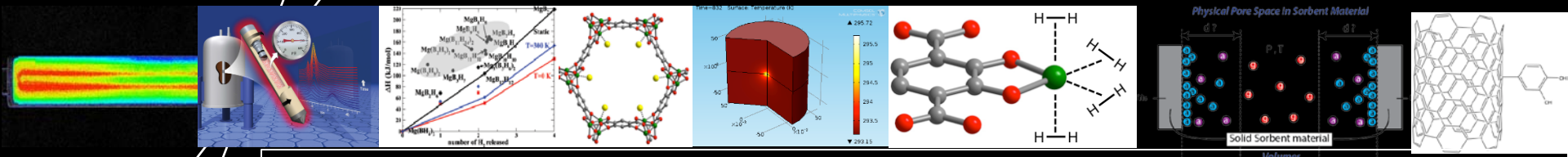
NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Project ID: ST131

H_2 Storage Characterization and Optimization Research Effort



DOE—EERE-FCTO Annual Merit Review

June 8, 2016

NREL Team: Rory Andrykowski, Jeff Blackburn, Arrelaine Dameron, Mira Dimitrievska (NIST), Suzanne Ferrere, Katie Hurst, Michele Olsen, Phil Parilla, Steve Robbins, Jacob Tarver (NIST), Jerry Tynan, Tom Gennett (PI)

NREL NATIONAL RENEWABLE ENERGY LABORATORY

BERKELEY LAB

Pacific Northwest NATIONAL LABORATORY

NIST

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

Overview

Timeline*

Start: October 2015
End: TBD
% complete FY 16: ~65%

*previously a component of NREL's materials development program and supported annually since 2006

Budget

Funding FY15: **$575k**
Funding FY16: $1.206M

Total Multi Performer Project
Funding FY16: $2.806M#
#Includes LBNL, PNNL and NIST

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 Chemi- sorption;
O. Test Protocols and Evaluation Facilities.

Collaborators

NIST - Craig Brown, Terry Udovic
PNNL - Tom Autrey, Mark Bowden,
LBNL - Jeff Long, Martin Head-Gordon
HyMARC
LANL - Troy Semelsberger
H2Technology Consulting, USA - Karl Gross
H_2ST^2, USA - Hydrogen Storage Tech Team
IEA-HIA Task 32 - Michael Hirscher, Darren Broom

Relevance

An NREL-led National Laboratory collaboration and synergistic research effort between:

NREL, LBNL, PNNL, NIST

- **To *Develop* and *Enhance* Hydrogen Storage Core Capabilities, i.e. Characterization Techniques**
- **To *Validate* claims, concepts, and theories of hydrogen storage materials**

Tom Gennett, Phil Parilla Jeff Long, Martin Head-Gordon, Tom Autrey, Mark Bowden, Craig Brown Terry Udovic

Relevance

Project Objectives:

Develop new characterization capabilities.

- **NMR, DRIFTS, PCT, TC, TPD, Calorimetry, Diffraction and Scattering**

Validate "performance claims and theories" critical to the design of new hydrogen storage materials.

Impact:

Access to advanced characterization and validation capabilities will accelerate research progress.

Rational design of new materials.

- Unique opportunity to better understand the properties of gas-solid interactions in high surface area materials
- Provide insight into the kinetic and thermodynamic bottlenecks in complex hydrides and hybrid materials.

Benchmarking theory.

- Couple theory with experiment to benchmark and validate the computational predictions. (HyMARC collaboration).
- Unravel complex phenomena, guide experimental work and accelerate progress.

Approach (All Partners)

NREL ST131a and ST014

- Validation and characterization of sorbent physiochemical properties
  - Advanced PCT analysis
  - Thermal Conductivity (TC) with T = 77-400 K, $P \leq$ 100 bar He/H_2
- Mechanistic validation:
  - can exposed cations in carbon-based sorbents reach target of ΔH = –15 kJ/mol?
  - is it possible to control sorbent desorption temperature?
- Validate computational predictions of H_2 binding energies and capacities

Pacific Northwest NATIONAL LABORATORY ST132

- NMR (i) solid state with precise H_2 dosing at T = 10-300 K; (ii) in-situ MAS with T to 400 K and $P \leq$ 200 bar (iii) variable pressure liquid with T to 300 K and $P \leq$ 500 bar
- Reaction Calorimetry with T to 400 K and $P \leq$ 20 bar.
- Mechanistic validation of reversible pathways in $Mg(BH_4)_2$
- Validation of calculated enthalpy of hydrogenation of triazine.

Berkeley Lab ST133

- IR spectroscopy (DRIFTS) with precise H_2 dosing at T = 10-300 K, $P \leq$ 100 bar
- Accurate modeling of H_2 adsorbed within porous materials
- Mechanistic validation:
  - can exposed cations in adsorbents reach target of ΔH = –15 kJ/mol?
  - is it possible to adsorb two, three, or four H_2 per metal cation?

NIST ST135

- Neutron diffraction with precise D_2 dosing at T > 5 K, $P \leq$ 100 bar
  - Determine crystal structures
- Inelastic neutron scattering at T > 5 K, $P \leq$ 100 bar
  - Understand the local environment for chemical-H and physisorbed-H_2
- Other neutron methods as applicable as applicable

Approach: The Role of NREL

Validation

- H_2 storage materials performance metrics
- Computational methods for predicting hydrogen storage properties

Characterization

- the physiochemical properties of emerging hydrogen storage materials
- new concepts for hydrogen storage mechanisms

- **Validation and characterization of sorbent physiochemical properties**
  - PCT analysis with P≤ 200 bar H_2 and temperature control from 50 – 350K
  - Thermal Conductivity (TC) with T = 77 - 400 K, $P \leq$ 100 bar H_2/He
- **Mechanistic validation:**
  - can exposed cations in carbon-based sorbents reach target of ΔH = –15 kJ/mol?
  - is it possible to control sorbent desorption temperature?
- **Validate computational predictions of H_2 binding energies and capacities.**

Approach – characterization

Thermal Conductivity (FY 16), Poster ST014

- **Design and construct a TC apparatus capable of measuring the thermal conductivity of hydrogen storage materials under expected operating conditions:**
  - Temperature range from 77 K to 400 K
  - Pressures up to 100 bar hydrogen
  - Capable of measuring pucks and powders and small-volume samples (down to ~ 0.5 cm^3)
  - Develop measurement hardware and “best practices” procedures (LANL)

PCT Analysis (FY 16 - 17) Poster ST014

- **Develop recommended PCT measurement, analysis and reporting protocols**
  - Volumetric and Gravimetric capacities of hydrogen storage materials
- **Design and construct a modified variable-temperature PCT Apparatus**
  - Variable temperature range from 50 K to 350 K
  - Capable to achieve up to 200 bar hydrogen overpressure
  - Ability of measuring sample sizes from 200 mg to >1 gram.

