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Metal-Organic Frameworks II

Lecture 37

Metal-organic frameworks: structures and structural properties

Lecture 38

Metal-organic frameworks: surfaces and host-guest chemistry

Lecture 39

Metal-organic frameworks: magnetic, electronic ion transport and spin switching properties

Metal-Organic Frameworks (MOFs)

Two connecting ligand



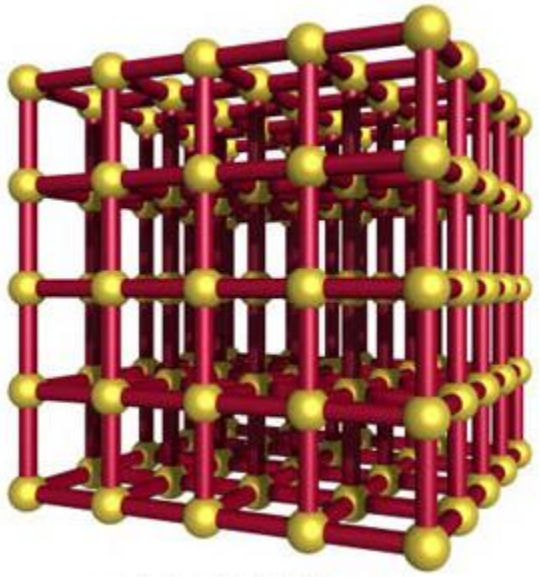
+

Six connecting **metal**

Octahedral



=



Cubic framework
(three-dimensional)

Nature, **402**, 276 (1999)

Highly porous MOFs are host-guest systems

MOFs can host "guest" molecules in their structure. E.g., MOF-5 has 19 Å cavities that is stable to 300 °C.

'MOF-5'

Cluster of 4 metal ions at **corners** $[Zn_4O(O_2CR)_6]$

1,4-benzene dicarboxylate **linker**

cavity

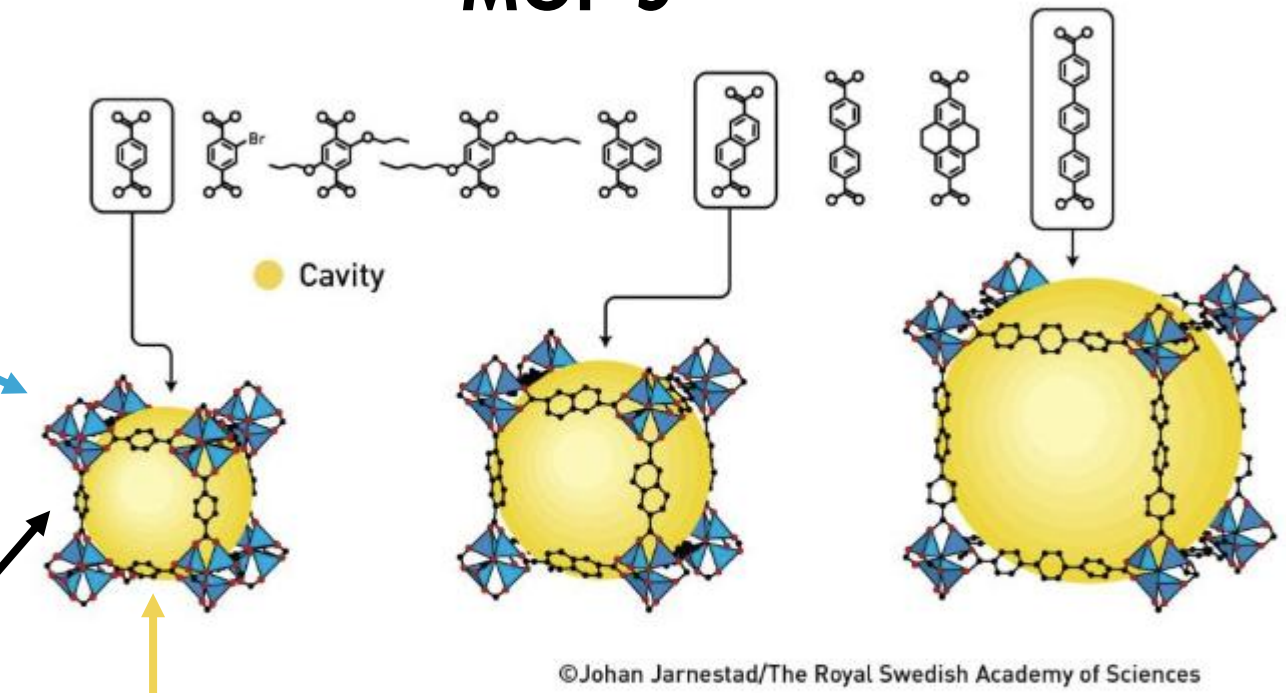


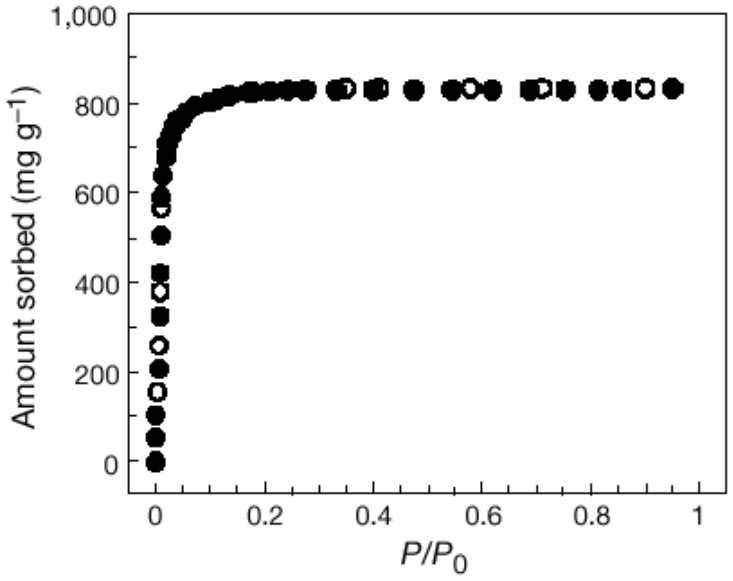
Figure 6. In the early 2000s, Yaghi showed that it is possible to produce entire families of MOF materials. He varied the molecular links, which resulted in materials with different properties. These include 16 variants of MOF-5, with cavities of various sizes. ©Johan Jarnestad/The Royal Swedish Academy of Sciences

Nature, **402**, 276 (1999)

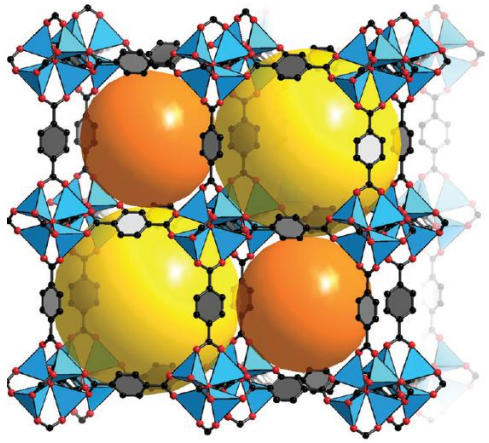
Gas sorption in MOFs

Measuring gas **isotherms** quantifies the uptake and release of gas.

Nanoporous materials do this reversibly, leaving the host lattice intact.



'MOF-5'



8 cavities per unit cell

Table 1 Gas and liquid vapour sorption in desolvated MOF-5

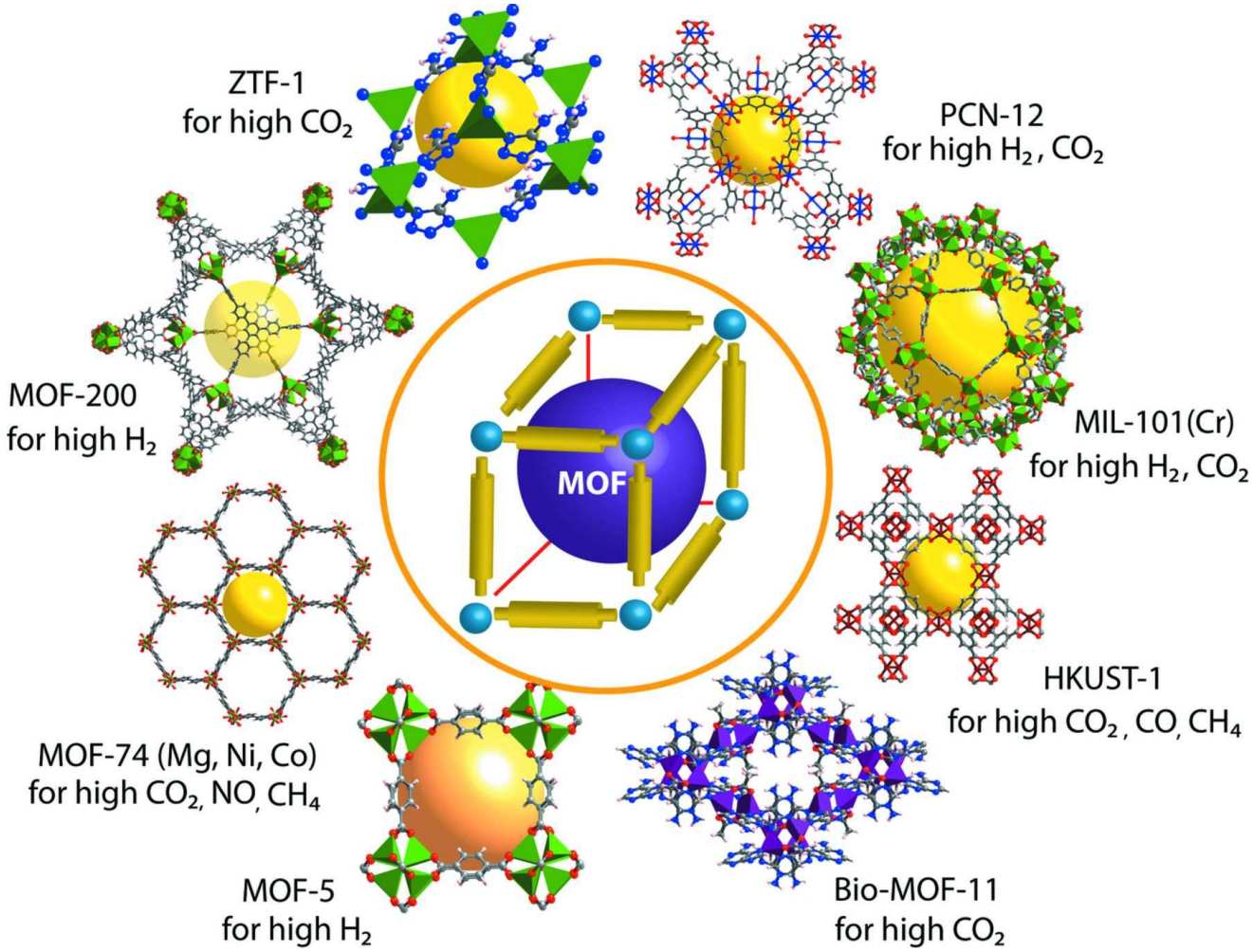
Sorbate	*T* (°C)	Amount sorbed (mg g^{-1})	Sorbate molecules per unit cell	Free volume (cm^3 g^{-1})	Free volume (cm^3 cm^{-3})
Ar	−194	1,492	230	1.03	0.61
N_2	−194	831	183	1.04	0.61
CH_2Cl_2	22	1,211	88	0.93	0.55
$CHCl_3$	22	1,367	71	0.94	0.55
C_6H_6	22	802	63	0.94	0.55
CCl_4	22	1,472	59	0.94	0.56
C_6H_{12}	22	703	51	0.92	0.54

Gas sorption in MOFs

By tuning the structure of MOFs, we can optimse their adsorption/desorption properties.

This lecture:

- H_2
- CO_2
- CH_4



Hydrogen as a fuel

Opportunities

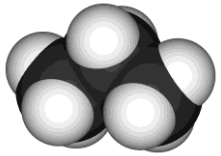
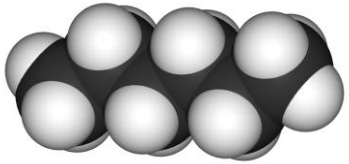
- High energy density per weight
- "Green" if produced with renewable energy
- Clean emissions with fuel cell

  ($H_2 + ½O_2 \rightarrow H_2O$)
- Efficient conversion from chemical energy to electrical energy
- Typical "fuel" may make it helpful to decarbonise tricky industries (e.g., aviation)

Challenges

- Low energy density per volume at room temperature and pressure
- Energy losses in producing, compressing, storing H_2
- Storage is challenging due to size and properties of H_2

Storing fuels

	Hydrogen	Methane	Propane	Hexane
				
Boiling point (BP)	-253 °C	-161 °C	-42 °C	69 °C
Critical temperature (T_c) *	-240 °C	-83 °C	97 °C	254 °C
	Even trickier due to lower BP and T_c	*Tricky to liquify at RT as T_c well below RT. Piped as a gas.*	*Pressurised to liquid at RT*	*Liquid at room temperature (RT)*

* Highest temperature a substance can exist as a liquid, regardless how much pressure is applied.

Numerical values are for interest only.

