelerate spillover materials development to meet DOE targets.
- NREL identified potential issues that produce irreversibilities and cause irreproducible hydrogen sorption measurements. An improved understanding of surface functionalization will enhance spillover.
- NREL improved measurement capabilities to provide more accurate and unique H<sub>2</sub> storage materials characterization at high throughput.

# Summary Table

## Summary of NREL Materials Development for the Last Year

Storage Parameters/ Materials	Specific Energy (Net, wt%)	Volumetric Energy (Net, g/L)	Binding Energy (KJ/mol)	Conditions	Besides Cost, other targets of issue	Comments
Li/THF co-int. Graphite (T)	5-7		5-20			
Li/THF co-int. Graphite (E)	0.5	NA		77K 2 bar		Need to remove excess THF
Li/THF co-int. Aerogel (E)	2.4	NA		77K 2 bar		Down selected, not working
BC <sub>x</sub> (E)	1.4	1	11	77K, 2 bar		Only 240 m <sup>2</sup> /g, 3 x more than AC with same SSA
2.7 H <sub>2</sub> -Ti-Amor-silica (T)	NA	NA	31	2.4 H <sub>2</sub> /Ti		Agrees w/ 2.7 H <sub>2</sub> /Ti Exper.
Li-BC <sub>8</sub> (E)	NA	NA	10-15	RT, 1 bar		10 X gain over AC, 5 m <sup>2</sup> /g
CaC <sub>14</sub> (H <sub>2</sub> ) <sub>8</sub> (T)	>10	>100	20-40	RT		Proof of unique Ca properties
CaCOF(H <sub>2</sub> ) <sub>4</sub> (T)	5.6	44		RT		Viable synthesis material
Hopping spillover kinetics (T)	NA	NA	~30	RT		1 <sup>st</sup> viable kinetic mechanisms
Hole assisted Kinetics (T)	NA	NA	~50	RT		1 <sup>st</sup> viable kinetic mechanisms
Ru, Pt, Pd-AC spillover (E)	1.2	6	20	RT, 80 bar	Catalyst, rate	Spillover on AC reproduced, 5X increase low P, higher rate
Ni(BF <sub>4</sub> ) <sub>2</sub> (PPh <sub>2</sub> ) <sub>2</sub> - SiO <sub>2</sub> aerogel (E)	~0.3	NA	20	77K, 2 bar		Model system that showed coordinated Ni-H <sub>2</sub> binding. Down Selected, low capacity
Sc,Fe,Cr-organometallics (T)	4-8	20-40	15-25	ambient		
Sc,Fe,Cr organometallics (E)	NA	NA	NA	ambient		Down selected, little progress
Templated Materials (E)	>6	40	5-8	77K, 30 bar		Working with partners to develop high SSA materials

T – Theoretical Predictions, E – Experimental Results

# Supplemental Slides

# Approach: NREL FY09 Milestones and Deliverables

- Report on the examination of missing storage capacities using different pressure and temperature routes. Compare to findings of Yue Wu at U. North Carolina. March 2009
- Verify accurate measurement at >100 bar. September 2009
- Quantify requirements of single element high specific surface area materials to meet DOE 2010 hydrogen storage targets. April 2009
- Demonstrate >7 wt% hydrogen storage in a high specific surface area material. September 2009
- Report on the synthesis of three new sorbents produced by gas phase synthesis, including boron-doped carbon structures and metal-dihydrogen complexes prepared by laser vaporization. April 2009
- Demonstrate 3 wt% hydrogen capacity at room temperature from gas-phase synthesized material. August 2009
- Demonstrate a successful reaction pathway that was developed as a result of employing theoretical calculations to guide experimental investigations. December 2008
- Demonstrate 2 wt% hydrogen storage that may be attributed to di-hydrogen ligands bound on transition metal atoms. April 2009
- Demonstrate 2 wt% hydrogen storage at room temperature with activated carbon materials. March 2009
- Determine the mechanism of enhanced hydrogen migration in carbon materials through simulations. Study the experimental results and test the proposed spillover mechanism, especially the evidences of kinetics enhancement through microscopic bridges and external vibrational forcefield. April 2009
- Study the recently synthesized organometallic molecules with Sc centers. Identify reaction pathways that may potentially assemble the molecules into a high-surface-area framework for hydrogen storage. September 2009
- Complete detailed Roadmaps with steering committee for HSCoE technology areas identifying outcomes of the center by 2010. November 2008
- Develop new collaborations with international groups (e.g. Thanos Stubos, Environmental Research laboratory, NCSR Demokritos) May 2009
- Complete outlines for each technology area (i.e. RC) that details issues to be addressed in the final go/no-go recommendations August 2009
- Deliver Technology development Roadmaps. December 2008
- Deliver HSCoE Contribution to DOE Annual Hydrogen Program Report. August 2009
- Deliver FY 2010 Annual Operating Plan. July 2009
- Deliver Quarterly Task Reports. 10/08, 01/09, 04/09, 07/09

