

Hydrogen Storage via Physisorption

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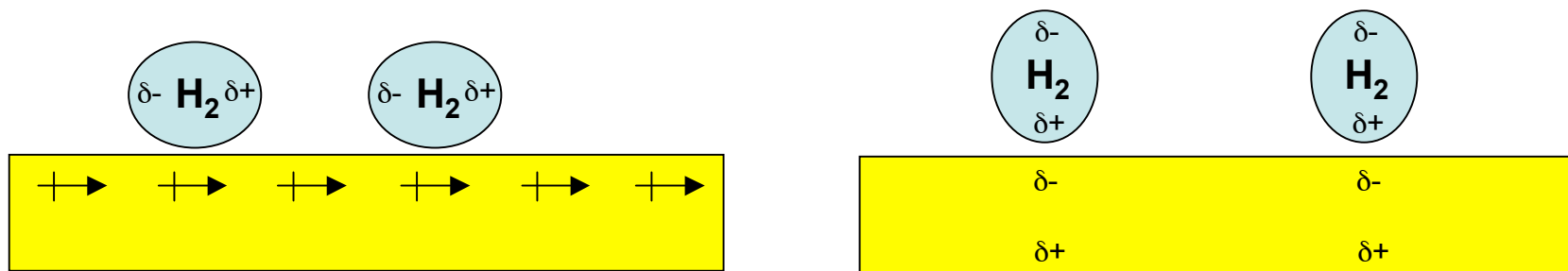
US DoE 2010 Hydrogen Storage Targets

gravimetric capacity	6 wt. % H₂
volumetric capacity	45 g H₂/L
operating temperature	-30 to 50 °C
maximum pressure	100 bar
refueling rate	1.67 kg H₂/min
cycle life	1000 cycles
cost	\$133 per kg H₂

Physisorption of H₂: Adsorption via van der Waals Interactions

typically:

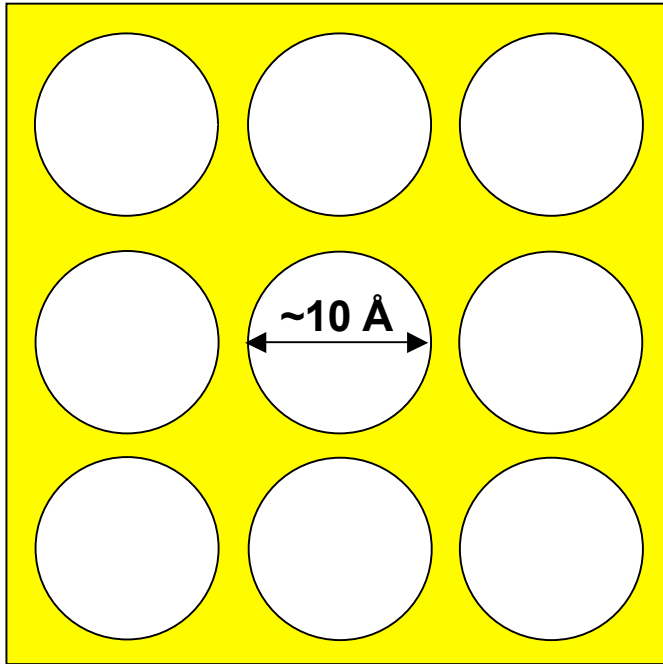
$$\Delta H_{\text{ads}} = 4\text{-}6 \text{ kJ/mol}$$



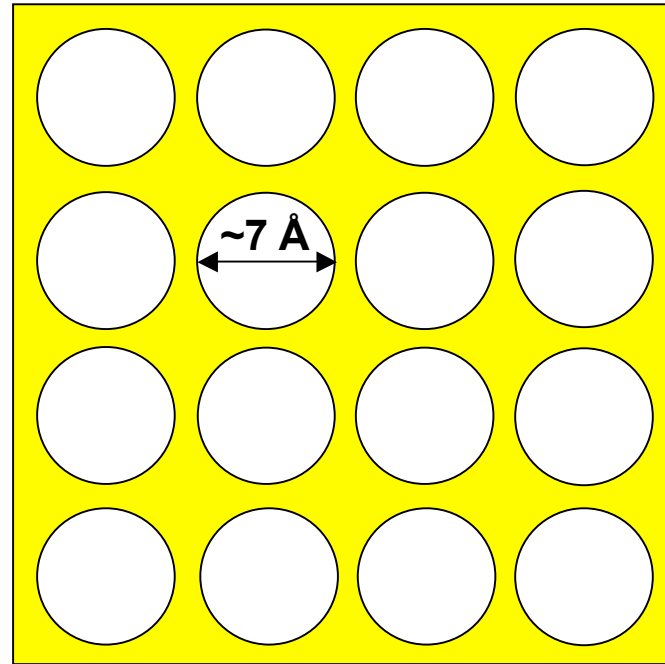
- Weak bonding of H₂ to solid surface through either dipole/induced-dipole or induced-dipole/induced-dipole interactions
- Need a high surface area:solid mass ratio to achieve a high gravimetric capacity

Optimum Pore Sizes

77 K



298 K



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

H₂ Storage in Microporous Forms of Carbon

Activated Carbon

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

Bénard, Chahine *Langmuir* **2001**, *17*, 1950

Carbide-Derived Carbon

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

Gogotsi, Dash, Yushin, Yildirim, Laudisio, Fischer *J. Am. Chem. Soc.* **2005**, *127*, 16006

