Hydrogen Storage in Nanostructured Materials for Automotive Applications

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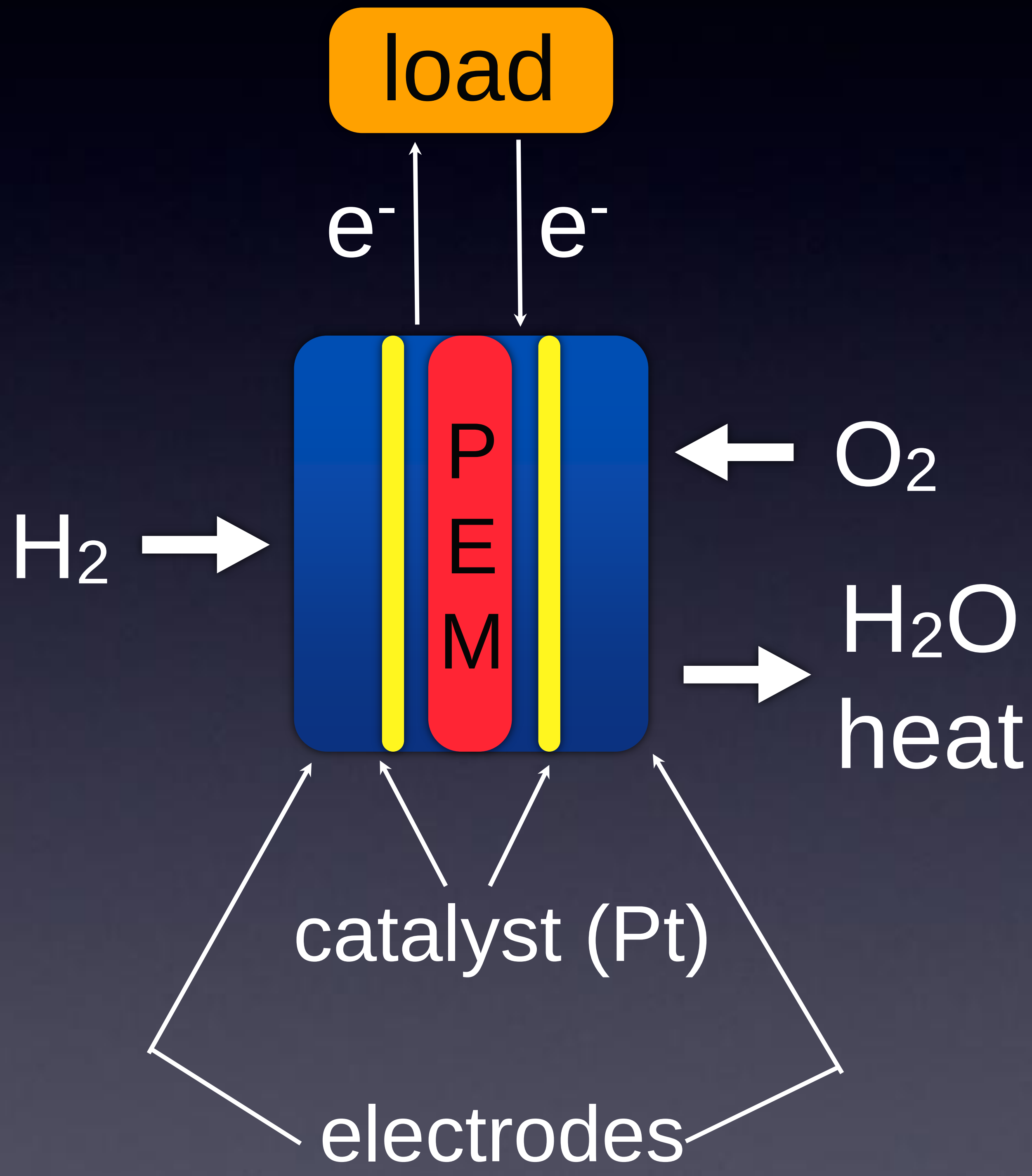
OUTLINE

- Need for efficient storage on board vehicles
- Overview of the most common storage strategies
- Focus on the advantages and potentialities nanostructured materials

Transportation without Fossil Fuels

A possible solution:

Electric vehicles powered by H_2 fuel cells



Chevrolet Sequel
(General Motors)

General Considerations

- High Energy density: $LHV (H_2) = 120.1$ MJ/kg
  LHV (gasoline) = 42.5 MJ/kg

- 500 km range vehicle → 6 kg of H_2

- U.S. Department of Energy (DOE) requirements for on-board storage:

  for 2010: 6 wt % , 45 kg/m^3
  for 2015: 9 wt % , 81 kg/m^3

- Storage solutions: efficient, safe, as cheap as possible

Possible Storage Strategies

Compression

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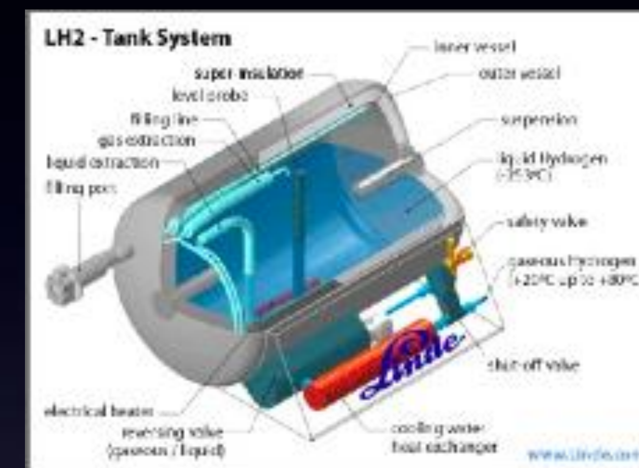
- compressed gaseous H_2
- 700 bar , 57 kg/m^3
- 15% of LHV lost in compression