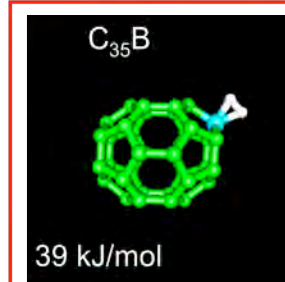
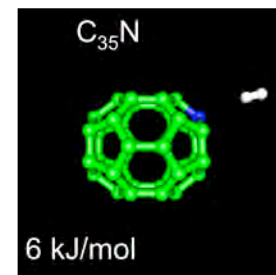
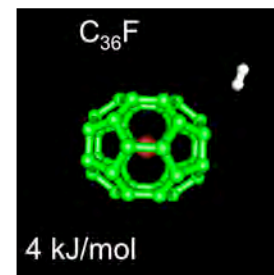
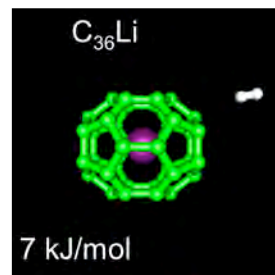


# Potential Substitutions in Carbon

– Kim et. al., PRL 96 016102 (2006)

- B and Be substitutions enhance  $H_2$  binding
- Binding decreases with number of  $H_2$  adsorbed
- Curvature affects binding

– Boron substitution also stabilizes metal atoms on the surface

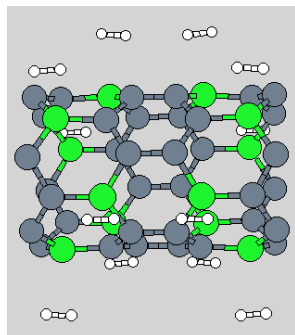


Enhanced binding

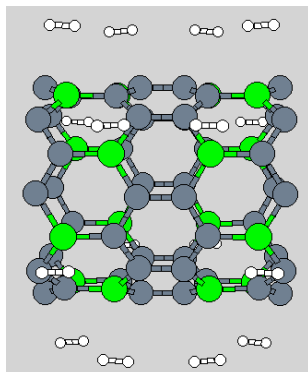
12 kJ/mol

11.1 kJ/mol

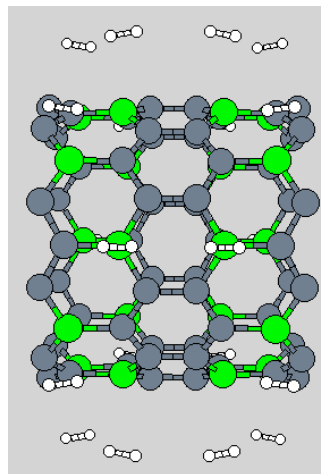
10.7 kJ/mol



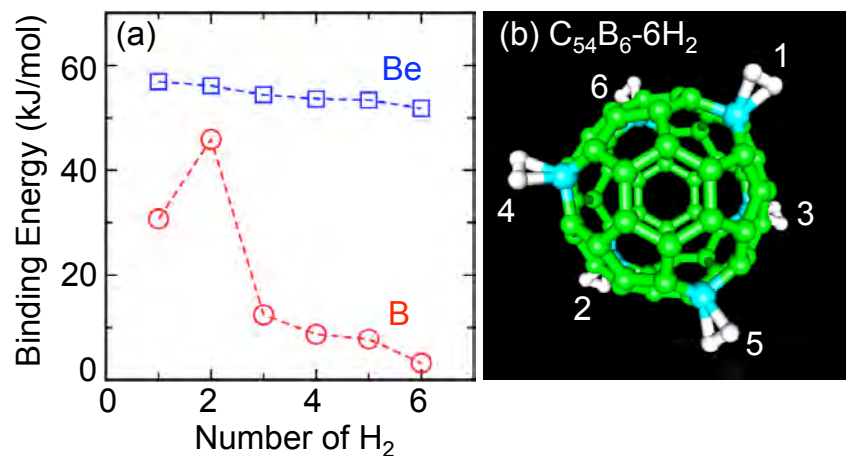
(3,0)



(4,0)



(5,0)



Surface curvature ( $sp^2$ - $sp^3$  hybridization) affects the binding.

# Background: Model and Experiment Agree

- For all known 3d M-H<sub>2</sub> materials, NREL models accurately predict the number and binding energy of that experimentally observed, including:

Bowers, M.T., *CLUSTER IONS - CARBON, MET-CARS, AND SIGMA-BOND ACTIVATION*. Accounts of Chemical Research, 1994. **27**(11): p. 324-332.

Table: Experimental binding energies in kJ/mol-H<sub>2</sub> (data taken from Ref. [Bowers]).