For interest only

Practical hydrogen storage targets

Considerations:

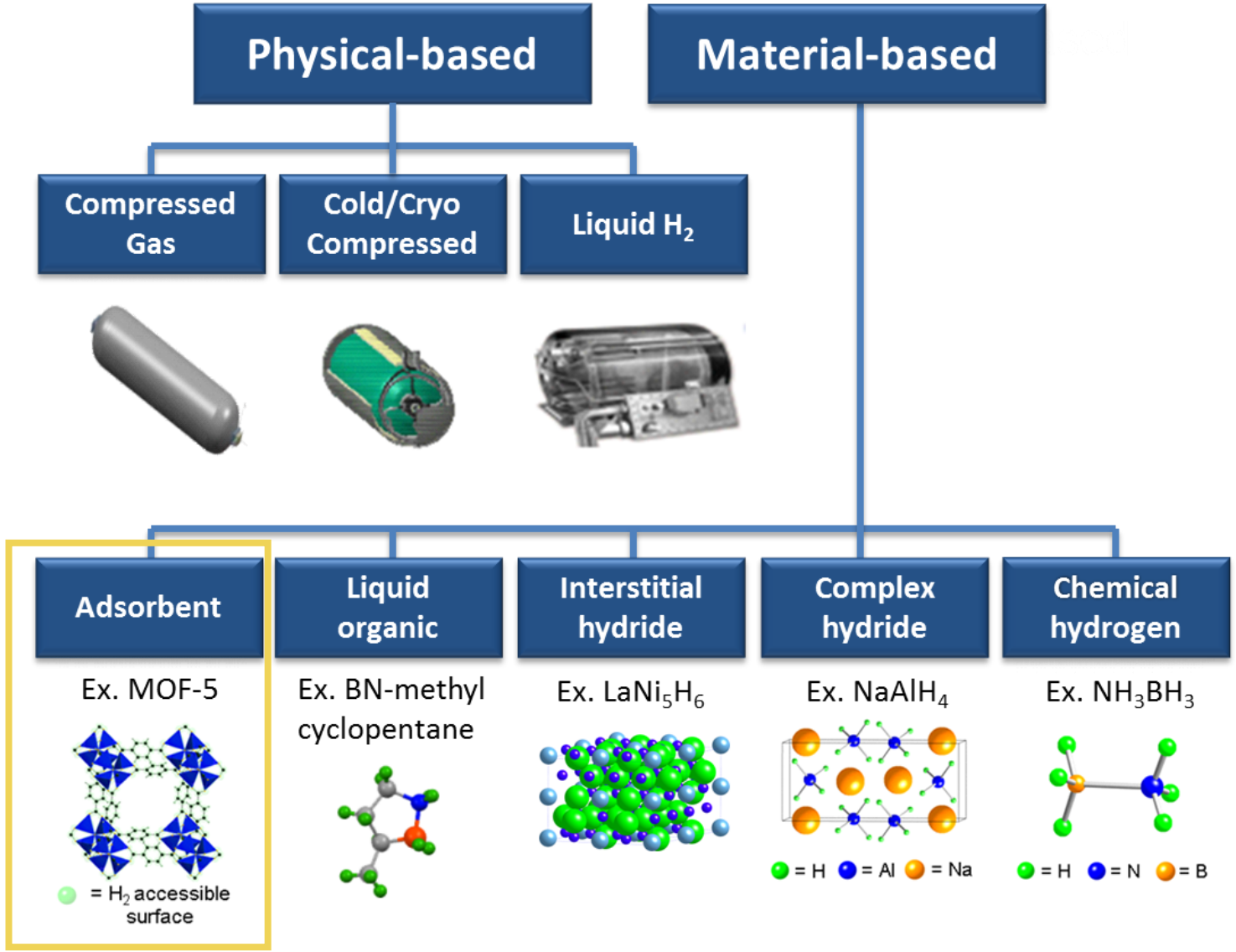
- high gravimetric and volumetric densities
- appropriate thermodynamics
- fast kinetics (quick uptake and release)
- long cycle lifetime for hydrogen absorption/desorption
- safety
- low cost

US Department of Energy Targets:

gravimetric capacity	6 wt. % H_2
volumetric capacity	45 g H_2/L
operating temperature	-30 to 50 °C
maximum pressure	100 bar
refueling rate	1.67 kg H_2/min
cycle life	1000 cycles
cost	$133 per kg H_2

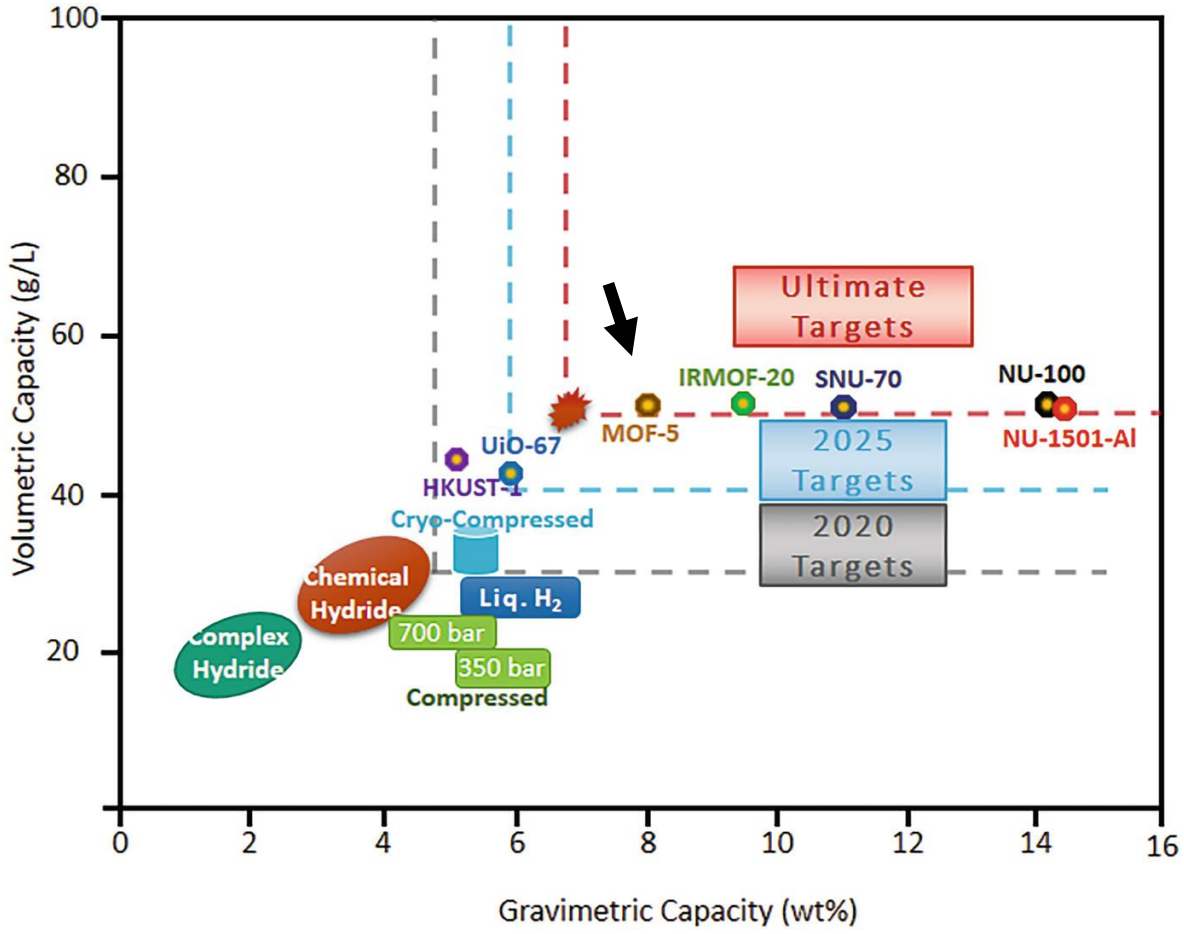
Ways to store hydrogen gas

- Liquid H_2 at 21 K.
- New cylinders withstand 700 atm.
- Liquification requires ~30% of energy.
- Thermal insulation to present boil off is expensive.



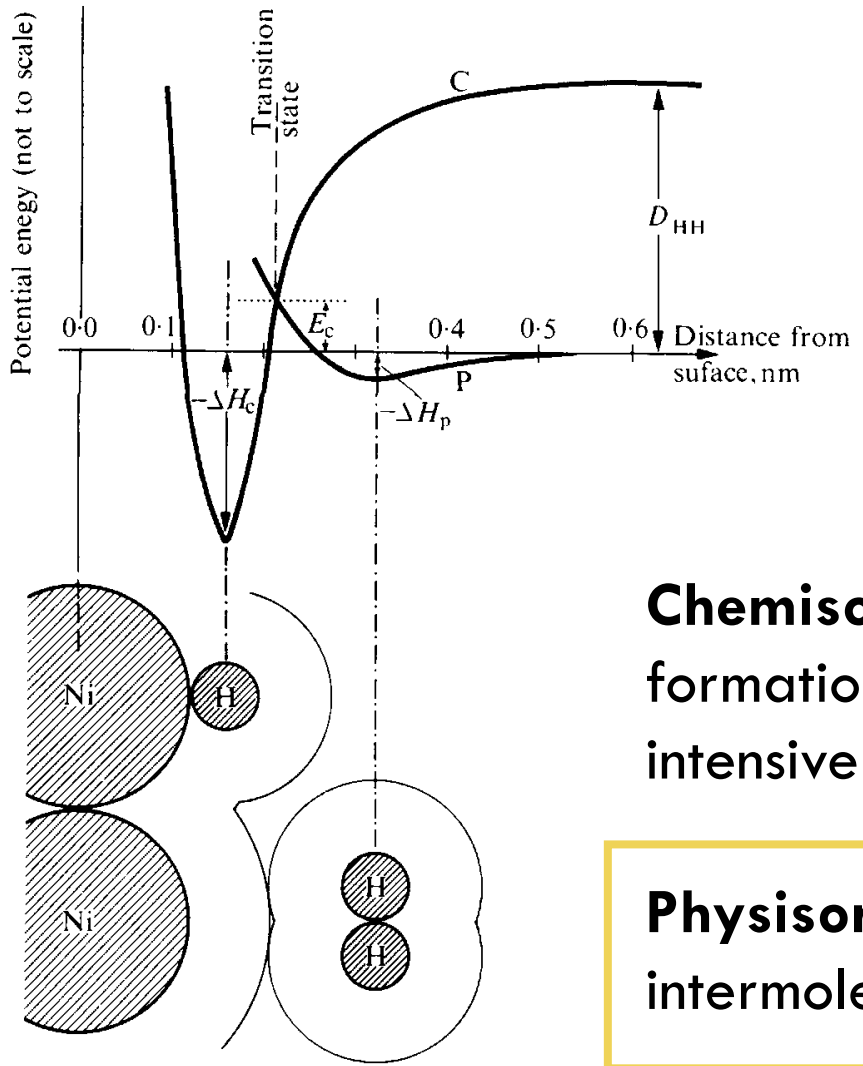
Hydrogen storage per mass and volume

MOFs (and other nanoporous materials) are competitive materials to reach energy density targets.



https://doi.org/10.1007/978-981-95-2947-6_90

Chemical storage of hydrogen

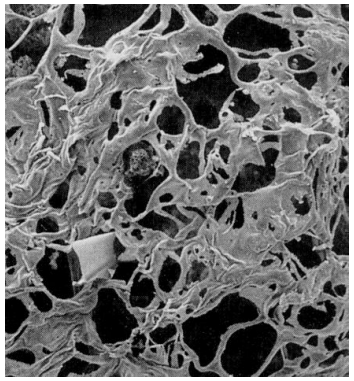


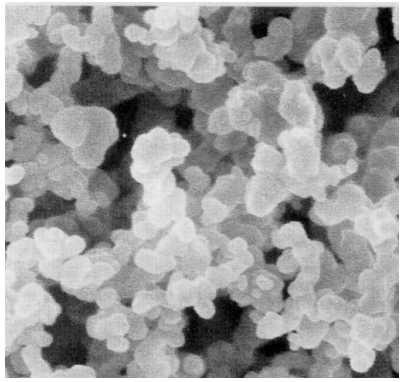
Chemisorption: Adsorption onto a surface through the formation of chemical bonds. Challenges include energy intensive and slow process.

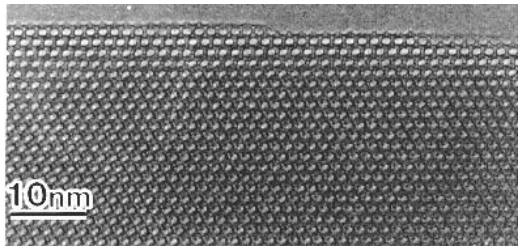
Physisorption: Adsorption onto a surface through weak intermolecular forces.

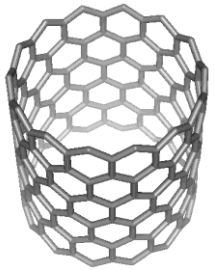
Material properties for H_2 storage by physisorption