Approach - validation

- **Gravimetric and Volumetric capacities (Poster ST014)**
  - **Validation of storage capacities for external samples**
  - **Inter-laboratory Volumetric Adsorption Measurement Study**
    - **15 participants from Industry, Academia and National Laboratories in USA, Europe, Asia and Oceania. (Prelim results at poster session)**
  - **Consensus on reporting volumetric capacities**

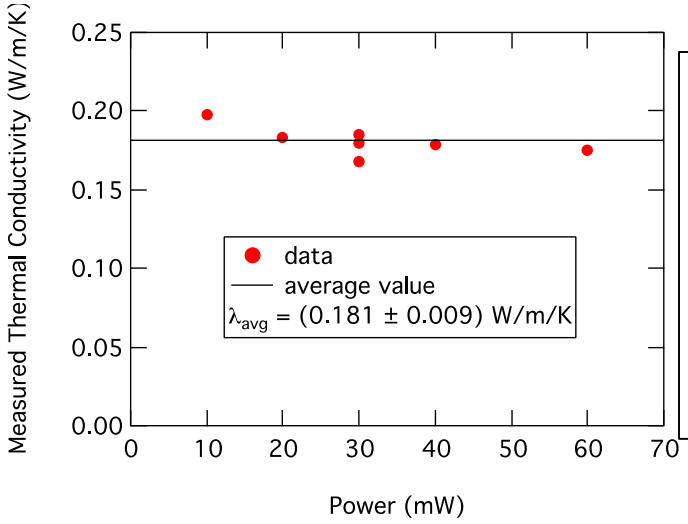
- **New approaches and materials that would enable H_2 uptake and release at ambient temperatures and moderate pressures, (i.e. validating theoretical models).**
  - **Control hydrogen desorption temperature with metal center**
    - **Multiple hydrogen molecules per metal center**
  - **Modified pore structure/chemistry to enable control of the hydrogen desorption temperature (thermodynamic and kinetic)**
    - **Control physisorption properties of high surface area sorbents**

Accomplishments: Thermal Conductivity Apparatus Design and construction (Poster ST014)

Designed and built an apparatus capable of measuring the thermal conductivity of hydrogen storage materials under ***expected operating conditions***:

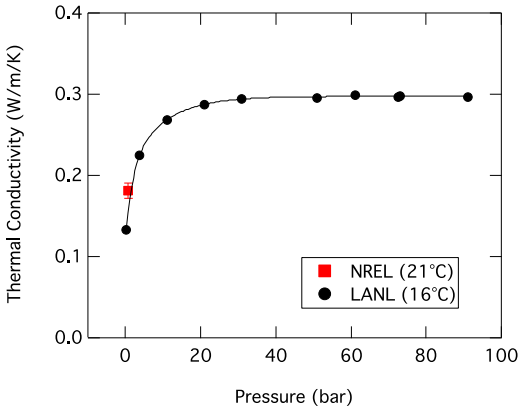
- ***Transient Plane Source Technique***
- 77 K to 400 K
- up to 100 bar
- capable of measuring pucks and powders (down to ~ 0.5 cm^3)

MOF-5 Measurements



Mathematical model fit the data well.

Reproducibility with different applied power.



MOF-5 Room temperature
He at 1 bar
Isotropic measurement
Matched LANL results

Accomplishments: Cryogenic Measurements (ST014)

We have demonstrated thermal conductivity measurements at cryogenic temperatures using BK glass samples (satisfies milestone).

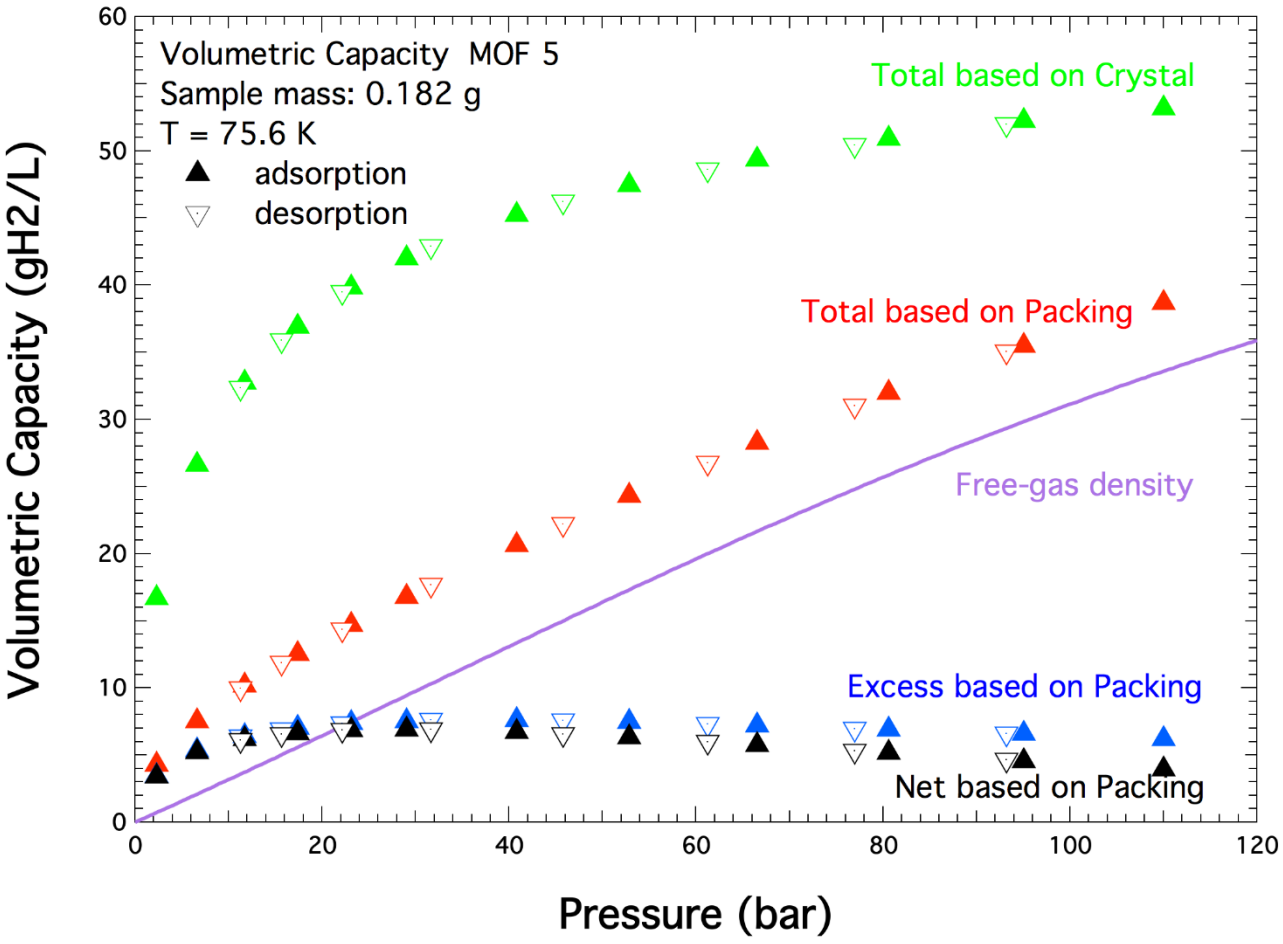
T (K)	Gas	Pressure (Torr)	K Measured (W/m-K)	K Accepted (W/m-K)†	Percent Deviation
75.6	He	615	0.47	0.45	+4.4%
75.6	He	210	0.46	0.45	+2.2%
295	He	615	1.15	1.1	+4.6%
295	Air	615	1.12	1.1	+1.8%

