# Room Temperature Hydrogen Storage in Nano-Confined Liquids

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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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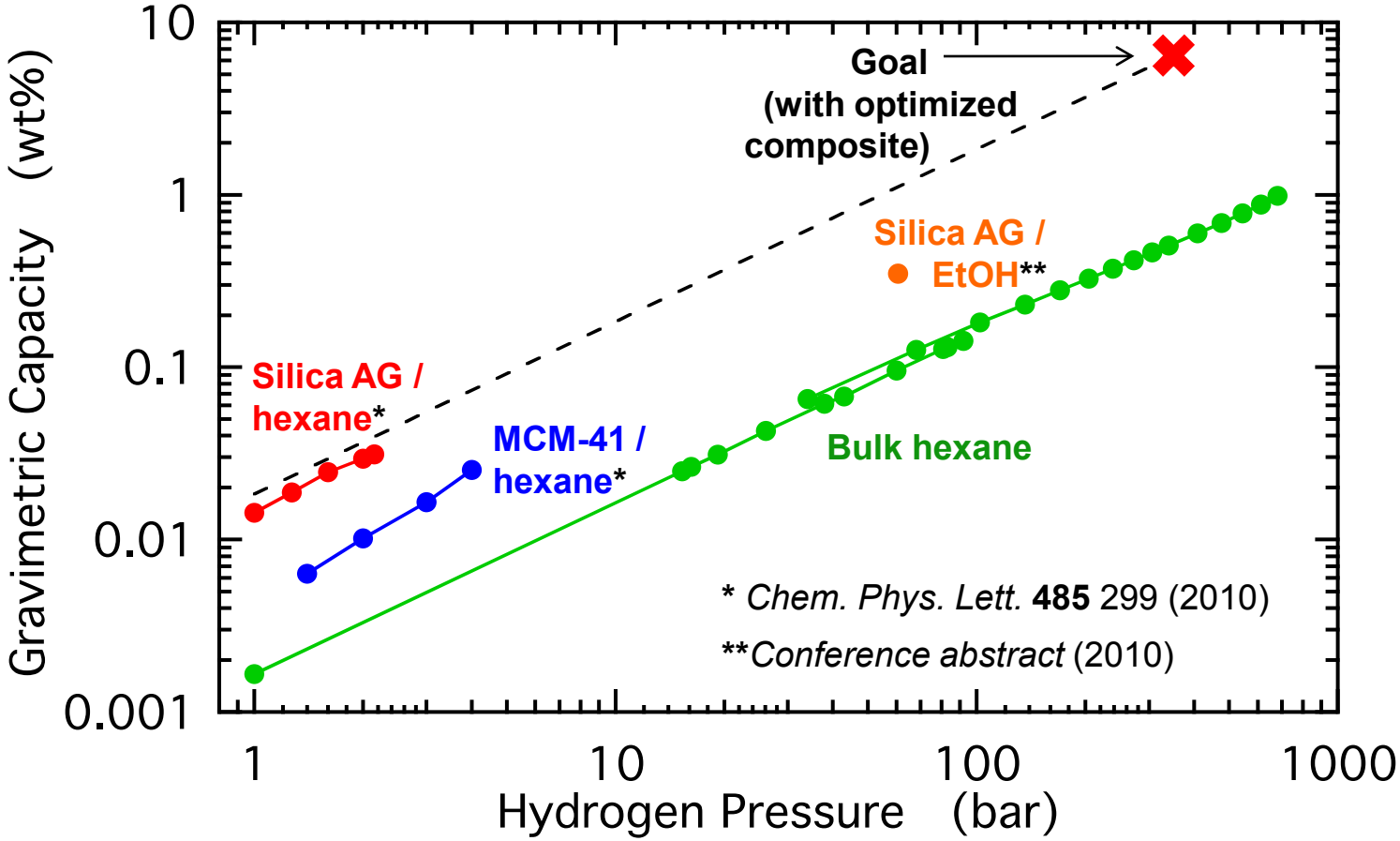
# Enhanced Solubility in Nano-Confined Liquids