1) Maximise the surface area per mass and per volume



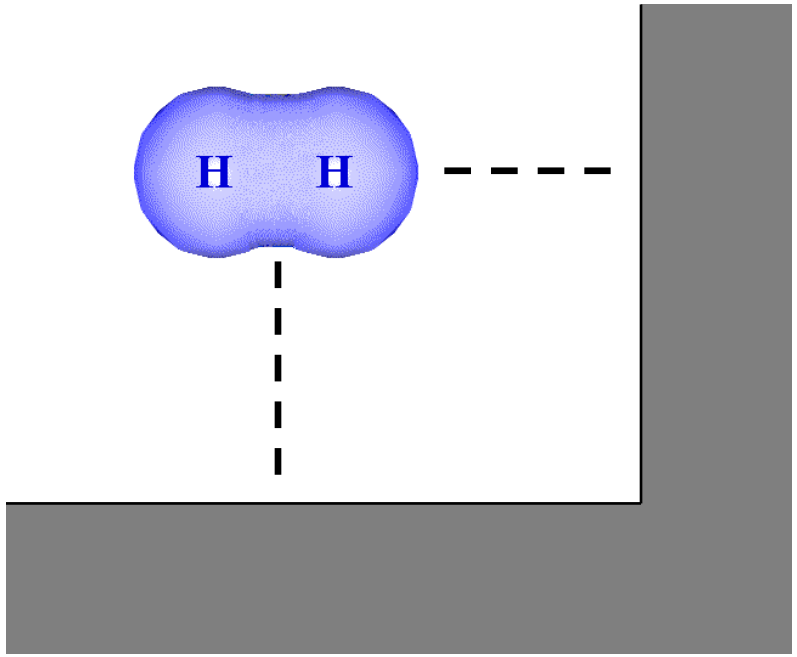






Ideally, surface area > 4000 m^2 g^{-1}

2) Maximise the strength of the physisorption interaction

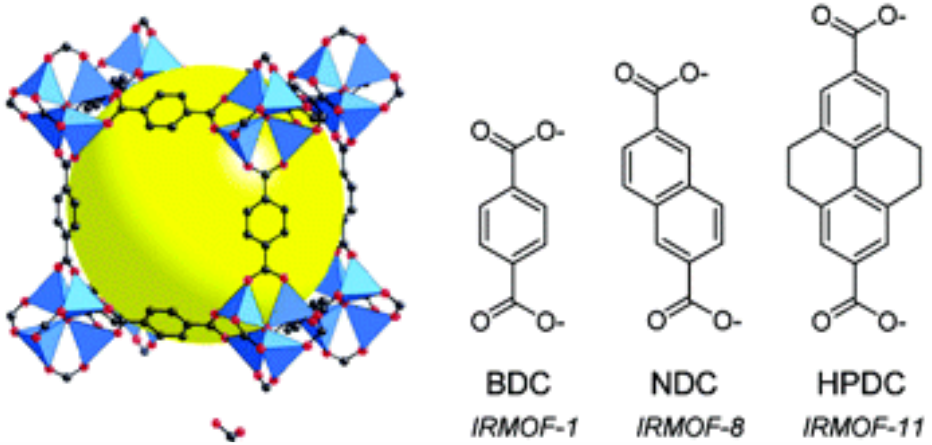


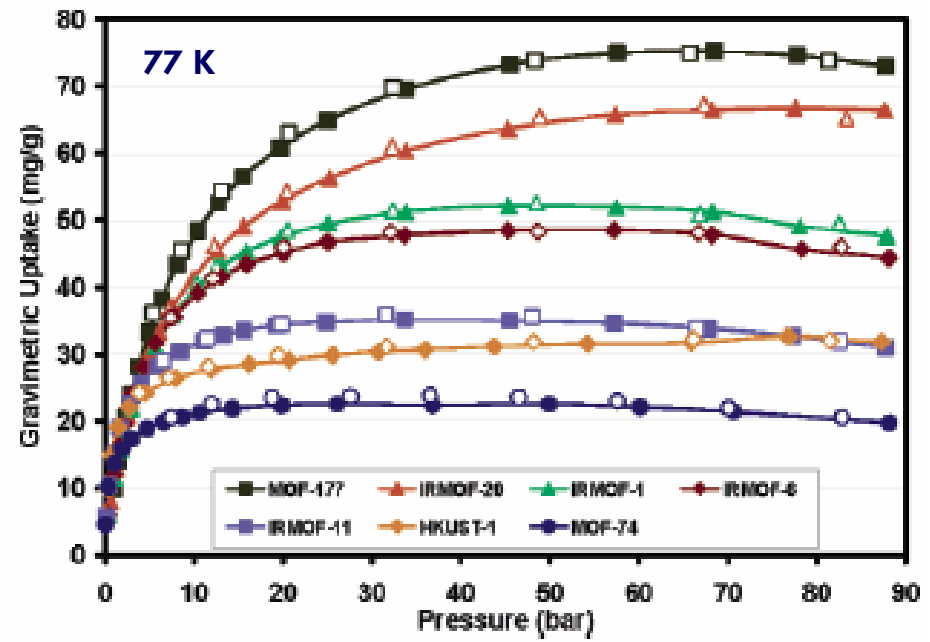
Ideally, $\Delta H \sim 14$ kJ mol^{-1}
Typically, $\Delta H \sim 4\text{-}6$ kJ mol^{-1}

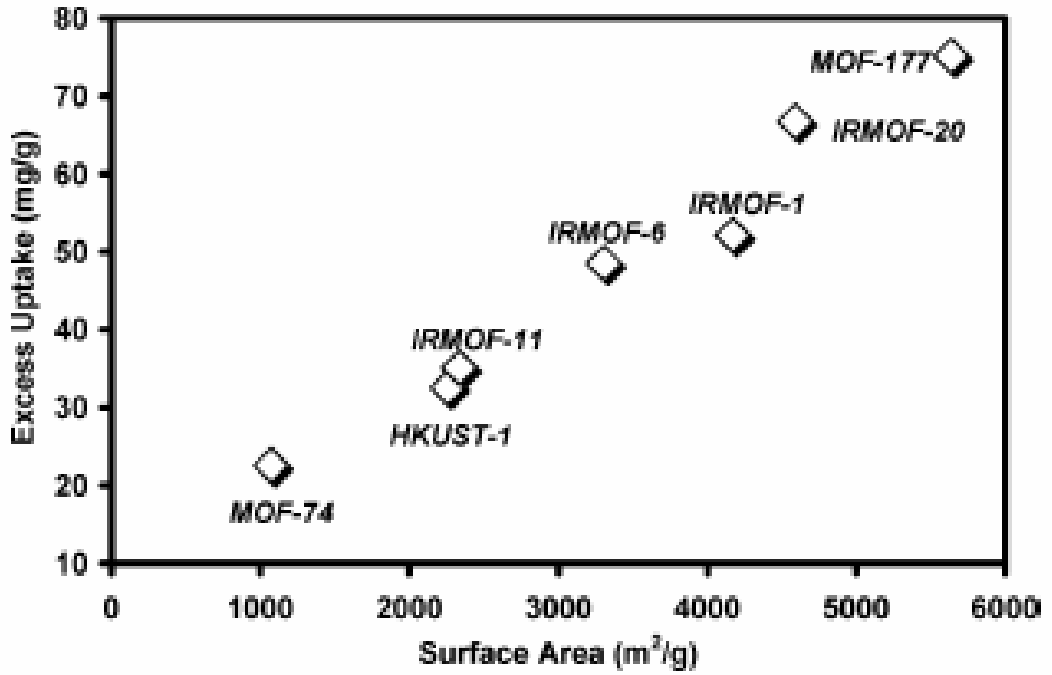
J. Am. Chem. Soc., **128**, 3494 (2006).

MOFs: Optimising surface area

- Framework structures have very high surface areas per mass
- H_2 forms a monolayer at low temperature and uptake scales with surface area.

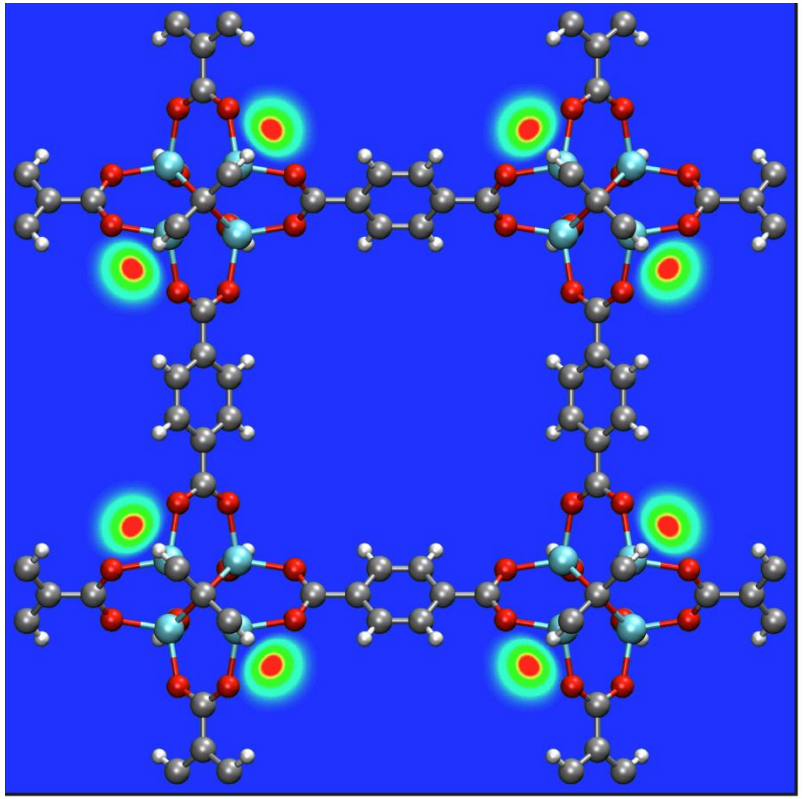






MOFs: Optimising the interaction energy

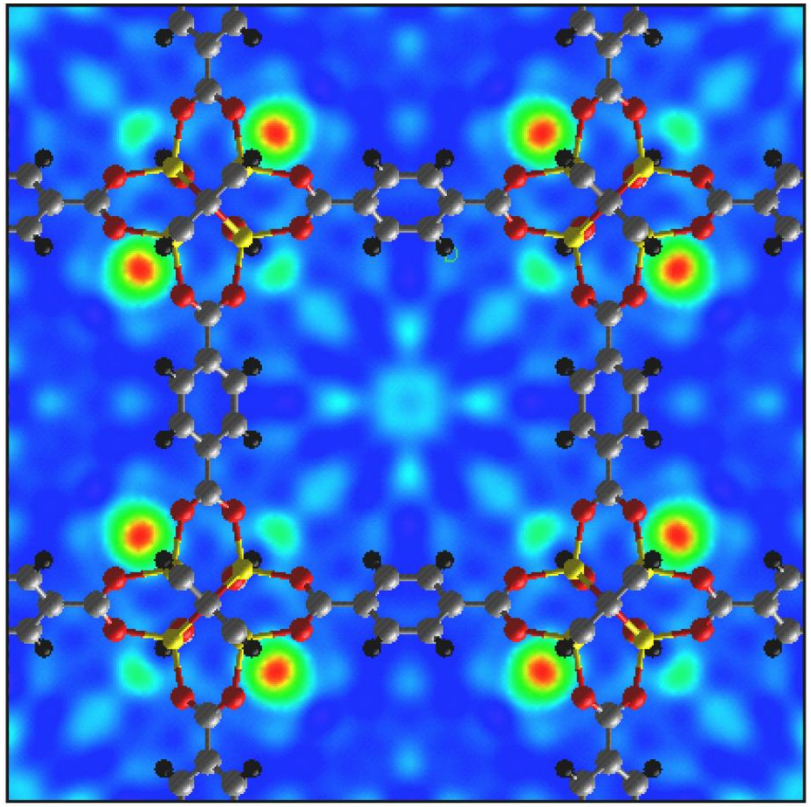
Where are the H_2 molecules?



Quantum diffusion Monte Carlo simulations

Calculation of the probability density for 1 H_2 per unit cell

J. Phys. Chem. A 2015, 119, 12166.



Neutron diffraction

Density maps for 32 D_2 molecules per unit cell

Phys. Rev. Lett. 2005, 95, 215504.

MOFs: Optimising the interaction energy

How strongly do the H_2 molecules bind?

For MOF-5:

The α binding site – a cup-shaped site with three Zn atoms

Binding energy:

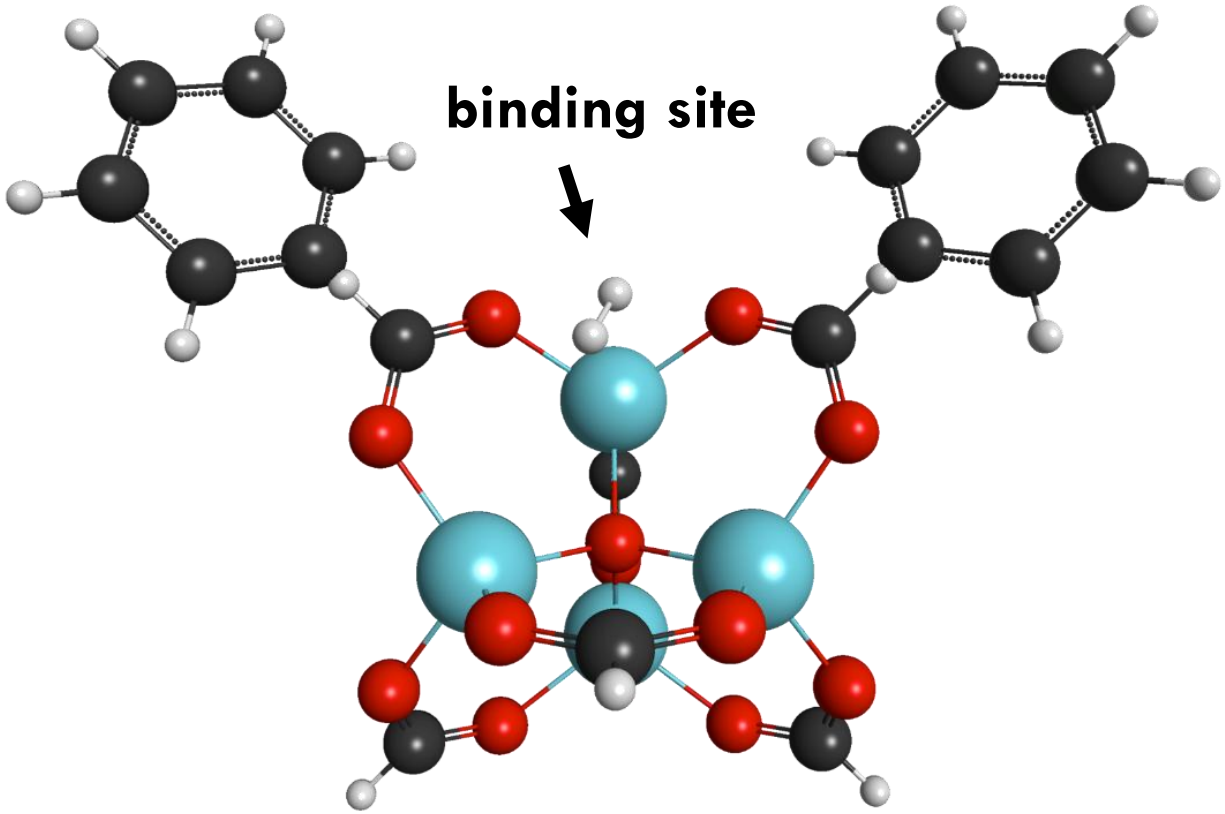
- By quantum simulation at 0 K

  $\Delta H_{ads} = -6.4$ kJ mol^{-1}

  At 0 K, a single H_2 molecule will adsorb here only.