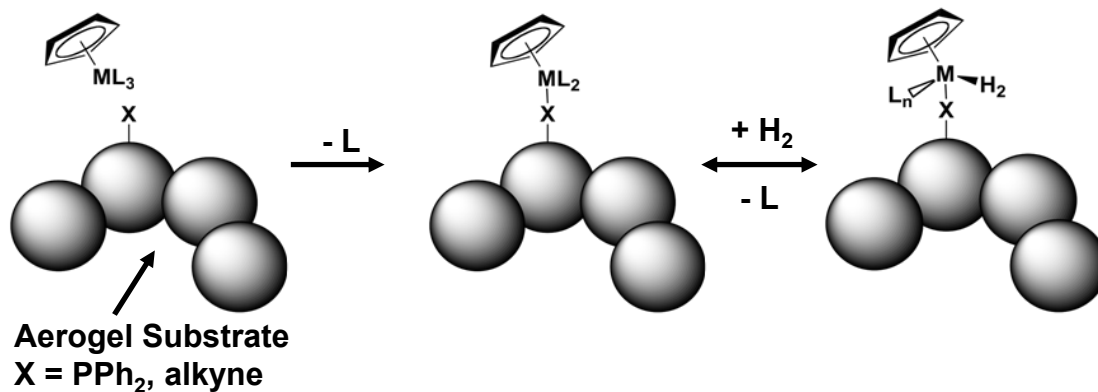
n	K <sup>+</sup>	Sc <sup>+</sup>	Ti <sup>+</sup>	V <sup>+</sup>	Fe <sup>+</sup>	Co <sup>+</sup>	Zr <sup>+</sup>	Nb <sup>+</sup>
1	6.1	8.8	31.4	42.6	52.7	76.1	69.0	61.9
2	5.6	28.8	41.8	44.7	69.8	71.1	49.3	65.2
3		22.6	38.9	36.8	35.5	40.1	48.1	59.8
4		20.9	39.3	37.6	41.0	40.1	46.0	64.4
5		18.8	40.6	17.6	11.3	18.0	44.3	69.4
6			39.7	40.1	10.9	16.7	43.1	59.8
7						3.3	41.4	56.0

## *Method:*

Electron ionization source float at 5 kV and are coupled to a reverse geometry magnetic / electric sector double-focusing machine used for mass analysis.

# Accomplishment: Inclusion of Transition Metal Fragments in High Surface Area Aerogels for Increased $H_2$ Storage

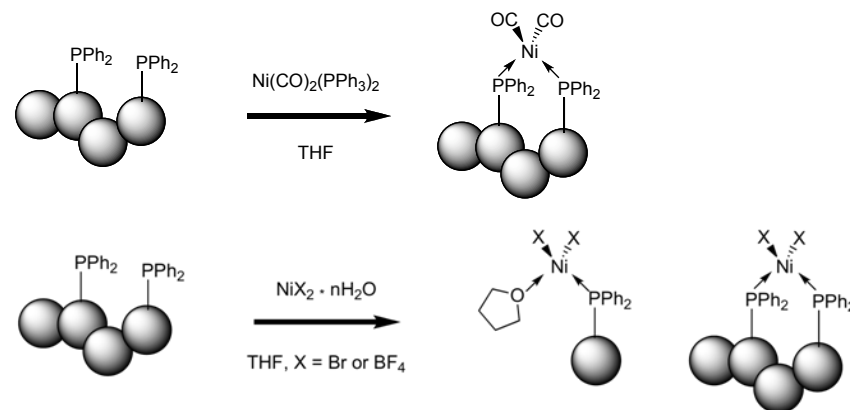
## Concept:



- Synthesized low-density  $SiO_2$  aerogels with pendant  $PPh_2$  groups
- SA:  $750 \text{ m}^2/\text{g}$ , presence of  $PPh_2$  groups confirmed by  $^{31}\text{P}$  NMR

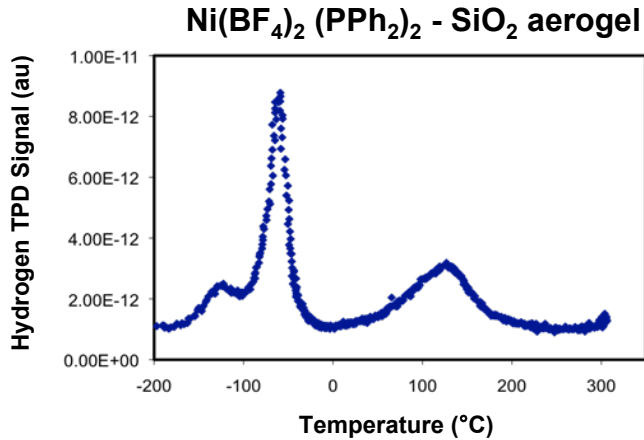
## Approach:

- Ligands must be easily displaced in the presence of  $H_2$  or by external processing controls such as heat or UV light
- Metal site must be electronically and coordinately unsaturated to bind multiple  $H_2$  ligands



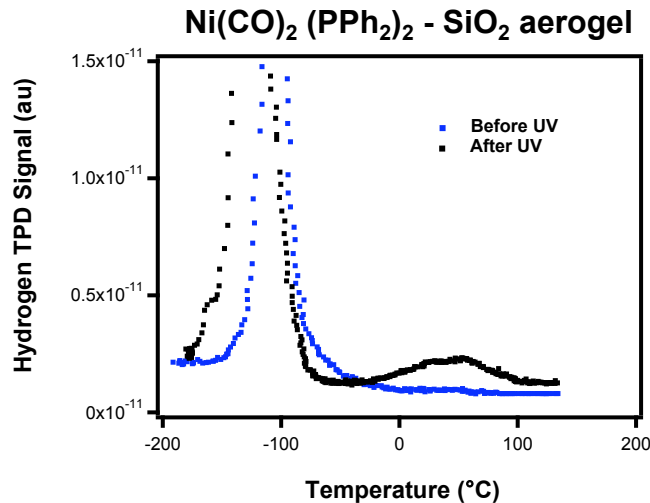
**Well-defined, site specific binding (pinning) of transition metal complexes to high surface area supports is now possible. Successfully developed reaction pathways to four novel Ni intermediates with ligands that were easily displaced.**

