New Carbon-Based Porous Materials with Increased Heats of Adsorption for Hydrogen Storage

Randall Snurr, Joseph Hupp,
Mercouri Kanatzidis, SonBinh Nguyen

Northwestern University

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Overview

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Timeline

- Start date: 9/1/2008*
- End date: 8/31/2012
- 0% complete*

Barriers

- Hydrogen storage
  - Gravimetric target
  - Volumetric target
  - Increased heat of adsorption

Budget

- Total project funding
  - DOE share: $1,295,493
  - Contractor share: $321,833
- FY08 Funding: $0
- FY09 Funding: $385,812

Partners

- No official partners
- Collaborators listed below

* 9/1/2008 is official start date. Funding not received until March 2009.

Relevance

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Overall Project Objectives

- Develop new materials to meet DOE volumetric and gravimetric targets for hydrogen storage
  - Metal-organic frameworks (MOFs)
  - Polymer-organic frameworks (POFs)
  - Tight integration of synthesis, characterization, and modeling
- Increase heats of adsorption as a means to meet volumetric and gravimetric targets at ambient conditions

Relevance

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Objectives for Current Year

- Metal-organic frameworks
  - Measure heats of adsorption and hydrogen uptake in existing cation-containing MOFs
  - Develop a new class of cation-containing MOFs
- Polymer-organic frameworks
  - Develop new POFs with high heats of adsorption
  - Use building blocks that increase microporosity and can bind lithium ions
- Modeling
  - Determine whether catenation is beneficial
  - Develop model for cation-containing MOFs

Approach

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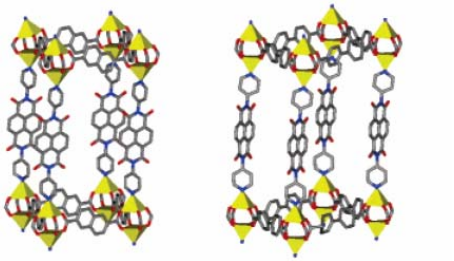
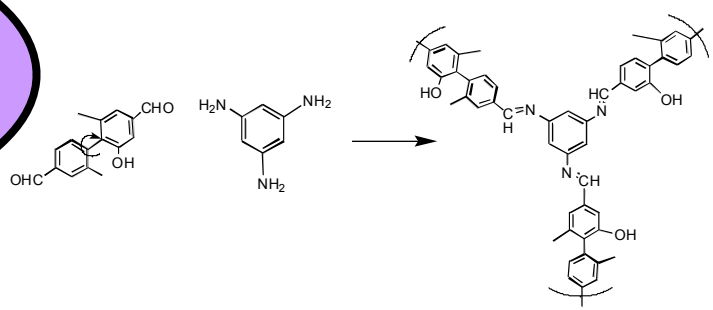


Snurr
Computational elucidation, design and modeling

Hupp
Synthesis and characterization of MOFs

Kanatzidis
Synthesis and characterization of POFs

Nguyen
Design and synthesis of SBUs for MOF and POF assembly



Approach

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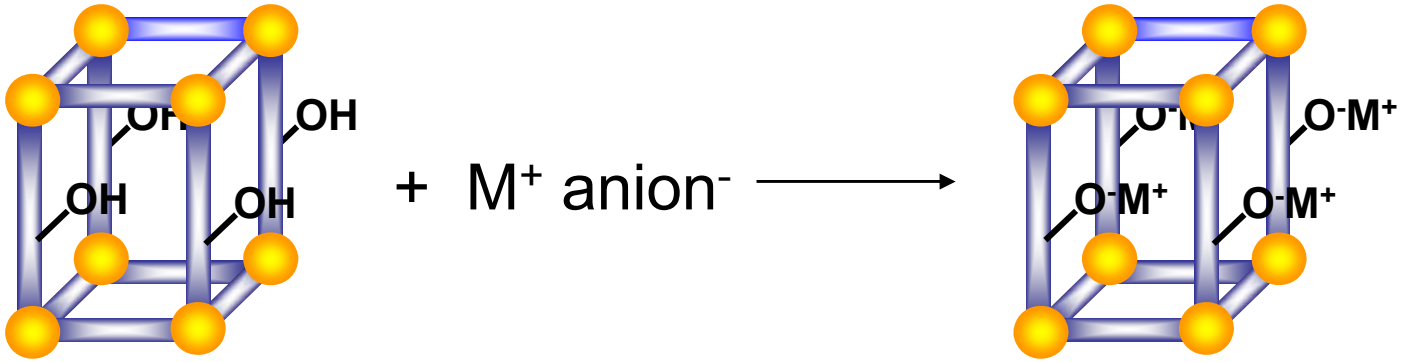
Enhance H_2 uptake via introduction of cations