- Measured values are well within the required 10% of accepted values.
- Additional investigation is needed to determine error bars for measured values.

† Ekin J 2006 *Experimental techniques for low-temperature measurements* (Oxford: Oxford University Press)

Volumetric Results Depends on Assumptions

Normalization affects volumetric data



Graph shows the same raw data calculated with different H_2 capacity determinations.

Note the difference between the Total capacities based on crystalline and packing densities.

Accomplishment: Inter-laboratory Volumetric Capacity Hydrogen Adsorption Measurement Study

H_2 sorption measurements on two distinct sorbent samples measured at 77K and ambient temperature.

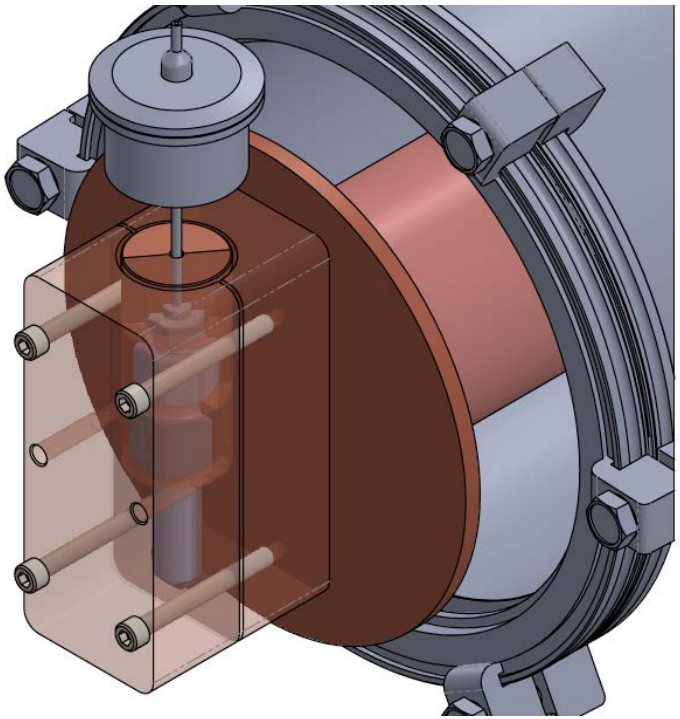
- Includes both excess and total volumetric capacities
- Builds on smaller previous study focused on excess gravimetric capacity

  (K.E. Hurst, P.A. Parilla, K.J. O'Neill, T. Gennett *Appl. Phys. A* 122; 42, 2016.)
- ~5 grams of each material were distributed to participants in February 2016
- 15 confirmed participants (including NREL) Includes Academia, Industry and National Laboratories from USA, Europe, Asia and Oceania.

(Poster ST014) for preliminary results

Accomplishment: Variable Temperature PCT Cryostat Design

Progress toward FY 17 Milestone



Modification of one of our current PCT instruments includes a cryo-cooler for controlling the sample temperature from 50K to 350K with H_2 pressures ≤ 200 bar .

This required a new design for the sample holder, cyro-cooler configuration and software.

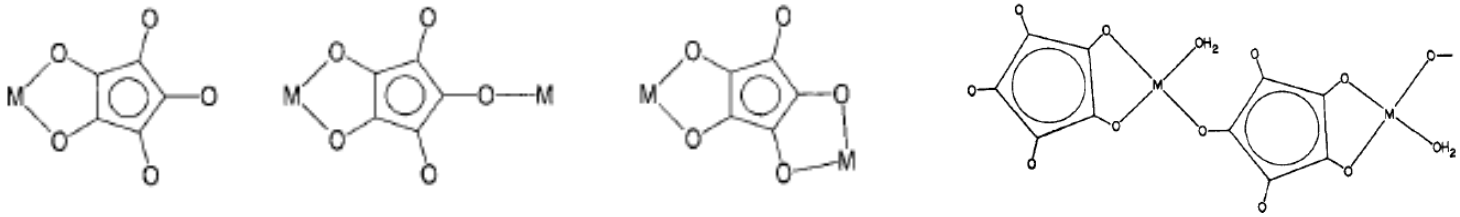
This design expands NREL's core characterization capabilities to include PCT measurements from 50 to 350K and enable the determination of the heats of adsorption.

Accomplishment: Effect of metal cation on hydrogen desorption temperature

Oxocarbon ions are cyclic compounds of the general formula $(C_nO_n)^{2-}$

2 – oxalate 3 – deltate 4 – squarate 5 – croconate 6 – rhodizonate

The electronic delocalization provides the possibility of pi-stacking interactions between the oxocarbon rings and unusual electronic and vibrational properties.