# Accomplishment: Evidence for Enhanced $H_2$ Binding in Ni Phosphine Complexes on $SiO_2$ Aerogels



Gravimetric Capacities <sup>a</sup> :	77 K, 2 bar
PPh <sub>2</sub> -SiO <sub>2</sub> <sup>b</sup>	0.67 wt%
NiBr <sub>2</sub> -PPh <sub>2</sub> -SiO <sub>2</sub> <sup>c</sup>	0.33 wt%
Ni(BF <sub>4</sub> ) <sub>2</sub> -PPh <sub>2</sub> -SiO <sub>2</sub> <sup>d</sup>	0.29 wt%

**Notes:** <sup>a</sup> Samples degassed to 300 °C prior to RT  $H_2$  dose. SA: 750<sup>b</sup>, 481<sup>c</sup>, 193<sup>d</sup> m<sup>2</sup>/g



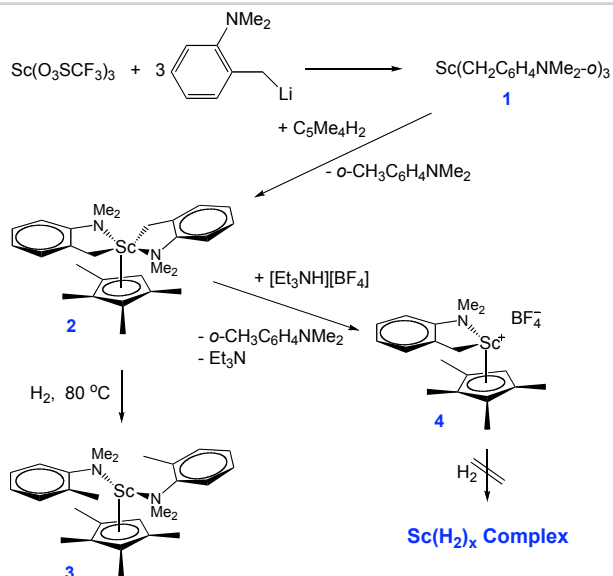
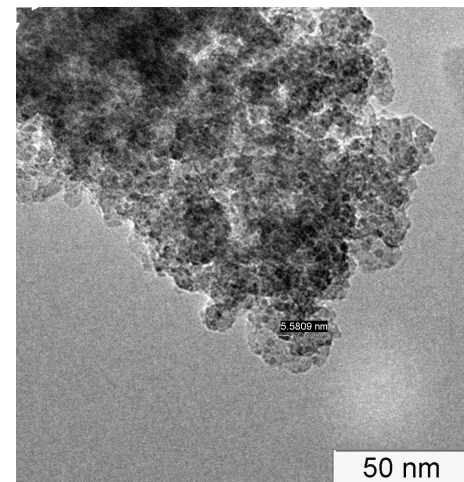
- Gravimetric capacities and BET surface areas decreased after utilizing solution-based chemistries
- Observed enhanced binding energies in two Ni decorated inorganic aerogels
- CO ligands were easily displaced by UV light
- A new  $H_2$  binding site in the Ni(CO)<sub>2</sub> aerogel was observed only after photolysis

Incorporated new  $H_2$  binding sites in two novel metal decorated inorganic aerogels with enhanced binding energies. The binding enthalpy reached as high as 20.5 kJ/mol at low  $H_2$  coverage.

# Material Downselect: Solution-Phase Synthesis of Supported Transition Metal Complexes that Bind Multiple H<sub>2</sub> Ligands

## Synthesis of Supported Phosphine-Transition Metal Complexes

- Successfully developed novel reaction pathways to stabilize TM complexes on phosphine functionalized inorganic aerogel supports.
- Ligands on metal centers were easily displaced in the presence of H<sub>2</sub> or by external processing controls such as heat or UV light.
- Temperature programmed desorption measurements revealed new H<sub>2</sub> binding sites with enhanced binding energies.
- Metal agglomeration was not avoided, 2-5 nm metal particles were observed.
- These types of solution-phase synthesis of supported Phosphine-TM complexes will no longer be pursued.



## Synthesis of a Sc Metal Complex with Multiple H<sub>2</sub> Ligands

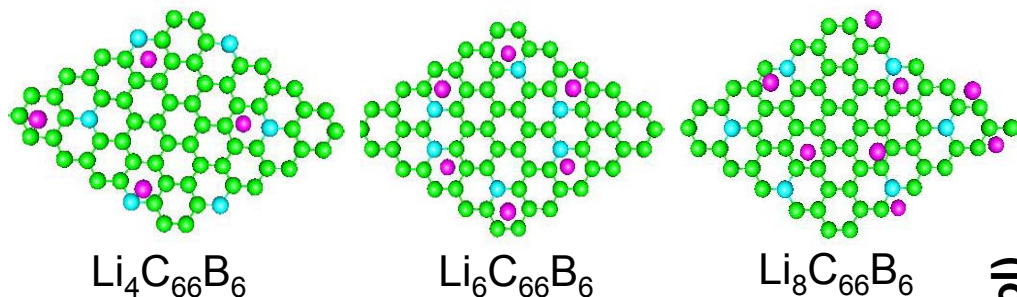
- The aminobenzyl ligands were not easily displaced from the Sc metal center (**2**) by H<sub>2</sub>. In addition, calculations at NREL indicated that the presence of the bulky aminobenzyl ligands hinder the adsorption of H<sub>2</sub> (i.e., sterically hinder).
- The reaction of a weakly coordinated cationic Sc center (**4**) with H<sub>2</sub> produced only the insoluble bridging Sc-H-Sc complex.
- We are no longer pursuing tractable reactions involving organometallic Sc complexes.