- Two approaches for introducing cations
  - Framework reduction
  - Alkoxide functionalization
- Mechanisms for increased uptake
  - Enhanced London dispersion interactions due to enhanced framework polarizability?
  - Enhanced adsorption due to increase in electric field?
  - Enhanced adsorption due to charge/quadrupole interactions?
  - Enhanced adsorption due to ion-induced displacement of catenated frameworks?

Approach

Metal-organic Frameworks



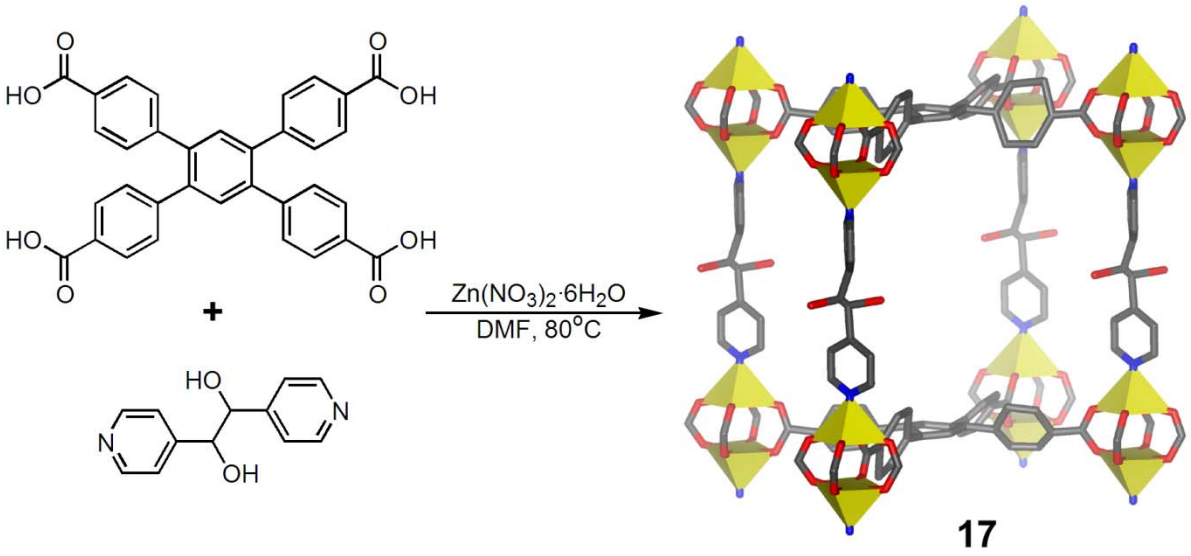
- Introduce charge via desirable cations
- Cation placement known and controllable
- Alkoxide formation should not greatly alter structure
- Alkoxide frameworks not air sensitive

Approach

Metal-organic Frameworks

Milestones for FY09

- Achieve 8 kJ/mol heat of adsorption at low coverage
- Achieve 8 kJ/mol heat of adsorption with little drop-off at higher coverages
- Achieve 10 kJ/mol heat of adsorption at low coverage



Hydroxyl-functionalized MOFs

Mulfort, Farha, Stern, Sarjeant, Hupp, *J. Am. Chem. Soc.*, 2009.