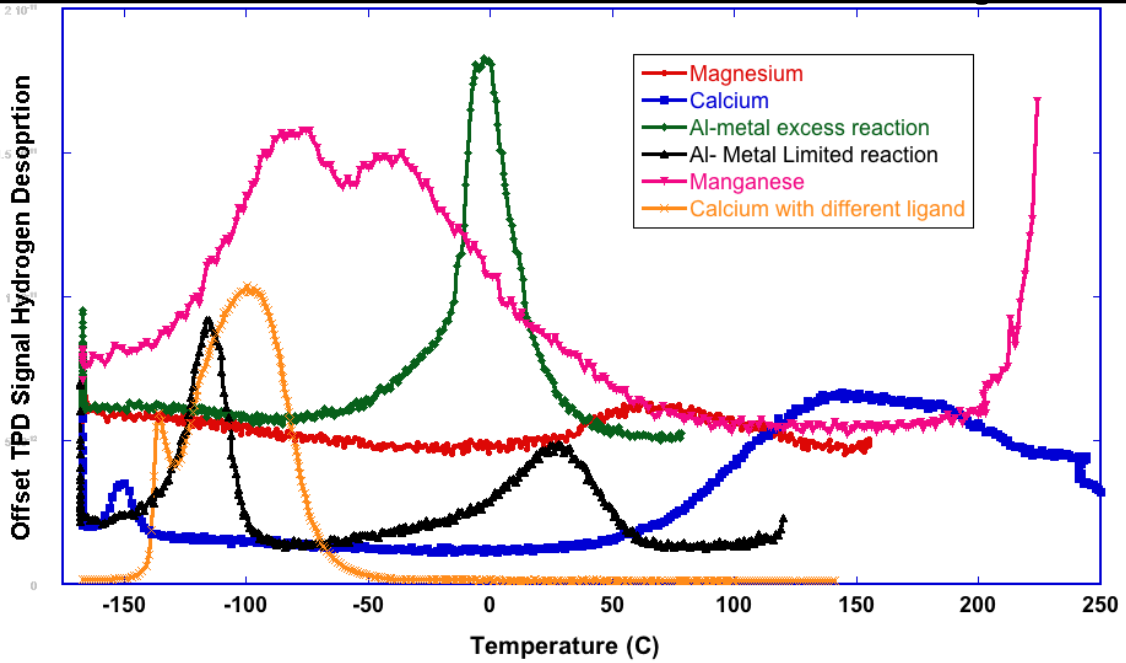


Synthesis:

- **Reaction of the respective metal nitrate or chloride with the sodium oxocarbon salt in water, methanol and/or anhydrous methanol.**
- **Various ratios and concentrations of reagents were used in attempts to alter the binding interaction and chain lengths.**
- **Transition metal complexes are predicted to be high-spin.**

Metals investigated to date include: Manganese, Magnesium, Beryllium, Calcium, Nickel and Aluminum.

Effect of Metal on Desorption Temperature



Metal/Ligand	Desorption Temperature (K)	Gravimetric capacity (1 bar) %w/w approximate
Be/mixed oxalate	150 K	<0.2%
Al/mixed oxalate	125 - 175 K (small pk 273K)	0.1 – 0.3%
Ca/mixed oxalate	150 – 225K	0.4 – 0.8%
Mg/croconate	340K	< 0.1%
Ca/Croconate	350 – 473 K	< 0.1%
Al/Croconate (a)	265 – 290 K	0.5 – 0.8%
Al/croconate (b)	140 – 170 K, 273 – 320K	0.1 – 0.3%
Mn/Croconate	200 K and 225 K (2 peaks)	0.2 – 0.4%

Demonstrated the ability to alter the hydrogen desorption temperature

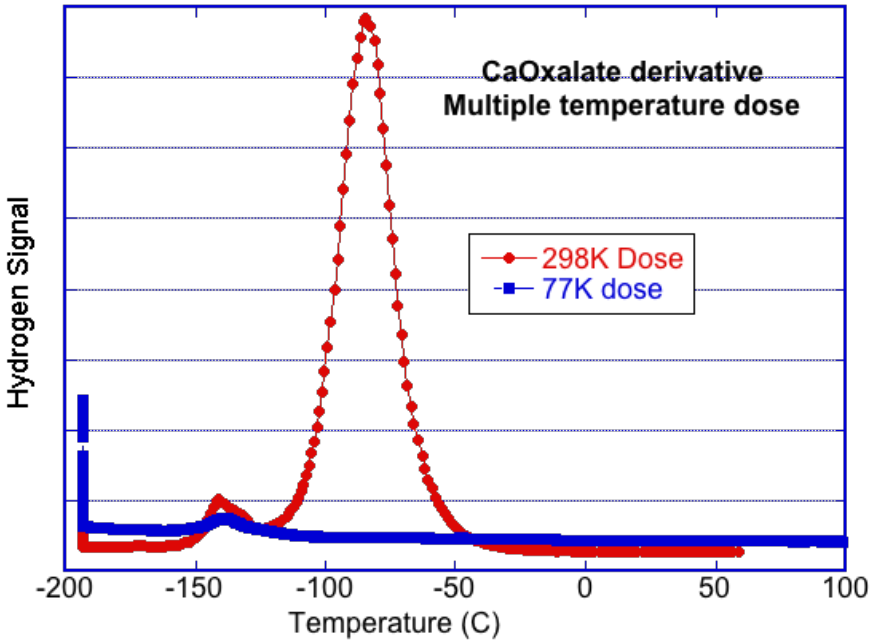
Will now determine extent of kinetic and thermodynamic contributions

Will now work to improve capacity.

Accomplishment: Ultramicroporous materials

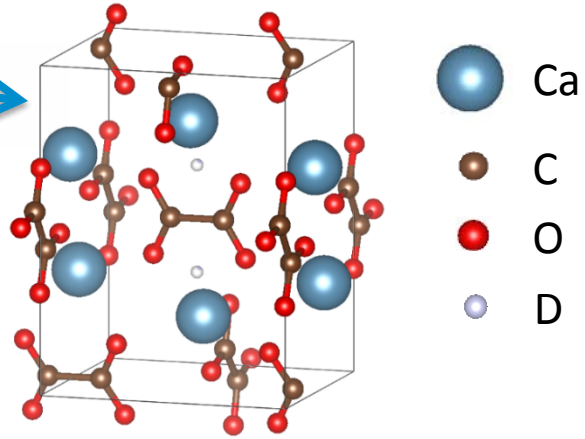
CaOxalate Derivative.

- Must dose at temps above 175K and pressures >250 torr
  - Established in joint PNNL/NIST/NREL efforts
- BET surface area 4 m^2/g, yet capacity approaches 1% w/w (≈1.5% theoretical for 1 H_2/Ca)
- Collaborative effort with NIST established no structural changes with temperature
- Appears is first ultramicroporous material with high (150K) desorption temperature (past materials were at 50 K, Hirscher, 2009 MgFormate)
- Kinetic versus thermodynamic effect
  - Binding energy vs. "diffusion" limits
- Need to establish pore sizes
  - Is their a structure change with temp
  - Metal or ligand "trapped" hydrogen
- Modeling (working with LBNL)