- Experimentally at 77 K:

  $\Delta H_{ads} = -3.8$ to -4.8 kJ mol^{-1}

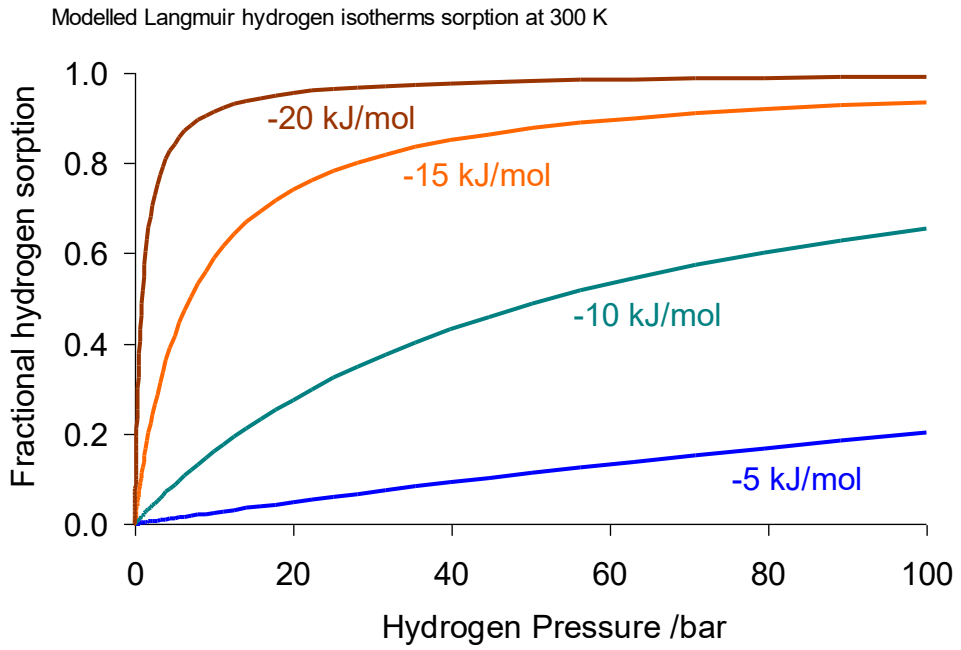


Adv. Funct. Mater. 2006, *16*, 520.
J. Am. Chem. Soc. 2006, *128*, 1304.

MOFs: Optimising the interaction energy

Back-of-envelope calculations can be used to determine the optimum interaction energy ($\Delta H°$) by considering the Langmuir H_2 isotherms at 298 K with respect to binding energy.

$$\text{Fractional sorption} = \frac{KP}{(1+KP)} \quad \textit{where} \quad K = (e^{\Delta S°/R})(e^{-\Delta H°/RT})/P_\circ \quad \text{and} \quad \Delta S° \cong -8R$$

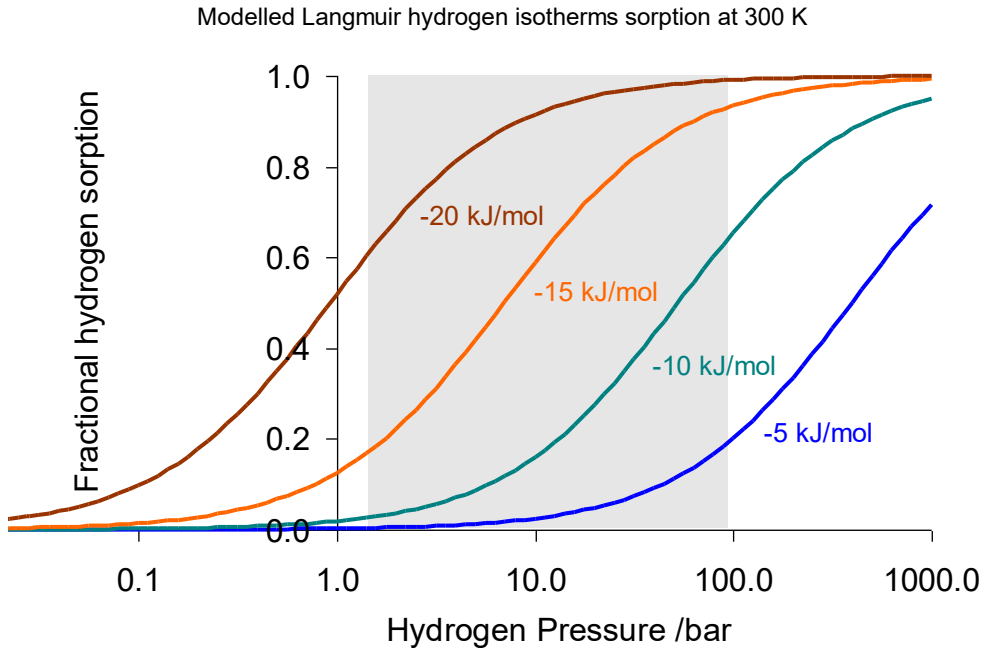


With low interaction energy (-5 kJ/mol): Small uptake of H_2, even at high pressure.

MOFs: Optimising the interaction energy

Back-of-envelope calculations can be used to determine the optimum interaction energy ($\Delta H°$) by considering the Langmuir H_2 isotherms at 298 K with respect to binding energy.

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Plotting pressure on a log scale shows similar shaped isotherms, shifted along the x-axis.

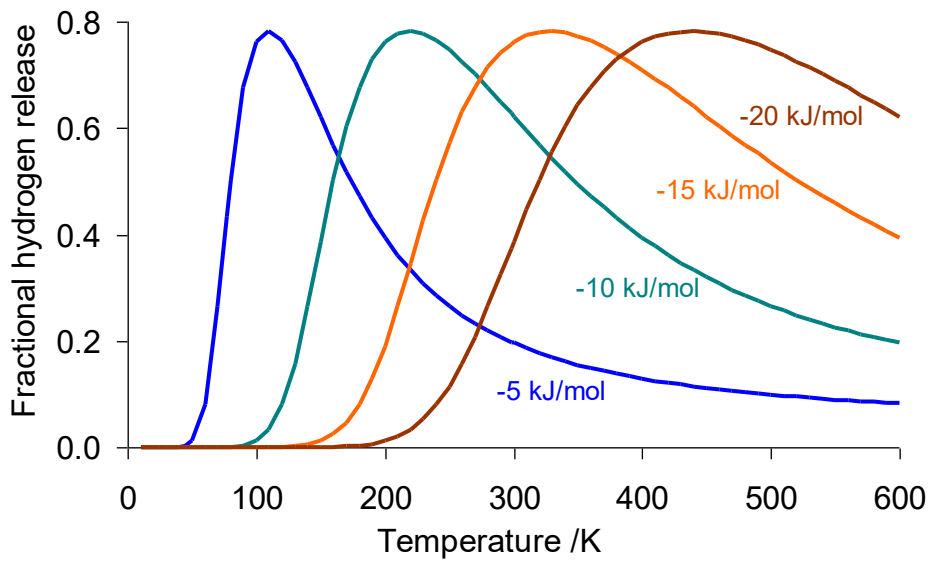
With high interaction energy (-20 kJ/mol), pressures <1 bar needed for full H_2 release.

The ideal binding energy for H_2 uptake (by increasing pressure) and release (by lowering pressure) within the practical pressure limits (1.5-100 bar) is ~15 kJ/mol.

MOFs: Optimising the interaction energy

Back-of-envelope calculations can be used to determine the optimum interaction energy ($\Delta H°$) by considering the Langmuir H_2 isotherms at 298 K with respect to binding energy.

$$\text{Fractional sorption} = \frac{KP}{(1+KP)} \quad \textit{where} \quad K = (e^{\Delta S°/R})(e^{-\Delta H°/RT})/P_\circ \quad \text{and} \quad \Delta S° \cong -8R$$



Temperature plays a role on the amount of H_2 uptake/release between the practical pressure limits ($1.5 \leq P \leq 100$ bar) for a given interaction energy.

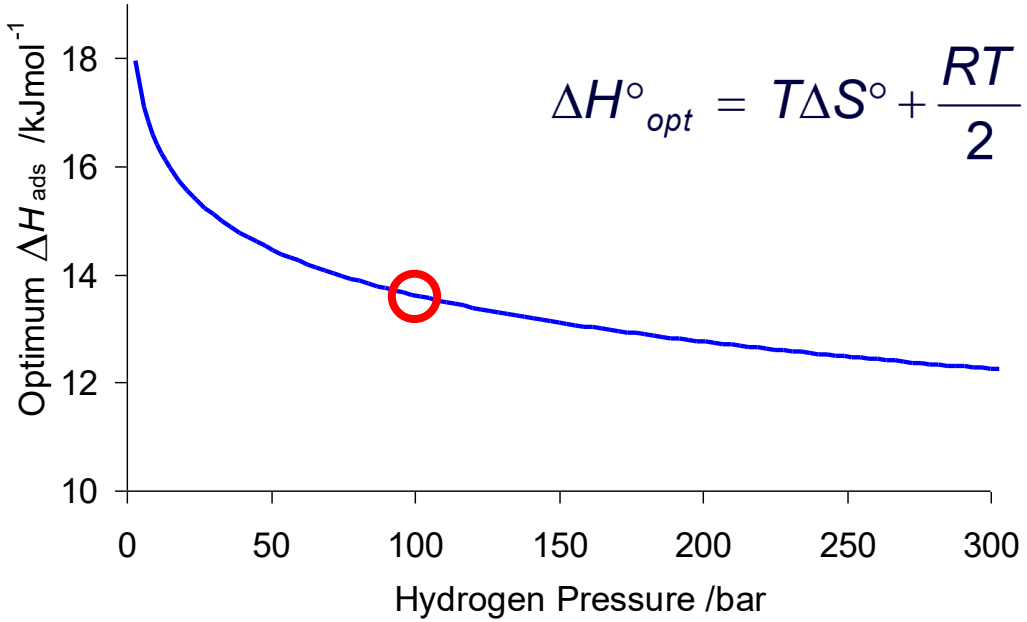
The interaction energy giving the highest H_2 release at room temperature is ~15 kJ/mol.

MOFs: Optimising the interaction energy

Back-of-envelope calculations can be used to determine the optimum interaction energy ($\Delta H°$) by considering the Langmuir H_2 isotherms at 298 K with respect to binding energy.

$$\text{Fractional sorption} = \frac{KP}{(1+KP)} \quad \text{where} \quad K = (e^{\Delta S°/R})(e^{-\Delta H°/RT})/P_\circ \quad \text{and} \quad \Delta S° \cong -8R$$

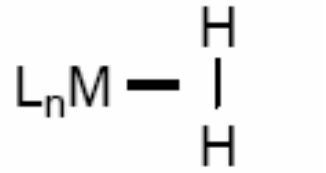
The optimum interaction energy can be determined precisely. For T = 298 K:



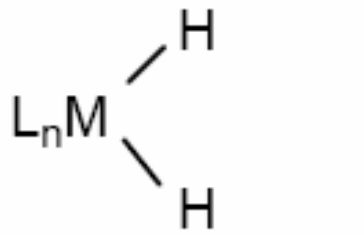
$$\Delta H°_{opt} = T\Delta S° + \frac{RT}{2}\ln\left(\frac{P_1P_2}{P_\circ^2}\right) = -13.6 \text{ kJmol}^{-1}$$

MOFs: Optimising the interaction energy

Finding inspiration to increase binding energy from metal hydride materials



η^2-H_2 complex



hydride complex

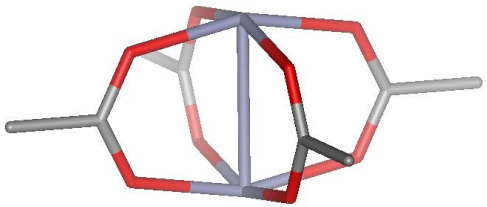
M	ΔH (kJ/mol)
$Li^+_{(g)}$	27
$Na^+_{(g)}$	10
$K^+_{(g)}$	6
$Ti^+_{(g)}$	37
Cu^+ in chabazite	56
CuCl surface	93
$Cr(CO)_5$	78
$Mo(CO)_5$	81
$Cr(CO)_3(PCy_3)_3$	31
$Mo(CO)_3(PCy_3)_3$	27
$W(CO)_3(PCy_3)_3$	42
$OsH_2(CO)(P^iPr_3)_2$	82

Materials that undergo chemisorption, forming metal hydrides via chemical bonds with H_2, have interaction energies that are too high.

Can the design principle of metal sites be incorporated into MOFs to increase their interaction energy?