Approach

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Polymeric-organic Frameworks

- Tailorable, microporous polymers containing π-conjugated phenyl groups linked together
- Modular construction
  - Two synthesis methods
    - Schiff's base chemistry
    - "Click" chemistry
  - Components chosen to produce loosely-packed, extended 3D networks
- Attributes of POFs that make them attractive for hydrogen storage
  - Very low density
  - Three-dimensional semi-rigid character
  - Designed microporosity through inefficient packing of polymer chains
  - Built-in functional groups for tuning H_2 interaction
  - Ability to generate systematic series of materials will provide increased understanding of gas adsorption and ultimately optimization

Approach

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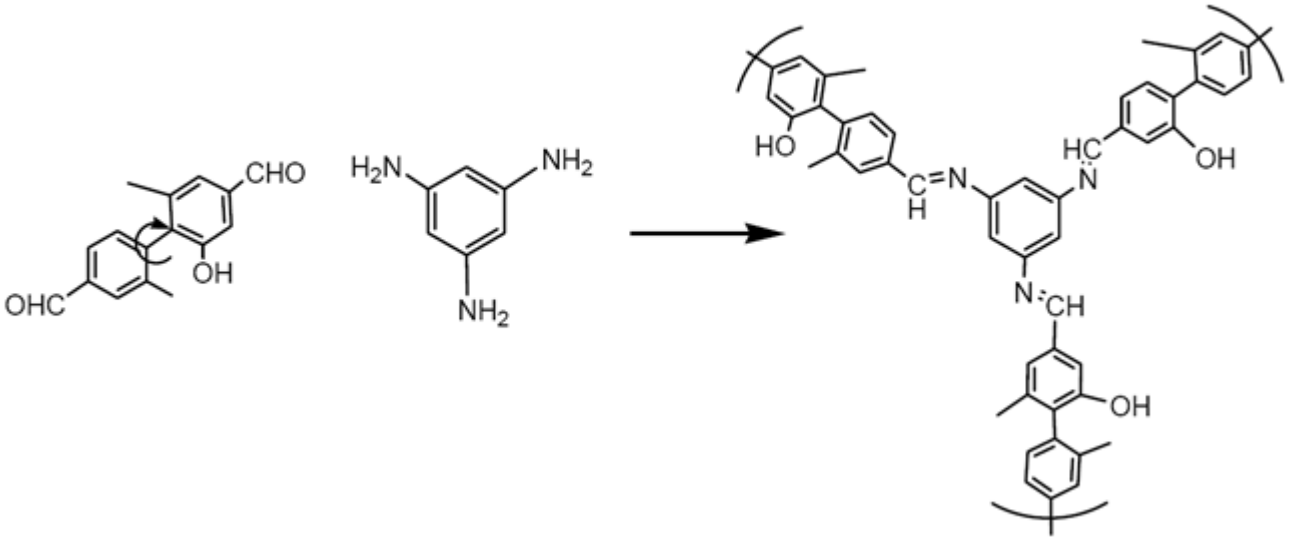
Polymer-organic Frameworks

Milestones for FY09

- Synthesize POFs with surface areas > 1500 m^2/g
- Introduce Li ions into POFs
- Demonstrate tunability of microporosity
- Achieve 8 kJ/mol heat of adsorption at low coverage



Approach

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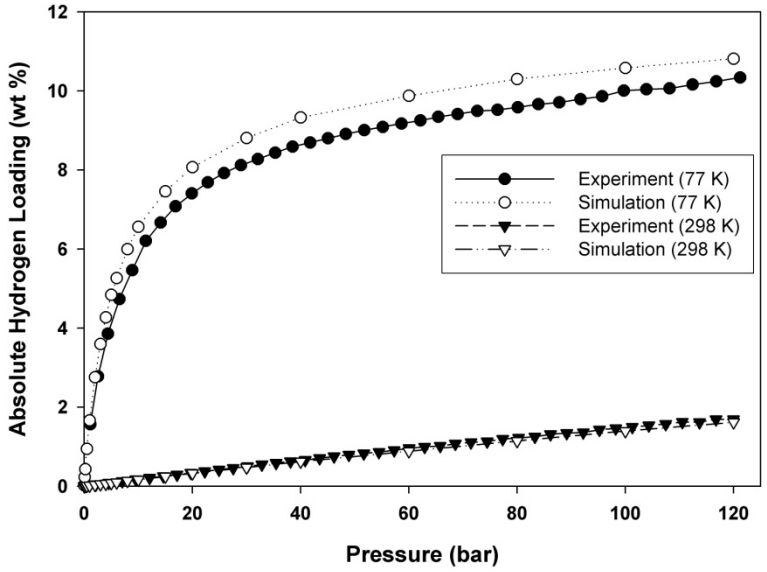
Molecular Modeling