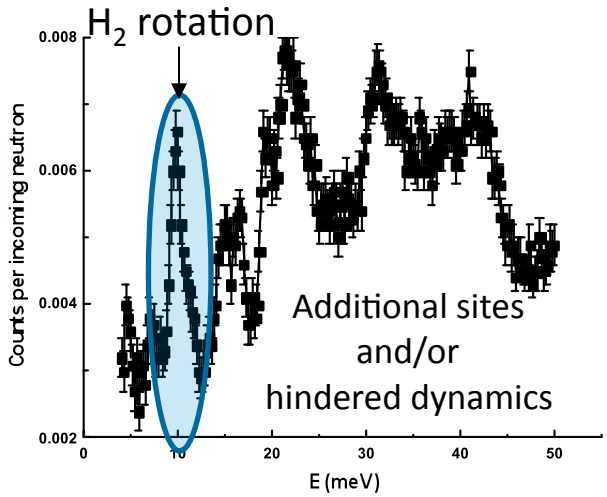


Accomplishment: Neutron characterization of calcium oxalate derivative (ST135)

- **Neutron Powder Diffraction**
  - Anhydrous calcium oxalate derivative confirmed as dominant phase
  - Changes in relative intensity of reflections upon dosing with D_2 reveal crystallographic planes in which hydrogen resides
  - Accurate refinement and precise determination of hydrogen adsorption sites complicated by additional crystal phases

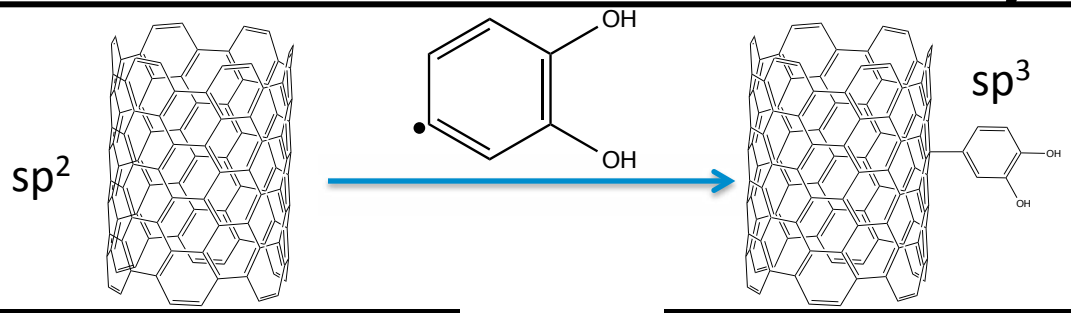


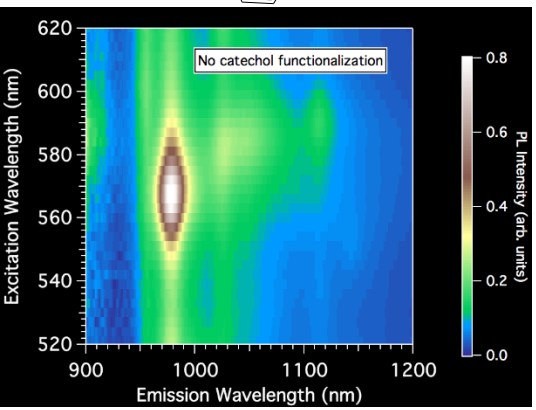
- **Inelastic neutron spectroscopy**
  - Sensitive almost exclusively to hydrogen
  - Loading pressure has a strong influence on adsorption properties
  - Adsorption of H_2 at atmospheric pressure suggests multiple binding sites and/or hindered dynamics

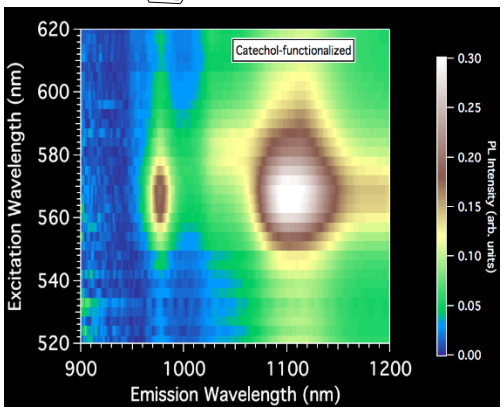


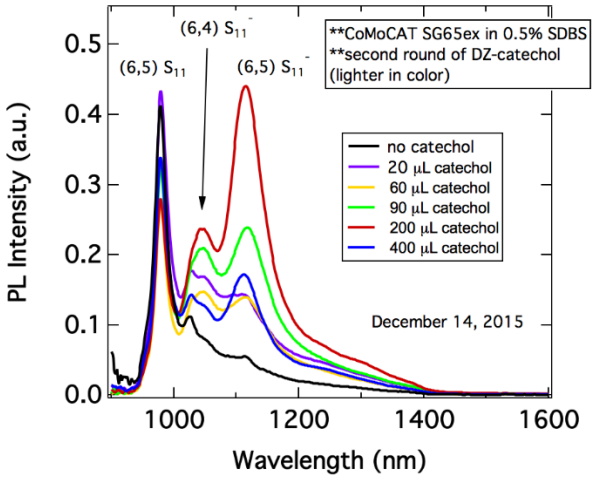
Neutrons locate adsorbed D_2 possibly in micropores