# Accomplishment: “Strong Binding of H<sub>2</sub> via Li Intercalated B-Graphite”

## Intercalation of B doped Graphite

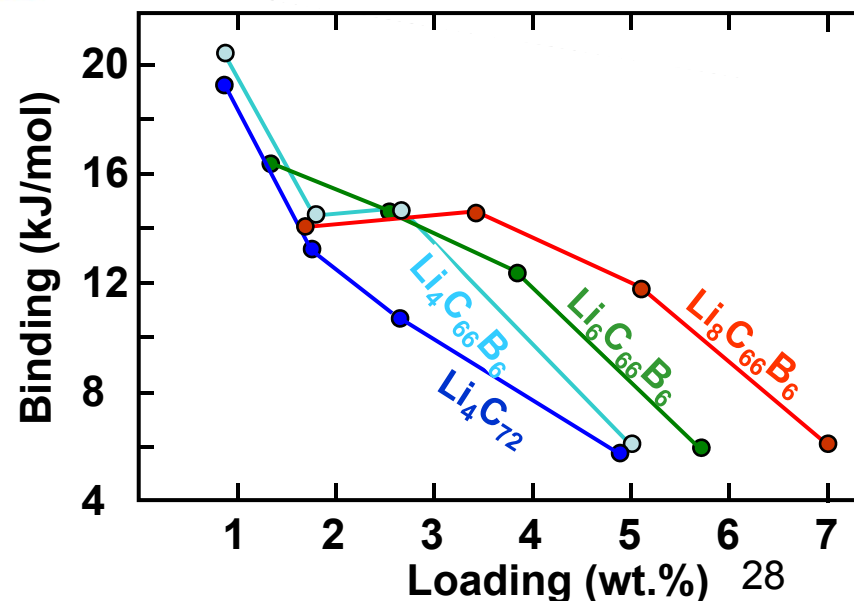
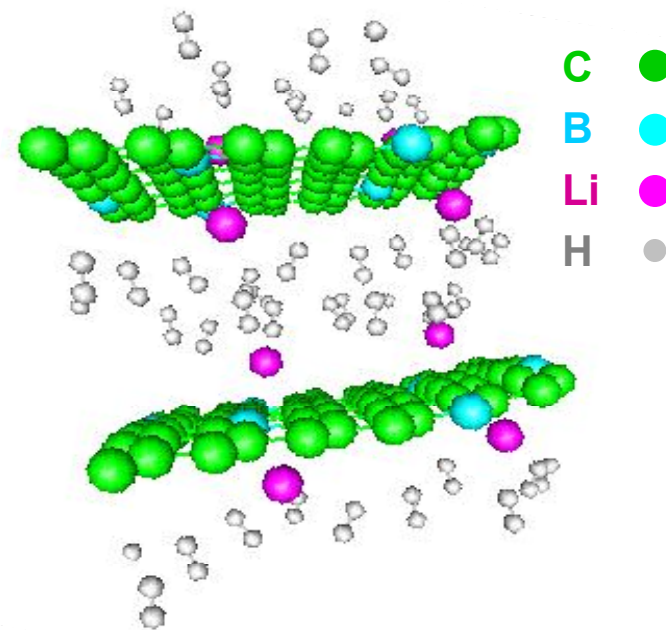
**Total energy (eV)** of metal-clustered structures relative to the metal-dispersed structures and nearest Li – Li distance (Å).

	Li <sub>4</sub> C <sub>66</sub> B <sub>6</sub>	Li <sub>6</sub> C <sub>66</sub> B <sub>6</sub>	Li <sub>8</sub> C <sub>66</sub> B <sub>6</sub>	Li <sub>10</sub> C <sub>66</sub> B <sub>6</sub>
Cluster	1.7/5.2	2.3/3.2	0.49/2.8	-0.26/2.4
Dispersed	0/7.4	0/6.1	0/5.7	0/5.1