- Determine effect of catenation on H_2 adsorption in Northwestern paddlewheel MOFs using
  - grand canonical Monte Carlo (GCMC) simulations
  - existing force fields that have been validated for other MOFs
- Develop model for cation-containing MOFs
  - Determine H_2/cation interactions with quantum chemical methods
    - DFT for geometries
    - MP2 with large basis set for energies → heat of adsorption
  - Fit QM results to analytic forms for GCMC
  - Use GCMC to predict effects of different cations, cation loading, pore size, etc. on hydrogen uptake

Approach

Molecular Modeling

- Milestones for FY09
  - Determine whether catenation is beneficial for hydrogen uptake in MOFs without cations
  - Develop model for cation-containing MOFs



Example: Hydrogen in IRMOF-1

Simulations: Ryan, Broadbelt, Snurr, *Chem. Comm.*, 2008.
Experiments: Kaye, Dailly, Yaghi, Long, *J. Am. Chem. Soc.,* 2007.

Technical Accomplishments and Progress: Previous Work

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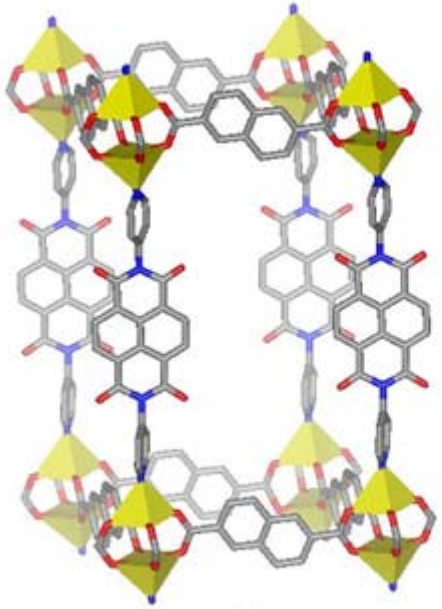
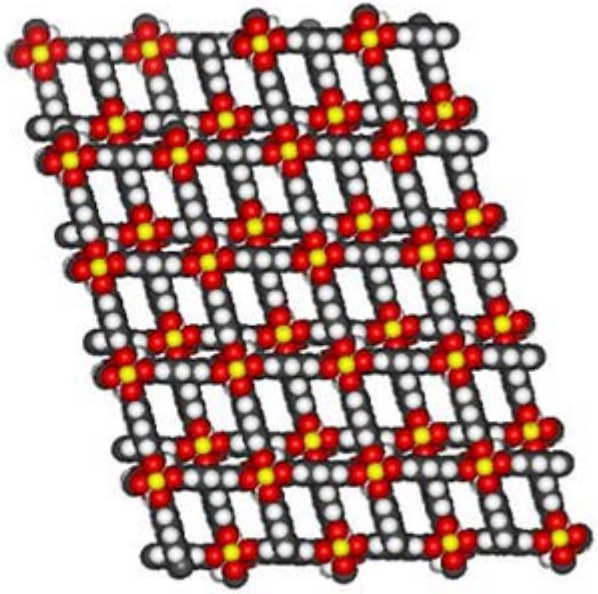


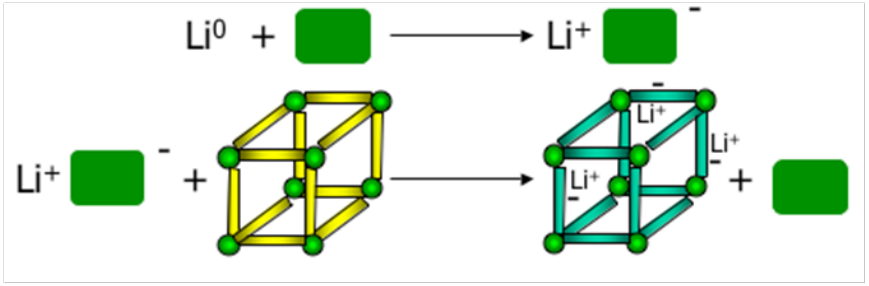
A



B

- Synthesis of a reducible-framework material
- Struts can be reduced with lithium.

