Room Temperature Hydrogen Storage in Nano-Confined Liquids

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15 May 2013

Project ID #
ST102

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Overview

Timeline

- Project start date: 05 March 2012
- Project end date: 15 February 2015
- Percent complete: 30%

Technical Barriers

- A. System weight and volume
- C. Efficiency
- E. Charging and discharge rates

Budget

- Total project funding
  - DOE share: $1.2M
  - Contractor share: $0.3M
- Funding received in FY12:
  - $450K (DOE)
  - $78K (Contractor)
- Funding for FY13:
  - $200K (DOE)
  - $93K (Contractor)

Partners

- No formal partners
- Tom Autrey (PNNL)
- David Farrusseng (CNRS)

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Project Goals and Objectives

Goal

Develop hydrogen storage materials with (*material basis*) hydrogen densities of ≥ 6 wt% and 50 g/l at room temperature and <350 bar that are compatible with the vehicle engineering and delivery infrastructure for compressed gas storage

Overall Objective

Use measurements and simulations to characterize, understand, and optimize the (*enhanced*) hydrogen storage capacity of nano-confined liquids (*liquids confined within nanoporous scaffolds*)

Objectives March 2012 – March 2013

- **Establish procedures for measuring hydrogen sorption (*solubility*) in liquids and liquid-based composites at pressures up to ~100 bar**
- **Validate procedures with bulk solvents**
- **Determine enhanced solubility of nano-confined liquid composites**
- **Develop simulation scheme to understand enhanced solubility effect**

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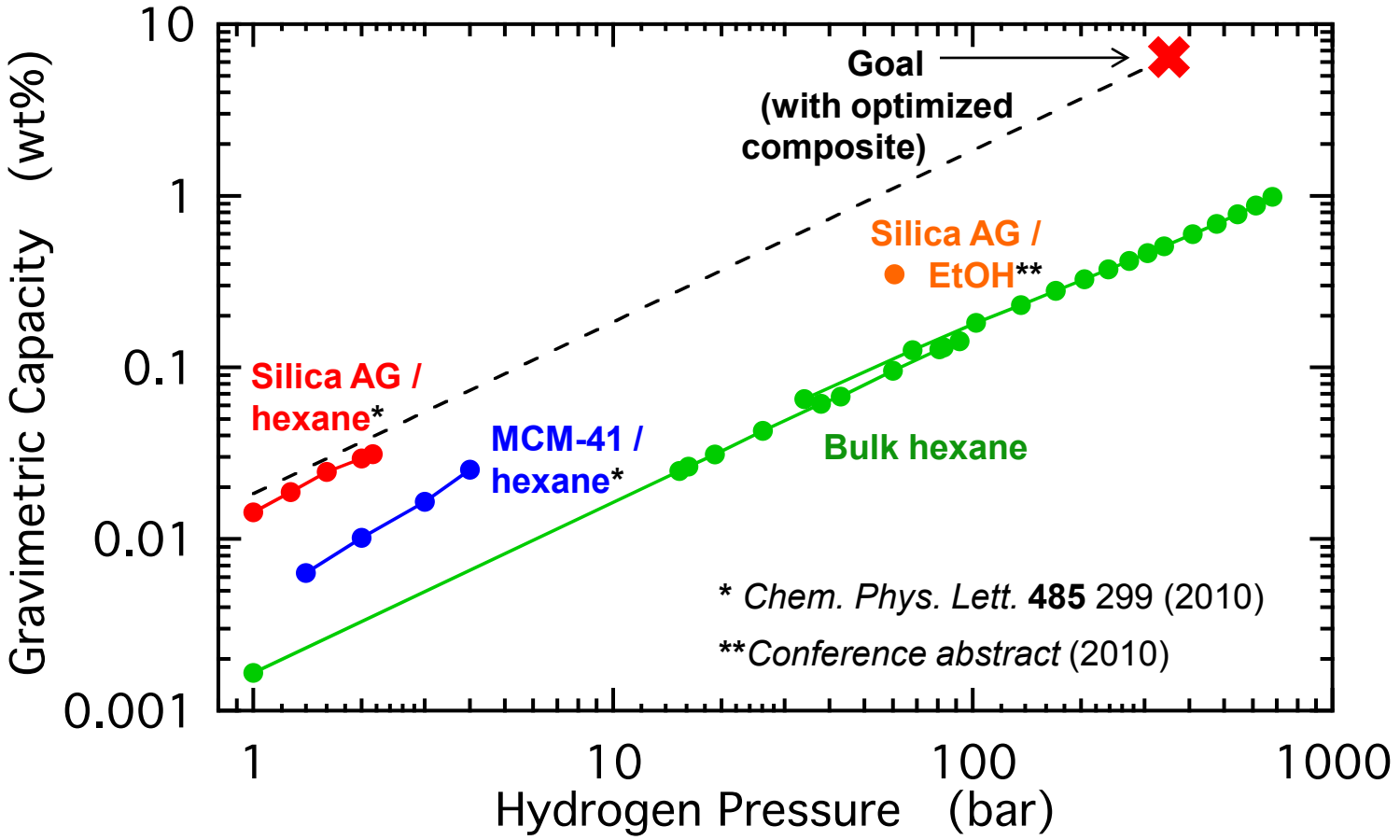
Enhanced Solubility in Nano-Confined Liquids