Liquefaction



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- liquid H_2 at 20 K
- 1 bar , 73 kg/m^3
- 30% of LHV lost in liquefaction

* http://www.fuelcell.no/hydrogen_storage_eng.htm

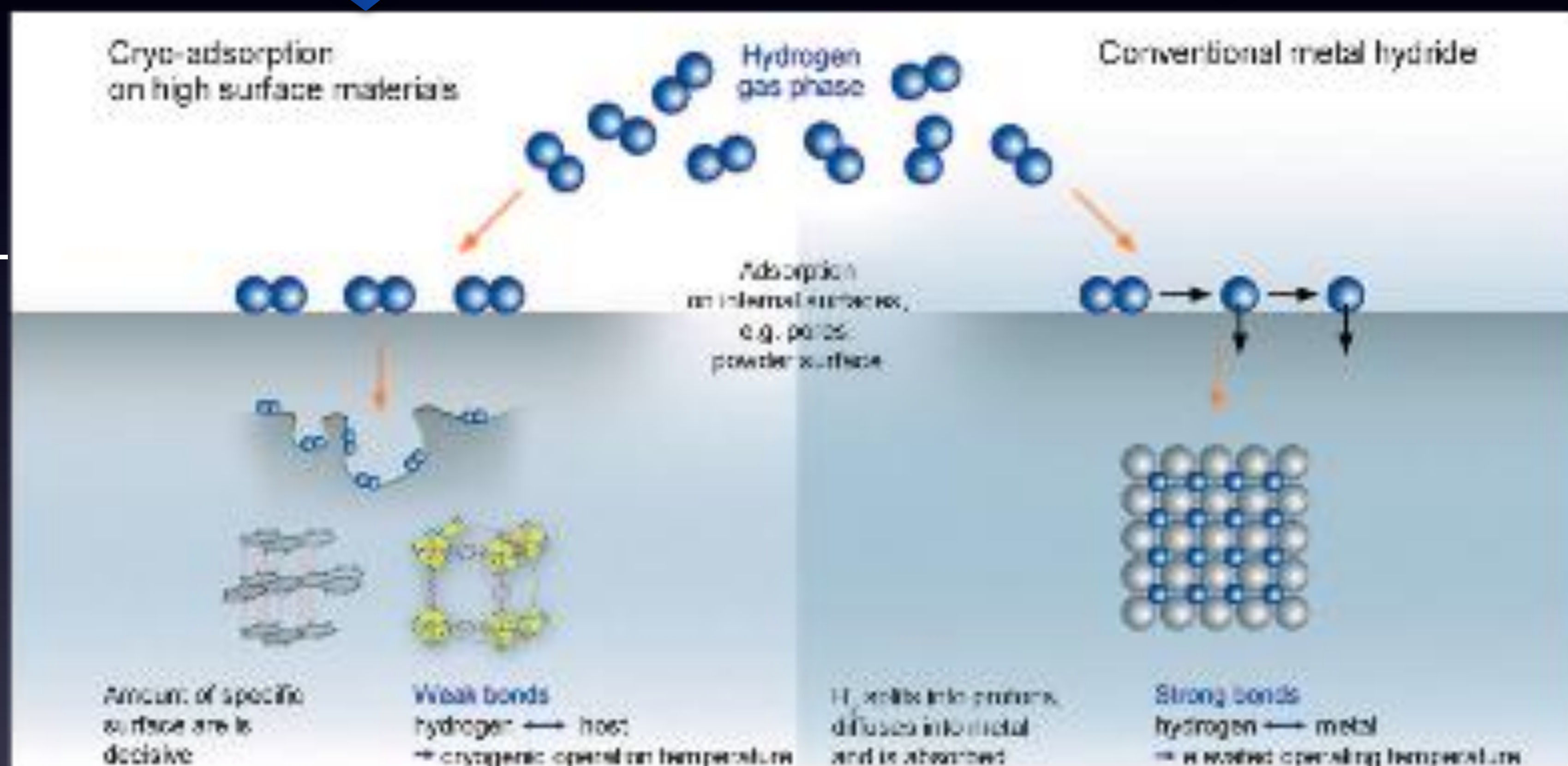
** http://www. eere.energy.gov

Possible Storage Strategies

Cryo-adsorption on high surface area materials

Metal Hydrides

U. Eberle *et al.;* Angew. Chem. Int. Ed. 2009, 48, 6608-6630



- too weak H_2 - surface bond (physisorption)
- low T required for uptake (77 K)