Zeolite-Templated Carbon

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

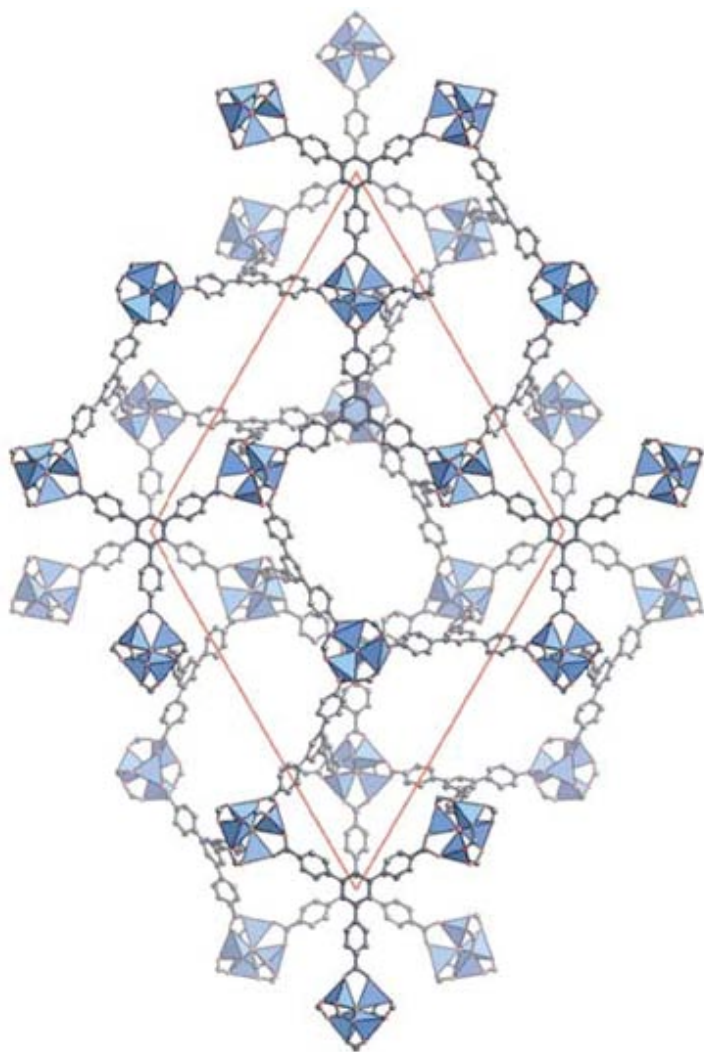
Yang, Xia, Mokaya *J. Am. Chem. Soc.* **2007**, *129*, 1673

Carbon Nanotubes

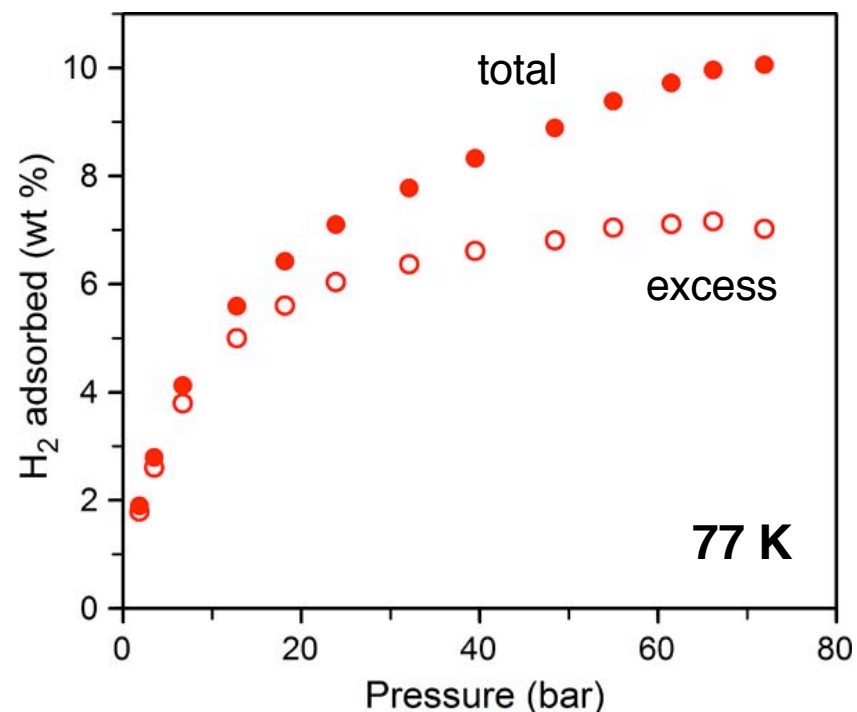
HF treated SWNT: $SA_{\text{BET}} = 1555 \text{ m}^2/\text{g}$, 4.6 excess wt % at 77 K

Bénard, Chahine *Scripta Mater.* **2007**, *56*, 803

H₂ Storage in a Metal-Organic Framework

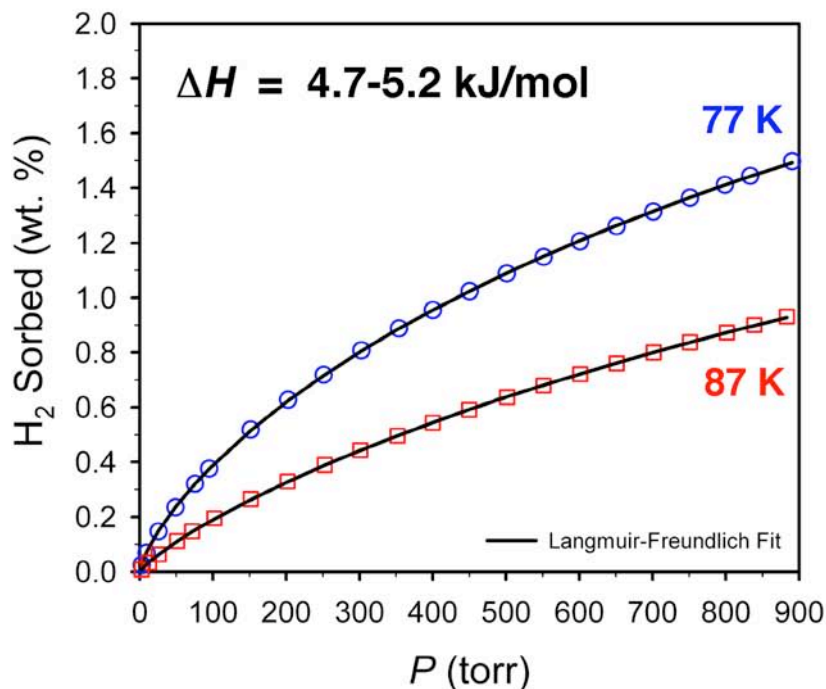


Zn₄O(1,3,5-benzenetricarboxylate)₂
(MOF-177)