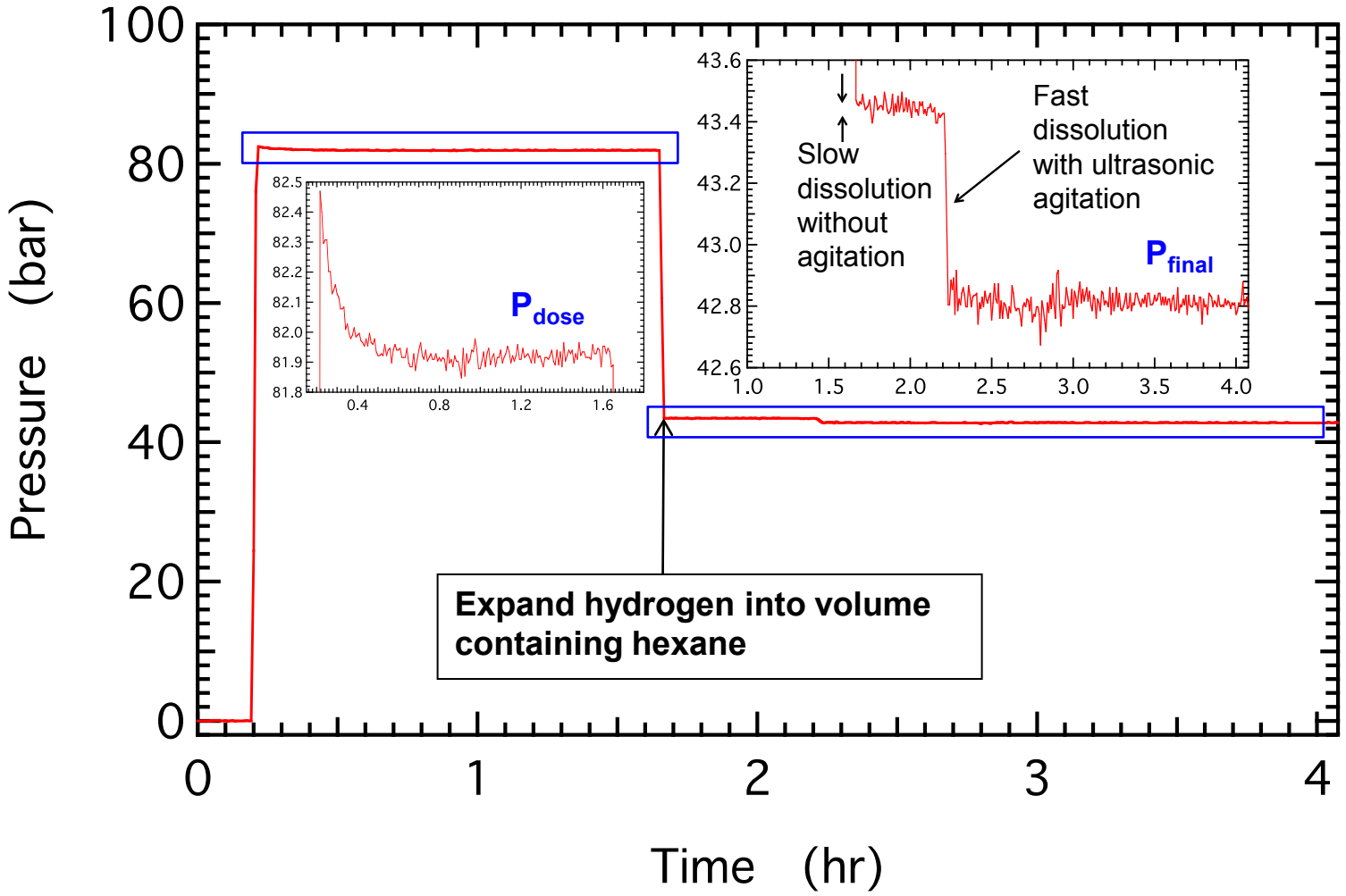
Hydrogen storage in nano-confined solvent/porous scaffold composites



- **Validate and understand (*experimentally and computationally*) the enhanced solubility effect**
- **Optimize and advance effect to achieve storage targets**

Gas/Liquid Solubility Measurement Procedure

Dissolution of hydrogen in bulk (liquid) hexane



Calculations

- **Convert P_{dose} and P_{final} into moles (m)**
- **$\Delta m = m_d - m_f$**
- **Gravimetric solubility (wt%) ~ $2 \cdot \Delta m / mass_{hex}$**
- **Volumetric solubility ($mmol/cm^3$) ~ $\Delta m / vol_{hex}$**

- **Technique (*including ultrasonic agitation*) also works for nano-confined solvent / porous scaffold composites**