- too strong H - Metal bond (chemisorption)
- high T required for H_2 release

Intermediate H_2 - substrate bond strength: is it possible?

stronger than physisorption → lower pressure needed

weaker than chemisorption → lower desorption T

Understanding the H_2 - substrate interaction

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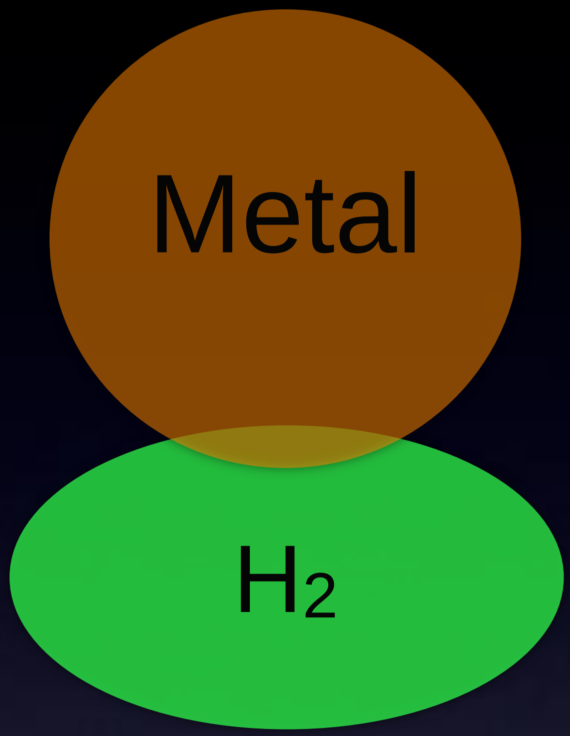
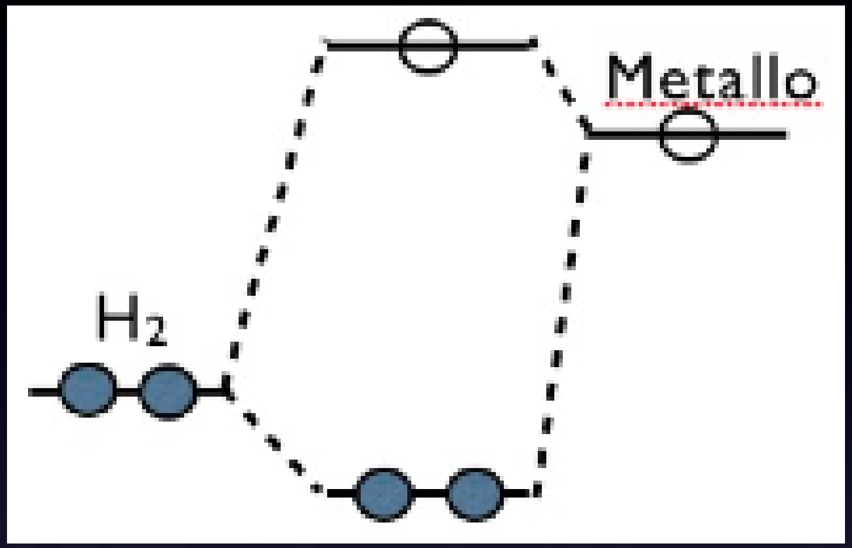
nanostructured materials with *ad hoc* properties