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

Isosteric Enthalpy of H₂ Adsorption in Zn₄O(BDC)₃



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

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

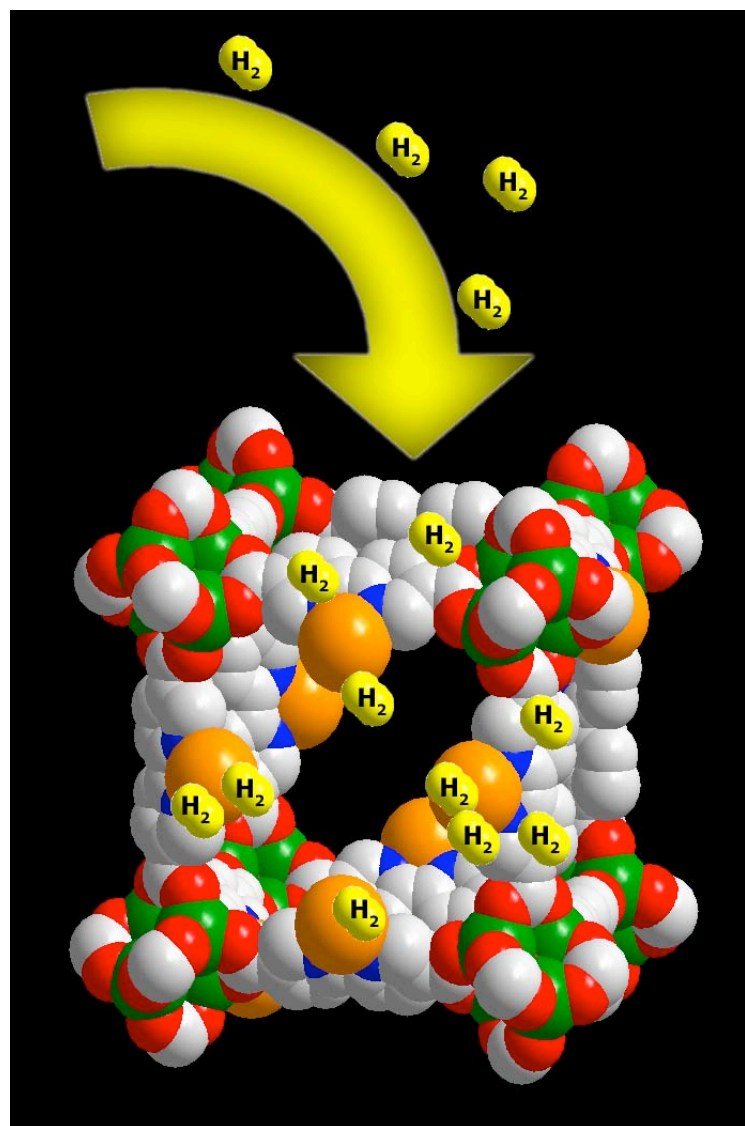
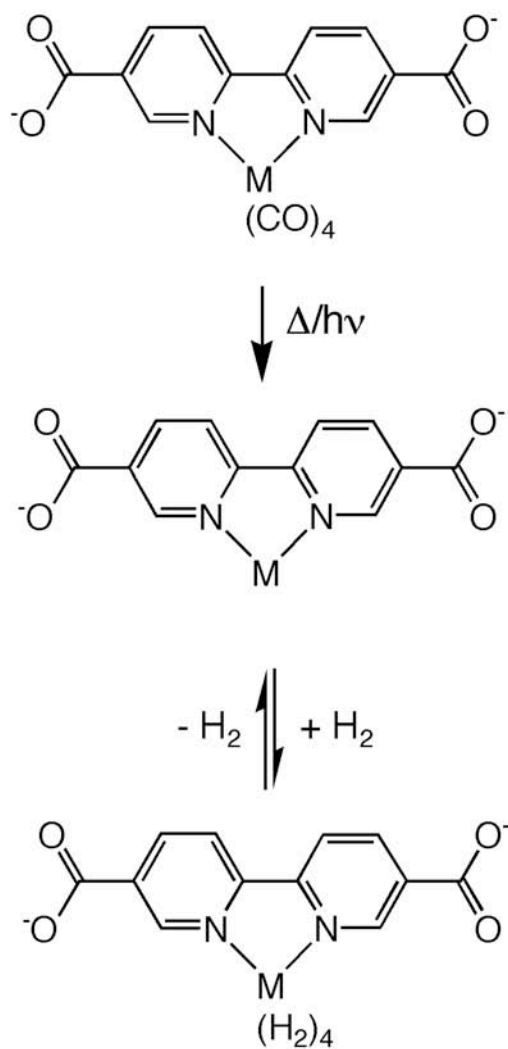
where: Q = moles adsorbed
 Q_{sat} = moles adsorbed at saturation
 P = pressure
 B and t = fit constants

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
 $R = 8.315 \text{ J/K}\cdot\text{mol}$

Generating Open Metal Adsorption Sites



H₂ Adsorption Enthalpies at Metal Centers



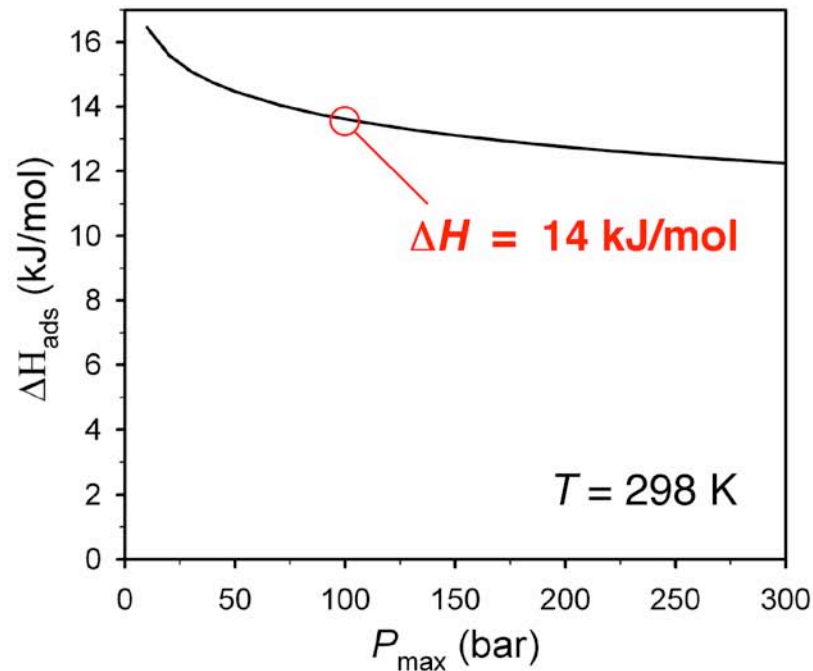
- Naively, one would like to achieve saturation of the material at 298 K and 1 atm
- Assuming no activation barrier for H₂ uptake and release, and a standard H₂ formation entropy of $S^\circ = 130.68 \text{ J/mol}\cdot\text{K}$, then at equilibrium:

$$\begin{aligned} \Delta H &= T\Delta S^\circ \\ &= \mathbf{38.9 \text{ kJ/mol}} \end{aligned}$$