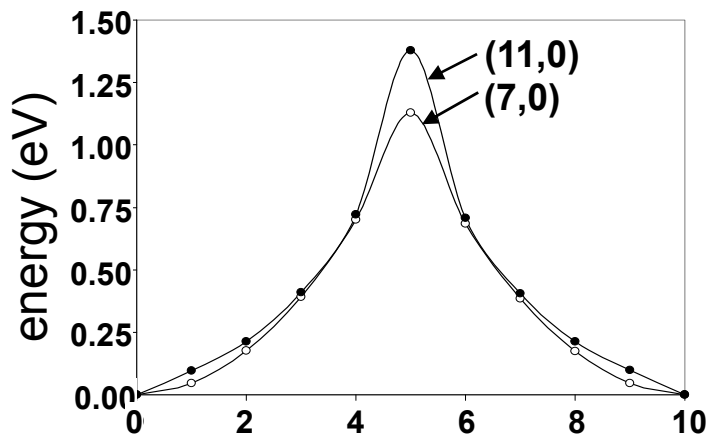
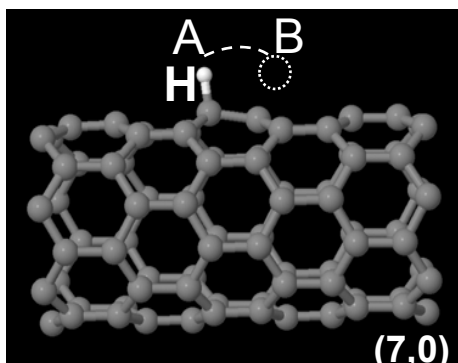
With 8 atm% B substitution, the non-clustering Li density increases, therefore, H capacity increases. Boron doping enhances both Li-to-sheet charge transfer and hydrogen binding.

H<sub>2</sub> binding energy can be effectively tuned by the interlayer distance

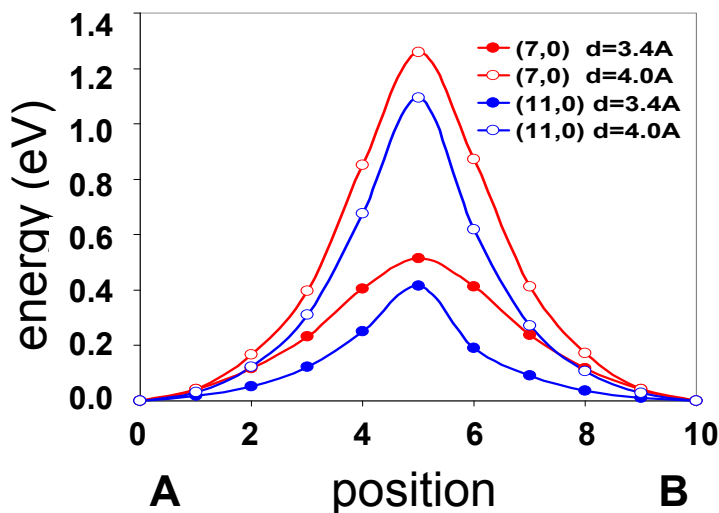
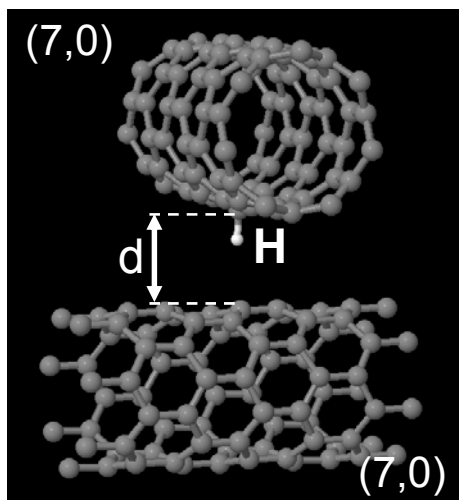
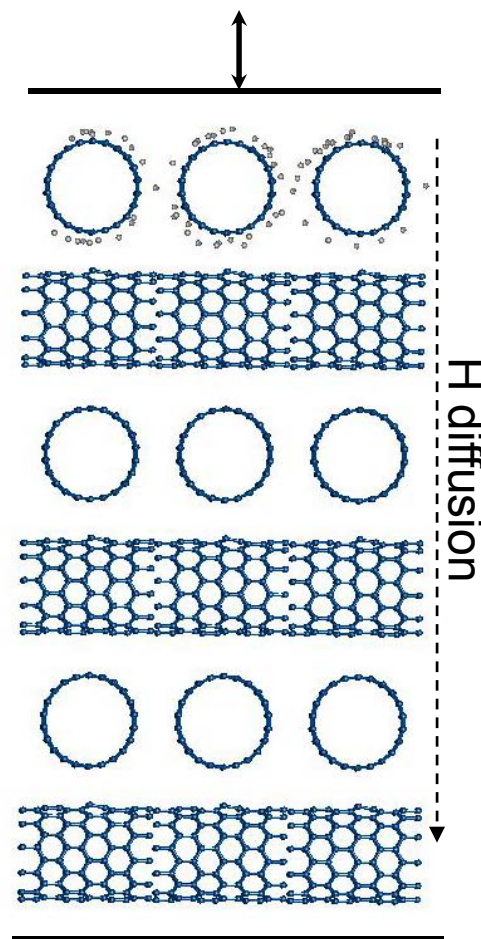




# Mechanism for H Transport for Spillover



External oscillation Force



**New mechanism proposed: hopping between CNTs (bottom) can be much faster than H diffusion on the CNT wall (upper), when the CNT-CNT side wall distance is getting closer. That means H migration in nanoscale carbon materials can be mediated by the neighboring carbon atoms. Extension of this concept indicates that hopping between two close surfaces (e.g. tight corner, small pore, or closely spaced planes) is viable mechanism for H diffusion for spillover.**