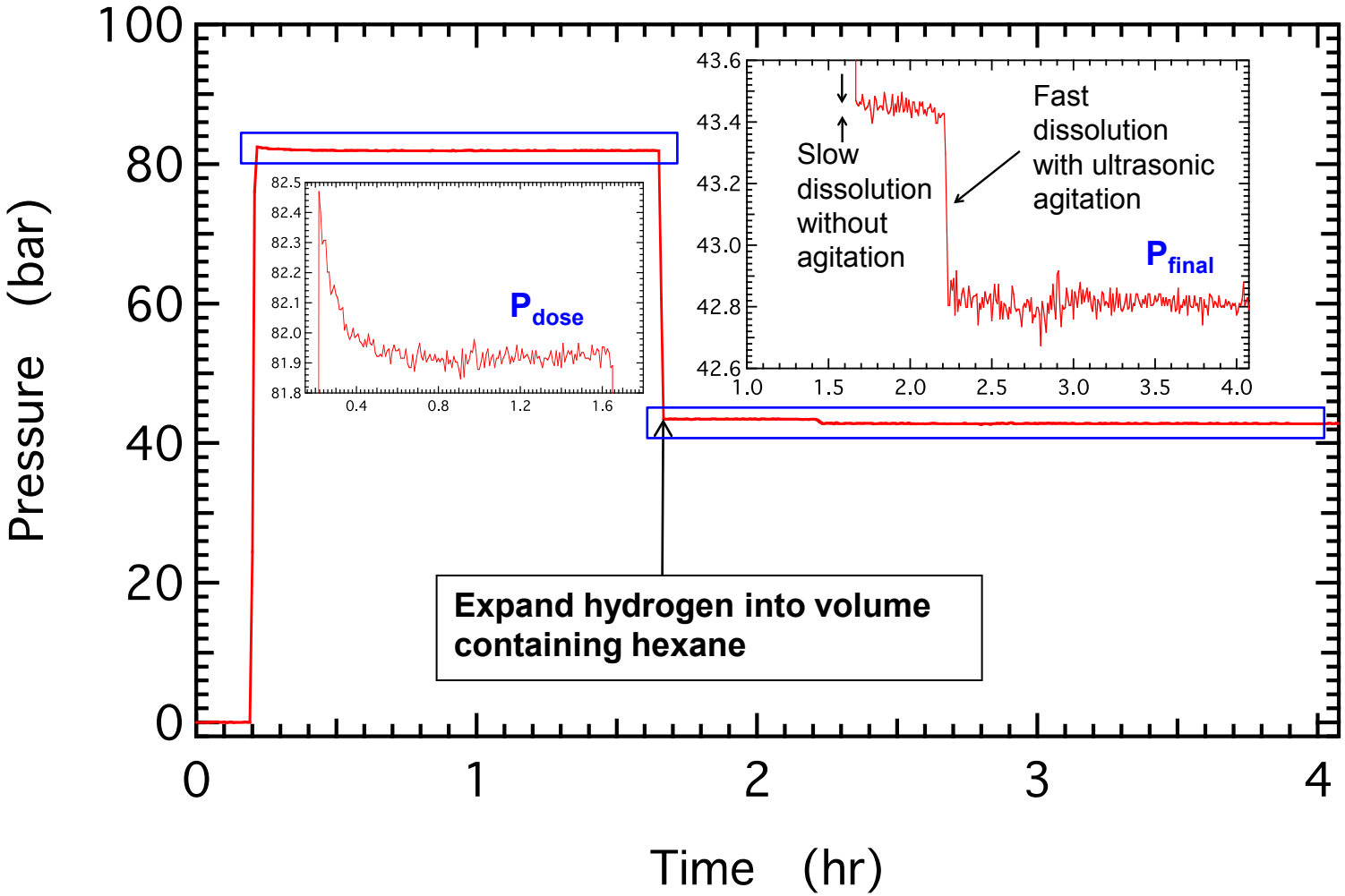
## Hydrogen storage in nano-confined solvent/porous scaffold composites