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

M	ΔH (kJ/mol)
Li ⁺ (g)	27
Na ⁺ (g)	10
K ⁺ (g)	6
Ti ⁺ (g)	37
Cu ⁺ in chabazite	56
CuCl surface	93
Cr(CO) ₅	78
Mo(CO) ₅	81
Cr(CO) ₃ (PCy ₃) ₃	31
Mo(CO) ₃ (PCy ₃) ₃	27
W(CO) ₃ (PCy ₃) ₃	42
OsH ₂ (CO)(P ⁱ Pr ₃) ₂	82

Optimum Enthalpy for H₂ 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: $\Delta S^{\circ} = -8R$

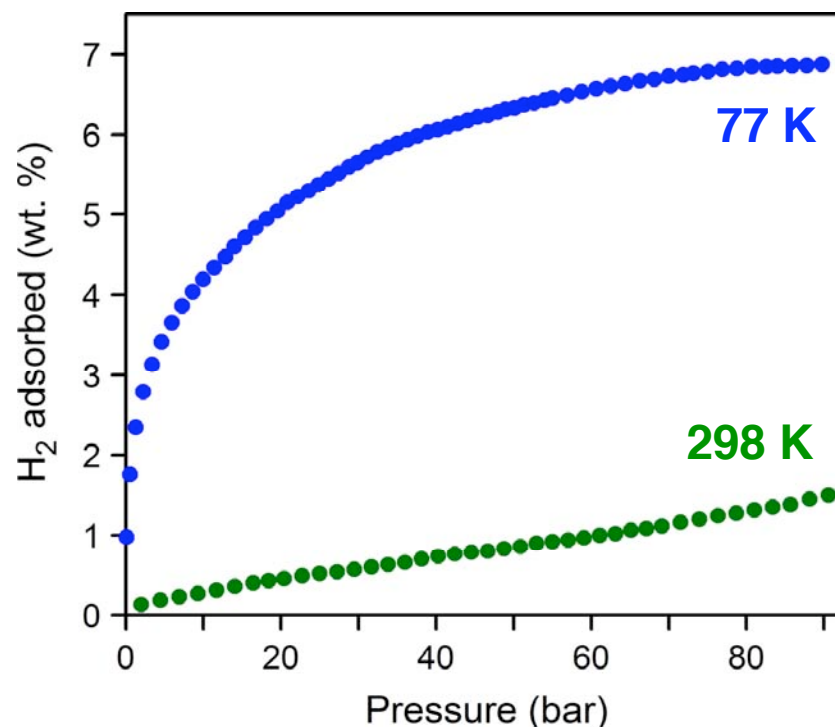
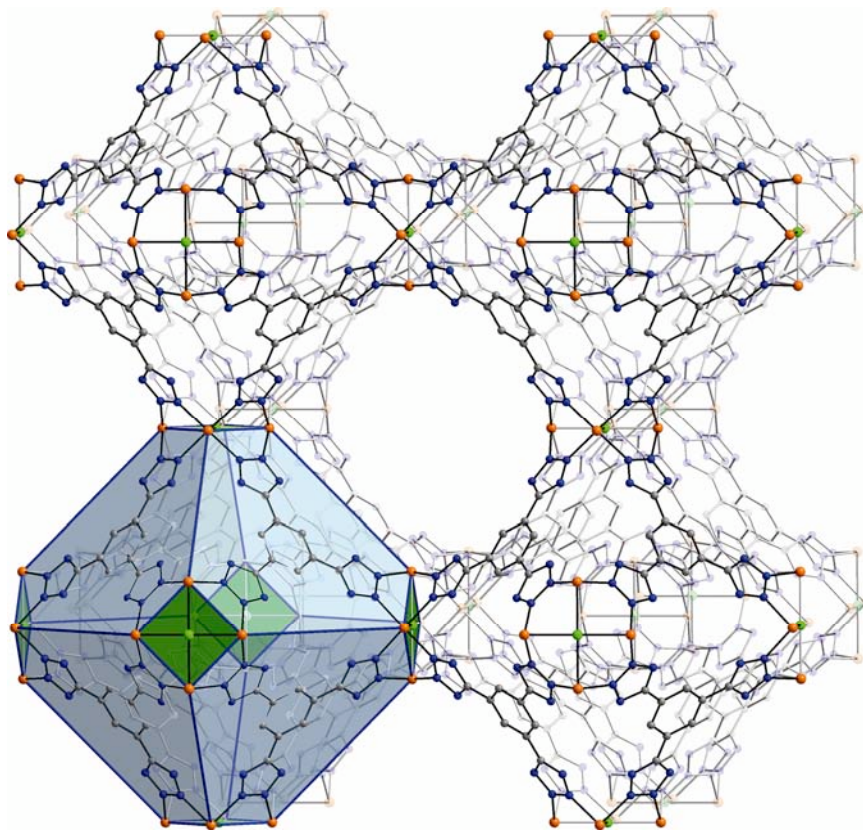
$$P_{\text{min}} = 1.5 \text{ bar}$$