Accomplishment: Modified sorbent pore structure/chemistry







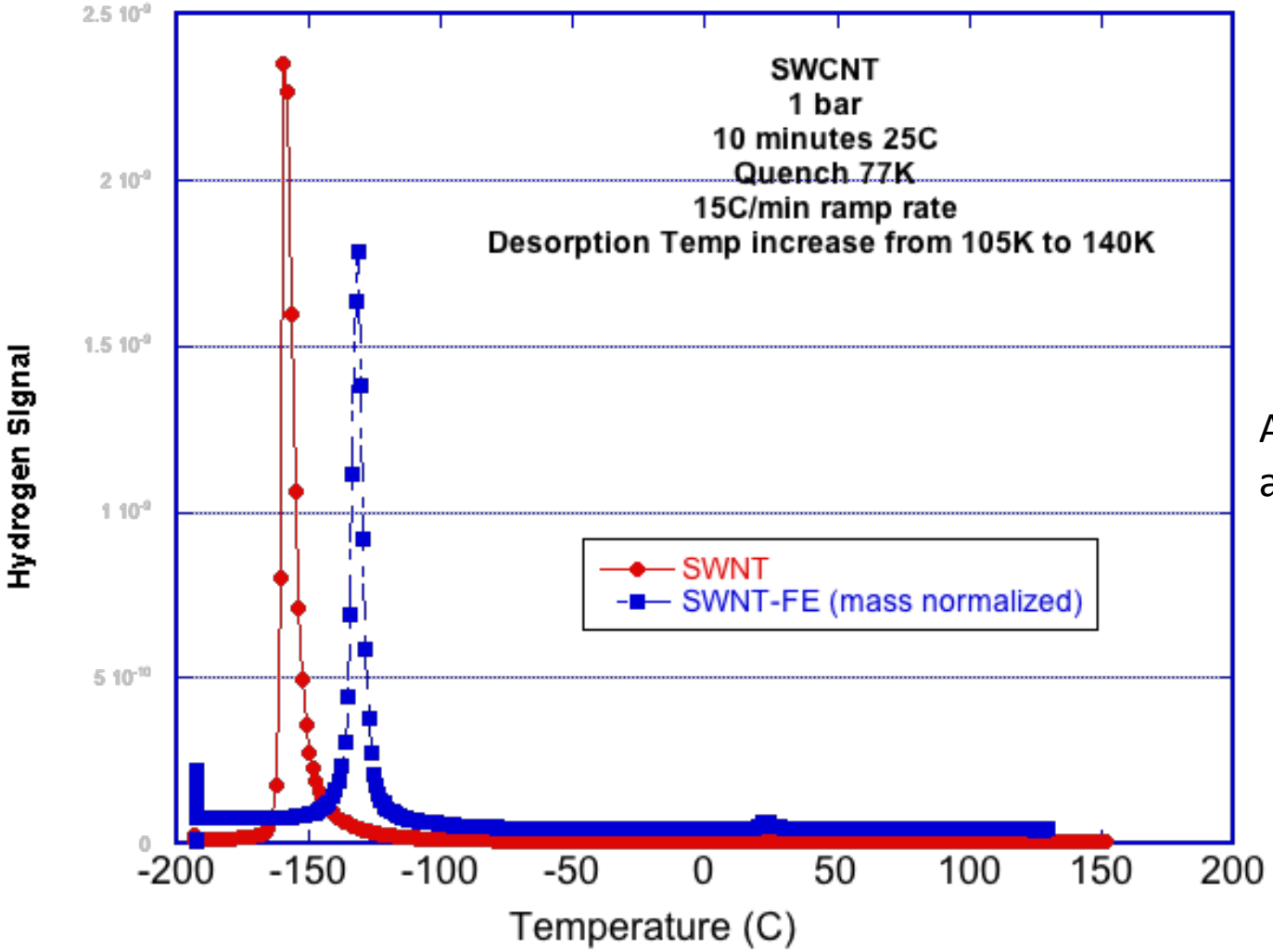


PL dominated by emission at 990nm from sp^2 for pristine SWCNTs

PL intensity by emission at 1100nm from sp^3 SWCNTs after modification allows for determination of extent of catechol incorporated

PL intensity plots allow for determination of catechol substitution levels.

Accomplishment: Increase Desorption Temperature of SWCNT sorbent



Approx. 1%w/w capacity at 1 bar)

Internal Collaboration Efforts

- **Collaboration of LBNL and NREL on verifying hydrogen adsorption isotherms, measuring thermal conductivities, measuring temperature programmed desorption data. (joint paper planned)**
- **Collaboration of LBNL, NREL and PNNL on measuring hydrogen adsorption in multiple materials using solid state NMR spectroscopy. (several papers planned in near future)**
- **Collaboration of LBNL and NIST on characterizing hydrogen adsorption in framework (MOFs) materials using neutron diffraction and neutron scattering spectroscopy. (joint paper submitted)**
- **Collaboration of NREL and NIST on characterizing ultramicroporous materials using neutron diffraction and neutron scattering spectroscopy. (joint paper planned)**
- **Collaboration of NREL and LBNL on the modeling of hydrogen sorption in hybrid ultramicroporous materials**
- **Collaboration of NREL with NIST and LBNL to characterize various materials at the APS facility. (joint papers planned)**
- **Collaboration of PNNL and NIST: dynamics models to fit experimental NMR data using insight from QENS and INS, (planned)**

Collaborations with HyMARC

- NIST Collaborations with SNL: Developing Spectroscopic Signatures for $Mg(BH_4)_2$
- NIST Collaborations with SNL: Determining products of hydrogenated Li_3N in nanoporous carbon
- Collaboration of PNNL and Sandia: sample exchange: standards for x-ray: B_3H_8, B_3H_8, $B1_0H_{10}$, $B_{11}H_{14}$, a mix of $B_{11}H_{14}$ + B_9H_{14} + B_3H_8, dehydrogenated $Mg(BH_4)_2$ and $B_{12}H_{12}$
- Collaboration of PNNL and LLNL: Comparison of ^{11}B NMR for release of H_2 from $Mg(BH_4)_2$ with H_2 uptake by MgB_2
- Collaboration of NREL and HyMARC (LLNL) for the modification of advanced carbon based sorbents by solution and PVD techniques. (exchange of materials and techniques to verify applicability)

Remaining Challenges and Barriers

- **Achieving more direct collaborations with HyMARC Team**
- **Achieving a collaborative balance with the new FOA initiated projects**
- **Designing autonomous software for both the advanced TC and PCT systems**
- **Achieving an International consensus on reporting volumetric and gravimetric capacities**
- **More interaction of theorists and experimentalists.**
- **Application of the advanced NMR, DRIFTS and Neutron capabilities to a broad base of sorbent materials**
- **Exhibiting control over kinetics in sorbent systems**
- **Exhibiting control over thermodynamics in sorbent systems**
  - Binding energies
- **Improved capacities of multi-hydrogen systems**
  - Increase to beyond two hydrogen molecules per metal center
- **Control over "useable" hydrogen stored in sorbent materials**
- **Improved cost considerations**

Proposed Future Work

TC Next steps:

- **Measurements at controlled temperatures down to 77 K**
  - Isotropic versus anisotropic
- **Measurements with pressurized H_2 up to 100 bar**
- **Autonomous software completion**

PCT Next Steps

- **Analyze data and publish results from the inter-laboratory volumetric hydrogen measurement study**
- **Validate measurements for hydrogen sorption.**
- **Develop new capabilities for measuring the hydrogen sorption with increased temperature range (50K – 350K).**
  - Need to finalize system design of cryostat and sample holder for VT- PCT system
  - Develop new Lab-view instrument software
  - Validate isosteric heat of adsorption measurement

