Gas Adsorption in Metal Organic Frameworks: an experiment using the NCNR Disk Chopper Spectrometer

Craig Brown, John Copley, and Yiming Qiu

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Overview

• **Issues** with Energy Storage:
  – The how and the why.

• **Applications** of Neutron Scattering
  – Locations of molecules
  – Dynamics/binding strengths

• **Outlook** for this experiment

• **Conclusion**

Overview  Issues  Application  Outlook  Conclusion
Why?

Why alternative fuels?

- Reduce dependence on foreign oil
- New opportunities for agriculture
- Reduce transportation costs
- Harness renewable energy sources
- Clean air in cities
- Reduce greenhouse gas emissions

What are alternative fuels?

- Ethanol (from corn, wood, …)
- Natural gas; 85% of NG used in U.S. is domestic (NG; from domestic gas/oil fields, deep-sea methane hydrate fields, landfills, biomass)
- Biodiesel (from soybeans, vegetable oils, …)
- Hydrogen (from NG, water & electricity, coal, …)
- Electricity (from nuclear/hydroelectric/solar/wind power plants)
Why?

Current natural-gas vehicles

• Low emission of
  – hydrocarbons (ozone, smog)
  – NO\textsubscript{x}
  – particulate matter
  – Up to 40% reduction of CO\textsubscript{2}

• Clean Cities Coalitions:
  – Los Angeles: 1500 CNG buses
  – Kansas City: 200 CNG public utility vehicles
  – U.S.: 130,000 CNG vehicles
  – worldwide: over 5 million CNG vehicles

Alternative fuel systems (BAF Tech.)

In 2006, Gasoline was $2.84 per gallon, diesel was $2.98 per gallon, and CNG was $1.90 per gasoline gallon equivalent!

http://www.eere.energy.gov/afdc/resources/pricereport/price_report.html
Fuel Storage
Compressed natural gas (CNG) is stored on board vehicles at high-pressure (3,000 psi)

Liquefied natural gas (LNG) must be cooled to −162 °C.
LNG requires only 30 percent of the space of CNG to store the same amount of energy.

Why?
Why?

$1.2 Billion to develop the technology needed for commercially viable hydrogen-powered fuel cells (2003)
However:

$\text{H}_2$ has 3x energy content by **MASS** c.f. gasoline

Gasoline has 4x energy content by **VOLUME** c.f. $\text{H}_2$

Targets

Methane

180 (cc CH\textsubscript{4})/cc 35bar (500 psi)/25K

-achieved using carbonized corncobs
  (Pfeifer, University of Missouri, 2007)

-IRMOF-6 155 cc/cc
  (Eddaoudi, Science 2002)

-IRMOF-1 ~115 cc/cc
  (Zhou, in prep.)

Hydrogen

<table>
<thead>
<tr>
<th>Parameter</th>
<th>'07</th>
<th>'10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy\textsubscript{(system)} (wt%)</td>
<td>4.5</td>
<td>6</td>
</tr>
<tr>
<td>Volumetric (g/L)</td>
<td>36</td>
<td>45</td>
</tr>
<tr>
<td>Fuel cost ($ per gge)</td>
<td>3</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Reversible, safe …

gge: gallon gasoline equivalent

Gravimetric and volumetric of best MOFs @77K
~7 wt\%, ~36g/L (e.g. Dinca, JACS, 2006) – NOT SYSTEM
Hydrogen Storage in MOFs

MOF-5 (IRMOF-1) can adsorb ~10 wt% H₂ (<10 K)

(Wong-Foy et al. JACS 128, 3494 (2006))

(Yildirim et al. PRL 95, 215504 (2005))
## Hydrogen Adsorption Enthalpy

<table>
<thead>
<tr>
<th>Material</th>
<th>Enthalpy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HKUST-1</td>
<td>~6.6</td>
</tr>
<tr>
<td>Prussian blue analogue</td>
<td>~7.4</td>
</tr>
<tr>
<td>MOF-74</td>
<td>~8.3</td>
</tr>
<tr>
<td>Zn$_3$(1,4-benzeneditetrazolate)$_3$</td>
<td>~8.7</td>
</tr>
<tr>
<td>IRMOF-11</td>
<td>~9.1</td>
</tr>
<tr>
<td>Cu$_{1.5}$[(Cu$_4$Cl)$_3$BTT$_8$]</td>
<td>~9.4</td>
</tr>
<tr>
<td>PCN-9</td>
<td>~10.1</td>
</tr>
<tr>
<td>Mn$_{1.5}$[(Mn$_4$Cl)$_3$BTT$_8$]</td>
<td>~10.1</td>
</tr>
</tbody>
</table>

~15 kJ/mol would be ideal for hydrogen storage material working at room temperature.  

Reference:
The Cu atoms in the fully dehydrated phase are coordinatively unsaturated.