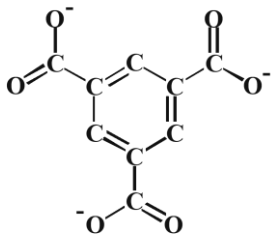
MOFs: Optimising the interaction energy

Hydrogen storage in $Cu_3(btc)_2$ ("HKUST-1")



$[Cu_2(Ac)_4]$

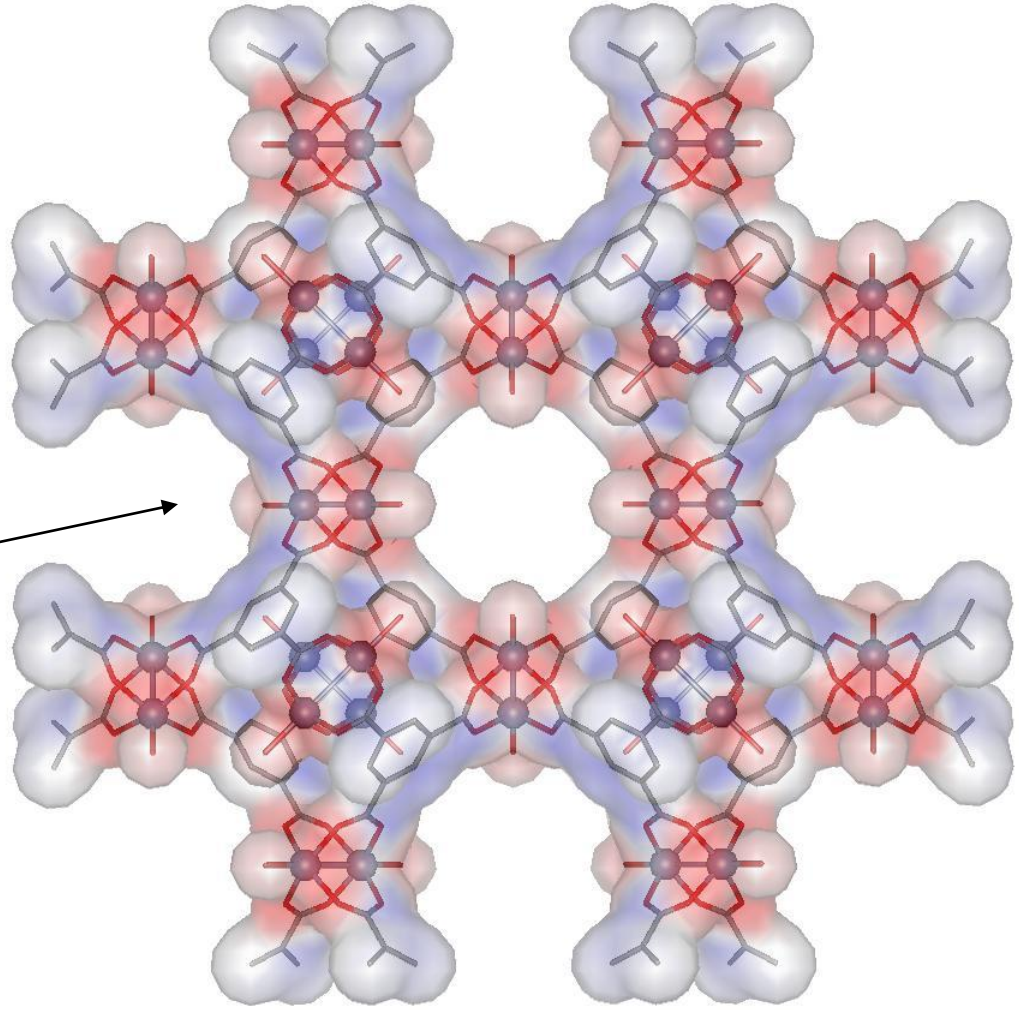
+



btc

(1,3,5-benzenetricarboxylate)

Synthesised with bound water coordinated to Cu

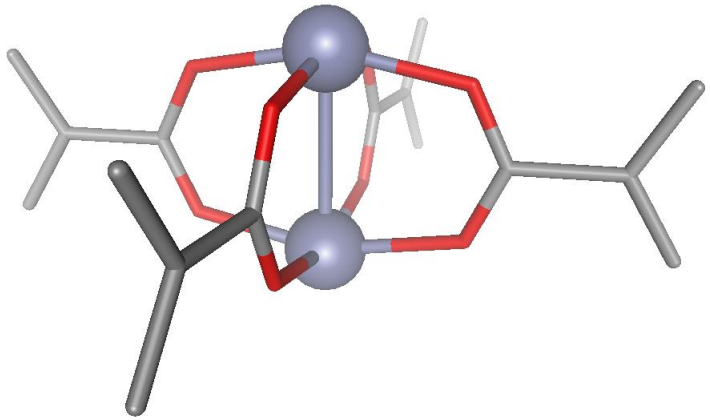


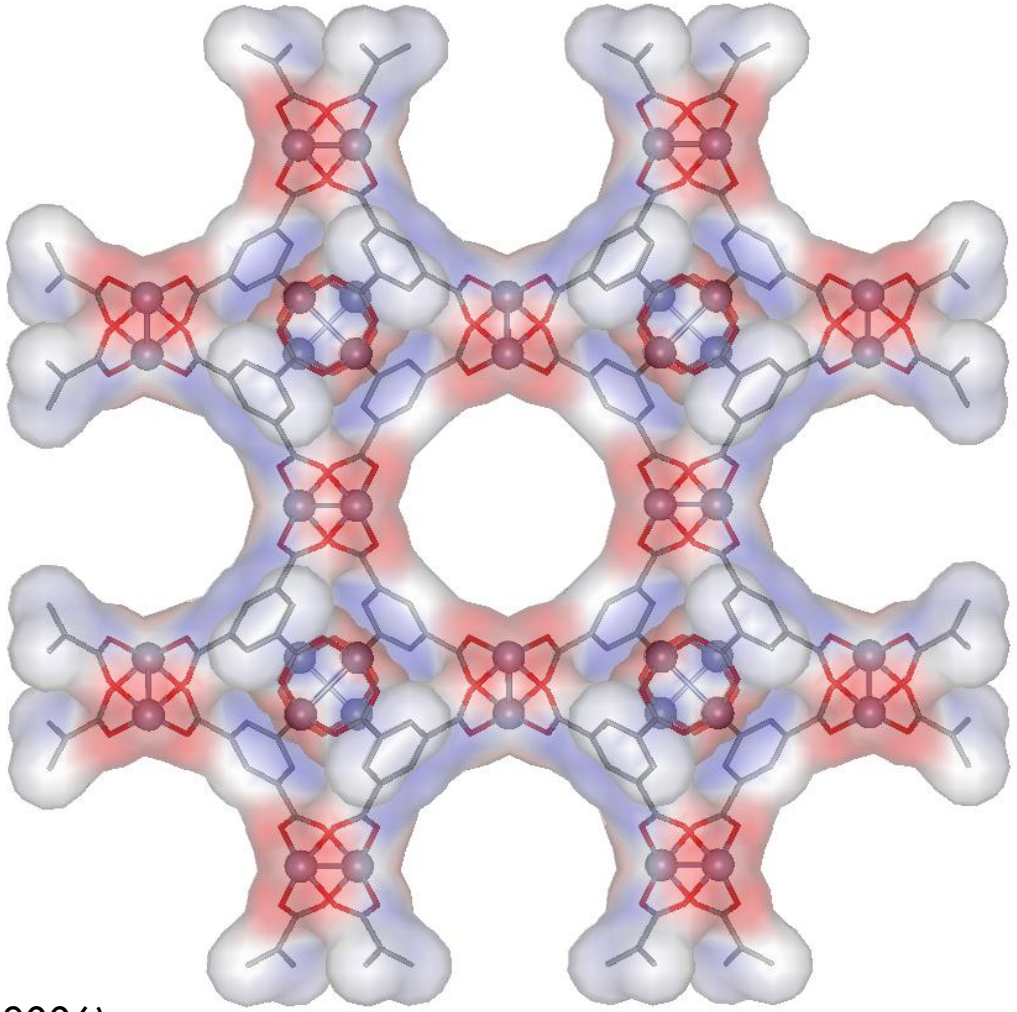
Williams *et al.*, *Science*, **283**, 1148-1150 (1999).

MOFs: Optimising the interaction energy

Hydrogen storage in $Cu_3(btc)_2$ ("HKUST-1")

Heating removes the water leaving undercoordinated Cu, i.e., a bare metal site.

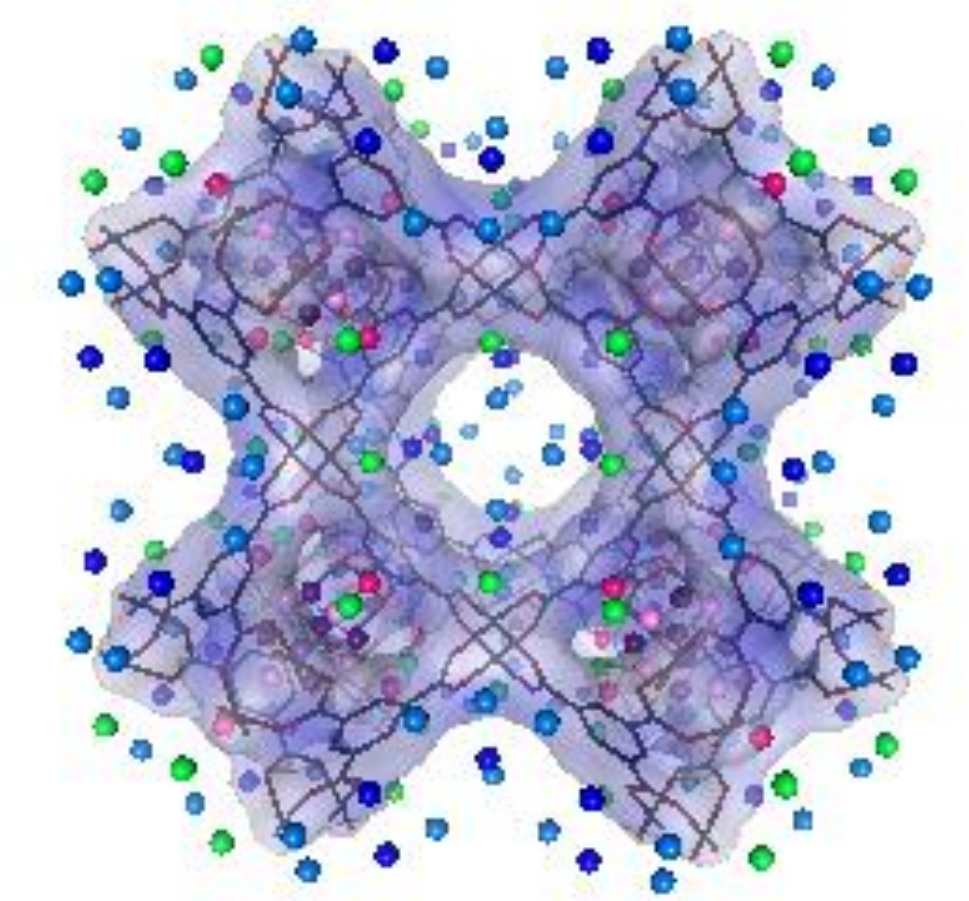




J. Am. Chem. Soc., **128**, 15578 (2006).

MOFs: Optimising the interaction energy

Hydrogen storage in $Cu_3(btc)_2$ ("HKUST-1")



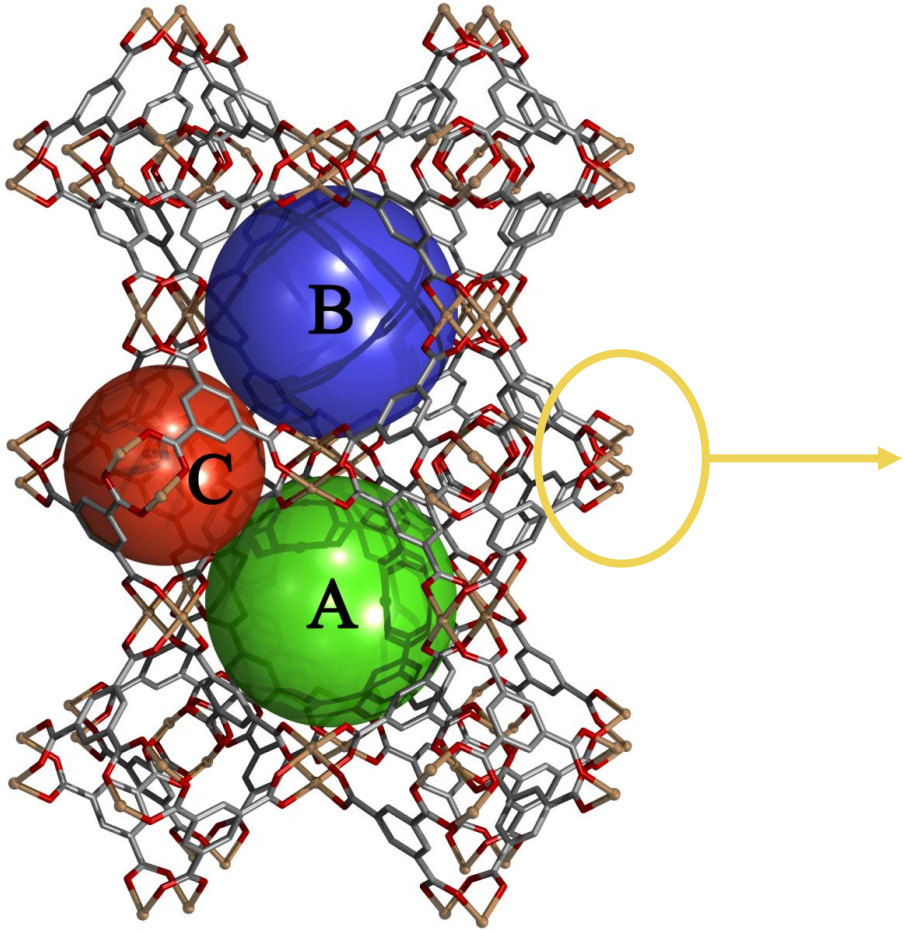
Neutron diffraction shows the sites in the structure that H_2 occupies and the order in which they are filled.

H_2 binds to the bare metal sites (green balls) first, due to a more favourable interaction energy, and then fills the pores (blue balls).

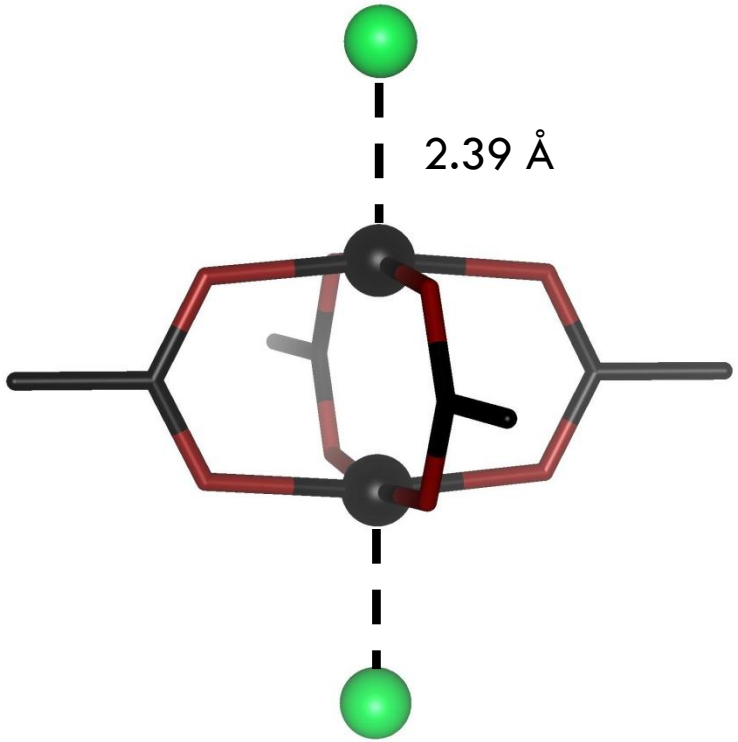
J. Am. Chem. Soc., **128**, 15578 (2006).