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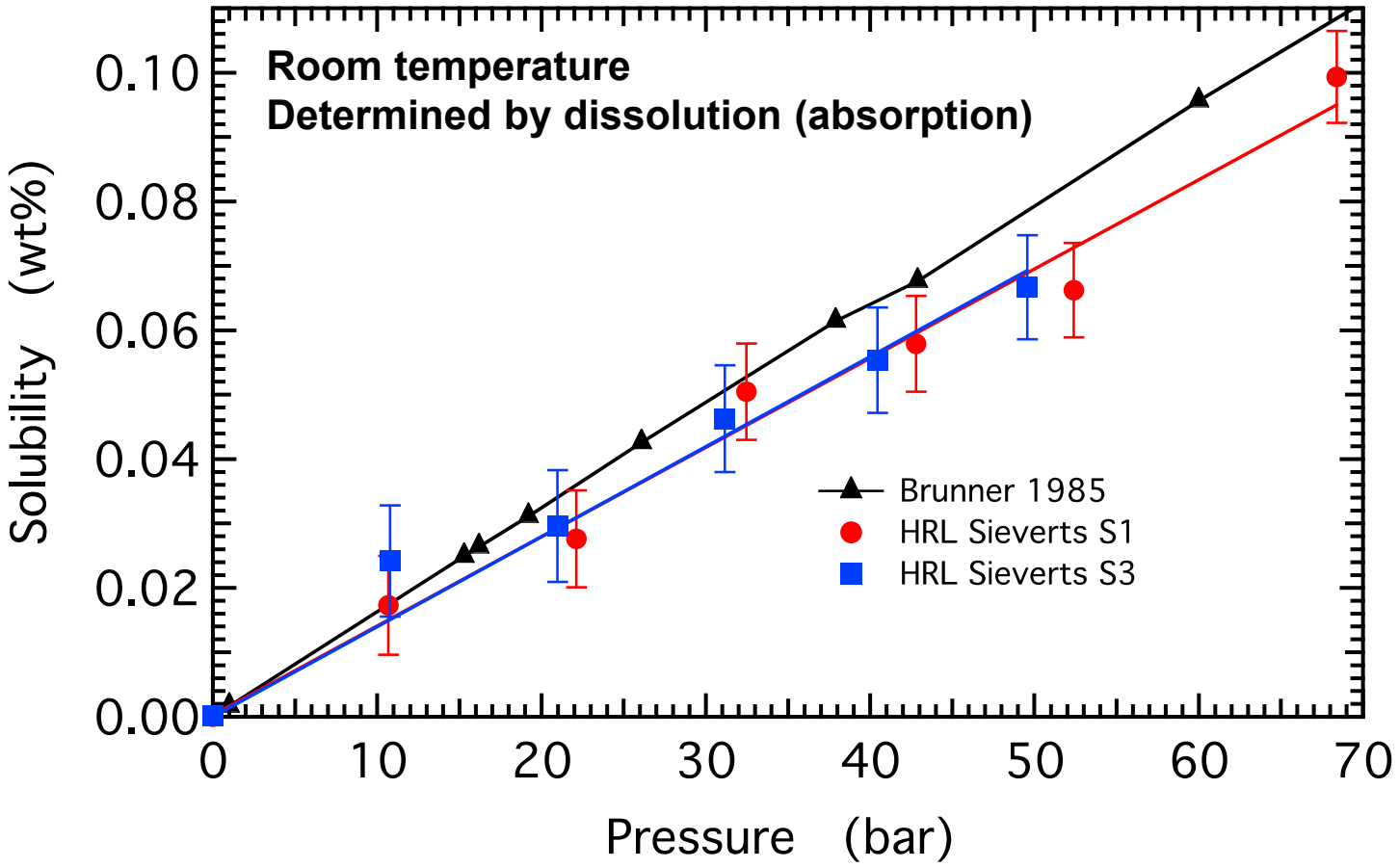
H_2 Solubility in Bulk Hexane

Samples prepared by helium purging and LN2 freeze/pump/thaw cycles



- **Average values agree with literature values within ~15%**
- **Errors reflect uncertainty in correction for hexane vapor pressure**

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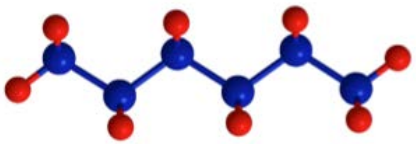
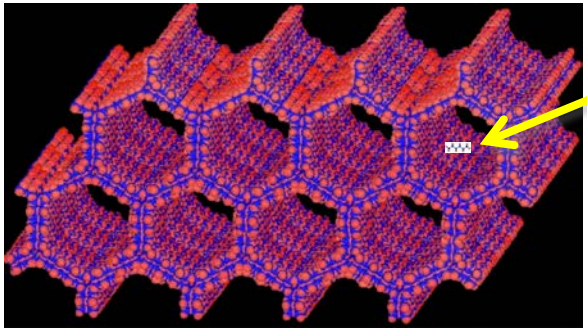
H_2 Solubility in Nanoconfined Solvent Composites

Begin with a reported system to validate effect:



n-hexane solvent
(*~0.8 nm long***)**

MCM-41 scaffold
(*3.4 nm diameter, 1-D pores; commercially available***)**



Approximate actual Pore : Solvent size ratio (4.4)

	Bulk n-Hexane* (mmol/cm^3)	Empty MCM-41* (mmol/cm^3)	Composite Hexane/MCM-41* (mmol/cm^3)	Capacity wrt bulk hexane	Capacity wrt empty MCM-41
CNRS Chem Phys Lett 2010 JACS 2012	**0.17**	**0.87**	**2.7** (*60 vol%*)	**15.9** x large enhancement	**3.1** x large enhancement
HRL	**0.185**	**0.4 ± 0.1**	*0.19 (52 vol%)* *0.18 (76 vol%)* *0.18 (84 vol%)*	**1.03** x **0.97** x **0.97** x no enhancement	**0.48** x **0.45** x **0.45** x lower

- **Bulk hexane and empty scaffold capacities agree approximately**
- **Composite capacities do not agree (***large enhanced capacities not validated***)**
- **Solubility in nanoconfined hexane is similar to bulk**