- **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*



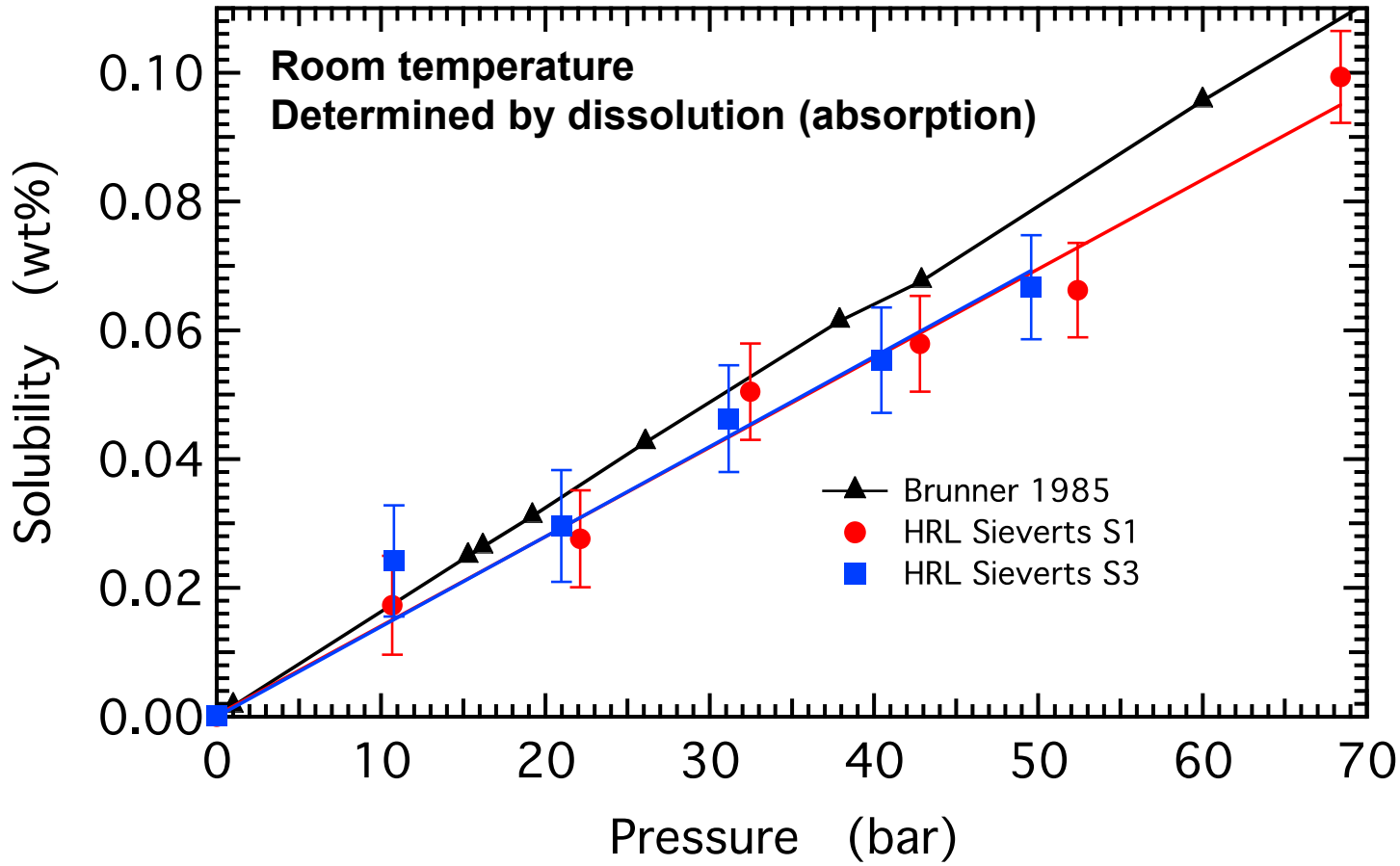

**Calculations**

- **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**

# $H_2$ Solubility in Bulk Hexane

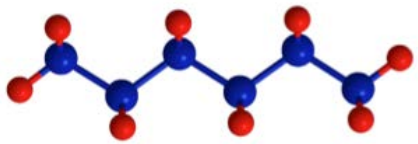
*Samples prepared by helium purging and LN2 freeze/pump/thaw cycles*




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

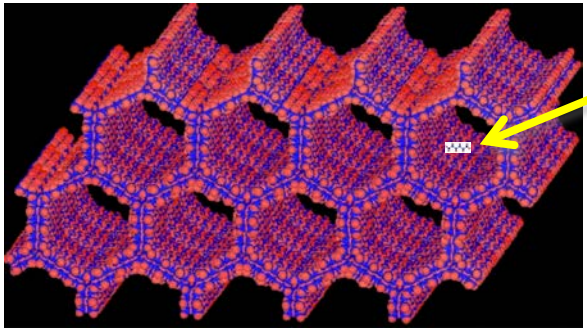
# $H_2$ Solubility in Nanoconfined Solvent Composites

*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)