Kubas complexes





H_2 donates 2 e^- to an empty orbital of the metal

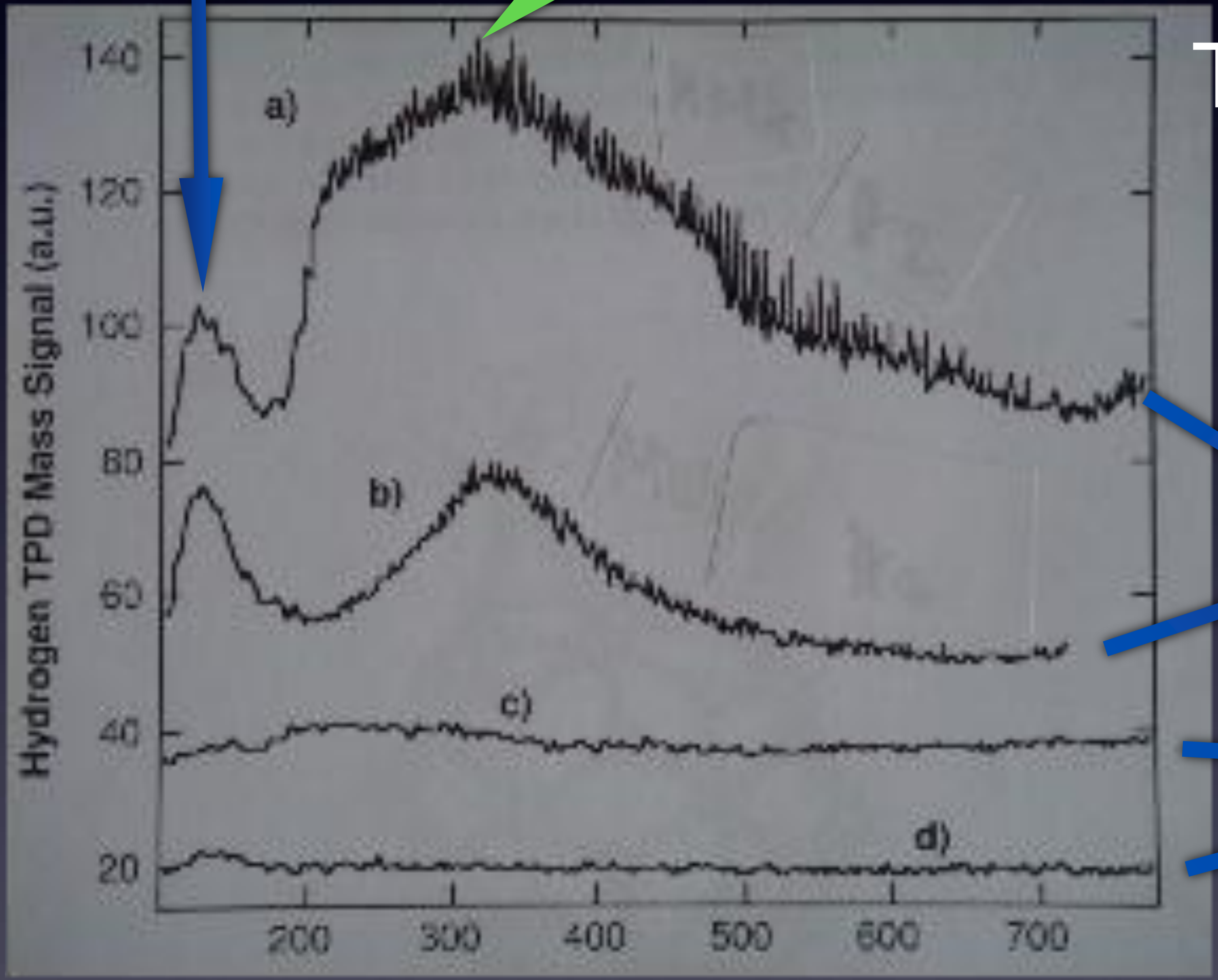
As a result, the H-H bond elongates

G. Kubas, Acc. Chem. Res., 21, 120, 1988

An Interesting Experimental Result

H_2 bound to Fe nanoparticles desorbes at room T!

Physisorbed H_2



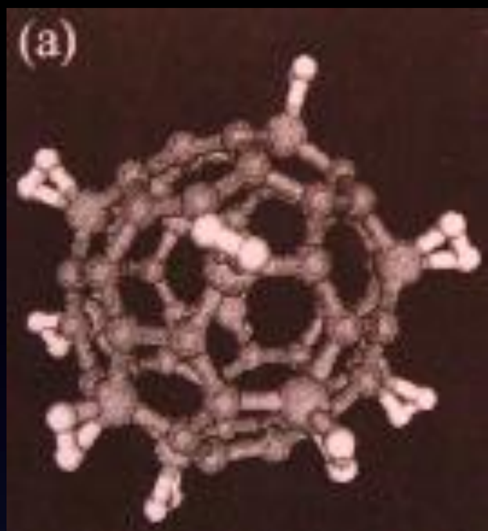
Thermal Desorption Spectroscopy

H_2 from MWCNTs with residual Fe nanoparticles

H_2 from Fe nanoparticles: nothing happens!

A.C. Dillon *et al.*; Mater. Res. Soc. Symp. Proc. vol. 837 (2005), N 4.2

Some examples:



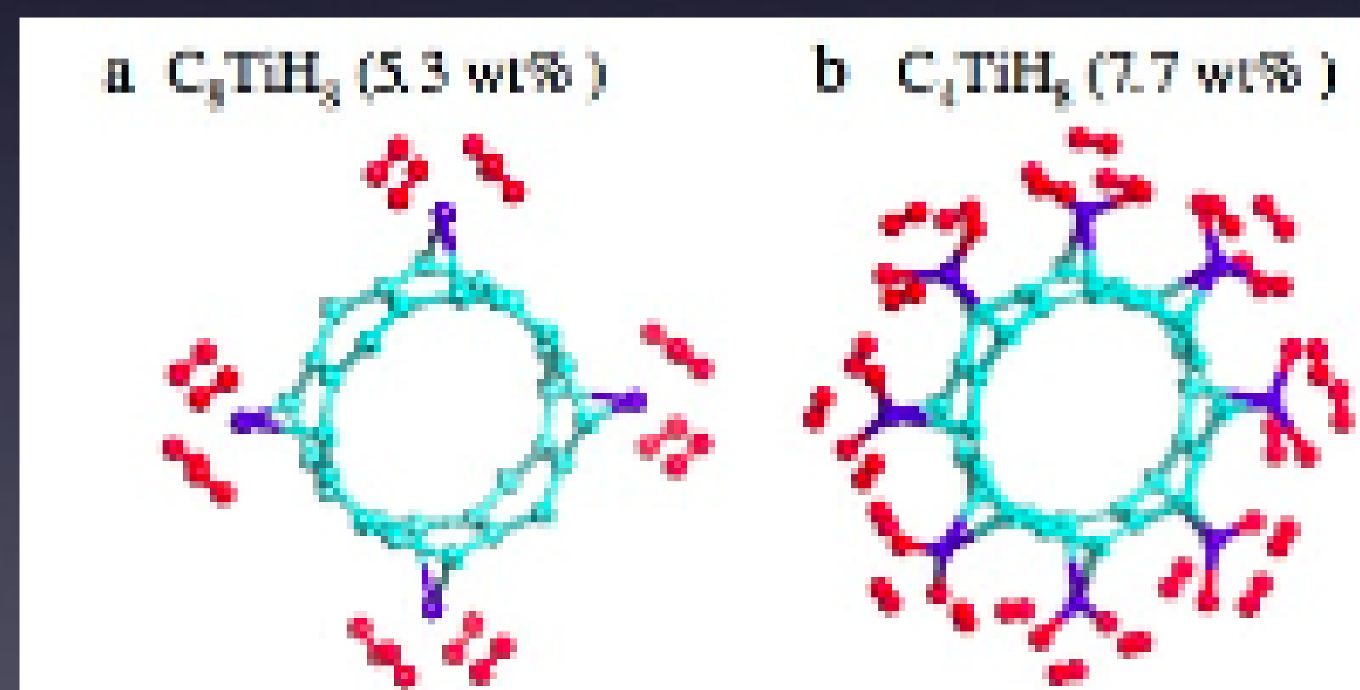
$C_{48}B_{12}$

- one H_2 molecule per B atom
- 3.3 wt%

ong-Hyun Kim *et al.;* Mater. Res. Soc. Symp. Proc. vol. 837 (2005), N3.21

“Ti-decorated” CNTs

- 4 H_2 per Ti atom
- up to 7.7 wt% : larger than 2010 DOE requirement of 6 wt%

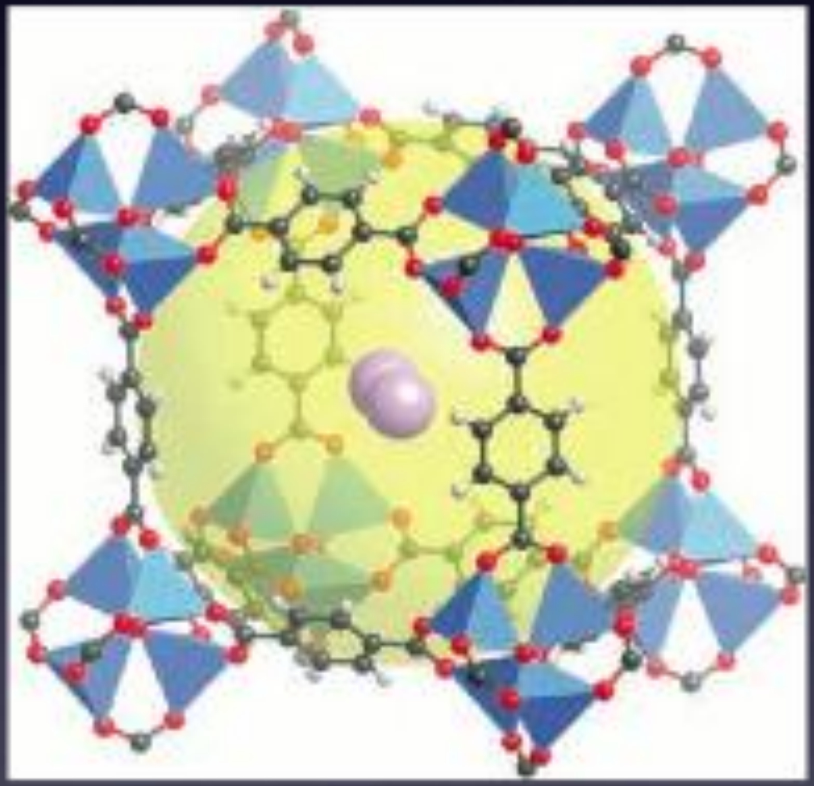


T. Yildirim, S. Ciraci; PRL 94, 175501 (2005)

A Promising Alternative:
Metal Organic Frameworks (MOFs)