*All measurements at ~35 bar

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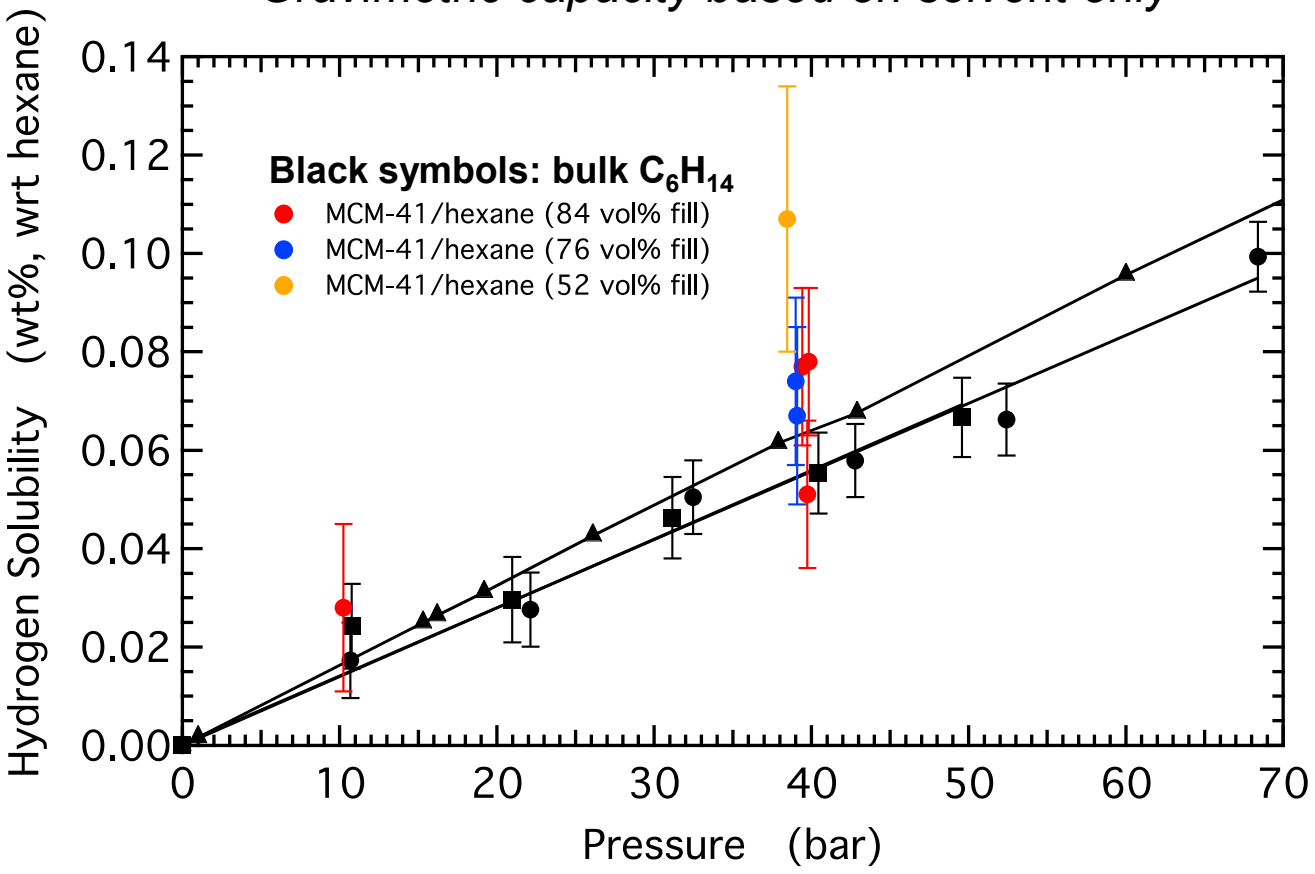
H_2 Solubility in Hexane/MCM-41 Composites

Gravimetric capacity based on solvent only



- **Solubility in composite is similar to bulk (*no large enhancement*)**
- **52 vol% composite capacity may be influenced by open scaffold**

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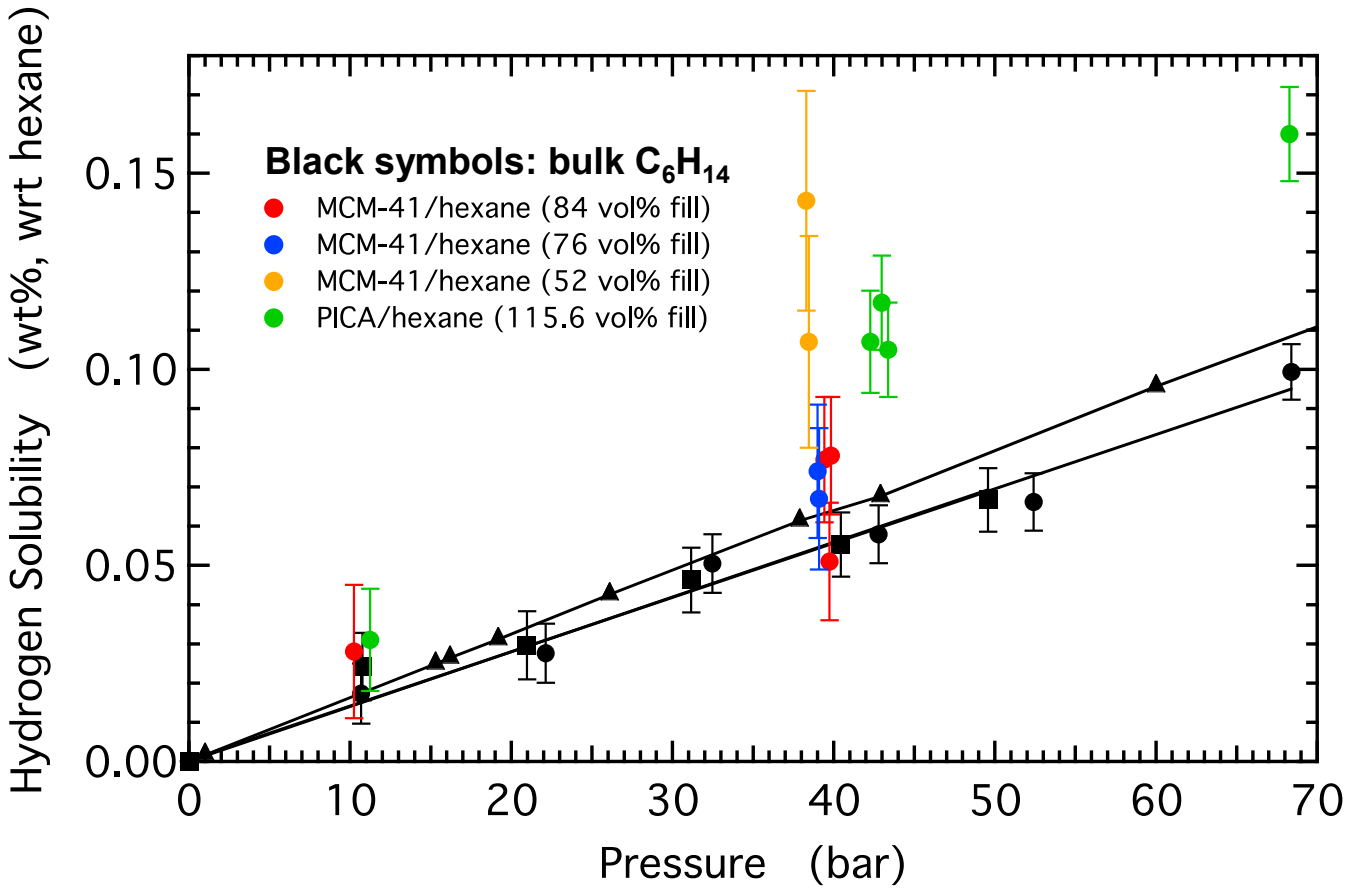
Smaller Pore: Hexane/Activated Carbon