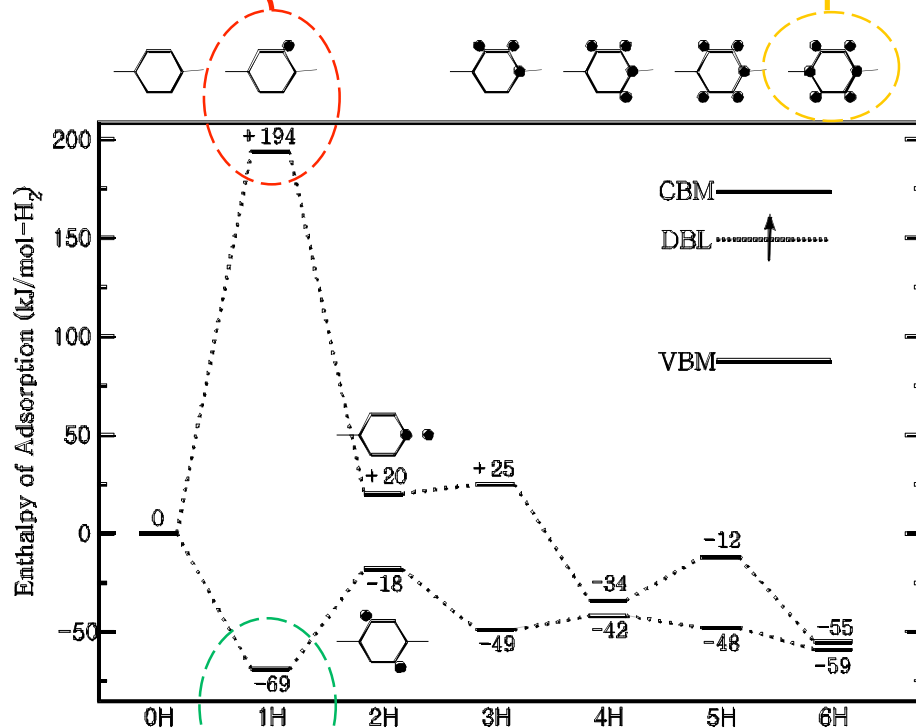


# Hole in the Valence Band is Essential for the Spillover

1. **Inaccessible high-energy 1H state** due to the strong **negative- $U$**  behavior of atomic H

2. **Free hole** can lower the energy of the 1H state by eliminating the unpaired electron from its dangling bond level.

3. Up to six H atoms are stored in the **benzene ring** (2.4 wt% & 17 g/L)



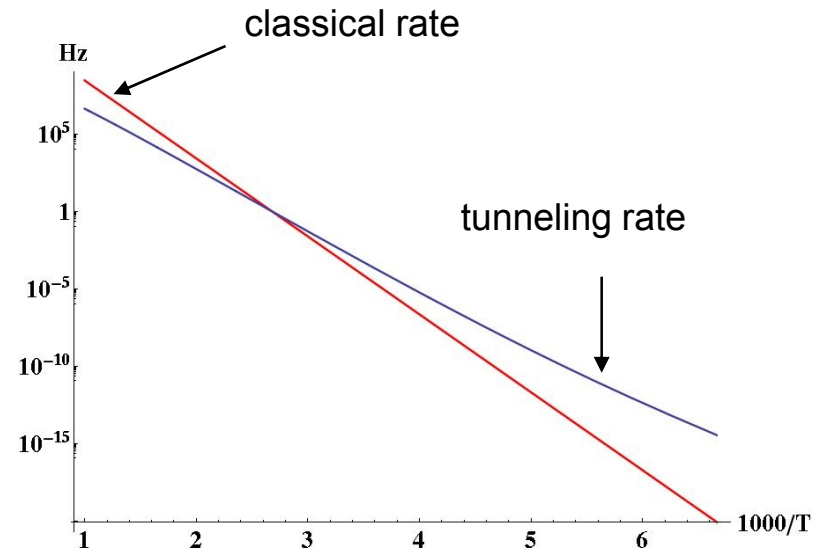
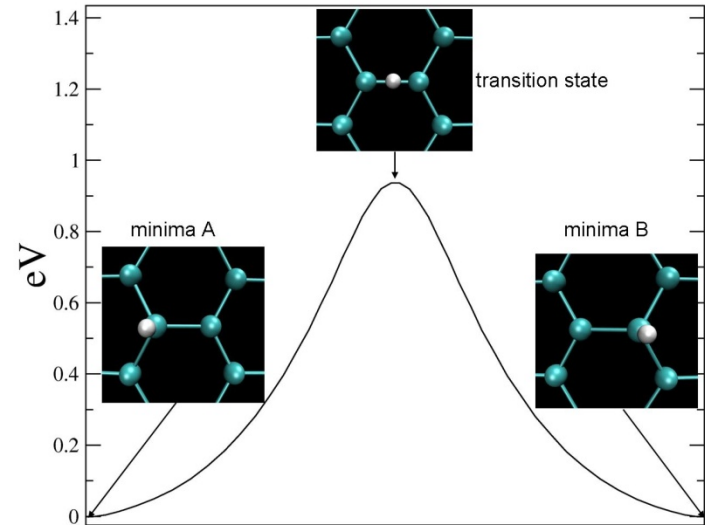
# Hydrogen motion: classical hopping or tunneling?