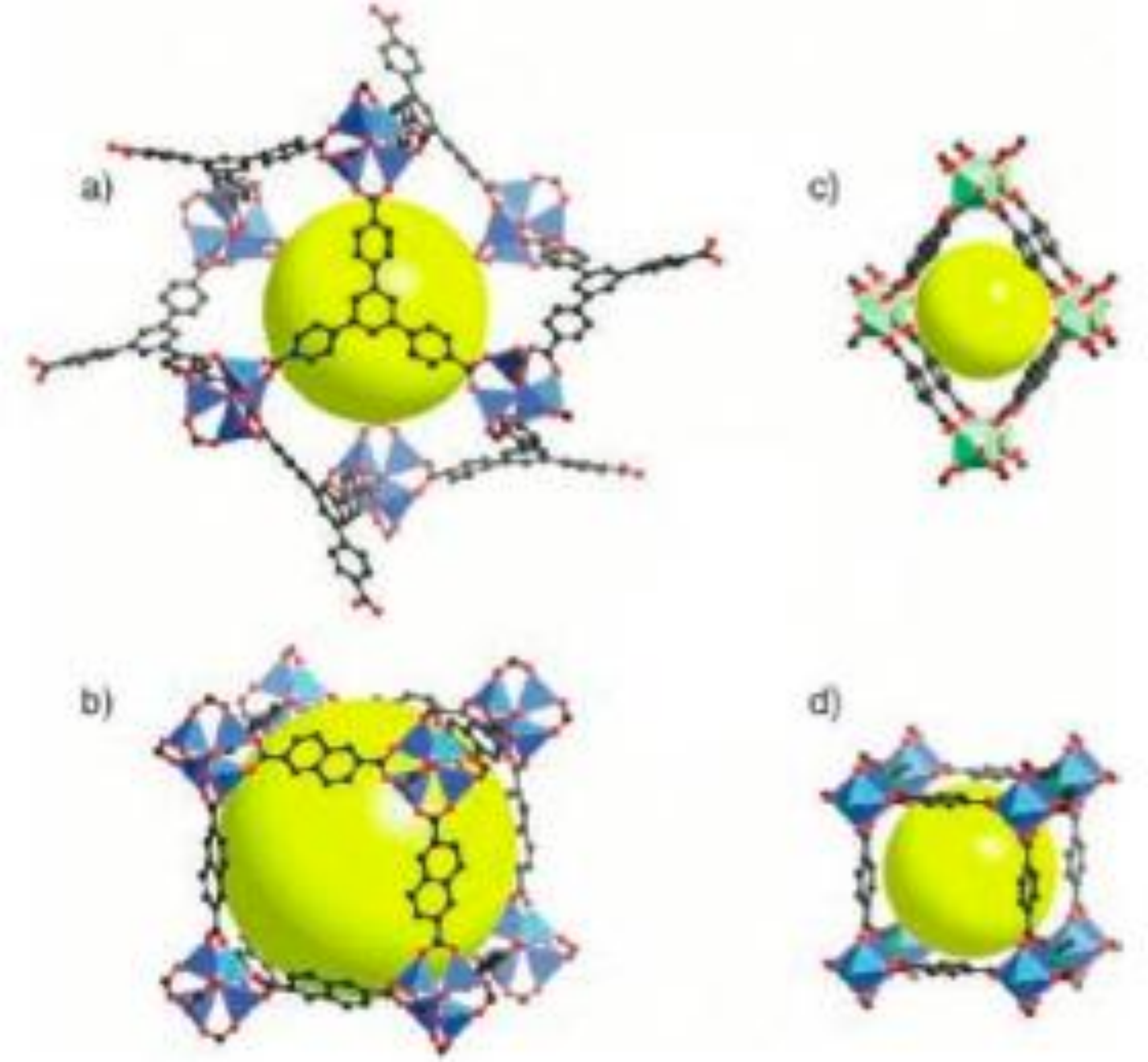
MOFs : crystalline solids assembled by connecting metal clusters through molecular bridges

- high surface area ⟶ PORES
- synthesis is easily achieved
- control on chemical and geometrical properties
- tunable H_2 storage capacity
- MOFs are cheap



MOF-5

.C. Roswell, O.M. Yaghi; Angew. Chem. Int. Ed. 2005, 44, 4670-4679


a)
b)
c)
d)