PICA activated carbon: <2 nm pore size (2.5 vs. 4.4 pore:solvent size ratio)



- **This appears to be an experimentally significant enhancement – of 2x**
- **Lower size ratio may further increase enhancement (*will be tested*)**

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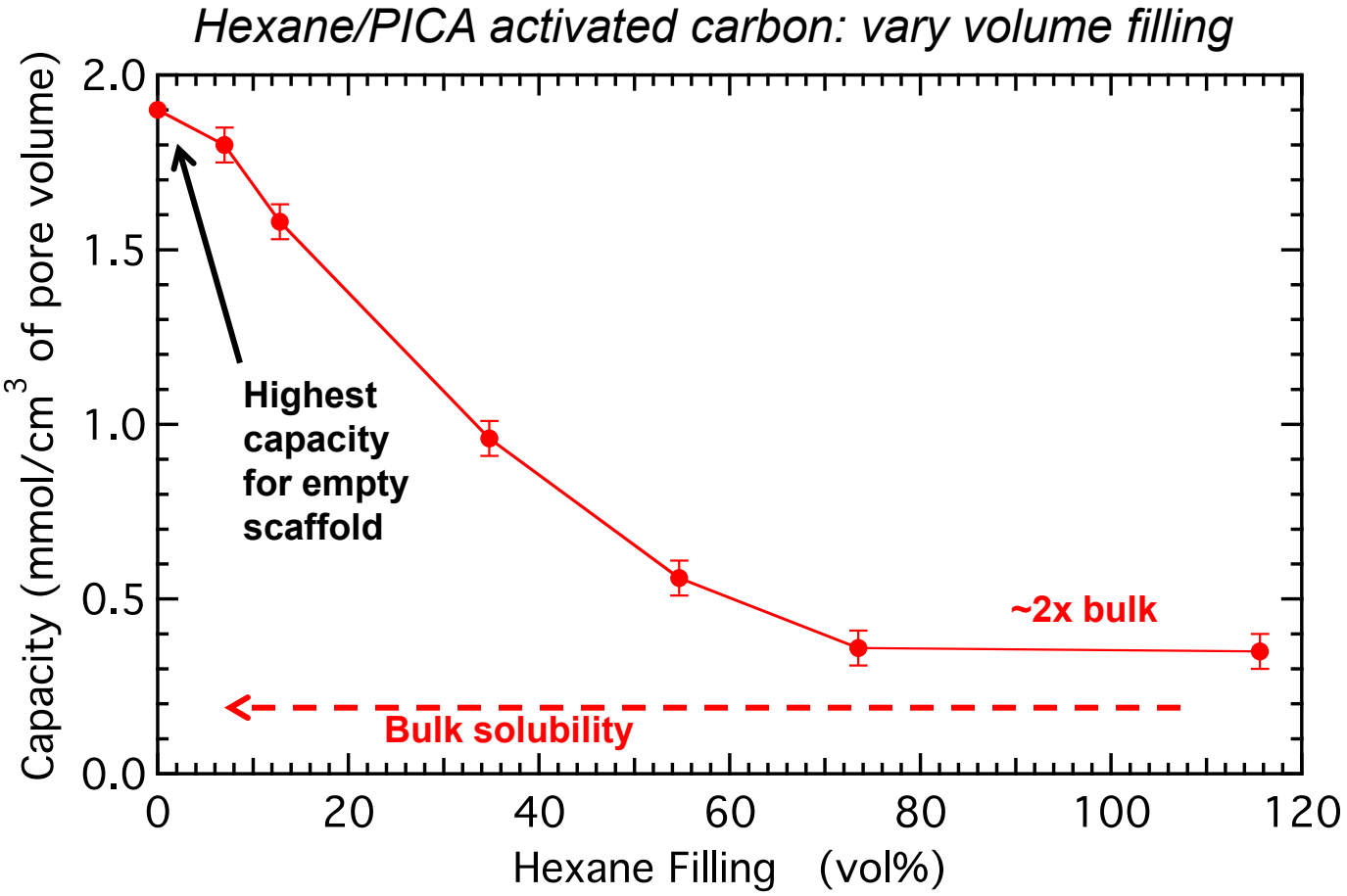
Hexane/Activated Carbon: Filling Dependence



- **Limit of high filling shows 2x enhancement**
- **However, volumetric capacity is still lowered compared to empty scaffold**
- **Higher pressures may favor composites (*will also be tested*)**

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Simulation of Enhanced Solubility Effect

- **Use molecular dynamics simulations of solvent/scaffold composites to quantify the effect of nano-confinement on the solvent properties**
  (*spatial density variations, orientational effects, thermodynamics***)**

- **LAMMPS molecular dynamics simulator (***classical, developed by Sandia***) with CHARMM forcefields (***Leonard-Jones with cutoffs***)**

- **Steps to full simulations :**
  - **bulk scaffold material (***silica***) Completed**
  - **empty nanoporous scaffold (***silica with 2 nm pore***) Completed**
  - **bulk solvent (***hexane***) Nearly completed, March 2013**
  - **solvent/scaffold composite (***hexane in 2 nm silica pore***)**
  - **additional pore diameters, H_2 solubility in composite**

- **Metrics used for validation of simulation :**
  - **density, pair correlation functions, thermodynamic quantities**