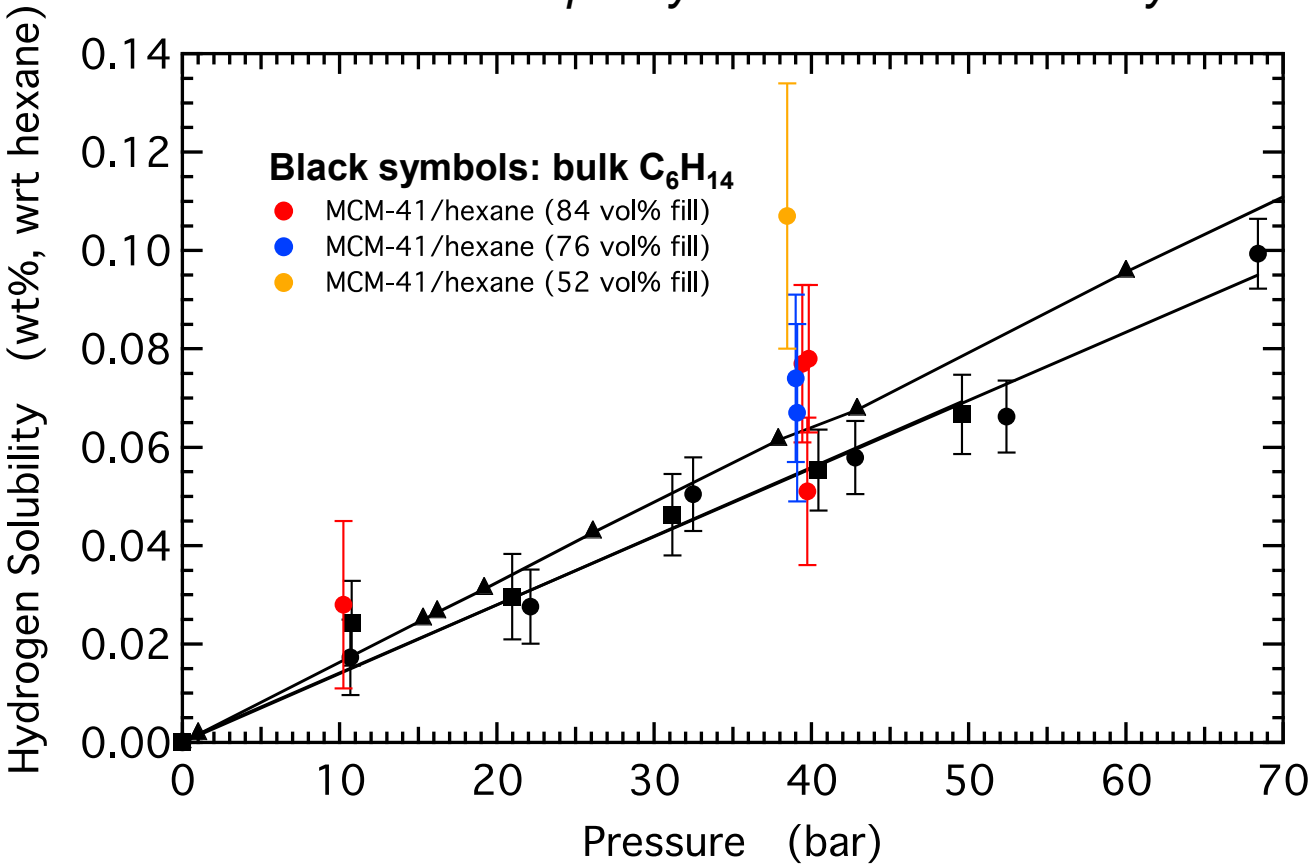
| | Bulk n-Hexane* ($mmol/cm^3$) | Empty MCM-41* ($mmol/cm^3$) | Composite Hexane/MCM-41* ($mmol/cm^3$) | Capacity wrt bulk hexane | Capacity wrt empty MCM-41 |
|---|---|---|---|---|---|
| **CNRS**<br>Chem Phys Lett 2010<br>JACS 