Hydrogen Storage via Physisorption

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# US DoE 2010 Hydrogen Storage Targets

<table>
<thead>
<tr>
<th>Property</th>
<th>Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravimetric capacity</td>
<td>6 wt. % H₂</td>
</tr>
<tr>
<td>Volumetric capacity</td>
<td>45 g H₂/L</td>
</tr>
<tr>
<td>Operating temperature</td>
<td>-30 to 50 °C</td>
</tr>
<tr>
<td>Maximum pressure</td>
<td>100 bar</td>
</tr>
<tr>
<td>Refueling rate</td>
<td>1.67 kg H₂/min</td>
</tr>
<tr>
<td>Cycle life</td>
<td>1000 cycles</td>
</tr>
<tr>
<td>Cost</td>
<td>$133 per kg H₂</td>
</tr>
</tbody>
</table>

Physisorption of H₂:
Adsorption via van der Waals Interactions

typically:
\[ \Delta H_{ads} = 4-6 \text{ kJ/mol} \]

- Weak bonding of H₂ to solid surface through either dipole/induced-dipole or induced-dipole/induced-dipole interactions

- Need a high surface area:solid mass ratio to achieve a high gravimetric capacity
Optimum Pore Sizes

77 K

- Calculated using Monte Carlo simulations with both cylindrical and slit pores

298 K

H₂ Storage in Microporous Forms of Carbon

**Activated Carbon**

AX-21: $SA_{BET} = 2800 \text{ m}^2/\text{g}$, 4.9 excess wt % at 30 bar and 77 K


**Carbide-Derived Carbon**

TiC-CDC: $SA_{BET} = 1800 \text{ m}^2/\text{g}$, 3.0 wt % at 1 bar and 77 K


**Zeolite-Templated Carbon**

From zeolite $\beta$: $SA_{BET} = 3200 \text{ m}^2/\text{g}$, 6.9 wt % at 20 bar and 77 K


**Carbon Nanotubes**

HF treated SWNT: $SA_{BET} = 1555 \text{ m}^2/\text{g}$, 4.6 excess wt % at 77 K

Bénard, Chahine *Scripta Mater.* 2007, 56, 803
H₂ Storage in a Metal-Organic Framework

Zn₄O(1,3,5-benzenetribenzoate)₂ (MOF-177)

- Record BET surface area = 4750 m²/g
- Framework density = 0.427 g/cm³
- Pore diameter ~17 Å
- Volumetric storage = 48 g/L

Wong-Foy, Matzger, Yaghi J. Am. Chem. Soc. 2006, 128, 3494
Isosteric Enthalpy of H₂ Adsorption in Zn₄O(BDC)₃

Sorption isotherms can be fit using the Langmuir-Freundlich equation:

\[
\frac{Q}{Q_{\text{sat}}} = \frac{B \cdot P^{(1/t)}}{1 + B \cdot P^{(1/t)}}
\]

where:
- \(Q\) = moles adsorbed
- \(Q_{\text{sat}}\) = moles adsorbed at saturation
- \(P\) = pressure
- \(B\) and \(t\) = fit constants

The binding enthalpy associated with a given quantity of H₂ adsorbed can then be determined using a variant of the Clausius-Clapeyron equation:

\[
\ln \left( \frac{P_1}{P_2} \right) = \Delta H \cdot \frac{T_2 - T_1}{R \cdot T_1 \cdot T_2}
\]

where:
- \(P_n\) = pressure for isotherm \(n\)
- \(T_n\) = temperature for isotherm \(n\)
- \(R = 8.315 \text{ J/K/mol}\)

Generating Open Metal Adsorption Sites

\[
\begin{align*}
\text{M (CO)}_4 & \xrightarrow{\Delta/\text{hv}} \\
\text{M} & \\
\text{M (H}_2)_4
\end{align*}
\]
H₂ Adsorption Enthalpies at Metal Centers

\[ MH_2 \rightleftharpoons M + H_2 \quad \Delta H \]

- Naively, one would like to achieve saturation of the material at 298 K and 1 atm
- Assuming no activation barrier for H₂ uptake and release, and a standard H₂ formation entropy of \( S^\circ = 130.68 \text{ J/mol} \cdot \text{K} \), then at equilibrium:

\[ \Delta H = T \Delta S^\circ \]
\[ = 38.9 \text{ kJ/mol} \]

- This enthalpy is highly variable, depending on choices of metal center and additional ligands