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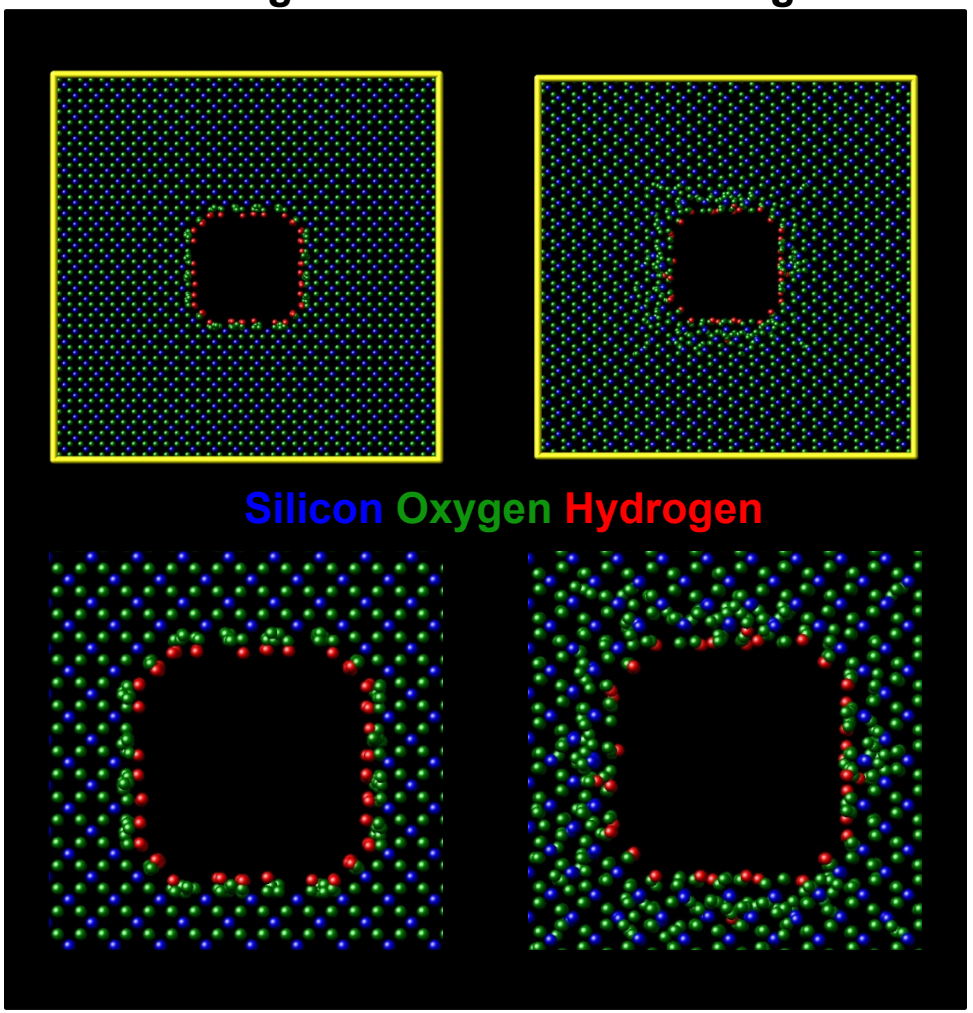
Simulation of Silica Scaffold

Top-down (2-D) views

Initial configuration **Final configuration**



Details:

- **~16 000 atoms**
- **~6.5 x 6.5 x 6.5 nm^3**
- **300 K**
- **~2 nm dia x 6.5 nm long pore**
- **Si-O-Si and Si-OH pore surface bonds**

- **Si-O bond length = 0.1626 ± 0.0027 nm** (*exp. = 0.1600 – 0.1615 nm*)

- **More disorder near pore**

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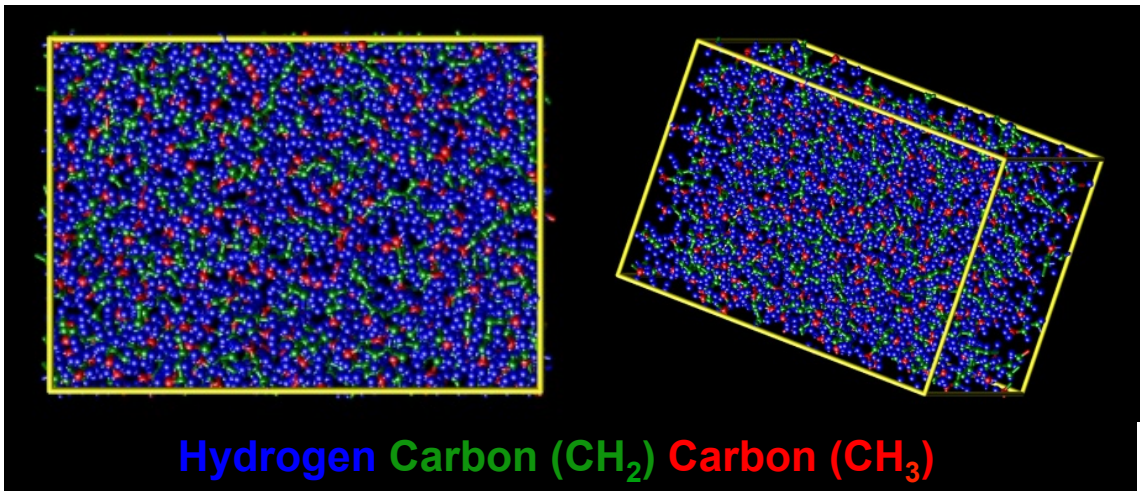
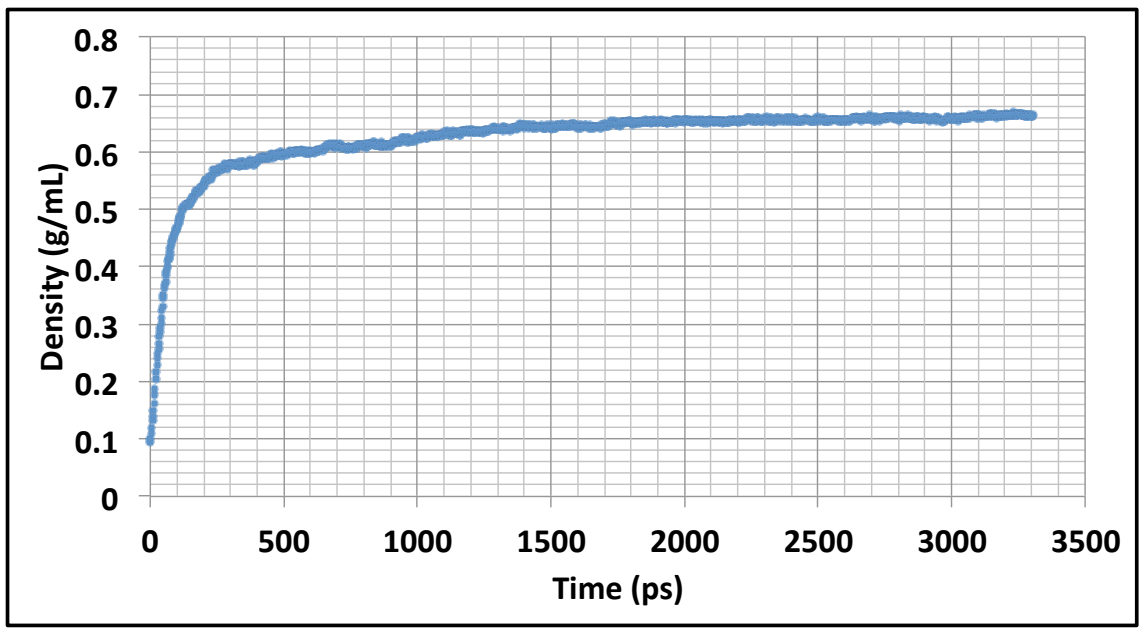
Simulation of Bulk Hexane