2012 | **0.17** | **0.87** | **2.7** (*60 vol%*) | **15.9** x<br>large enhancement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

# $H_2$ Solubility in Hexane/MCM-41 Composites

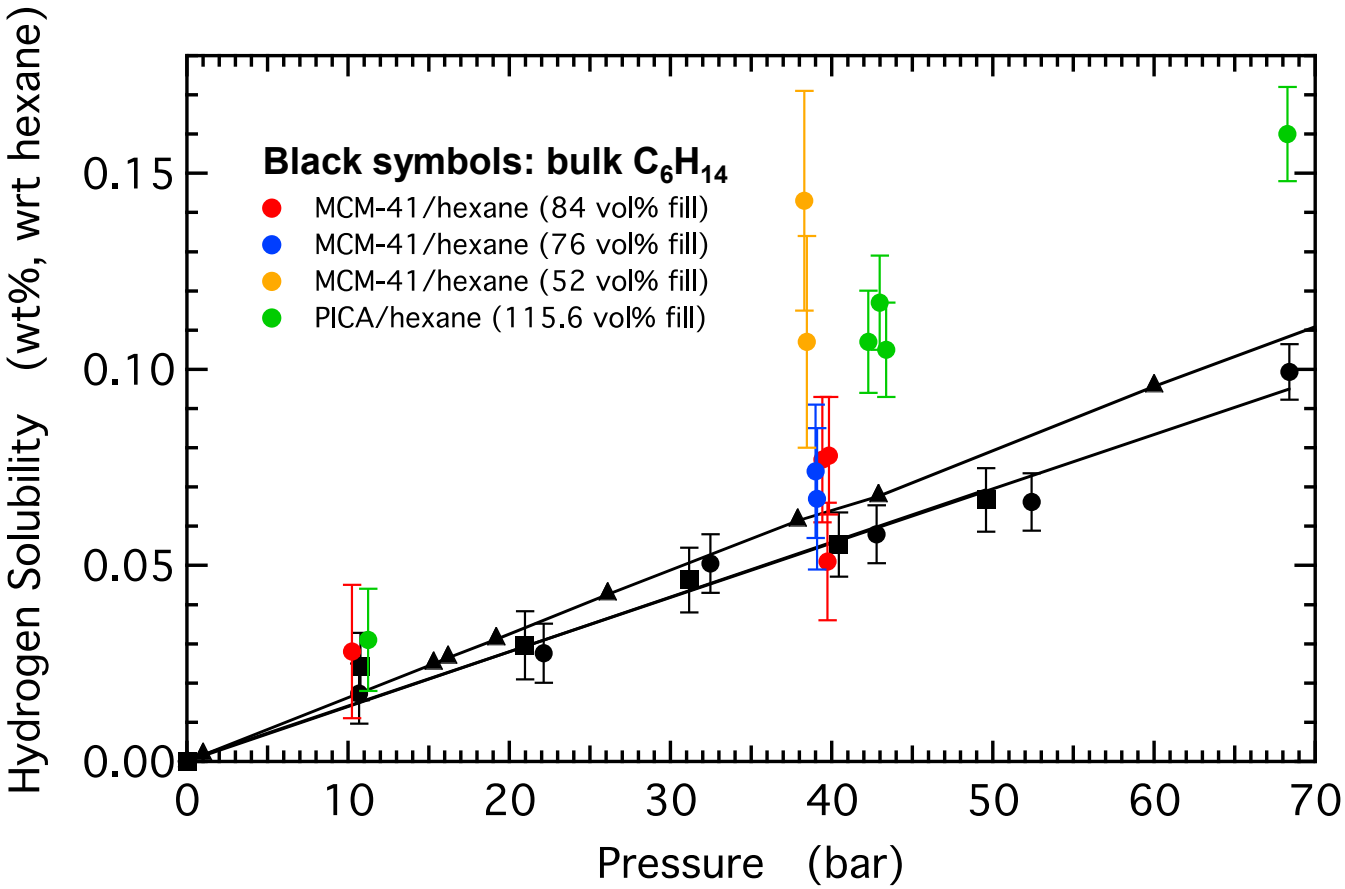
*Gravimetric capacity based on solvent only*