One of two identical networks shown



Technical Accomplishments and Progress: Previous Work

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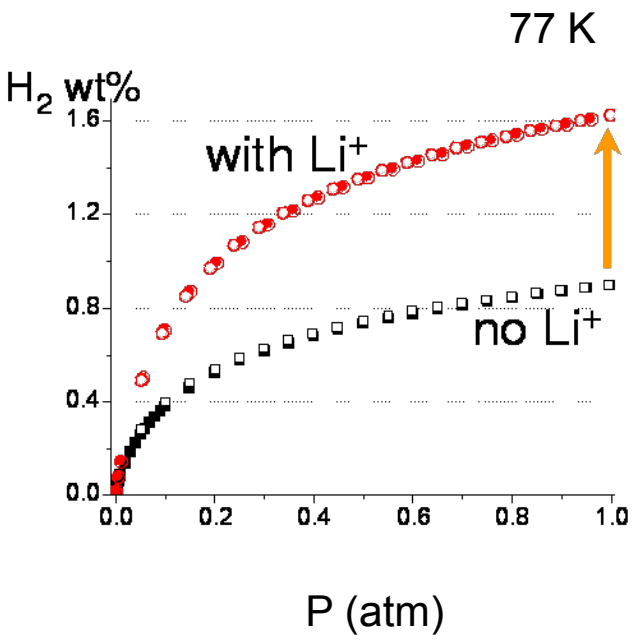
- $Zn_2(NDC)_2(diPyNI)$ MOF is reduced upon exposure to Li^0 in DMF
- H_2 uptake is nearly doubled with 5% doping
- Heat of adsorption substantially increases



Mulfort, Hupp, *J. Am. Chem. Soc.*, 2007.

Technical Accomplishments and Progress: Previous Work

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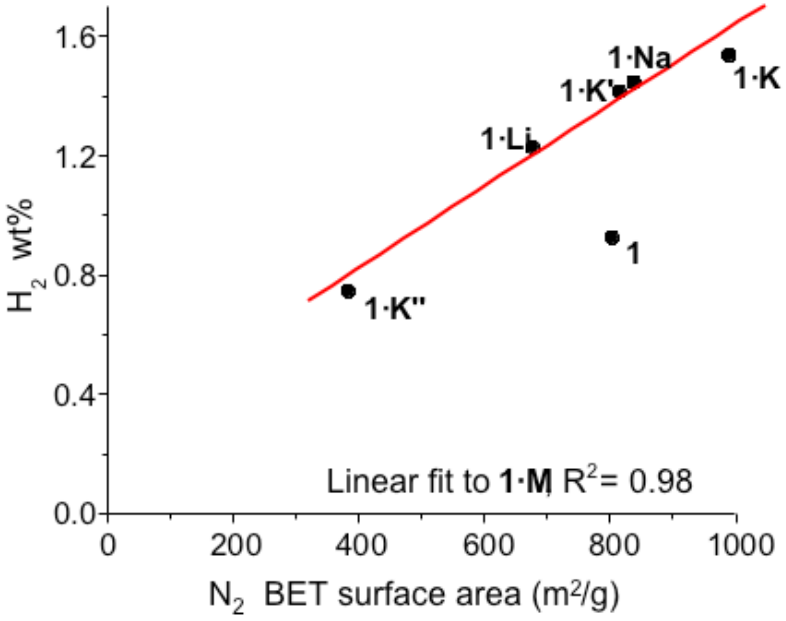
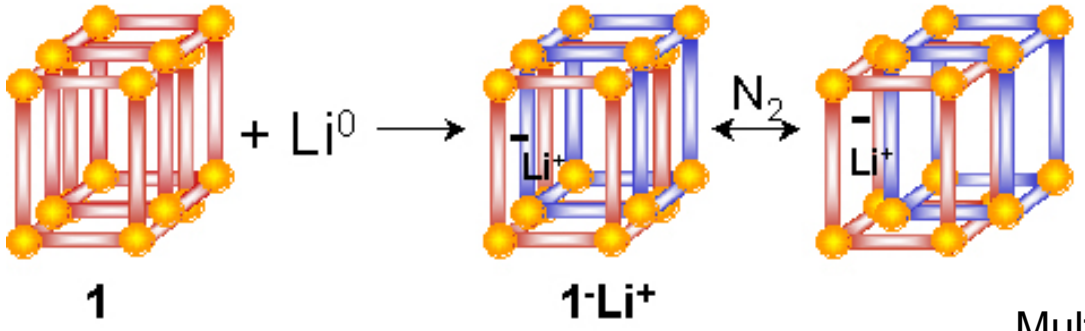
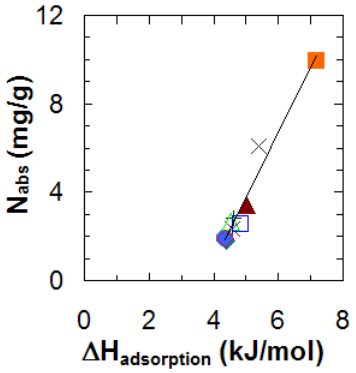
- Enhancement effects extend to other cations
- Enhancement effects extend to other MOFs
- Enhancements scale with cation-induced surface area modulation