Top-down view **3-D view**





Details:

- **250 hexane molecules**
- **Volume = 4.5 x 3.25 x 3.7 nm^3**
- **Temperature = 300 K**

- **Final bulk density = 0.662 g/cm^3 (*exp. = 0.659 g/cm^3*)**
- **Spatial density profiles, pair correlation functions, and thermodynamic parameters are being calculated**

Collaborations

- **No formal partners**

- **Informal collaborators**

  - Tom Autrey (PNNL)
  email correspondence and discussions
  (*possible effort on NMR and/or PDF of confined liquids***)**

  - David Farrusseng (CNRS)
  email correspondence

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Future Work

- **Continue to optimize enhanced solubility effect**
  - **vary pore : solvent size ratio (***test larger solvents, eg $C_{16}H_{34}$***)**
  - **test branched solvents (***eg iso-octane***)**
  - **test additional scaffolds (***eg MOFs, micoporous polymers***)**

- **Investigate effect of pressure (***to exceed scaffold adsorption***)**

- **Perform full solvent / scaffold simulations**
  - **hexane in 2 nm silica pore**
  - **vary pore and/or solvent size**
  - **consider including H_2 as solute**

- **Go/No-go decision (***Sept. 2013, month 18***)**
  - **demonstrate mechanism to achieve 1 wt% storage**

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Summary

- **Solubility enhancements of ~2x up to 50x have been reported for gasses, including H_2, in liquid solvents that are nano-confined in scaffolds having pore sizes <~10 nm**

- **An enhancement of ~20x at 350 bar with a scaffold pore volume of 4.0 cm^3/g would enable room temperature material-based hydrogen storage densities of 6 wt% and 50 g/L**

- **This phenomena has not been thoroughly explored or understood (*only a limited number solvents and scaffolds have been characterized*)**

- **This approach has the potential to significantly improve the capacity of compressed hydrogen systems with minimal changes to vehicle engineering and delivery infrastructure, thus facilitating technology transition**

- **Initial measurements have not validated reports of 15x enhancements for hexane/MCM-41 (*bulk values, ie 1x enhancements, were observed*)**

- **However, hexane/activated carbon appears to show a 2x enhancement**

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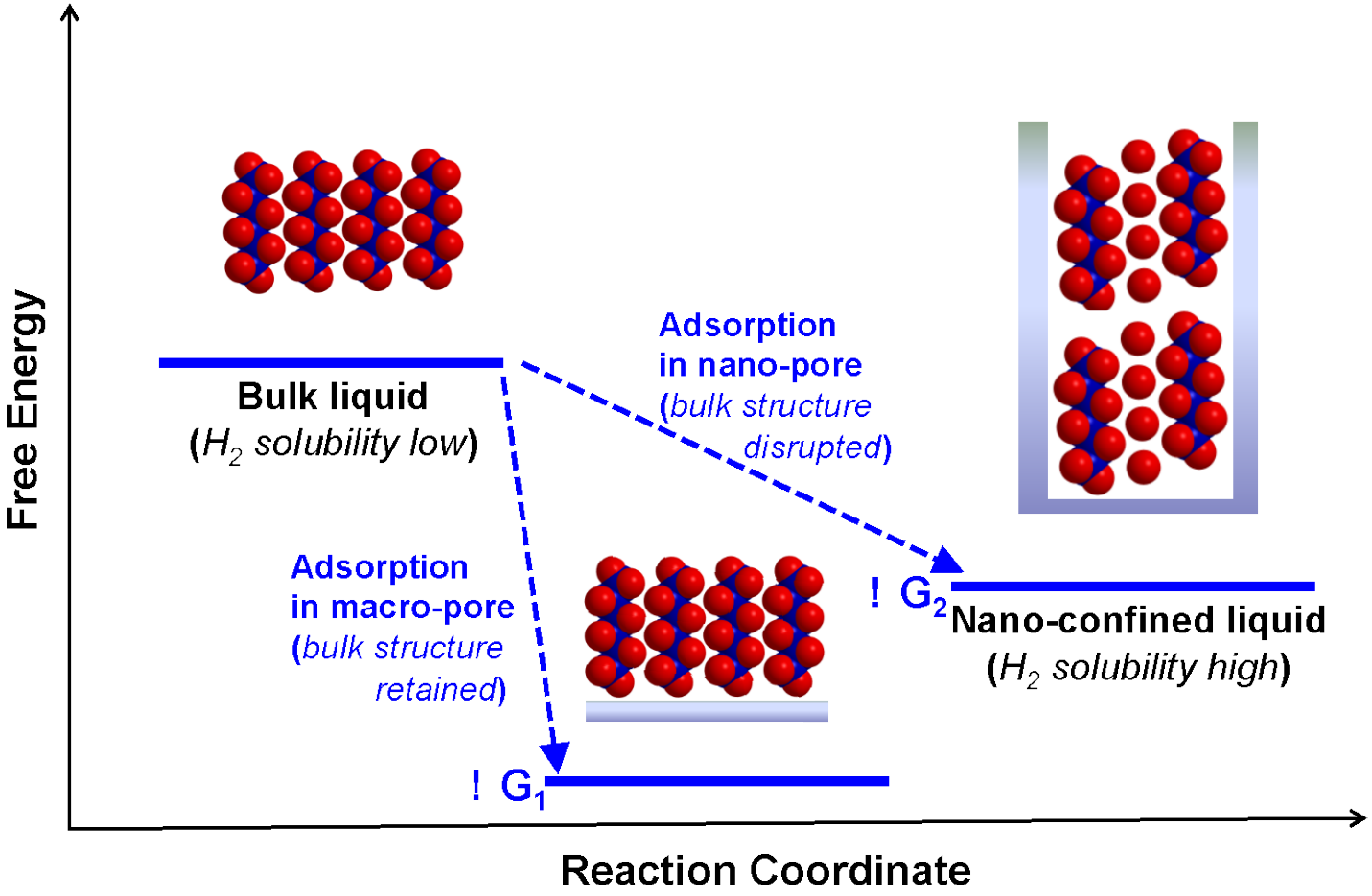
Technical Backup Slides