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

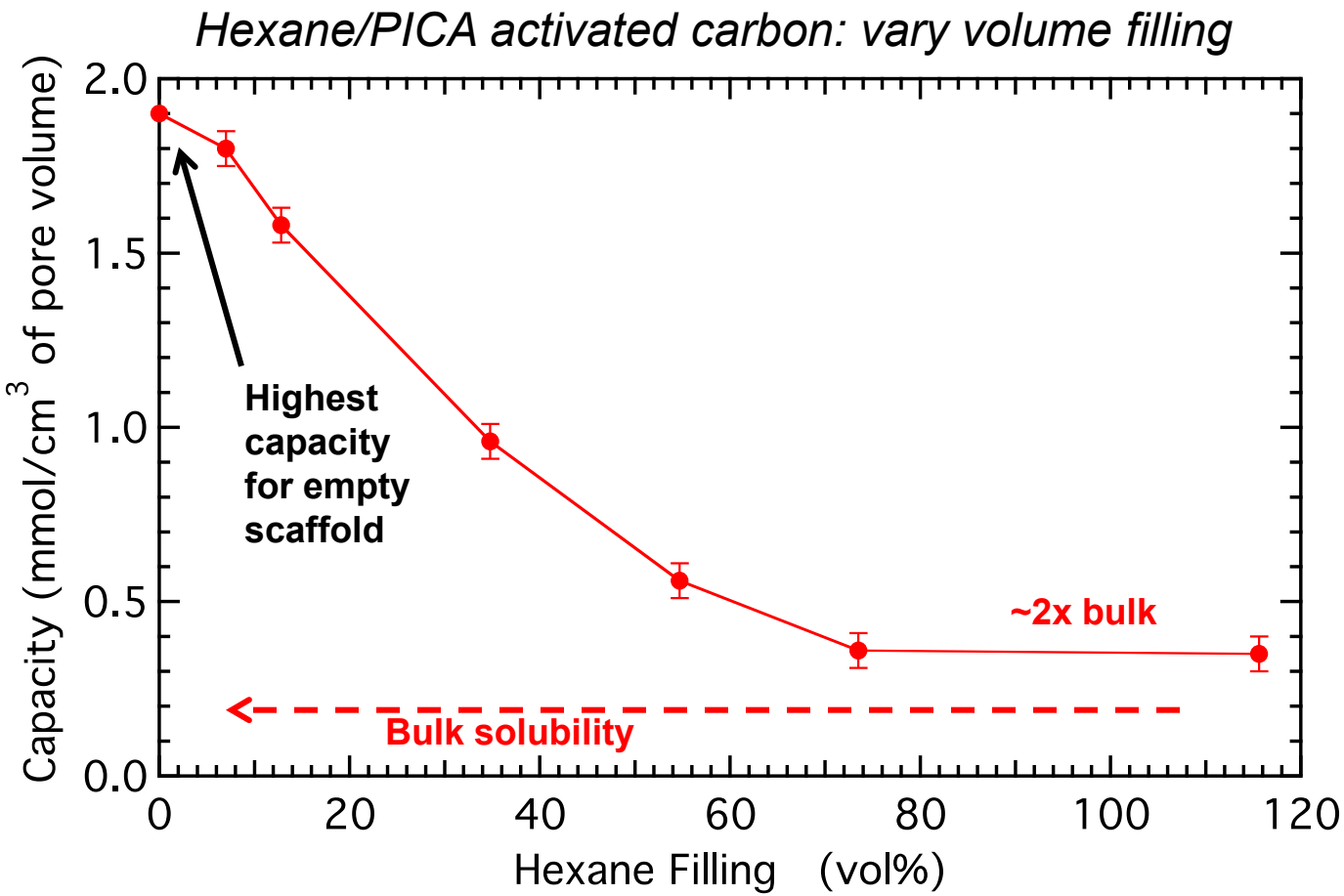
# Smaller Pore: Hexane/Activated Carbon

*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*)**

# 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***)**

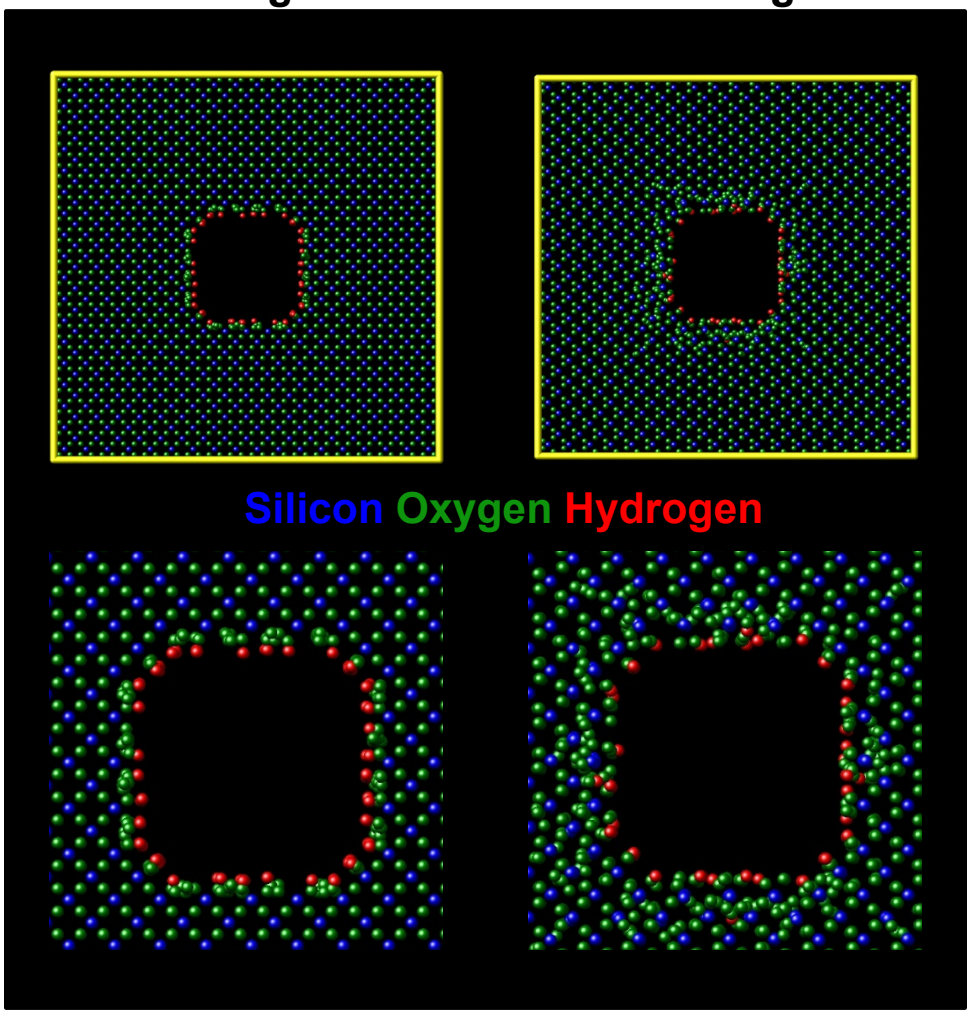
- **Steps to full simulations :**
  - **bulk scaffold material (***silica***) Completed**
  - **empty nanoporous scaffold (***silica with 2 nm pore***) Completed**
  - **bulk solvent (***hexane***) Nearly completed, March 2013**
  - **solvent/scaffold composite (***hexane in 2 nm silica pore***)**
 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