MOFs: Optimising the interaction energy

Hydrogen storage in $Cu_3(btc)_2$ ("HKUST-1")



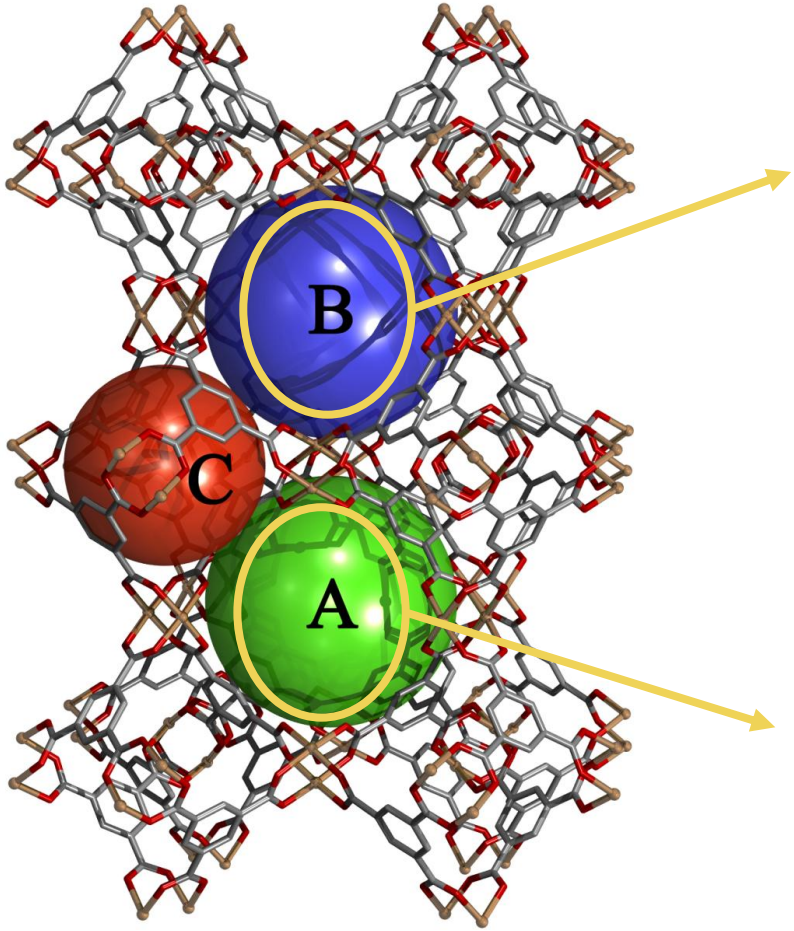
Bare metal sites



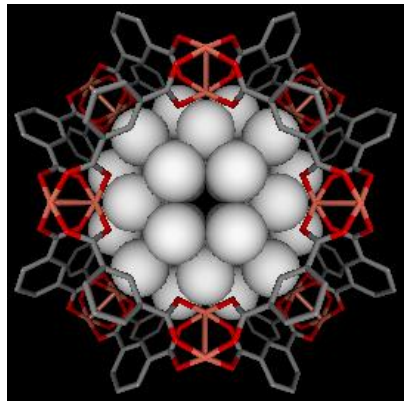
J. Am. Chem. Soc., **128**, 15578 (2006).

MOFs: Optimising the interaction energy

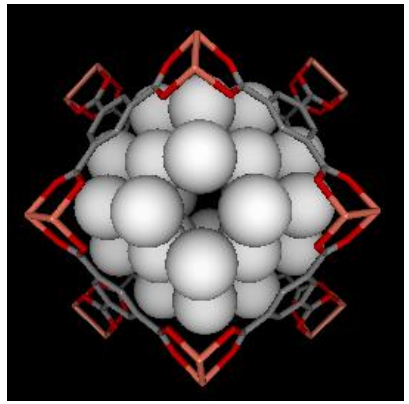
Hydrogen storage in $Cu_3(btc)_2$ ("HKUST-1")



Filling inside the pores



48 D_2: face-capped truncated rhombic dodecahedron



32 D_2: face-capped truncated octahedron

J. Am. Chem. Soc., **128**, 15578 (2006).

For interest only

Capturing CO_2 from post-combustion gas

Flue gas from post-combustion process is a complex mixture, which makes CO_2 capture challenging.

Molecule	Concentration (by volume)
N_2	73-77 %
CO_2	15-16 %
H_2O	5-7 %
O_2	3-4 %
SO_2	800 ppm
SO_3	10 ppm
NO_x	500 ppm
HCl	100 ppm
CO	20 ppm
hydrocarbons	10 ppm
Hg	1 ppb

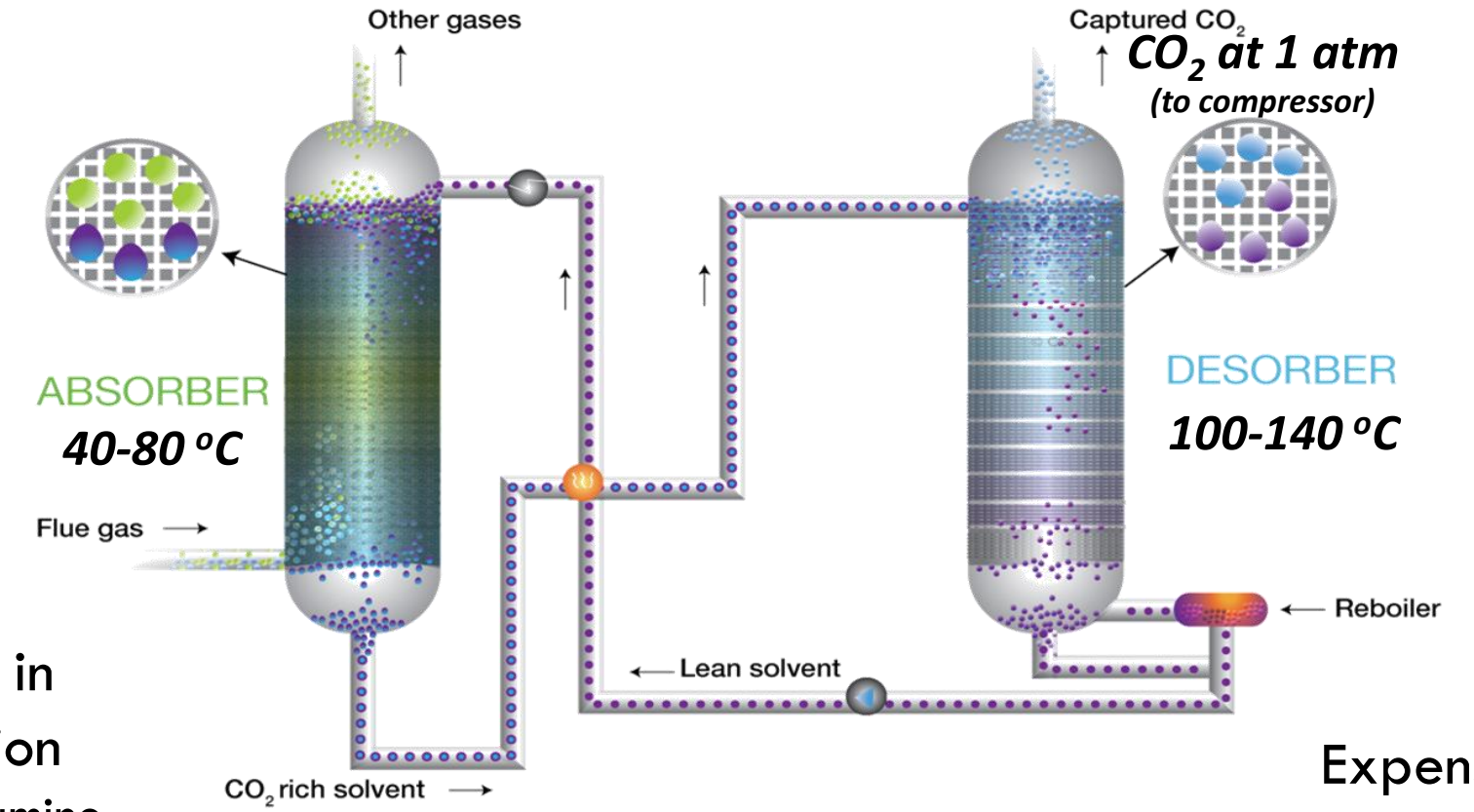
Conditions: Temperature 50-75 °C; Pressure 1 atm

- High volume of flue gas
- Low CO_2 concentration
- Corrosive solutions
- Poor recyclability
- Requires compression and transport
- CCS increases costs by 25-40%

Ind. Eng. Chem. Res. **2002**, *41*, 5470

For interest only

CO_2 capture by 'wet scrubbing'



Alkanolamine in aqueous solution
e.g., monoethanolamine

Expensive due to high heat capacity of water

R. R. Bottoms (Girdler Corp.), "Separating acid gases," U.S. Patent 1783901, 1930.

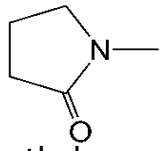
For interest only

New CO_2 capture technologies

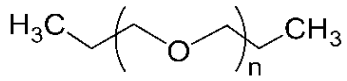
Physical Absorbents

Rectisol® (cold methanol,-40°C)

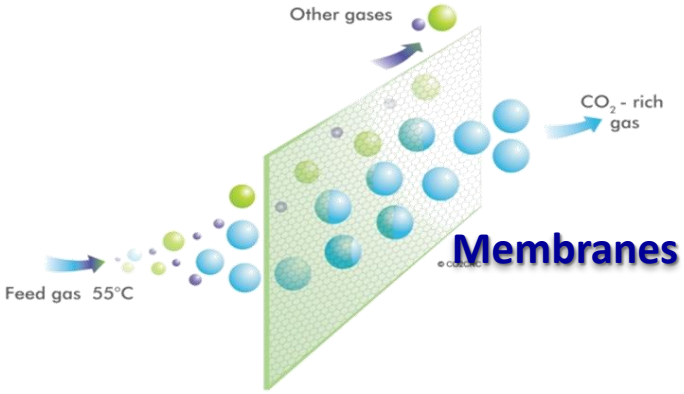
Purisol® (N-methyl-2-pyrrolidinone)



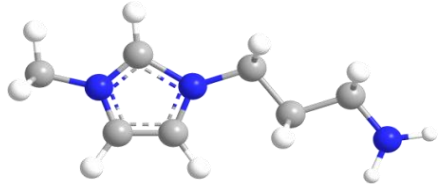
Selexol™ (mix of dimethylethers of polyethylene glycol)



Membranes

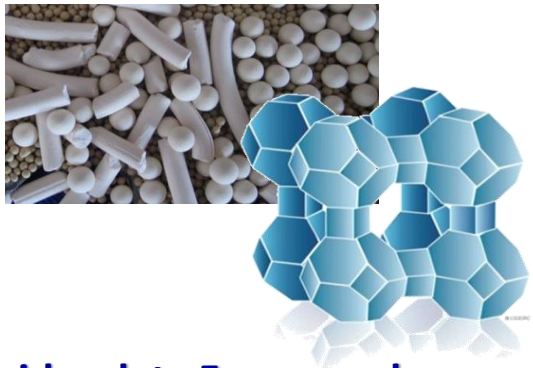


Ionic Liquids



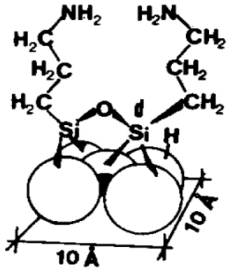
Zeolites

(up to1500 m^2/g)



Amine-Grafted Silicas

SBA-15



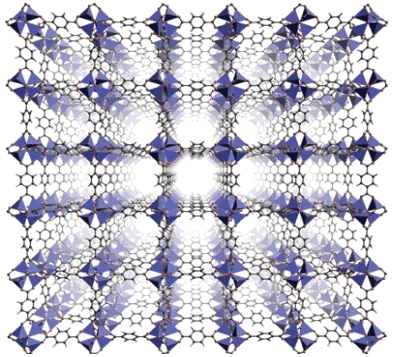
Hydrates and Carbonates of Ca and Mg

Activated Carbon

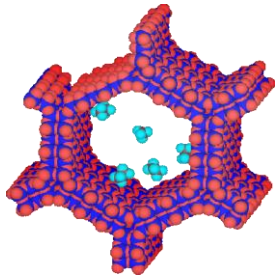
(400-1000 m^2/g)

Metal-Organic Frameworks

(up to 6000 m^2/g)

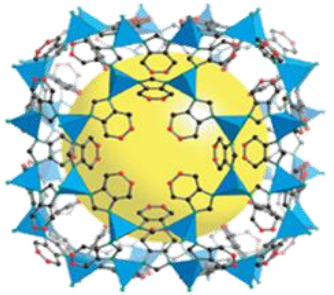


Amine-Impregnated Silicas



MCM-41, MCM-48 loaded with polyethyleneimine

Zeolitic Imidazolate Frameworks

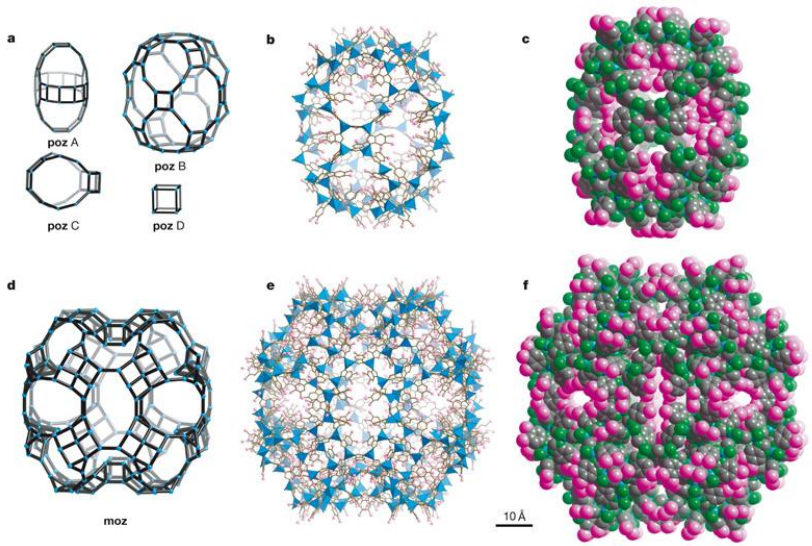


Angew. Chem. Int. Ed., **2010**, *49*, 6058-6082; *Pure Appl. Chem.*, **2011**, *83*, 57.