$$P_0 = \text{standard pressure} = 1 \text{ bar}$$

$$R = 8.315 \text{ J/K}\cdot\text{mol}$$

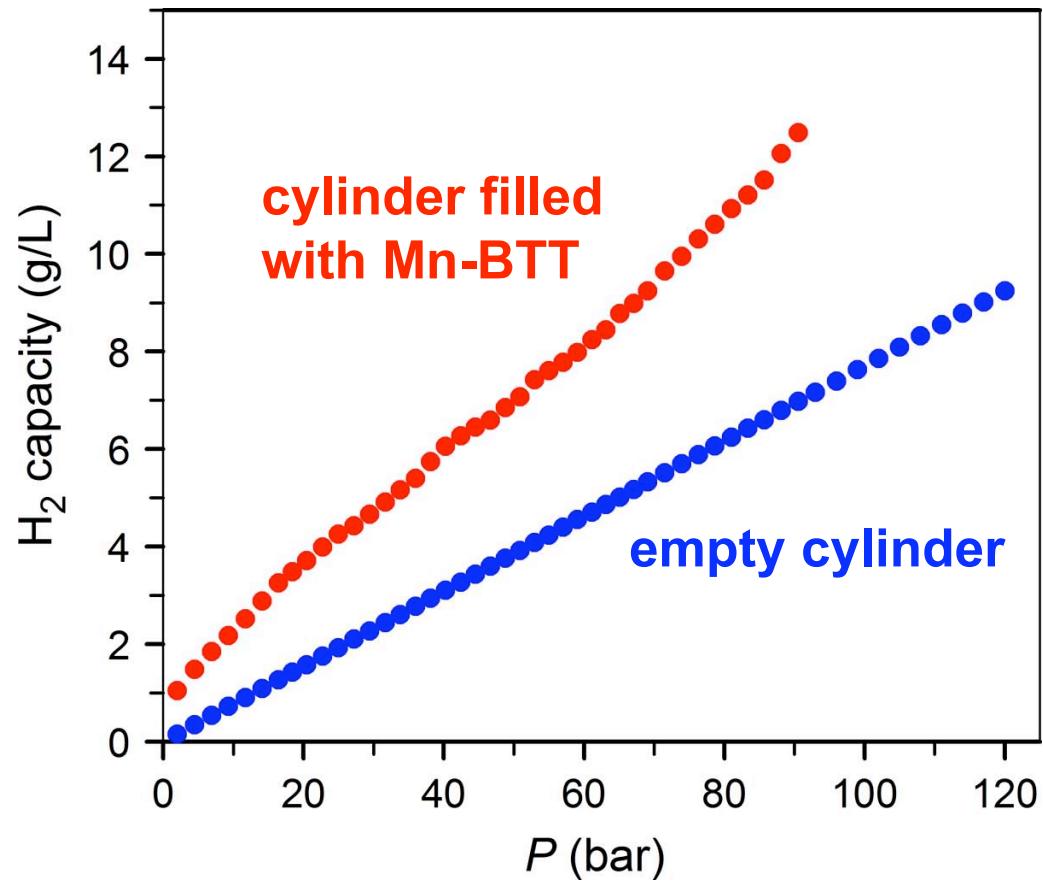
- Fuel cells typically operate at a minimum pressure of $P_{\text{min}} = 1.5$ bar
- For a constant temperature process, maximum delivery of H₂ is 63.5% of total storage capacity
- More complex adsorption models do not result in significantly different optimum enthalpies

A Tetrazolate-Bridged Framework with Exposed Mn^{2+} Sites



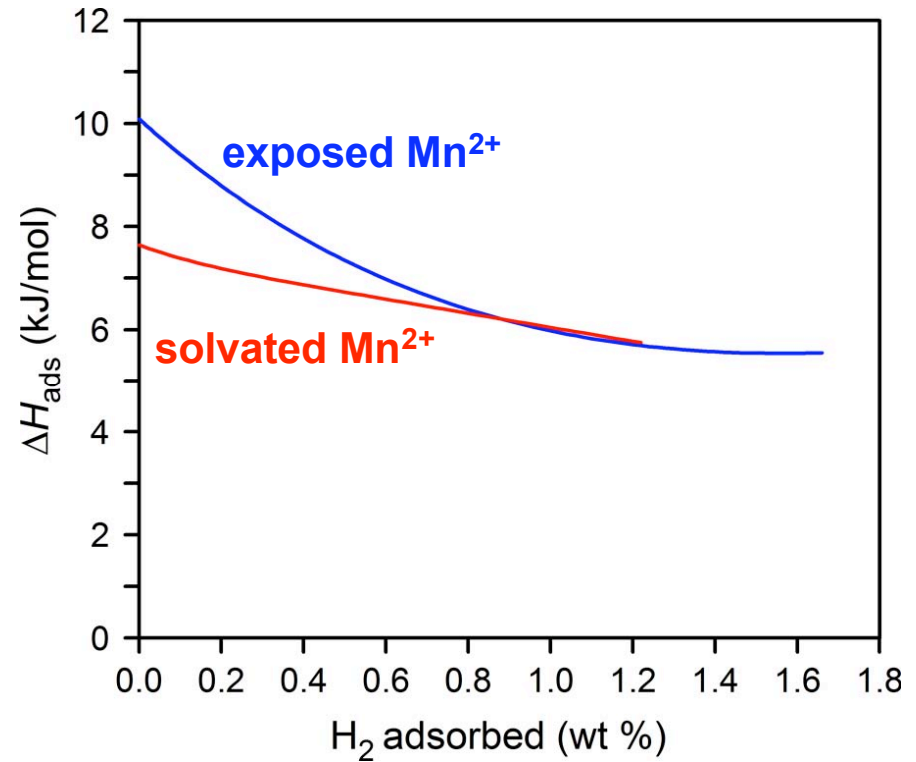
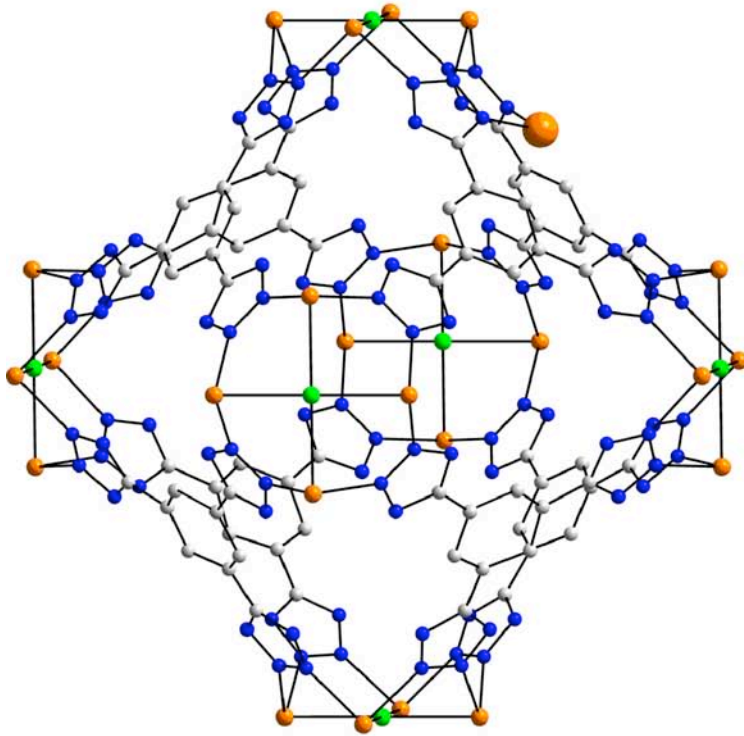
- Volumetric storage at 90 bar and 77 K is **60 g/L** (85% density of liquid H_2 at 21 K)
- Volumetric storage at 90 bar and 298 K is 50% greater than in an empty cylinder