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

# Simulation of Silica Scaffold

Top-down (2-D) views

Initial configuration Final configuration




**Details:**

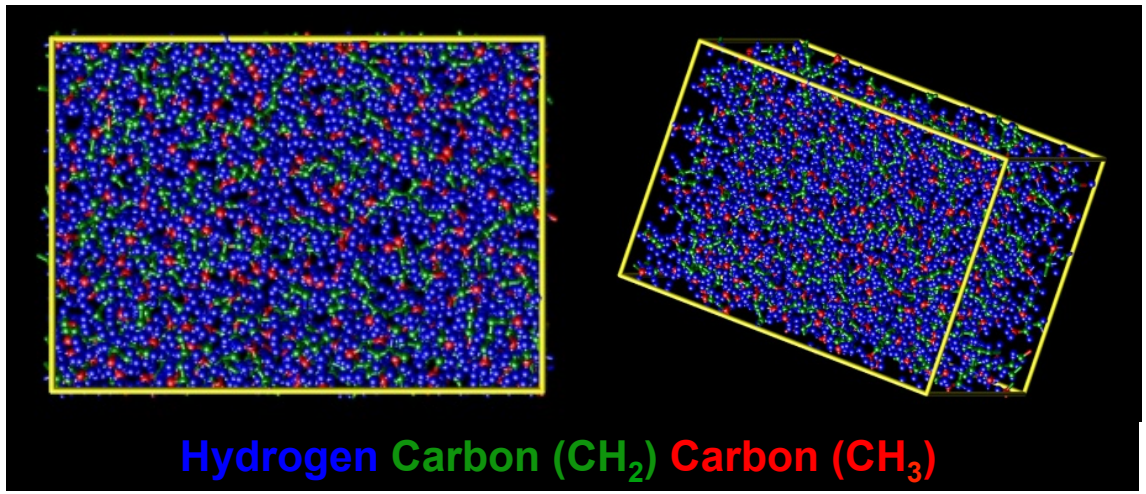
- **~16 000 atoms**
- **~6.5 x 6.5 x 6.5 nm$^3$**
- **300 K**
- **~2 nm dia x 6.5 nm long pore**
- **Si-O-Si and Si-OH pore surface bonds**

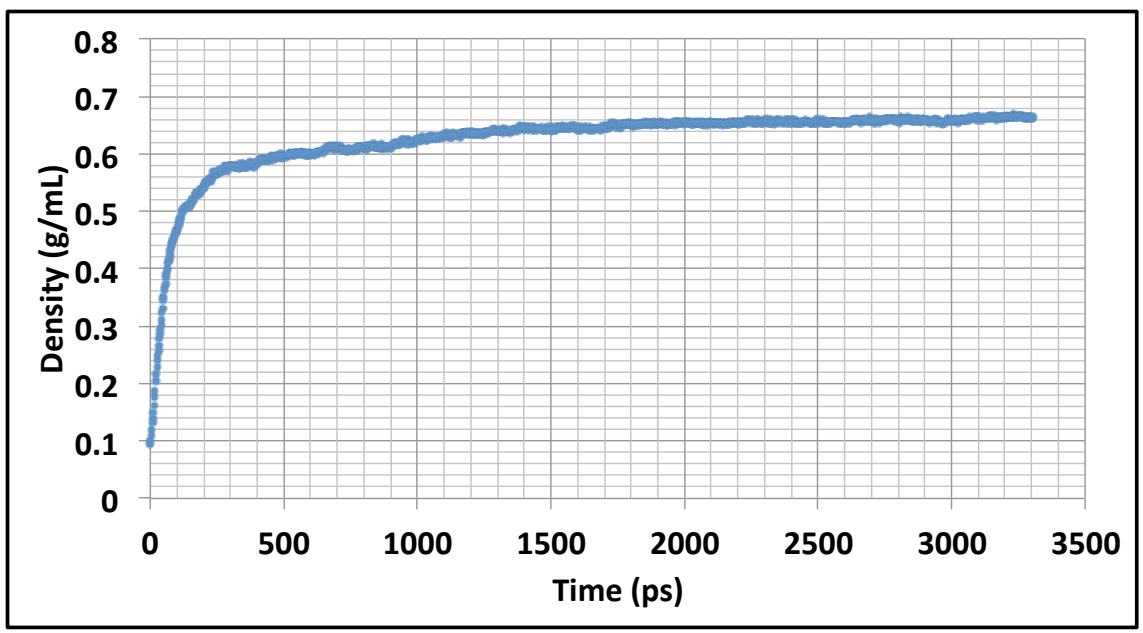
- **Si-O bond length = 0.1626 ± 0.0027 nm** (*exp. = 0.1600 – 0.1615 nm*)