Proposed Future Work

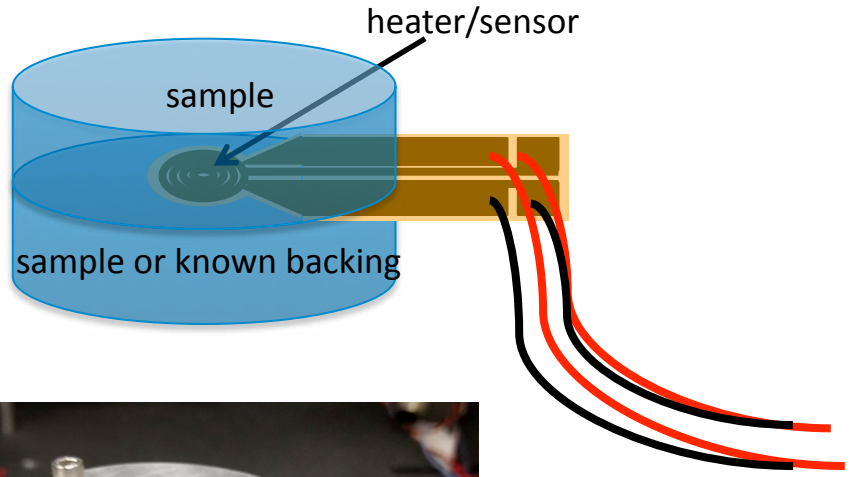
- **Modeling of various oxo-carbon materials (with LBNL)**
  - Validate models
- **Establish position of metal site within SWCNT-catechol materials (with NIST)**
- **Modify high surface area carbon materials with catechol (Materials from NREL and HyMARC (Ted Baumann))**
- **Identify position of hydrogen within oxo-carbon materials (NIST, PNNL, LBNL)**
- **Establish further control over metal-sorbent synthesis materials for enhanced capacity.**
  - Currently at approximately 1% w/w for model materials

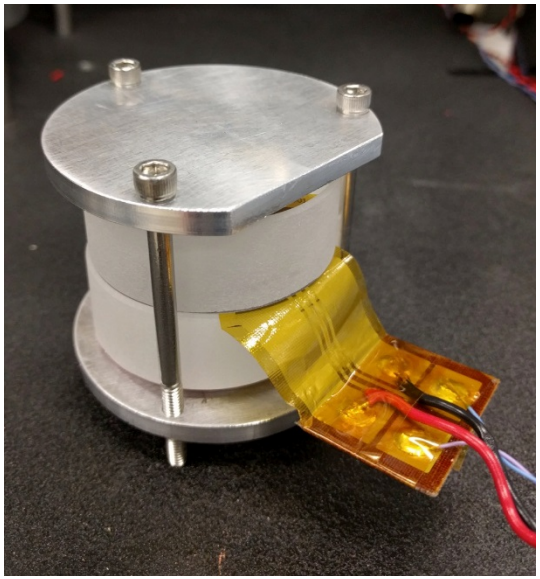
Mandatory Summary Slide: Highlights

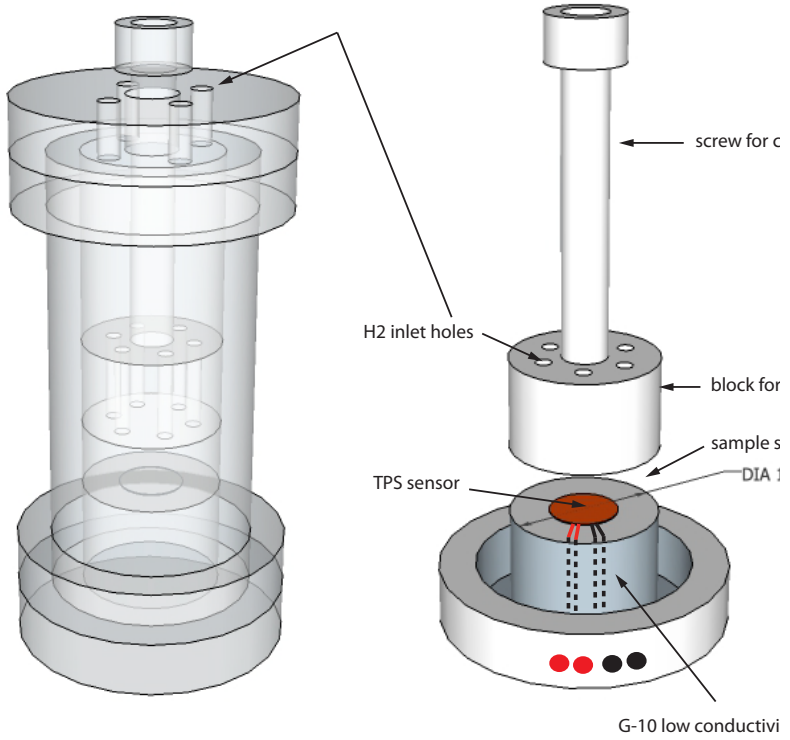
- **Kick-off meeting October 10, 2015 at LBNL, All participants present**
- **Joint NDA with HyMARC completed October 2066.**
- **Joint meeting with HyMARC at NREL November 3-5, 2015**
- **Joint Tech Team meeting with HyMARC, April 20-21, 2016**
- **Monthly conference calls (more often individual interactions)**
- **New Hires**
  - NREL, 2 postdocs, 0.5FTE
  - PNNL, 1.5 postdoc
  - LBNL, 3 postdoc, 3 graduate students
- **New advanced characterization and materials performances were observed at LBNL, PNNL, NIST and NREL. Several of the most important results are summarized herein.**
  - **NREL**
    - built and written software for an advance TC instrument for measuring the thermal conductivity of H_2 storage materials under operating conditions.
    - initiated a very important round robin volumetric study
    - completed designs for a new advanced variable temperature PCT system
    - synthesized novel catechol derivatized nanostructured carbon materials
    - exhibited control of desorption temperatures in metal-oxocarbon systems. (Collaboration with NIST, LBNL and PNNL)
  - **LBNL**: observed 2 hydrogen molecules on a metal center as characterized by NIST within framework material (paper submitted) (ST133)
  - **PNNL:** enhanced kinetics of the hydrogen interaction with borohydride materials (collaboration with HyMARC and Univ of Hawaii)(ST132)
- **All milestones on track and/or completed.**
- **11 publications (published, in-press or submitted)**
- **3 Records of Inventions submitted to protect IP.**