Enhanced Solubility: Mechanism



- **Simulations to test mechanism**

Details of Asymptote Calculation

What gravimetric and volumetric storage densities could be obtained?

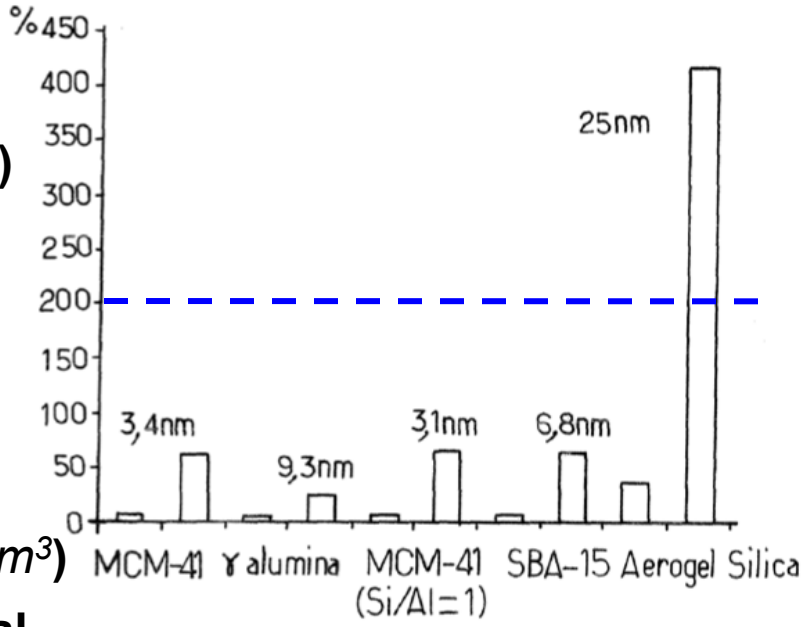
1) Assume a solubility = C_L/C_g of 200% for H_2 in, *eg*, nano-confined hexane
(*high, but within demonstrated range*)

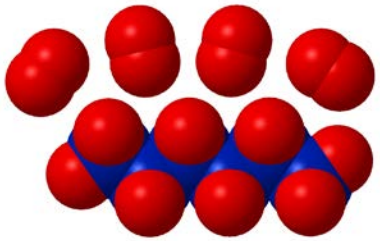
2) Assume 200% can be achieved at 350 bar
(*big assumption, but 156% at 60 bar reported*)

- **$C_g(H_2$@350 bar) = ~14.5 mol/L**
- **Therefore, C_L = 29 mol/L**

3) Assume 4.0 cm^3/g pore volume scaffold
(*very high but possible, demonstrated*)

- **4.0 cm^3 gives 2.64 g-hexane (*ρ = 0.66 g/cm^3*)**
- **1 g-scaffold + 2.64 g-hexane = 3.64 g-total**
- **29 mol/L in 0.004 L gives 0.23 g-H_2**
- **0.23 g-H_2/3.64 g gives ~6 wt% H_2 (*~3.5 H_2/C_6H_{14}*)**
- **0.23 g-H_2 in 0.0045 L gives 50 g-H_2/L**





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Issues/Opportunities

1) Achieving solvent/scaffold with sufficient H_2 solubility

- **only a small number of scaffolds tested (*mainly porous silica's and alumina's*)**
- **there is a large range of possible scaffold materials to try, *eg*:**
  - **carbon's (*activated, aerogel, mesoporous, templated*)**
  - **MOF's**
  - **porous polymers**
- **other than the relationship with pore size, what determines the solubility is unknown (*ie, why does hexane in 8.7 nm silica aerogel give 400%*), *eg*:**
  - **solvent size/pore size systematics**
  - **solvent functional groups**
  - **pore surface chemistry**

2) Recovered hydrogen will be contaminated by solvent vapor

- **engineering solutions (*eg, selective membrane/filter, condense and recycle*)**
- **material solutions:**
  - **use higher molecular weight solvents**
  - **use ionic liquids with alkyl side chains**
  - **polymerize or oligomerize solvent**
  - **tether solvent to scaffold**