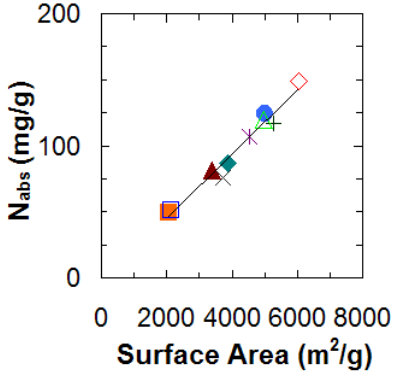


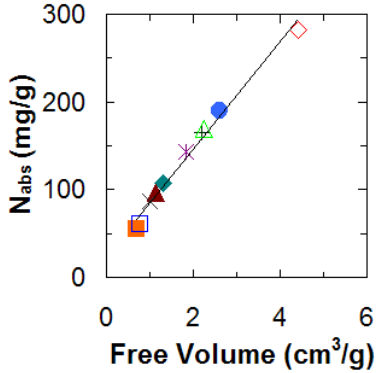


Mulfort, Hupp, *Inorg. Chem.*, 2008.

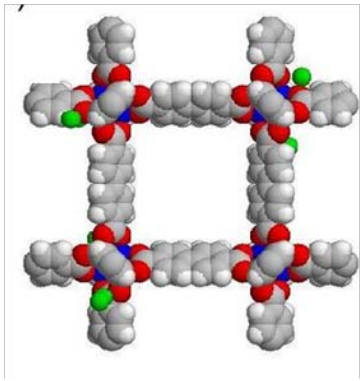
Technical Accomplishments and Progress: Previous Work

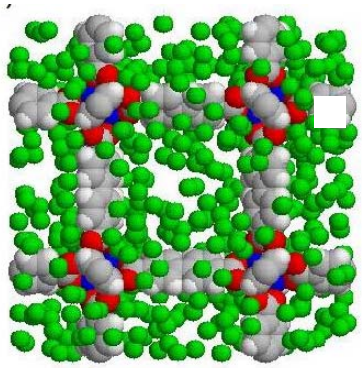


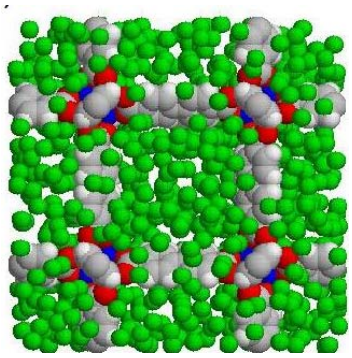




Using modeling, established that H_2 uptake in MOFs fall into 3 regimes:







- At low P, uptake correlates with heat of adsorption
- At intermediate P, uptake correlates with surface area
- At high P, uptake correlates with free volume

Frost, Düren, Snurr, *J. Phys. Chem. B*, 2006.

