HYDROGEN STORAGE IN METAL-ORGANIC FRAMEWORKS

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Overview

Timeline
- Project start date: 5/1/2005
- Project end date: 4/30/2009

Budget
- Total project funding: DOE $1.6 M
- Funding received FY 05: $112 K
- Funding for FY 06: 150 K
- Funding for FY 07: 430 K

Barriers addressed
Technical barriers addressed:
- Improved gravimetric and volumetric density of hydrogen uptake
- Hydrogen capacity and fast kinetics at 77K
- Improved hydrogen binding energy
- Synthesis scale up of MOFs to cubic meters

Technical system targets by 2010:
- Gravimetric capacity: 6 wt% and 1.5 kWh/L; Volume capacity: 45gH/L; operating temperature: -30° to 45°C

Partners (depends on funding)
- Juergen Eckert (UCSB)
- Joe Hupp (NW)
- Randy Snurr (NW)
Objectives and important directions

A. DESIGING POROSITY
1) Increased binding energy
2) Increase surface area without increase of dead volume
3) Cycling and kinetics of hydrogen charge and discharge
4) Impact of open-metal sites on binding energy and uptake capacity
5) Impregnation with polymers and nano-particles of light metals

B. MOFs AS MOLECULAR FUEL TANKS
1) Scale up of favored MOFs
2) Transfer of samples to DOE for independent verification of data
3) Establish a standard for hydrogen storage measurements
Reticular chemistry is concerned with linking of molecular building blocks (organic molecules, inorganic clusters, dendrimers, peptides, proteins,...) into predetermined structures in which such units are repeated and are held together by strong bonds.
DESIGN OF POROSITY

- Control of the organic link’s functionality
- Variation in metal-oxide units’ size and composition
- Control of pore-metrics
- Exposition of metal-sites within the pores
- Strategies for achieving high surface areas
- Control of dead volume
H$_2$ Adsorption in Non-Catenated MOFs

Functionality has little impact on uptake

![Graph showing H$_2$ uptake vs. Pressure for IRMOF-1, IRMOF-2, IRMOF-3, IRMOF-6, and IRMOF-8.](image-url)
H$_2$ Adsorption in Non-Catenated MOFs

Functionality has little impact on uptake

![Graph showing H$_2$ uptake versus pressure for IRMOF-20, IRMOF-1, MOF-177, and IRMOF-18.](image)
**H₂ Adsorption in Catenated MOFs**

Catenation increases uptake by 40% relative to non-catenated.

![Graph showing H₂ uptake vs. pressure (Torr) for different MOFs: IRMOF-1, IRMOF-8, IRMOF-9, IRMOF-11, and IRMOF-13. Each MOF is represented by a different marker and line color. The graph includes molecular structures of IRMOF-9, IRMOF-11, IRMOF-13, IRMOF-1, and IRMOF-8.]
MOF-9: $\text{Tb}_2(\text{ADB})_3[(\text{CH}_3)_2\text{SO}]_4 \cdot 16[(\text{CH}_3)_2\text{SO}]$
Large Free Volume in Interpenetrating Networks: The role of Secondary Building Units

Cell edge: $a = d + l$
van der Waals Radius of SBU = $\delta / 2$
For $n$ frameworks to interpenetrate with centers of the SBUs aligned along the body diagonal:
$n(d + \delta) \leq \sqrt{3} a$ thus $n \leq \sqrt{3} (d + l) / (d + \delta)$

Volume of the cell = $(d + l)^3$
Volume occupied by SBUs / cell = $n(\pi / 6)d^3$
Volume of the linkers / cell = $3n(\pi r^2)l$
Free Volume = $(d + l)^3 - n(\pi / 6)d^3 - 3n(\pi r^2)l$
IRMOF-62: Design of highly catenated MOF with Pore size favored for hydrogen

MOF-5 like framework
Quadra-interpenetrating
Small channel can be seen along crystallographic c-axis (5.2 Å in diameter)
Utilization of “edge” (diyne link)

3.5 Zn(NO$_3$)$_2$•4H$_2$O
1 eq. Et$_3$N
DMF

P3212
$a = 31.114(1)$ Å, $c = 39.280(3)$ Å
Cell Volume: 32931.2(2) Å$^3$
$d = 0.691$ g cm$^{-3}$
OPEN METAL SITES