Hydrogen Storage at 298 K



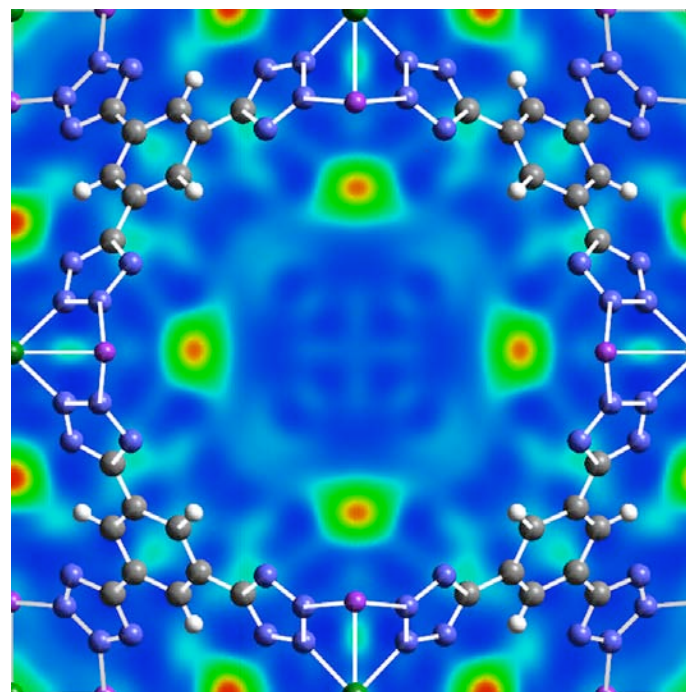
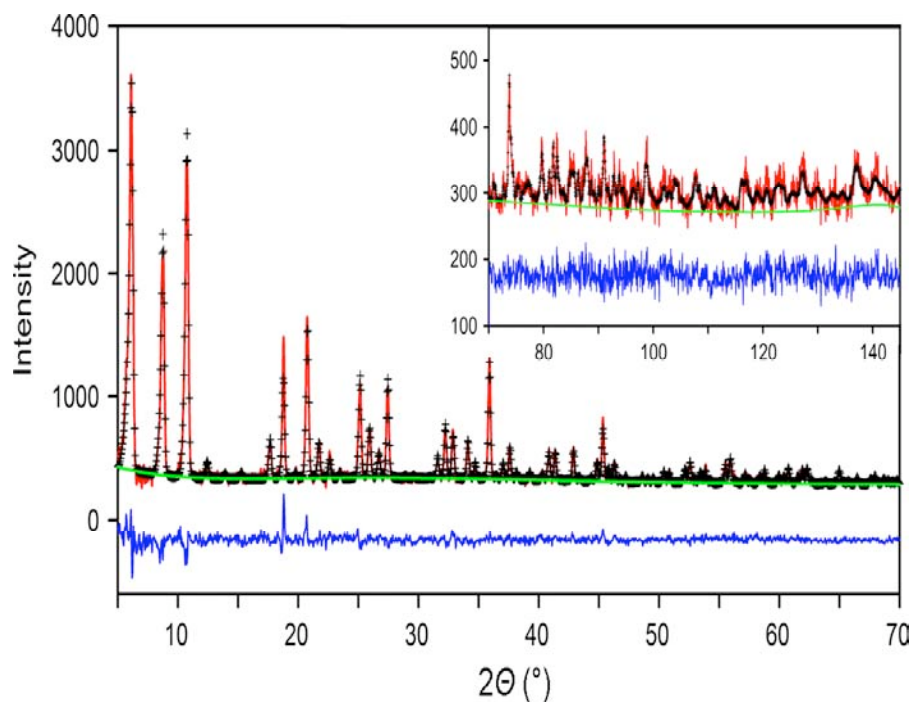
- Expect that approximately twice as much H₂ can be stored at the usual loading pressure of 120 bar