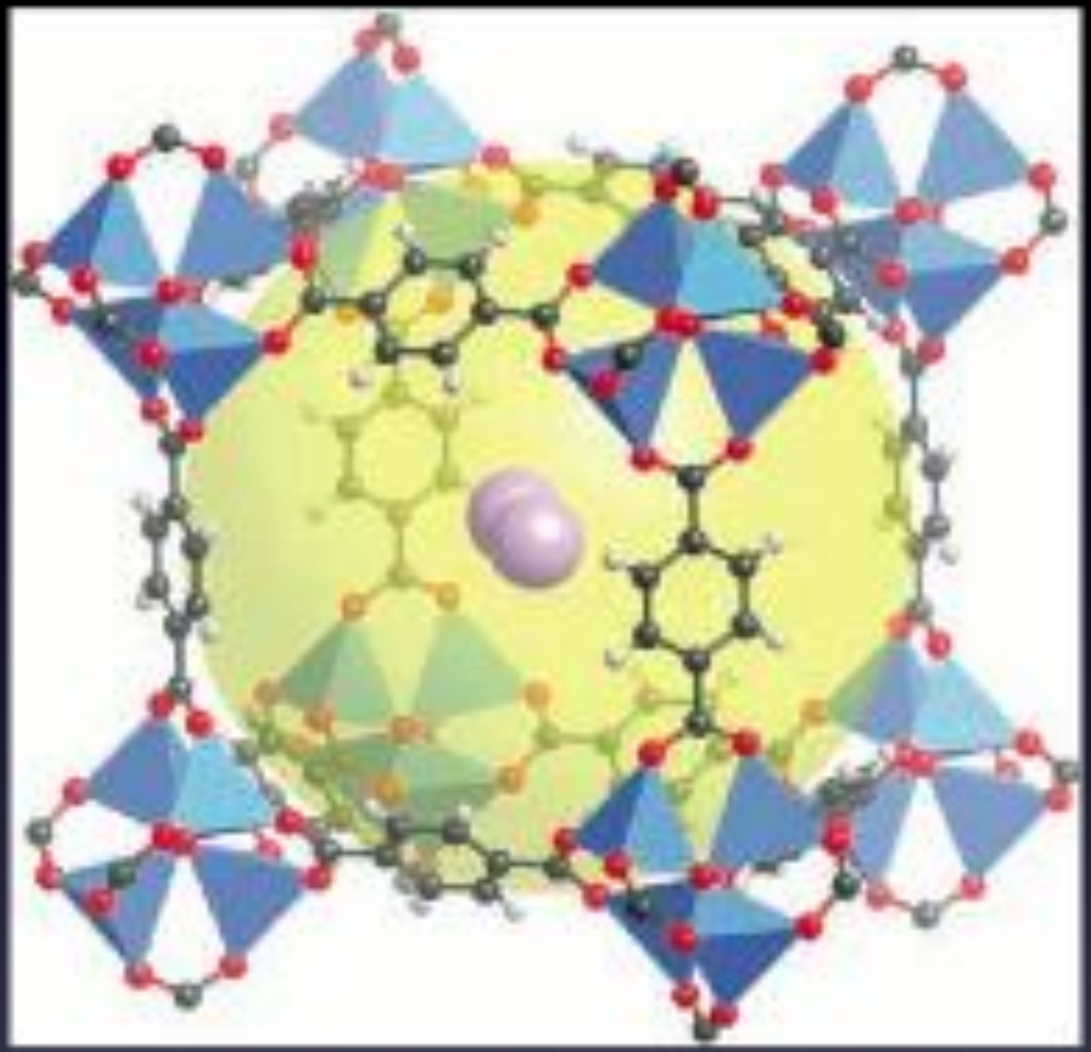
The Role of Pores

Ideal situation: pore diameter comparable to H_2 dimensions (1.2 Å)

maximization of van der Waals interaction with the whole pore surface

stronger H_2 absorption energy

larger volumetric capacity (H_2 stored/unit volume)



MOF-5
pore diameter: 15.2 Å

REDUCE PORE DIMENSIONS

J.L.C. Roswell, O.M. Yaghi; Angew. Chem. Int. Ed. 2005, 44, 4670-4

Techniques to Reduce Pore Dimensions

Impregnation

Diffusion of high surface area nanostructures into pores

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decreasing pores dimensions

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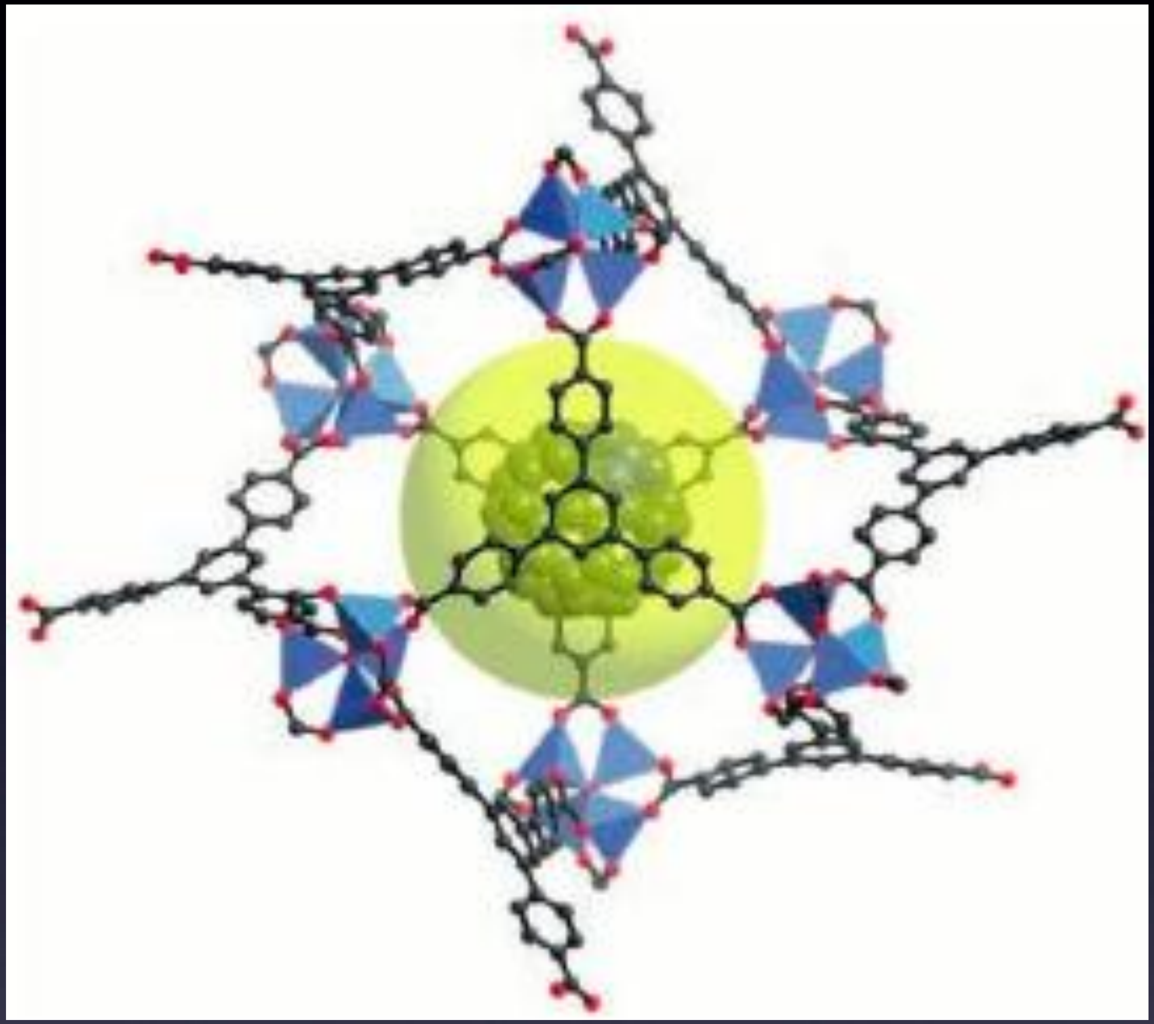
new absorption sites