Technical Accomplishments and Progress: Previous Work

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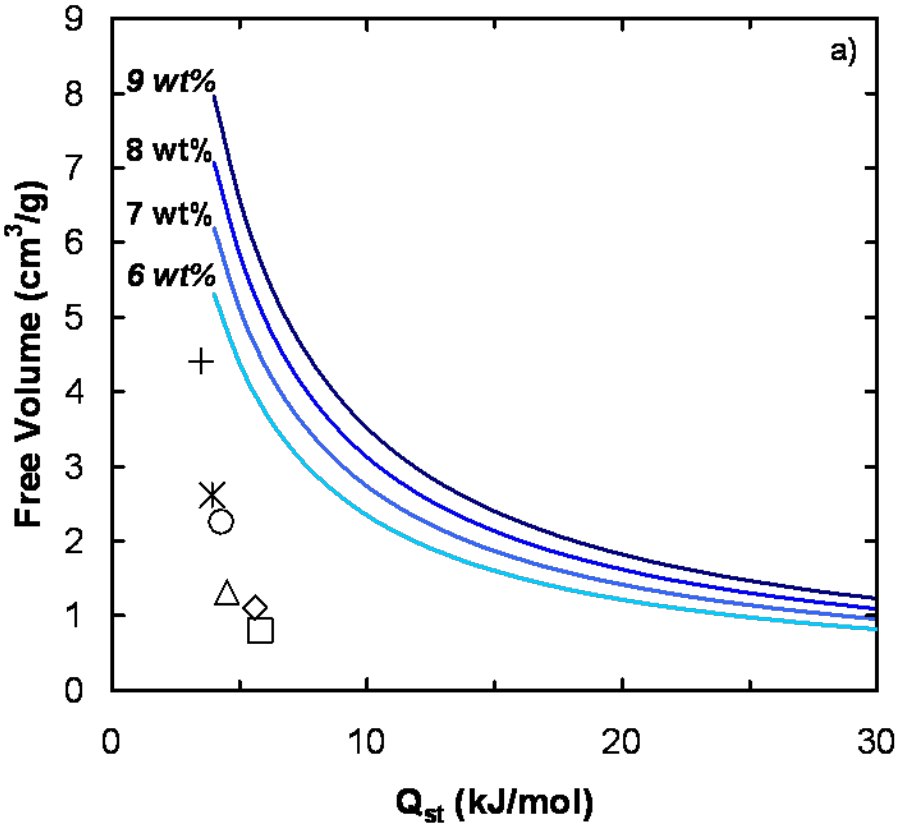
Using modeling, quantified the trade-off between free volume and heat of adsorption for H_2 storage in MOFs.

Both are necessary.



△ IRMOF-1; ◇ IRMOF-9; ∗ IRMOF-10; ○ IRMOF-14; + IRMOF-16; □ Cu-BTC

Frost and Snurr, *J. Phys. Chem. C*, 2007.

Collaborations

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- Argonne National Laboratory
  - Dr. Karen Mulfort: SAXS and other characterization
  - Dr. Peter Stair: Raman characterization
- Universidade Federal Ceara, Fortaleza, Brazil
  - Profs. Celio Cavalcante, Diana Azabedo, Mardonio Lucena: high pressure adsorption measurements, round-robin validation of uptake measurements
- Nature of the collaborations
  - We have existing relations with these groups, but the collaboration on hydrogen storage is just starting.
  - These groups are external to the DOE H_2 Program

Proposed Future Work

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- MOFs
  - Develop *non-catenated*, high-area, cation-containing MOFs
  - Continue to measure H_2 uptake and heats in new materials
- POFs
  - Develop new cation-containing POFs
  - Continue to measure H_2 uptake and heats in new materials
- Modeling
  - Validate model against experimental data
  - Extend modeling to POFs
- Go/No-Go Decision at end of FY10
  - Project will continue into Phase 2 if any materials have a volumetric capacity of 45 g/L at −40°C and 100 atm; or if any materials have a gravimetric capacity of 6 wt% at −40°C and 100 atm; or if any materials display heats of adsorption above 10 kJ/mol. Note that these are capacities of the materials alone.
  - The Phase 2 transition would include down selecting materials.

Summary

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- We are developing new materials to meet DOE hydrogen storage targets
  - Metal-organic frameworks (MOF)
  - Polymer-organic frameworks (POF)
- The new concept is to introduce cations into MOFs and POFs to improve the heats of adsorption, which will improve room temperature storage.
- We have already developed 2 strategies for introducing cations into MOFs.
- Integration of molecular modeling and experiment will aid in reaching our goals.