Increased H₂ Adsorption Enthalpy at Exposed Metals



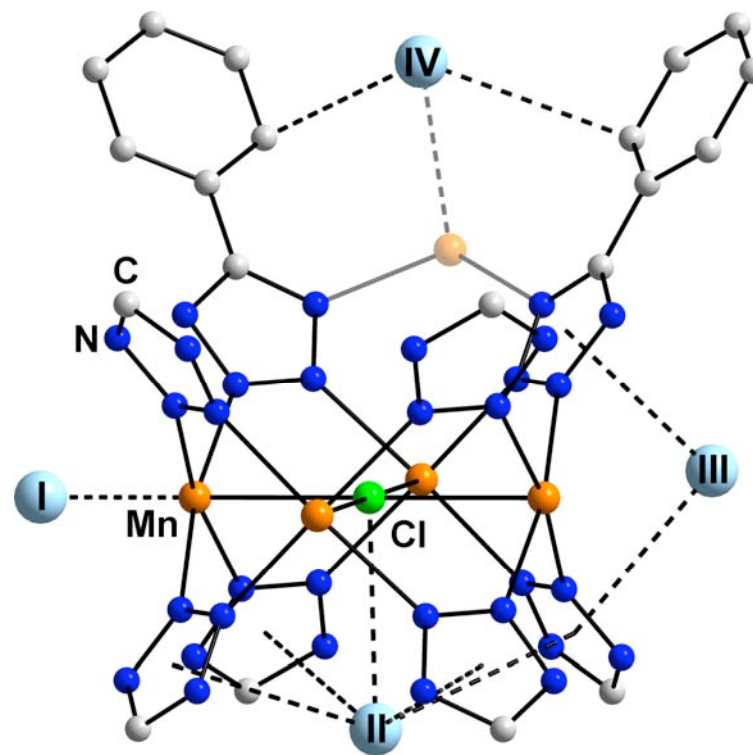
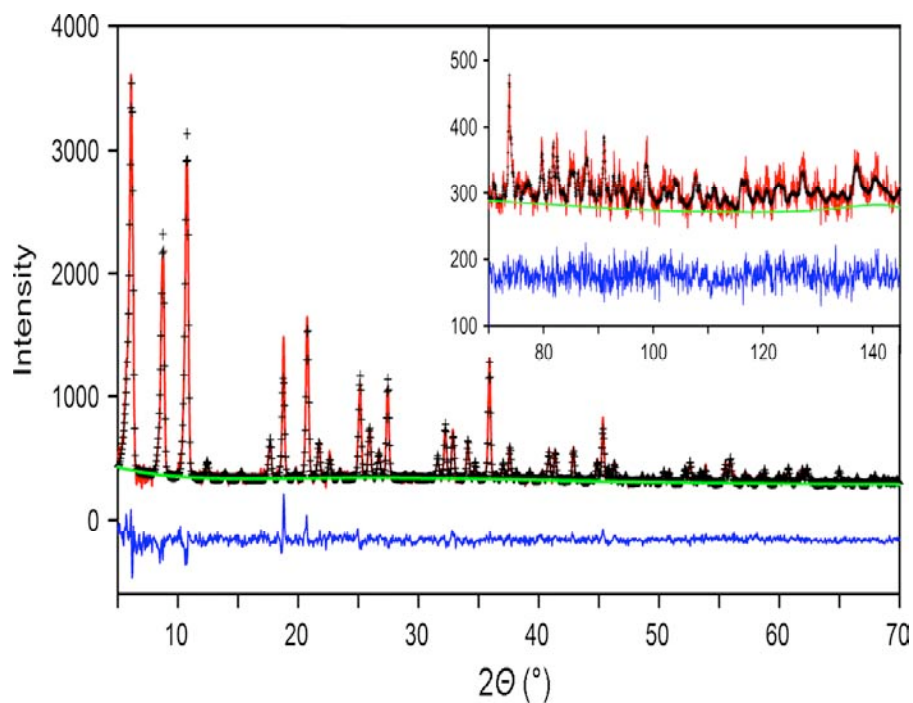
- Binding enthalpies at low loading are now as high as 10 kJ/mol
- Exposed Mn²⁺ coordination sites are only a small weight fraction of available sites
- Attempts to replace Mn²⁺ with stronger-binding cations (e.g. Cu⁺) are underway

Locating D₂ Adsorption Sites by Neutron Diffraction



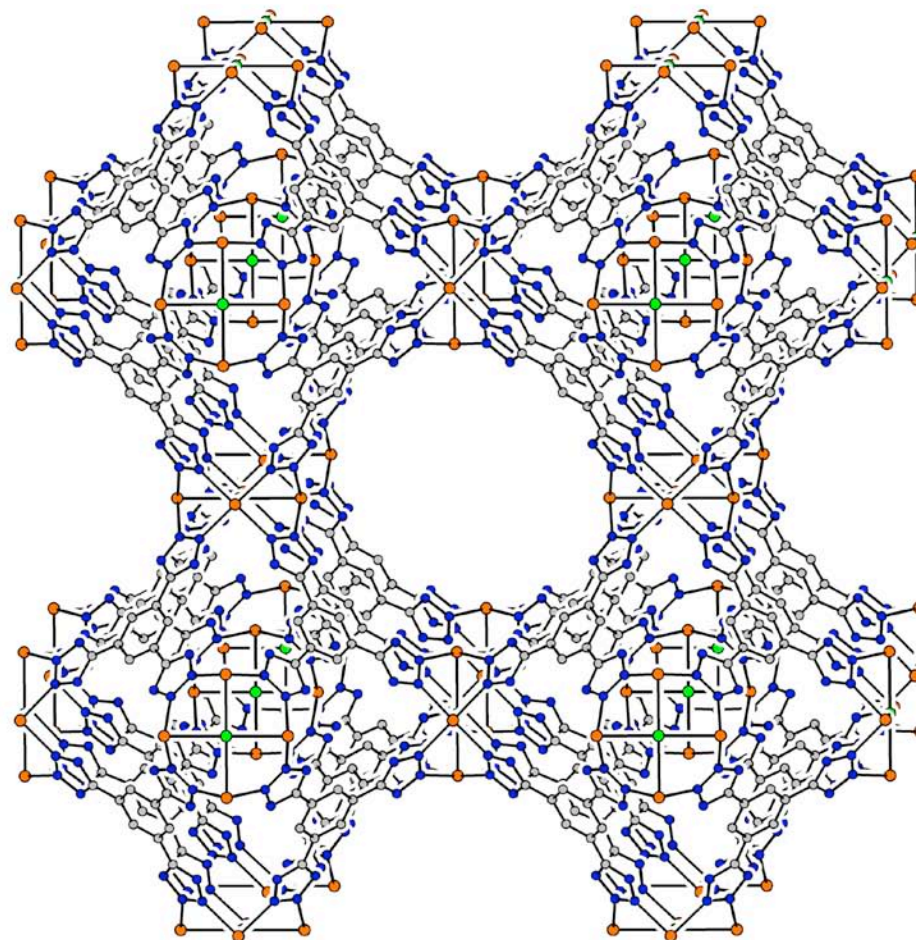
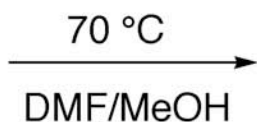
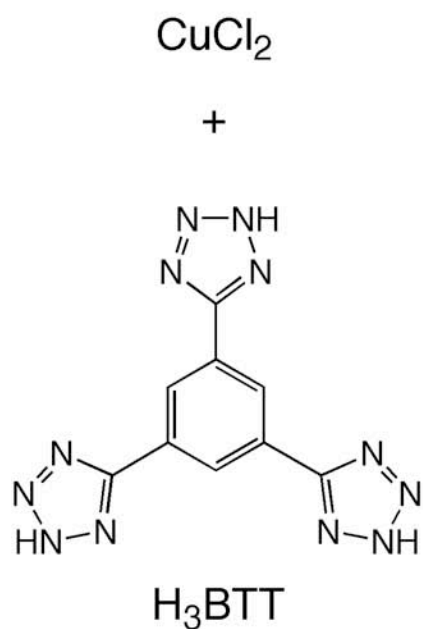
- Strongest D₂ binding occurs at sites I (Mn-D₂ = 2.2 Å) and II (Cl···D₂ = 3.5 Å)
- First direct observation of metal-D₂ interaction in a metal-organic framework