MOF material properties for CO_2 capture

1. High surface area
2. Large pore voids but small pore openings to achieve size selective gas adsorption with high uptakes

E.g., zeolitic imidazolate frameworks (ZIFs)



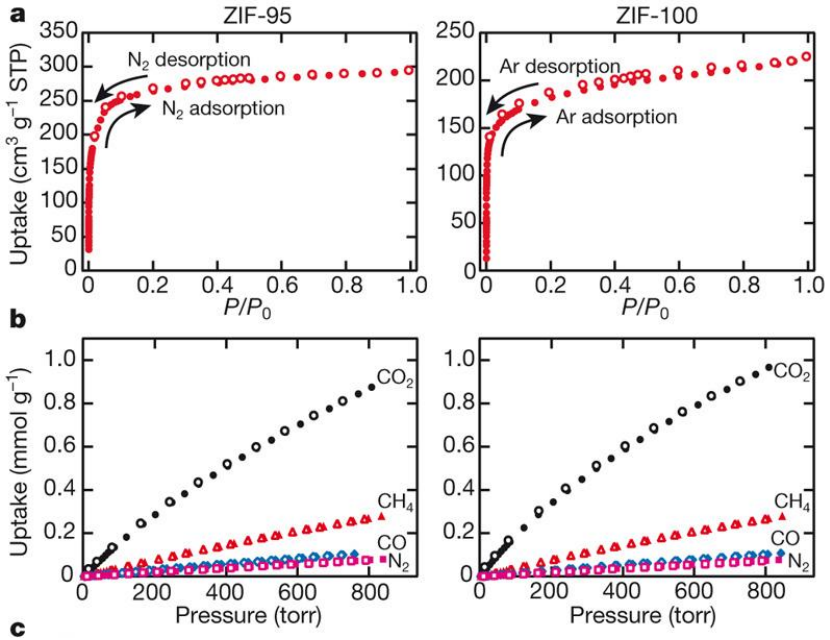


Table 2 | Gas separation selectivity of ZIFs and BPL carbon

Material	Gas pairs	ZIF selectivity*[28]	BPL carbon selectivity[25]	Ratio ZIF/BPL carbon*
ZIF-100	CO_2/CH_4	5.9 ± 0.4	2.5	2.4 ± 0.2
ZIF-100	CO_2/CO	17.3 ± 1.5	7.5	2.3 ± 0.2
ZIF-100	CO_2/N_2	25.0 ± 2.4	11.1	2.3 ± 0.2
ZIF-95	CO_2/CH_4	4.3 ± 0.4	2.5	1.7 ± 0.2
ZIF-95	CO_2/CO	11.4 ± 1.1	7.5	1.5 ± 0.1
ZIF-95	CO_2/N_2	18.0 ± 1.7	11.1	1.6 ± 0.2

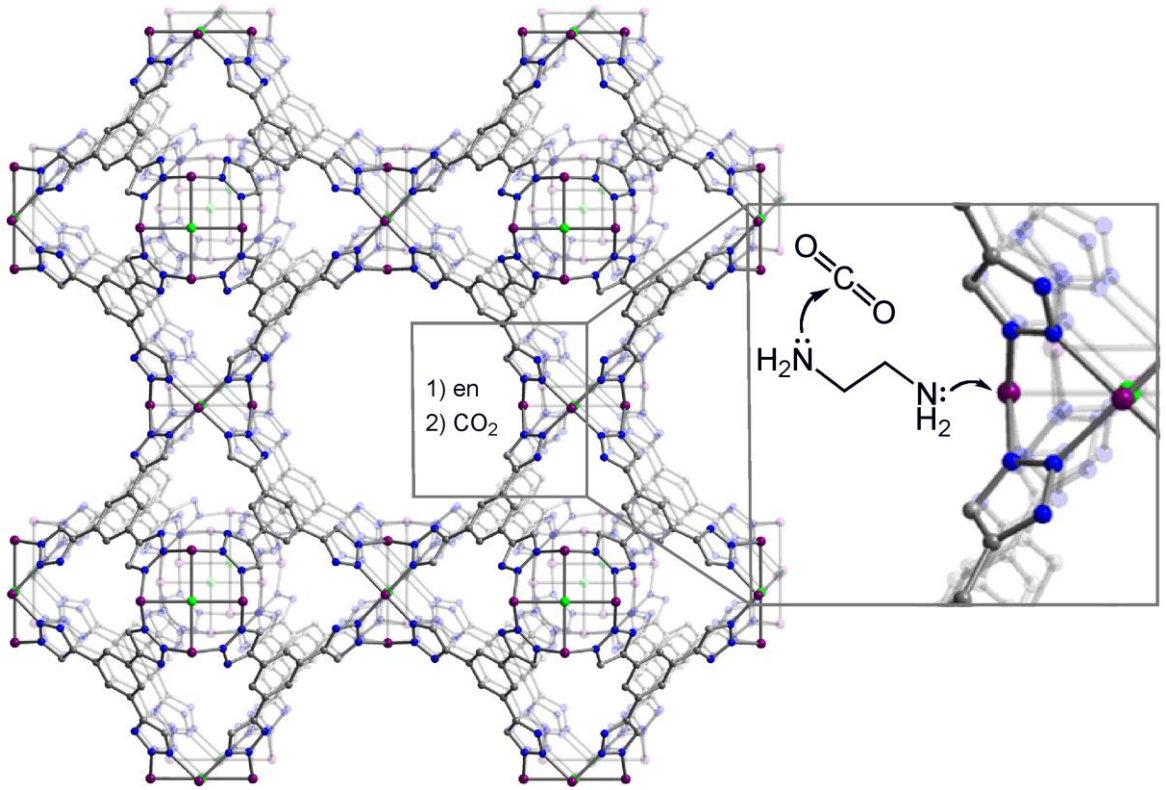
High CO_2 uptake and low N_2 uptake

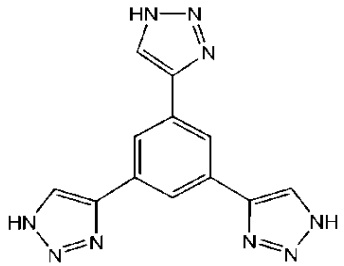
Nature, **453**, 207 (2008); *Science*, **319**, 893 & 939 (2008); *Langmuir*, **24**, 7245 (2008)

MOF material properties for CO_2 capture

3. Surface design to optimise CO_2 interaction

e.g., $H_3[(Cu_4Cl)_3(BTTri)_8]$





BTTri = 1,3,5-tris(1H-1,2,3-triazol-5-yl)benzene

- *Recall:* CO_2 bonds with amines.
- Bidentate amine ligand (e.g., ethylene diamine) can be tethered to the metal sites.
- The uncoordinated end can react with CO_2 to form carbonates.

J. Am. Chem. Soc. **2009**, *131*, 8784

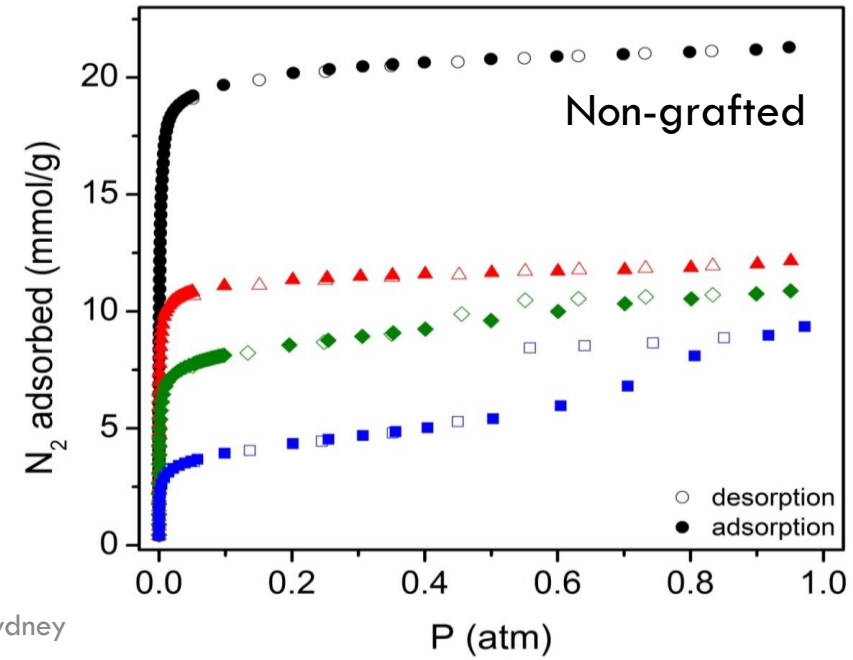
MOF material properties for CO_2 capture

3. Surface design to optimise CO_2 interaction

e.g., $H_3[(Cu_4Cl)_3(BTTri)_8]$

- Amine grafting reduces the surface area (disadvantage).

N_2 isotherms at 77 K



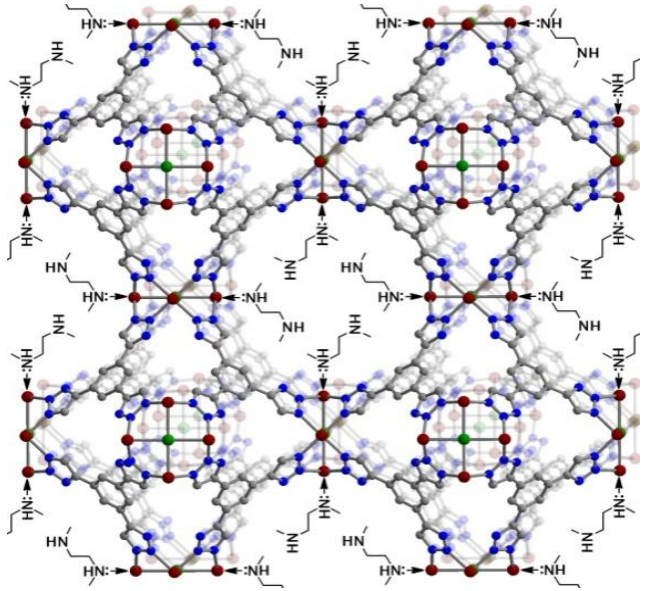
	BET Surface areas
Non-grafted	1770 m^2/g
en	345 m^2/g
pip	380 m^2/g
men	634 m^2/g
mmen	870 m^2/g
dimen	854 m^2/g

MOF surfaces designed for CO_2 capture

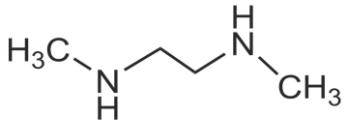
3. Surface design to optimise CO_2 interaction

e.g., $H_3[(Cu_4Cl)_3(BTTri)_8]$

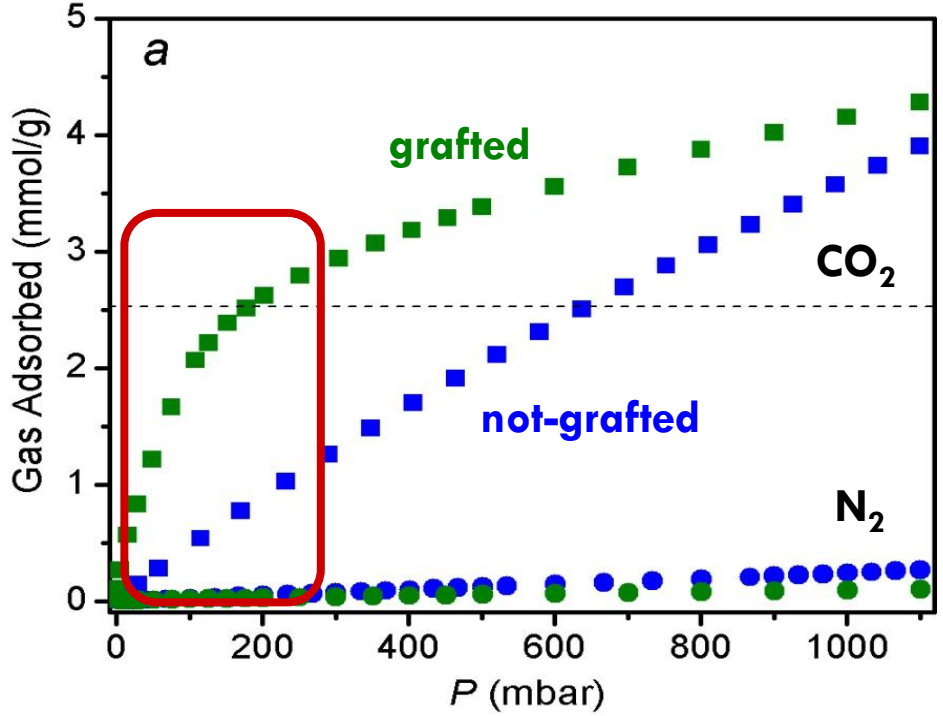
- Amine grafting increases the amount of CO_2 uptake and reduces the amount of N_2 uptake (overall advantage!)