- Design within MOF frameworks
- Impact on uptake capacity
- Impact on adsorption energy
MOFs with open metal sites

(a) = (b) = (c) = (d)
$\text{Cu}_2(\text{ATC}) \cdot 6\text{H}_2\text{O}$

$\text{Cu}_2(\text{ATC})$

JACS 2001 (Banglin Chen)
H$_2$ Uptake by MOFs with Open-Metal Sites

Open metal sites increase uptake by 70%

![Graph showing H$_2$ uptake vs. pressure for different MOFs](image)
Hydrogen Adsorption Sites

- Inelastic neutron scattering (reported last review)
- X-ray single crystal structure on N2 and Ar
- Single crystal neutron diffraction
Single crystal X-ray diffraction at 30 K for Ar guest
Data collected on VIVALDI (ILL) on 0.5 mm$^3$ crystal sealed under D$_2$
Appearance of D$_2$ on $\alpha$(CO$_2$)$_3$ site at 50 K, additional D$_2$ appears on $\beta$(ZnO)$_3$ at 5 K

Relationship of surface area to hydrogen uptake and reversibility of uptake

- Design of surfaces replete with adsorption sites

- Can high surface area and reduced dead volume (i.e. good volumetric capacity) be achieved in one material?

- Uptake capacities of MOFs under high pressure conditions and 77K

- 4. Reversibility of uptake
N$_2$ adsorption isotherm for Zn$_4$O(BTB)$_2$

Surface area = 4,500 m$^2$/g  
(5,500 m$^2$/g)

Pore volume = 1.59 cm$^3$/g  
(0.69 cm$^3$/cm$^3$)

Amount sorbed (mg/g)

N$_2$ sorption
N$_2$ desorption
MOF-200:
Zn_4O(BBC)_2
Trigonal, P-3
a = b = 51.45 Å
c = 41.80 Å
V = 95,822.1 Å³
S.A. = ‘8,000’ m²/g
7.5 wt % Hydrogen uptake at 77K
MOF volumetric H₂ uptake at 77 K

Volumetric Uptake (g/L) vs. Pressure (bar) for various MOFs:
- IRMOF-20
- MOF-177
- IRMOF-6
- IRMOF-1
- MOF-74
- HKUST-1
- IRMOF-11
Correlation of uptake with surface area

- MOF-74
- HKUST-1
- IRMOF-11
- IRMOF-6
- IRMOF-1
- IRMOF-20
- MOF-177

Uptake (mg/g) vs. Surface Area (m²/g)
Isosteric Heats of Adsorption

MOFs combining open metal sites with 7-8 Angstroms pore size are most favored

![Graph showing isosteric heats of adsorption for different MOFs](image)
H₂ Adsorption (high-P)

Poor room temperature uptake

<table>
<thead>
<tr>
<th>Temperature</th>
<th>wt%</th>
<th>mg/g</th>
<th>mmol/g</th>
<th>cc/g</th>
<th>cc/cc</th>
<th>g/L</th>
</tr>
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<tbody>
<tr>
<td>77 K</td>
<td>3.3</td>
<td>33</td>
<td>16.5</td>
<td>370</td>
<td>327</td>
<td>29.2</td>
</tr>
<tr>
<td>298 K</td>
<td>0.4</td>
<td>4</td>
<td>2</td>
<td>45</td>
<td>40</td>
<td>3.5</td>
</tr>
</tbody>
</table>
Kinetic Profile of Uptake and Release of hydrogen

(Fueling Time)
Completely Reversible Charge/Discharge of Hydrogen Adsorption in IRMOF-11

Fueling time 2.5 minutes
Typical IRMOF-62 kinetic profile (Fueling time 2 minutes)

Blue: applied pressure, red: weight change (without buoyancy correction)
Independent Verification of MOF-177 Hydrogen Uptake Capacity
(volumetric and gravimetric measurements verified, shown using gravimetric scale)
Volumetric H$_2$ uptake for IRMOF-62

IRMOF-62  Surface area: 2650 m$^2$/g, Pore volume: 0.95 cm$^3$/g
MOF
Hydrogen Storage Capacities (50 bar, 77K)

$g \frac{H_2}{L_{system}}$

- Al: 23 (2002)
- Zn: 42 (2005)
- Mn: 23 (2006)
- H$_2$, liq (1 bar, 20K)
- H$_2$, gas (700 bar, 298K)
- NaX
- H$_2$, gas (350 bar, 298K)
Nanocubes as molecular fuel tanks
BASOCUBES
Strategies for increasing adsorption energy