Locating D₂ Adsorption Sites by Neutron Diffraction



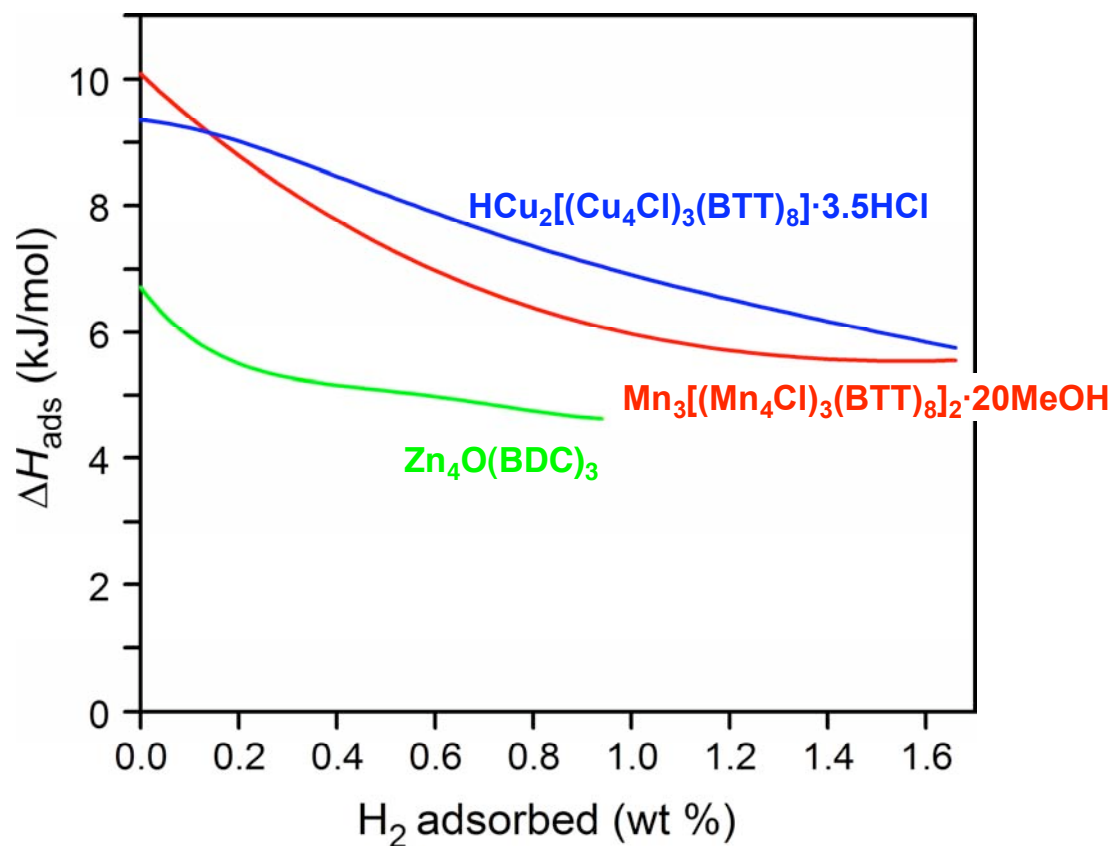
- Strongest D₂ binding occurs at sites I (Mn-D₂ = 2.2 Å) and II (Cl···D₂ = 3.5 Å)
- First direct observation of metal-D₂ interaction in a metal-organic framework

A Copper(II)-Containing Sodalite Framework



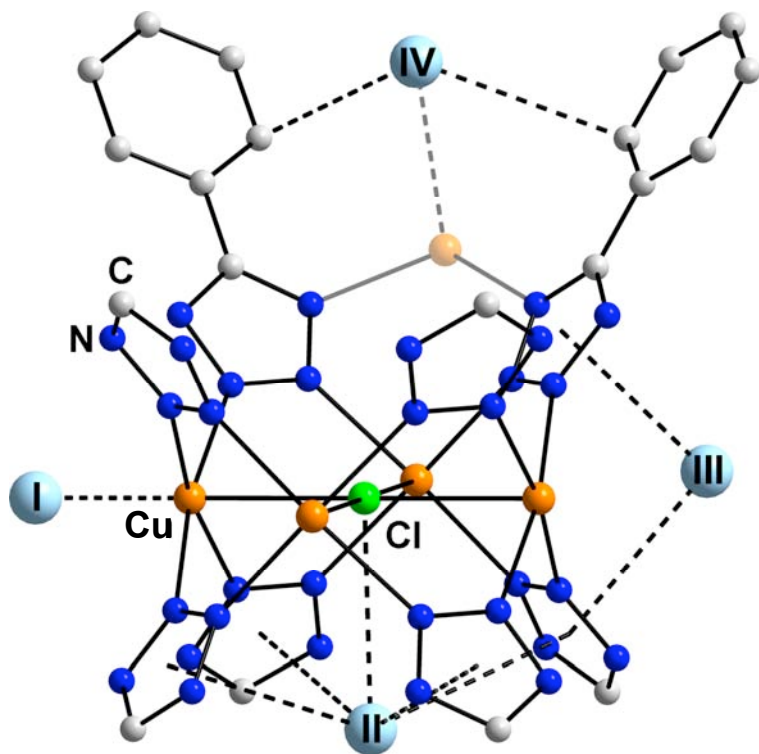
- Washing with methanol and heating under dynamic vacuum gives **fully desolvated** material

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

D₂ Adsorption in Cu-BTT Framework



D ₂ loading	site I	site II	site III	site IV
6	4.4(1)	3.1(1)	0	0
12	7.8(1)	5.2(1)	0	0
18	10.7(1)	5.7(1)	1.2(1)	0
30	11.1(2)	5.5(1)	8.0(2)	4.3(2)
sat.	12	6	24	24

- 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^{II}