- **More disorder near pore**

# 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**

# 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**

# 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***)**

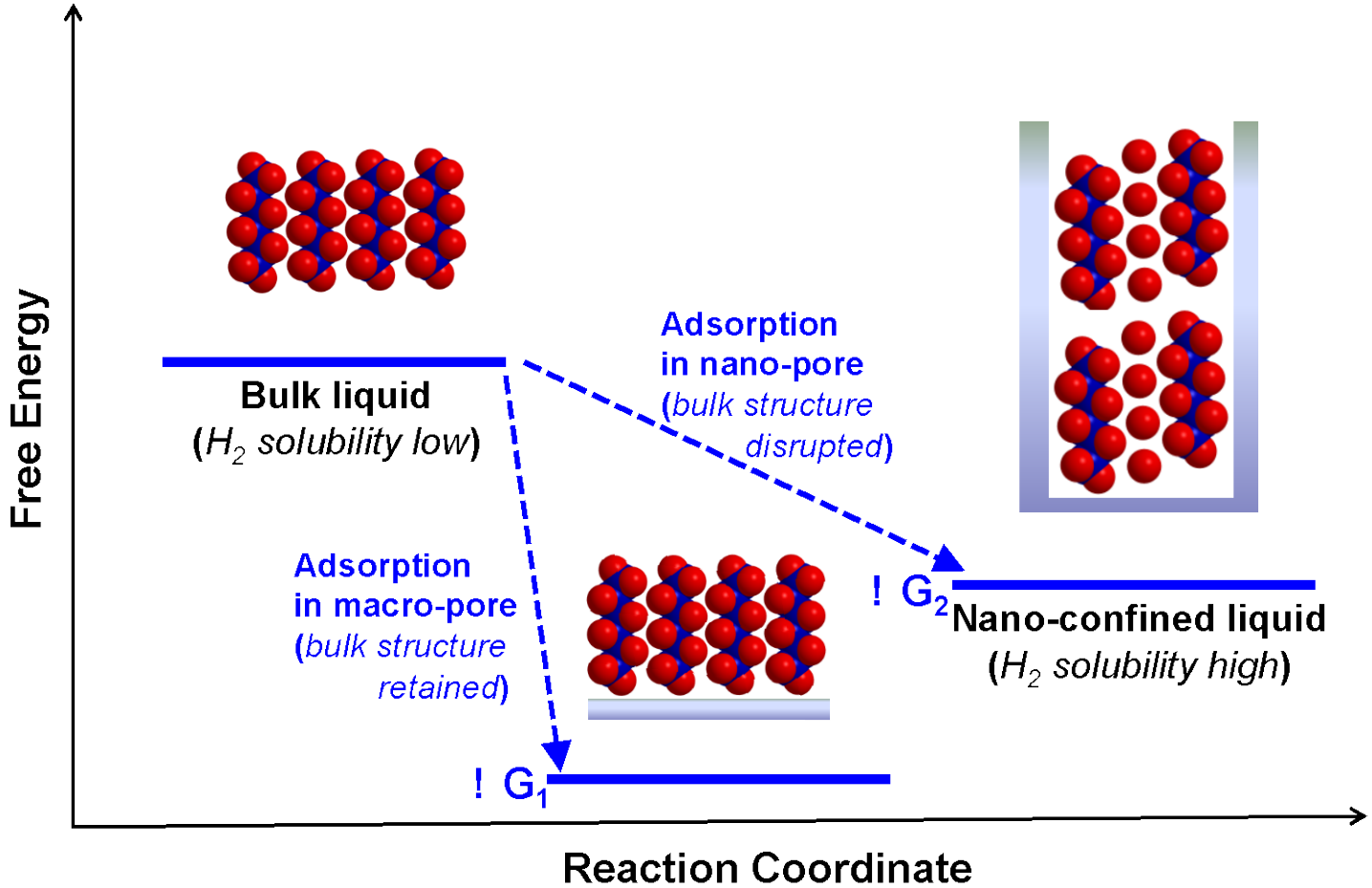
- **This approach has the potential to significantly improve the capacity of compressed hydrogen systems with minimal changes to vehicle engineering and delivery infrastructure, thus facilitating technology transition**

- **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**

# Technical Backup Slides

# Enhanced Solubility: Mechanism




- **Simulations to test mechanism**

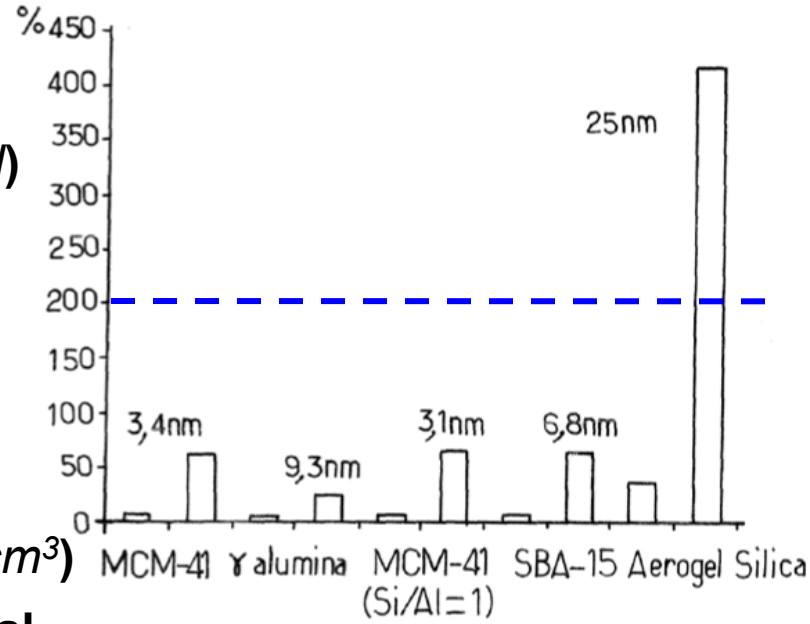
# Details of Asymptote Calculation

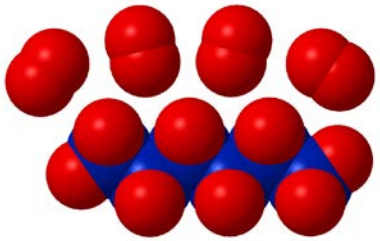
**What gravimetric and volumetric storage densities could be obtained?**

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** (*$\rho$ = 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**



# 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**