$H_3[(Cu_4Cl)_3(BTTri)_8(mmen)_{12}]$
"1-mmen"



CO_2 isotherms using 10 wt.% CO_2 at 25°C

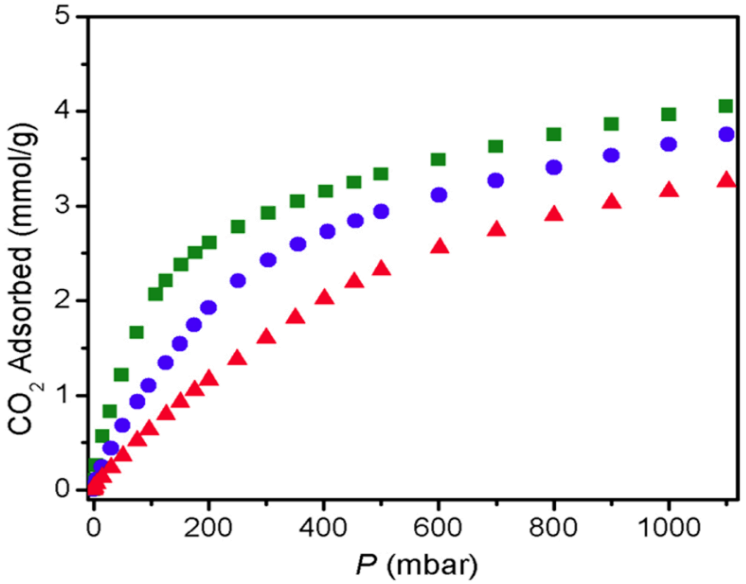


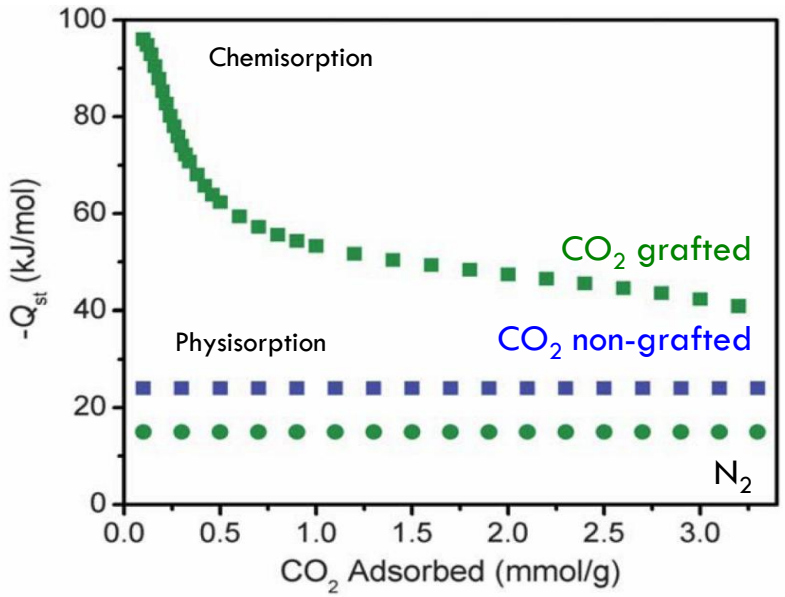
MOF surfaces designed for CO_2 capture

3. Surface design to optimise CO_2 interaction

e.g., $H_3[(Cu_4Cl)_3(BTTri)_8]$

- Changing the amine affects the amount of CO_2 uptake.
- Amine grafting changes the enthalpy of adsorption ($-Q_{st}$), indicating a change from physisorption to chemisorption.





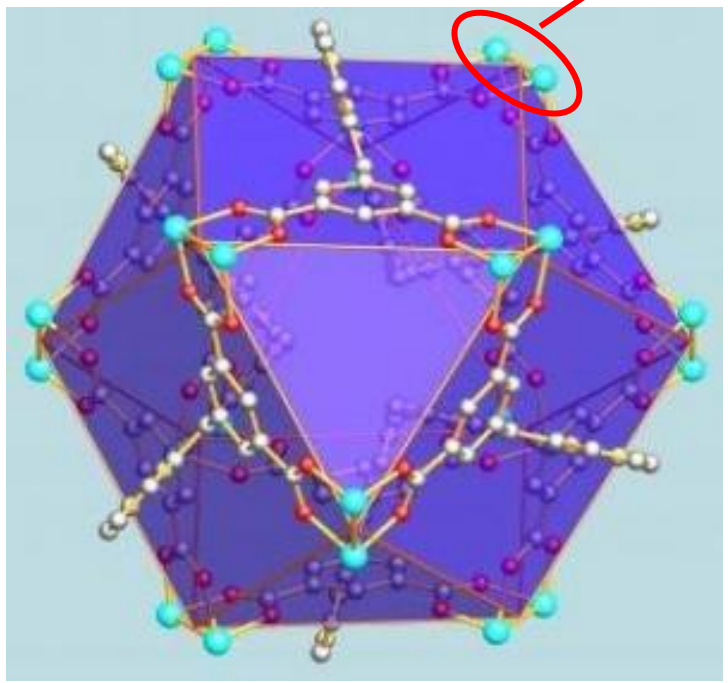
$-Q_{st}$ (zero coverage)	kJmol^{-1}
Non-grafted	21
en	90
pip	96
men	82
mmen	96
dimen	46

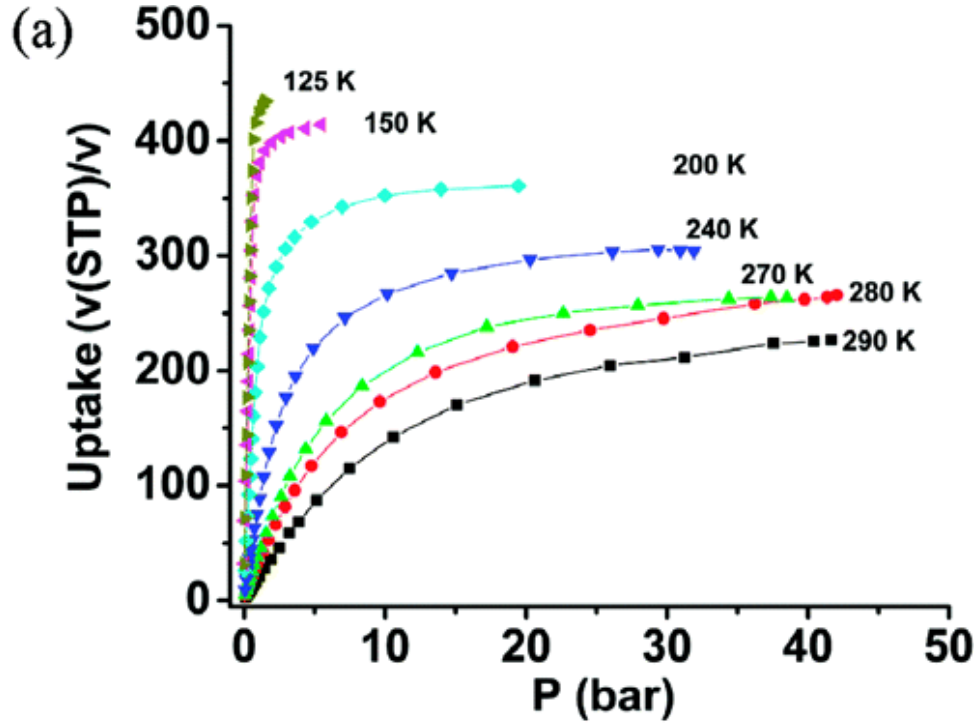
MOF material properties for CH_4 storage

1. High surface area
2. Favourable interaction energy and local structure.

E.g., 'PCN-14'

Structural feature: Cu – Cu dimers





J. Am. Chem. Soc., **130**, 1012 (2008).

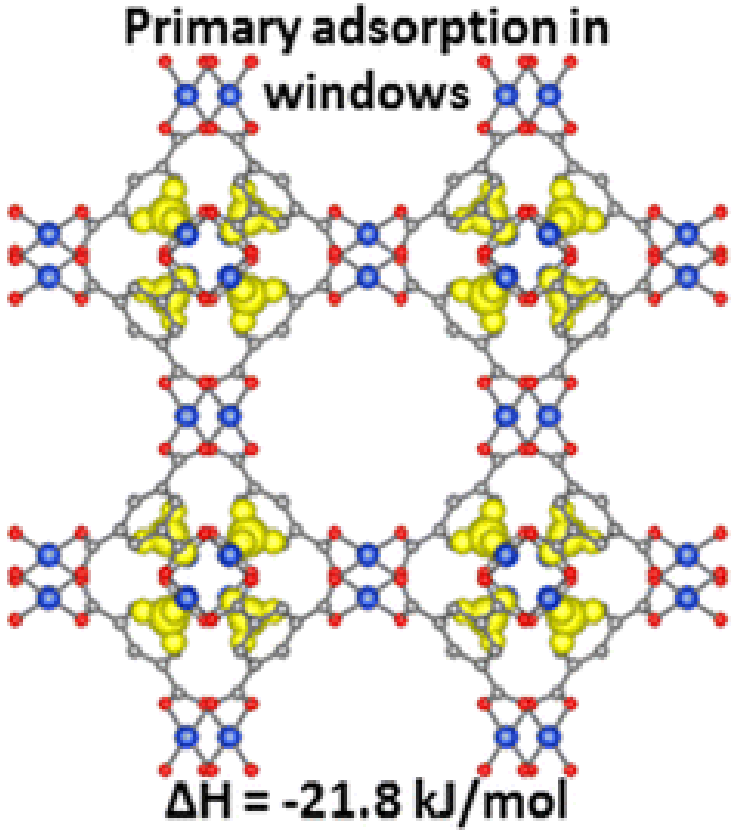
See http://www.sciencedaily.com/releases/2008/01/080121101027.htm

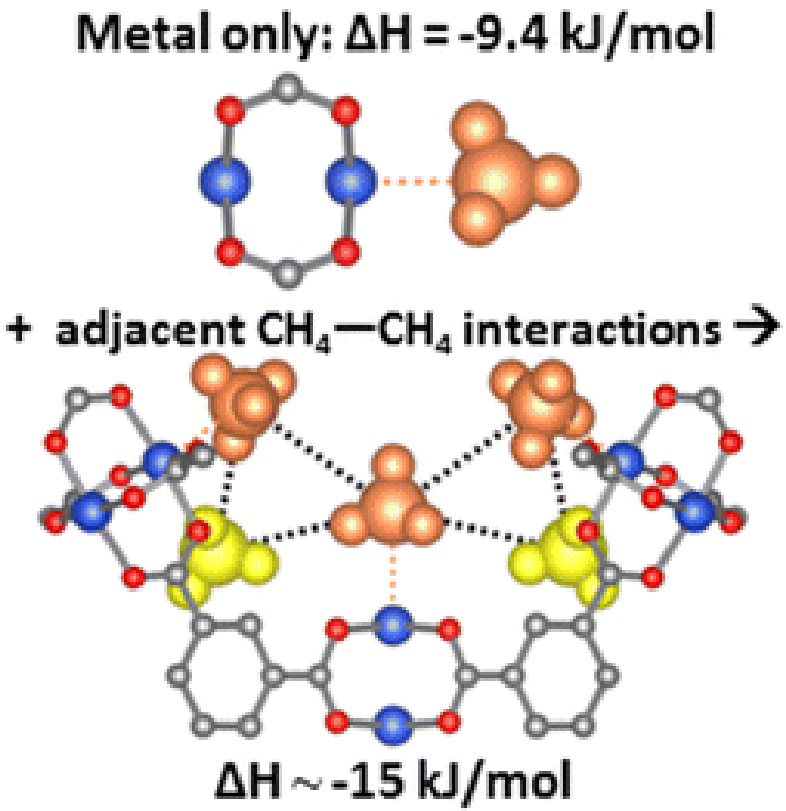
MOF material properties for CH_4 storage

1. High surface area
2. Favourable interaction energy and local structure.

E.g., $Cu_3(btc)_2$ ('HKUST-1')

- CH_4 binds to the bare metal site creating an ion-induced dipole on the guest molecule, strengthening the interaction.
- The local structure creates adjacent CH_4 – CH_4 interactions that further strengthen the interaction.



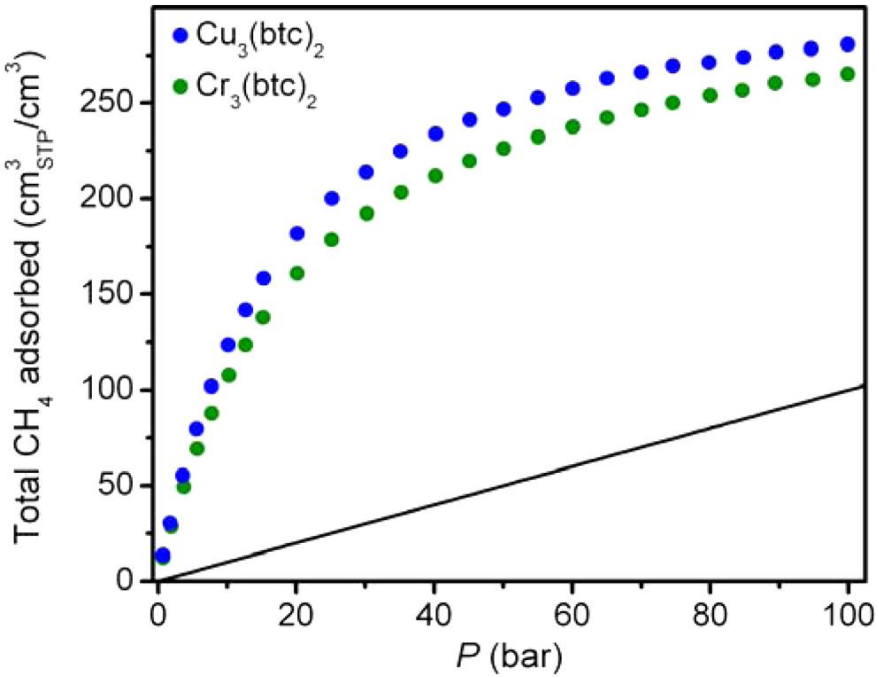


Chem. Eur. J., **16**, 5205 (2010).

CH_4 storage in MOFs

$Cu_3(btc)_2$ ('HKUST-1') exhibits the highest known room temperature volumetric methane uptake.

Total uptake: 230 $cm^3(STP)/cm^3$ at 35 bar and 270 $cm^3(STP)/cm^3$ at 65 bar, meeting volumetric target set by DOE.



Tank filled with MOF, filled with CH_4

Empty tank filled with CH_4

Nature Materials, **17,** 174 (2018).

Learning outcomes

After this lecture you should be able to

- Appreciate the porous nature MOFs, and understand that strategic design of these materials allows the achievement of very high surface areas with specific host-guest functions
- Broadly appreciate the performance requirements of gas storage and separation materials, and understand how MOF design can target the following technologies:
  - Hydrogen storage
  - CO_2 capture
  - Methane storage