- Desolvated crystals exhibit:
  - Total H₂ uptake of ~3 wt % at 77 K and 90 bar
  - At 27 g H₂/L provides a storage density <40% of that of liquid H₂
  - A maximum isosteric heat of adsorption of 6.6 kJ/mol

Chui, Science, 283, 1148 1999
Roswell, JACS, 128, 1304 2006
Wong-Foy, JACS., 128, 3494 2006
Metal Interactions

Isotherms at 77 K for H₂ in HKUST-1

HKUST-1, Cu₃(BTC)₂

- \( A_{Lang} \) = 2175 m²/g
- \( A_{BET} \) = 1507 m²/g
- \( V_p \) = 66%

Roswell, JACS, 2006, 128, 1304*
Metal Interactions
Diffraction patterns for D₂ in HKUST-1

Metal Interactions

Fourier Difference to locate $D_2$ in HKUST-1
Framework and DFT

Bare HKUST-1 Spectroscopy

Energy (meV)

Neutron Intensity (arb. units)

- LDA Cal. Bare HKUST
- FANS Cu
- FANS PG

unpublished

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Framework and DFT
Bare HKUST-1 Spectroscopy

6.2 meV = 50 cm⁻¹

unpublished
Framework and DFT
Bare HKUST-1 Spectroscopy

Neutron Intensity (arb. units)

Energy (meV)

LDA Cal. Bare HKUST
FANS Cu
FANS PG

unpublished

Overview Issues Application Outlook Conclusion
Para has a nuclear spin $I=0$. This constrains $J$ to be even.

Ortho has a nuclear spin $I=1$. This constrains $J$ to be odd.

Transition between ortho and para species can occur through flipping the nuclear spin.

\[ E_J = B J(J+1), \quad B_{\text{H}_2}=7.35 \text{ meV} \]
TOF spectroscopy
Disc Chopper Spectrometer

(1) The neutron guide

(2) The choppers

(3) The sample area

(4) The flight chamber and the detectors
Total Scattering

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Elastic peak
Quasielastic
Inelastic

$w_0$
Metal Interactions

HKUST-1 2 p-H2:Cu 1.81Å T=4K

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Metal Interactions

DCS

\[ I(Q) \propto e^{-Q^2 \langle u^2 \rangle^{1/3}} j_1(\frac{d_{HH} Q}{2})^2 \]

\[ j_1(x) = \frac{\sin x}{x^2} - \frac{\cos x}{x} \]

Overview

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The transition tells us about the symmetry and strength of the local potential. A larger rotational barrier implies a stronger binding.
Metal Interactions

Extract Intensity as fn of loading...

Hydrogen adsorption is complicated!
Do not load just the strongest adsorption sites in order

\[ \text{Counts} \]

\[ \text{H}_2/\text{Cu} \]

Liu et. al, J. Alloys Compounds
Outlook

• Experience Practical TOF spectroscopy
  – sample choice
  – geometry consideration
• Learn something about the instrument
  – Wavelength / Resolution / Intensity
• Data Reduction
• Data Analysis and Interpretation
  – Tunneling spectroscopy
  – Quasi-elastic spectroscopy
  • spatial and temporal information
The maximal excess adsorption capacity of CH₄ in MOF-5 is 51.7 wt%, or 24 CH₄ per MOF-5 formula (i.e., 4Zn). This is reduced to ~15 wt% (115 cc/cc) at room temperature, 35bar.

The excess isosteric heat of adsorption (calculated using the Clausius-Clapeyron equation) for the initial CH₄ adsorption in MOF-5 is ~12.2 KJ/mol. At high concentration, Qst increases with increasing amount adsorbed, indicating the importance of the interactions between adsorbed CH₄ molecules.

(Zhou, in prep.)
Where are the methane molecules?

The adsorption sites were directly determined from the difference-Fourier analysis of neutron powder diffraction data. Initial adsorption occurs at the MOF5 “cup site” with a well defined CH₄ orientation. We did not see any well-defined sites for additional adsorption.

The neutron powder diffraction pattern of MOF-5:4CD₄ at 4 K with the Rietveld refinement.

(Zhou, in prep.)
Where are the methane molecules?

The isosurface of the difference-Fourier (DF) neutron scattering-length density superimposed with the ZnO₄ clusters of the MOF-5 host structure, indicating the location of the first methane adsorption sites. This is a “direct measurement” (like taking a picture) of the methane molecules packed in the solid with a well defined orientation.

T-dependent neutron scattering is further used to visualize the methane orientational dynamics with increasing temperature.

(Zhou, in prep.)
Types of Experiments

- Translational and rotational diffusion processes, where scattering experiments provide information about time scales, length scales and geometrical constraints; the ability to access a wide range of wave vector transfers, with good energy resolution, is key to the success of such investigations.
- Low energy vibrational and magnetic excitations and densities of states.
- Tunneling phenomena.

- **Chemistry** --- e.g. clathrates, molecular crystals, fullerenes
- **Polymers** --- bound polymers, glass phenomenon, confinement effects
- **Biological systems** --- protein folding, protein preservation, water dynamics in membranes.
- **Physics** --- adsorbate dynamics in mesoporous systems (zeolites and clays) and in confined geometries, metal-hydrogen systems, glasses, magnetic systems.
- **Materials** --- negative thermal expansion materials, low conductivity materials, thermo-electrics, hydration of cement, carbon nanotubes, proton conductors, metal hydrides.
Conclusions

• Neutrons can tell us where atoms are located.

• Neutrons can tell us how a lattice vibrates—very sensitive to the local potential

• Neutrons can tell us adsorbate-framework interaction strengths