<table>
<thead>
<tr>
<th>M</th>
<th>( \Delta H ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺(g)</td>
<td>27</td>
</tr>
<tr>
<td>Na⁺(g)</td>
<td>10</td>
</tr>
<tr>
<td>K⁺(g)</td>
<td>6</td>
</tr>
<tr>
<td>Ti⁺(g)</td>
<td>37</td>
</tr>
<tr>
<td>Cu⁺ in chabazite</td>
<td>56</td>
</tr>
<tr>
<td>CuCl surface</td>
<td>93</td>
</tr>
<tr>
<td>Cr(CO)₅</td>
<td>78</td>
</tr>
<tr>
<td>Mo(CO)₅</td>
<td>81</td>
</tr>
<tr>
<td>Cr(CO)₃(PCy₃)₃</td>
<td>31</td>
</tr>
<tr>
<td>Mo(CO)₃(PCy₃)₃</td>
<td>27</td>
</tr>
<tr>
<td>W(CO)₃(PCy₃)₃</td>
<td>42</td>
</tr>
<tr>
<td>OsH₂(CO)(P^3Pr₃)₂</td>
<td>82</td>
</tr>
</tbody>
</table>
Optimum Enthalpy for $\text{H}_2$ Storage at 298 K

Applying the Langmuir model:

$$\Delta H^\circ_{\text{opt}} = T\Delta S^\circ + \frac{RT}{2} \ln \left( \frac{P_{\text{min}} P_{\text{max}}}{P_0^2} \right)$$

where: $\Delta S^\circ = -8R$
- $P_{\text{min}} = 1.5 \text{ bar}$
- $P_0 = \text{standard pressure} = 1 \text{ bar}$
- $R = 8.315 \text{ J/K\cdotmol}$

- Fuel cells typically operate at a minimum pressure of $P_{\text{min}} = 1.5 \text{ bar}$
- For a constant temperature process, maximum delivery of $\text{H}_2$ is 63.5% of total storage capacity
- More complex adsorption models do not result in significantly different optimum enthalpies

Bhatia, Myers *Langmuir* 2006, 22, 1688
A Tetrazolate-Bridged Framework with Exposed Mn$^{2+}$ Sites

- Volumetric storage at 90 bar and 77 K is 60 g/L (85% density of liquid H$_2$ at 21 K)
- Volumetric storage at 90 bar and 298 K is 50% greater than in an empty cylinder

Hydrogen Storage at 298 K

- Expect that approximately twice as much \( \text{H}_2 \) can be stored at the usual loading pressure of 120 bar.
Increased $\text{H}_2$ Adsorption Enthalpy at Exposed Metals

- Binding enthalpies at low loading are now as high as 10 kJ/mol
- Exposed $\text{Mn}^{2+}$ coordination sites are only a small weight fraction of available sites
- Attempts to replace $\text{Mn}^{2+}$ with stronger-binding cations (e.g. $\text{Cu}^+$) are underway
Locating $D_2$ Adsorption Sites by Neutron Diffraction

- Strongest $D_2$ binding occurs at sites I ($\text{Mn-}D_2 = 2.2 \text{ Å}$) and II ($\text{Cl} \cdots D_2 = 3.5 \text{ Å}$)
- First direct observation of metal-$D_2$ interaction in a metal-organic framework

Locating D₂ Adsorption Sites by Neutron Diffraction

- Strongest D₂ binding occurs at sites I (Mn-D₂ = 2.2 Å) and II (Cl···D₂ = 3.5 Å)
- First direct observation of metal-D₂ interaction in a metal-organic framework

A Copper(II)-Containing Sodalite Framework

\[
\text{CuCl}_2 + \text{H}_3\text{BTT} \xrightarrow{70 \degree C, \text{DMF/MeOH}} \text{HCu}_2[(\text{Cu}_4\text{Cl})_3(\text{BTT})_8]\cdot3.5\text{HCl}\cdot12\text{DMF}\cdot24\text{H}_2\text{O}\cdot16\text{MeOH}
\]

- Washing with methanol and heating under dynamic vacuum gives **fully desolvated** material

Comparison of H₂ Adsorption Enthalpies

- H₂ storage capacity for Cu phase is similar to that of Mn analogue
- Enthalpy increase of ca. 1 kJ/mol is apparent for higher H₂ loadings

Dinca, Han, Liu, Brown, Dailly, Long Angew. Chem. Int. Ed. 2007, 46, 1419
D₂ Adsorption in Cu-BTT Framework

- Strongest D₂ binding occurs at sites I (Cu-D₂ = 2.5 Å) and II (Cl···D₂ = 3.5 Å)
- Metal-D₂ interactions weakened owing to Jahn-Teller effect of Cu⁺⁺

Dinca, Han, Liu, Brown, Dailly, Long Angew. Chem. Int. Ed. 2007, 46, 1419