C_{60} - impregnated MOF-177

J.L.C. Roswell, O.M. Yaghi; Angew. Chem. Int. Ed. 2005, 44, 4670-4679

Techniques to Reduce Pore Dimensions

Catenation

Synthesis of two interpenetrating MOFs → reduction pf pore volume

interpenetration

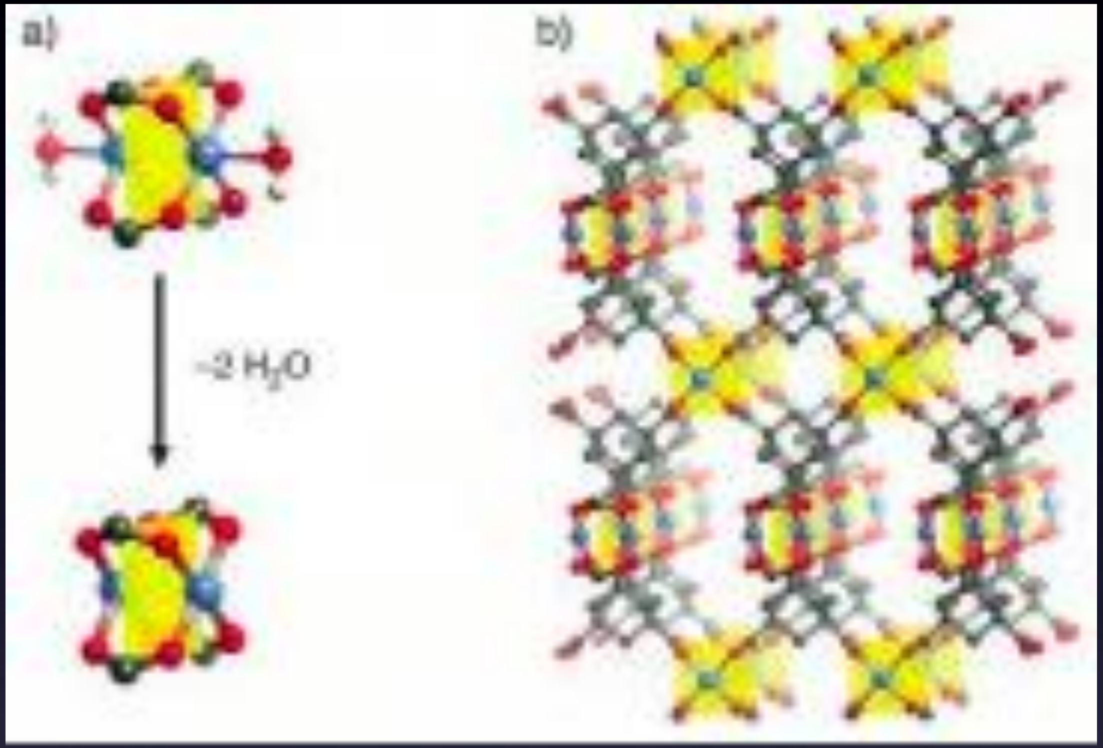
interweaving

functionalized linkers

J.L.C. Roswell, O.M. Yaghi; Angew. Chem. Int. Ed. 2005, 44, 4670-4679

Techniques to Reduce Pore Dimensions

Open Metal Sites



Cu^{2+} - H_2O

heating

H_2O is removed

new absorption sites

larger gravimetric capacity

J.L.C. Roswell, O.M. Yaghi; Angew. Chem. Int. Ed. 2005, 44, 4670-4679

Conclusions

- compression
- liquefaction
- metal hydrides

→

- low efficiency
- high costs
- scarcely tunable storage properties

Nanostructured materials → tailoring storage properties cheaper

Internal Combustion Engine → Oil Age

on-board storage solutions: efficient, safe, cheap

H_2 fuel cell → H_2 Economy