Technical Back-up slides

Approach: TPS Sample Holders



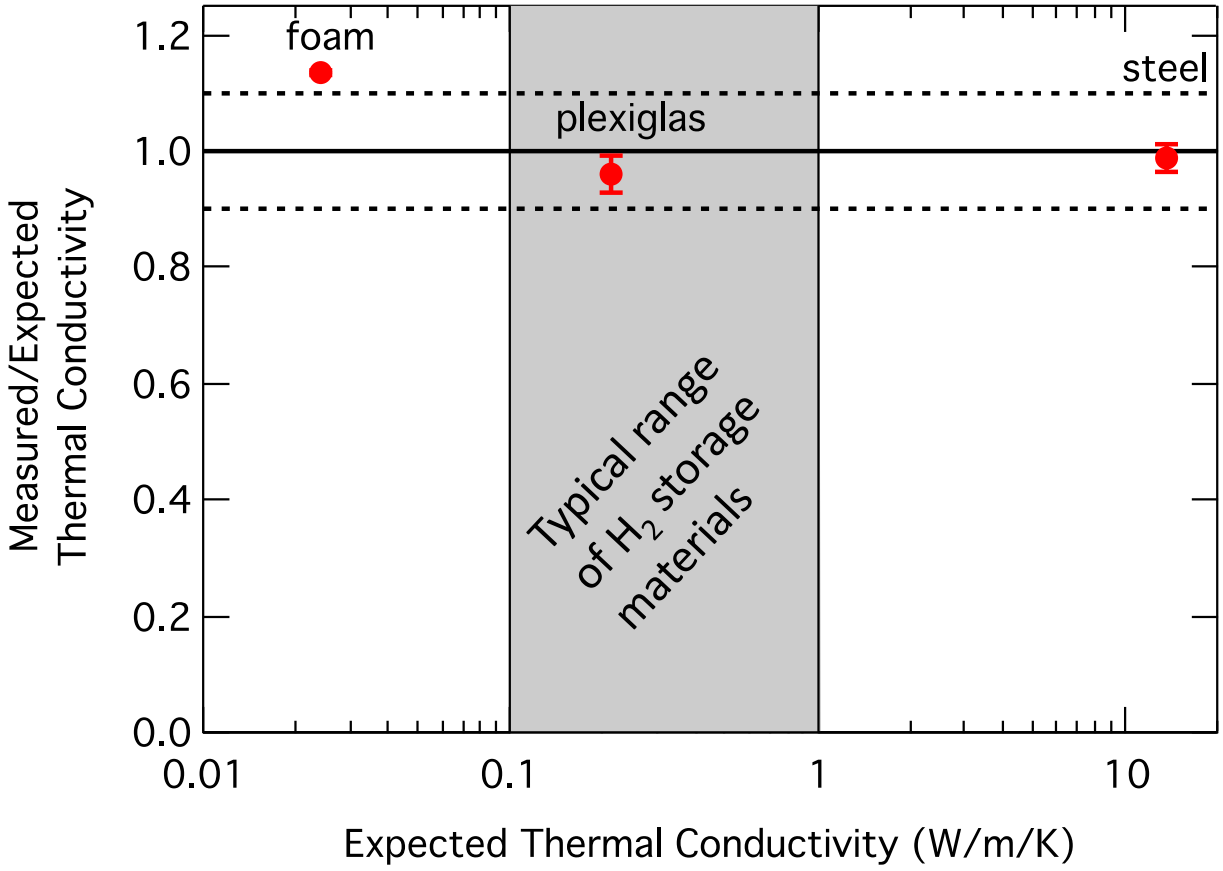




Possible design for powder samples.

The sample holder sits inside the pressure vessel, which mounts atop a cryostat.

Accomplishments: Measurement Validation



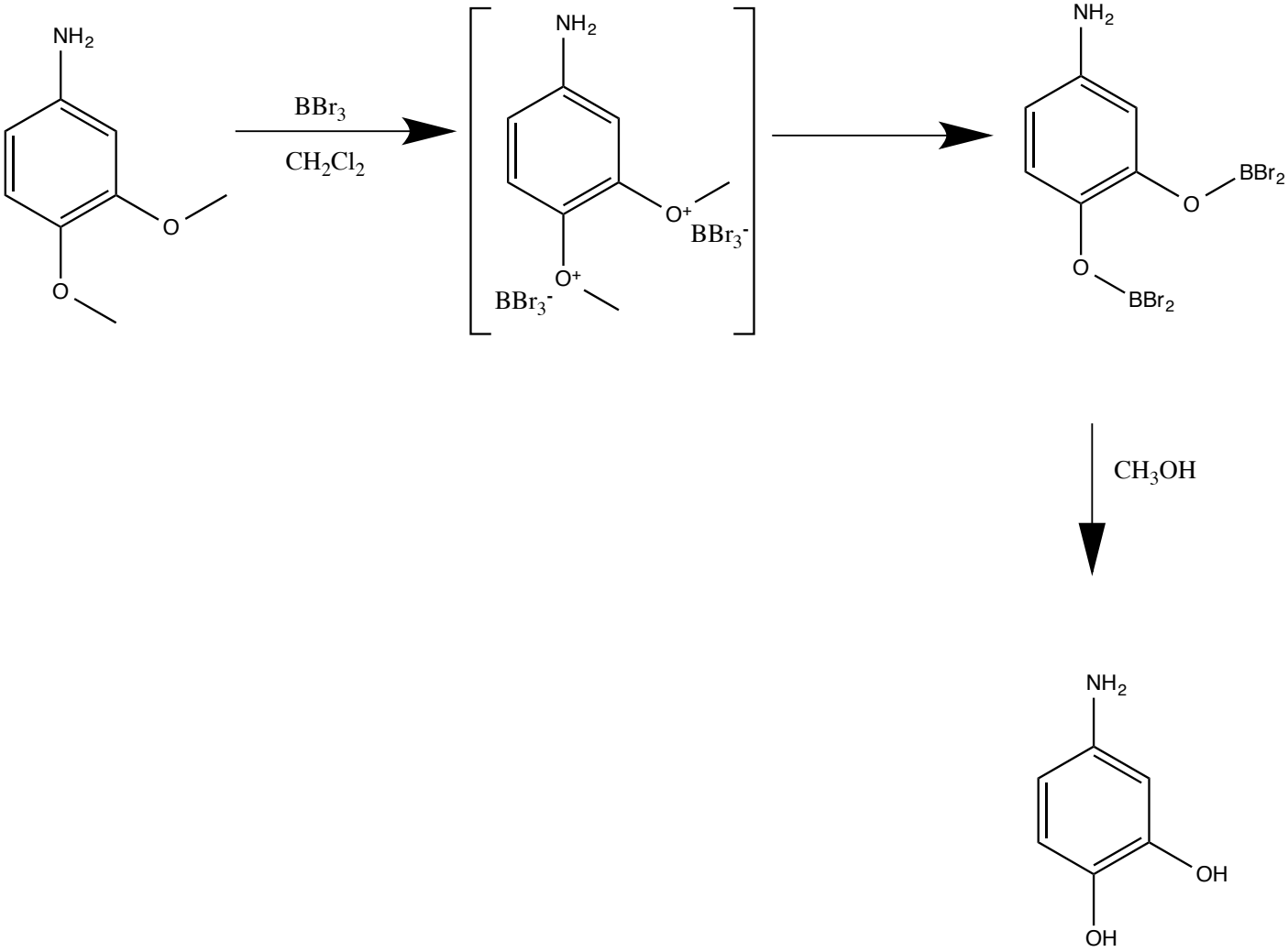
Reference materials:

- Stainless Steel
- Plexiglas
- Foam Insulation

(room temperature, atmospheric pressure)

Good agreement over 3 orders of magnitude

Accomplishment: Preparation of 4-aminocatechol



Accomplishment: Functionalization of carbon with catechol