- DFT barrier  $E_a = 1.04$  eV
- However,  $E_a$  is very similar to desorption barrier. MD simulation shows at elevated temperatures H prefers to desorb rather than hop.

**Given the light mass, can H diffuse by quantum tunneling?**

- Calculation reveals that indeed at RT tunneling is more important.
- Although the rate is too low for RT spillover, the calculation shows that H will diffuse on graphene before it desorbs.

West, et al. (to be submitted)



# Hole is essential to both energetics and transport

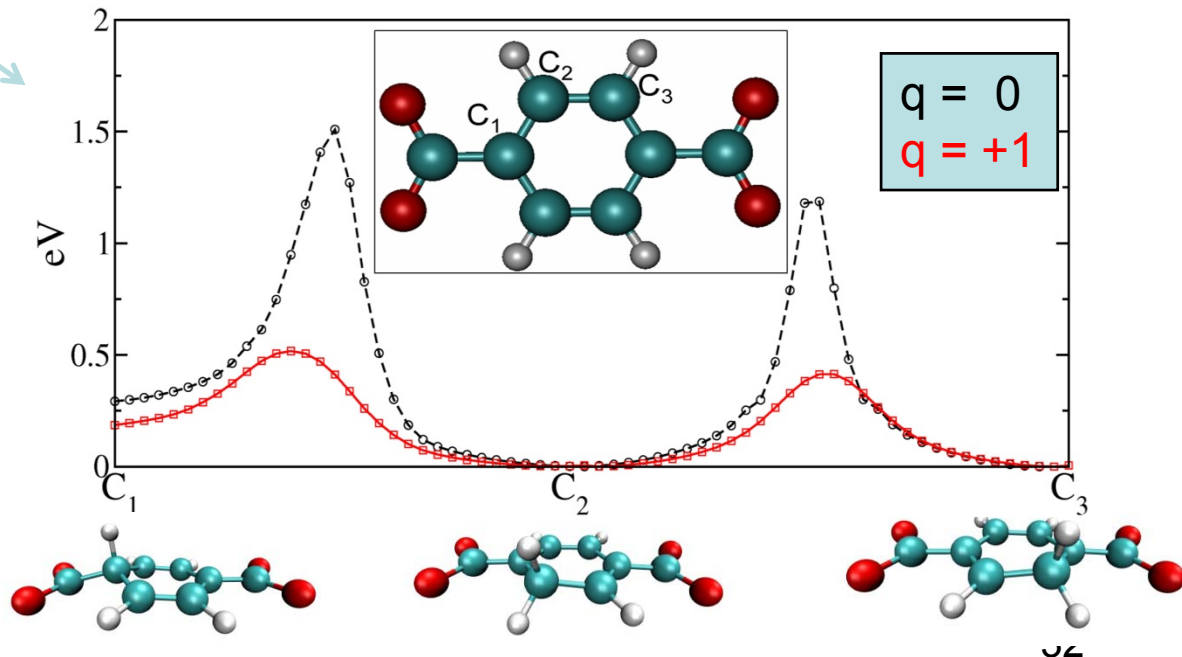
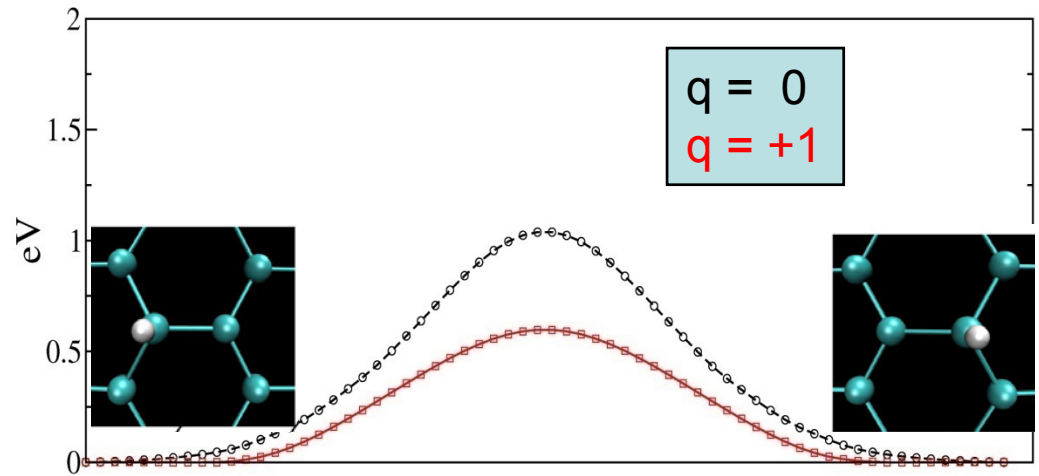
## Case 1: graphene

- barrier drops from 1.04 eV for  $H^0$  to **0.60 eV** for  $H^+$

## Case 2: MOF linker

- multiple paths but the largest barrier drops from 1.52 eV for  $H^0$  to **0.52 eV** for  $H^+$

**Conclusion:** H is indeed mobile at RT and spillover does take place should free-hole exists.



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