- Coordination with theory (Prof. Bill Goddard, Caltech)
- Impregnation strategies: (a) polar polymers, (b) clusters of light metals, and organo-metallic complexes
- Design of soft chemi-sorption within the pores: Proximal Lewis acid-Lewis base sites
Strategy 1:

Binding Li to six membered rings
High room temperature hydrogen uptake (5%wt) in Li-doped Zn-MOF systems

Predictions (Han and Goddard, Caltech)

At 300 K

Triangle: pure MOFs, Star: Li-doped MOFs
Cyan: MOF6, Blue: MOF10, Green: MOF16, Red: MOF22, Black: MOF30
Strategy 2A:

Impregnation with metal complexes having open metal sites
Proof of Concept
Successful Impregnation of CpW(CO)3 in MOF-5
Carbonyl groups can be removed by heating under vacuum, leaving behind open metal sites of W.
Strategy 2B:

Impregnation with polymers containing conjugation
Polymer impregnation MOF-177

1,4-Diphenylbutadiyne

Polymerization of monomer in MOF-177
Impregnation

Polydiphenyl-butadiyne (PDPB)

C≡C stretching

MOF-177 + PDPB

A. Single crystal of PDPB
B. MOF-177 + PDPB
C. Sliced MOF-177 + PDPB
Strategy 3:

Chemisorption *douce*
Fully Reversible Splitting of H₂

Heating to >100° C quantitatively reverses H₂ dissociation with change in color.

Reversible, Metal-Free Hydrogen Activation

Gregory C. Welch, Ronan R. San Juan, Jason D. Masuda, Douglas W. Stephan*

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Covalent Organic Frameworks (COFs)

3 boronic acid → -3 H₂O → boroxine anhydride

diboronic acid BDBA → -H₂O → COF-1
3 boronic acid + hexahydroxy triphenylene (HHTP) → triboronate ester

diboronic acid (BDDA) + hexahydroxy triphenylene (HHTP) → COF-5

27 Å
A: TBPM
B: TBPS
C: HHTP
D: $B_3O_3$ ring
E: $C_2O_2B$ ring
COF-108: Density = 0.17 g/cm³
Surface area = 4,700 m²/g

Science 2007
It’s all in the angle (145°)

1

M - IM - M

145°

2

Si - O - Si

145°
ZIF-8 sod
Thermal stability of ZIFs
Chemical stability of ZIF-8
(c) 7 days (Boiling H₂O)
5 days (Boiling H₂O)
3 days (Boiling H₂O)
1 day (Boiling H₂O)
As Prepared

2θ (degrees)
Trigonal Zn metal site next to Z-F bond both pointing to the center of pore
PROGRESS

1. Tuning porosity lead to tripling of hydrogen uptake in MOFs (excess 7.5% wt, absolute 12% wt)
2. The 35 grams H2/L achieved in MOF-177, clearly indicates that dead volume is none issue for MOFs
3. MOFs exhibit fast kinetics (1-3 minutes for charging and discharging)
4. MOF materials porosity and uptake are stable to charge/discharge cycling
5. Cubic meter scale of useful MOFs is now developed by BASF
FUTURE WORK

1. Higher adsorption energy by:
   (a) Design of Lewis-acid and Lewis-base sites
   (b) Doping with Li and impregnation with early T.M. complexes
   (c) Acetylene MOFs for high surface areas and stronger binding of hydrogen

2. Application of high throughput and characterization methods to search for specific structures

3. Testing new materials:
   (a) Zeolite imidazolate Frameworks (ZIFs)
   (b) Covalent organic frameworks (COFs)
Current Group Members

Thanks for putting up with Professor

Dr. C. Knobler  Dr. A. Côté  Dr. N. Aratani  Dr. R. Banerjee  D. Britt  E. Choi  L. Dudek  S. Duhovic

Dr. H. El-Kaderi  Dr. O. El-Kaderi  Dr. H. Furukawa  Dr. H. Hayashi  J. R. Hunt  Q. Li  J. Mendoza-Cortés  K. Park

Dr. Z. Ni  Dr. B. Ramachandran  Dr. Q. Wei  A. Phan  I. E. Rauda  D. Tranchemontagne  F. Uribe-Romo  B. Wang