INSTITUT DES MATÉRIAUX POREUX DE PARIS

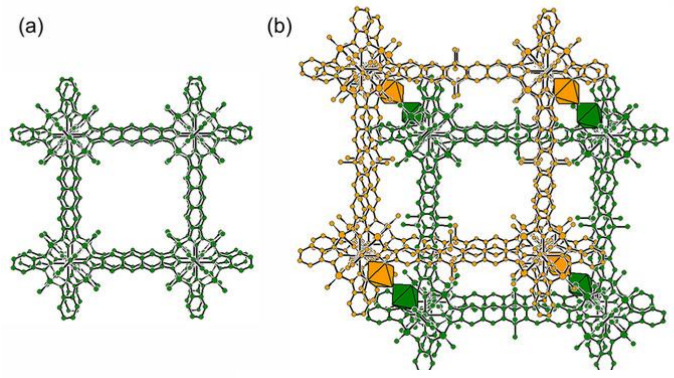
ÉCOLE NORMALE SUPÉRIEURE

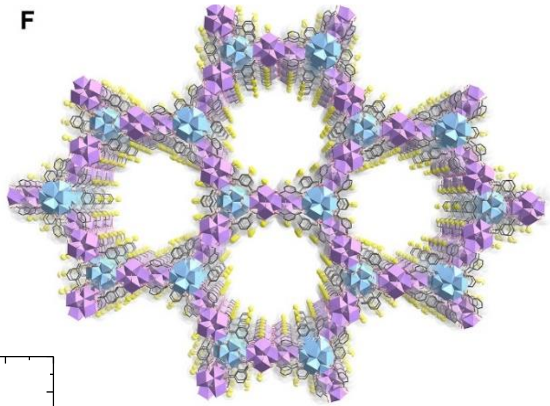
ESPCI PARIS

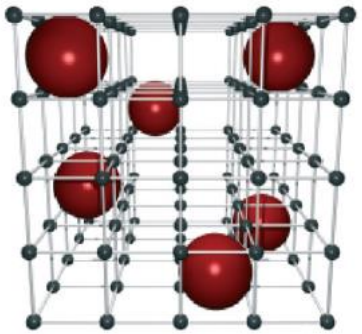
EDUCATION SCIENCE INNOVATION

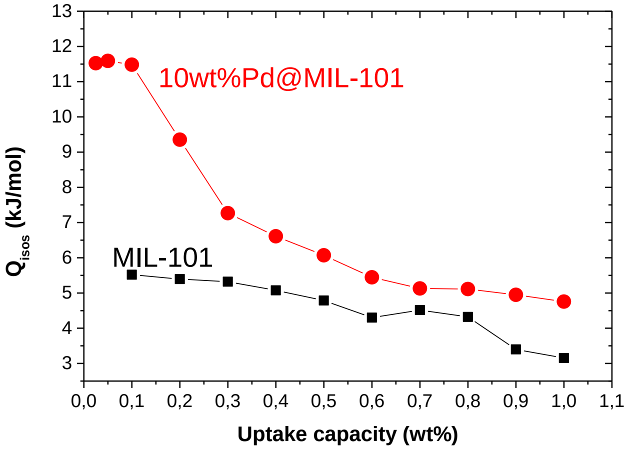
PSL UNIVERSITÉ PARIS

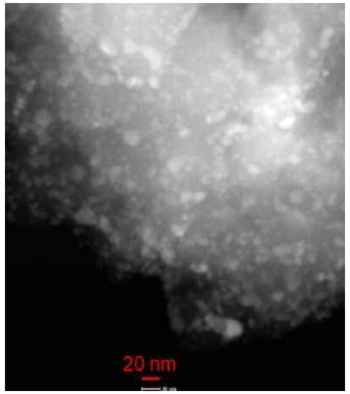
Hydrogen : from storage to production







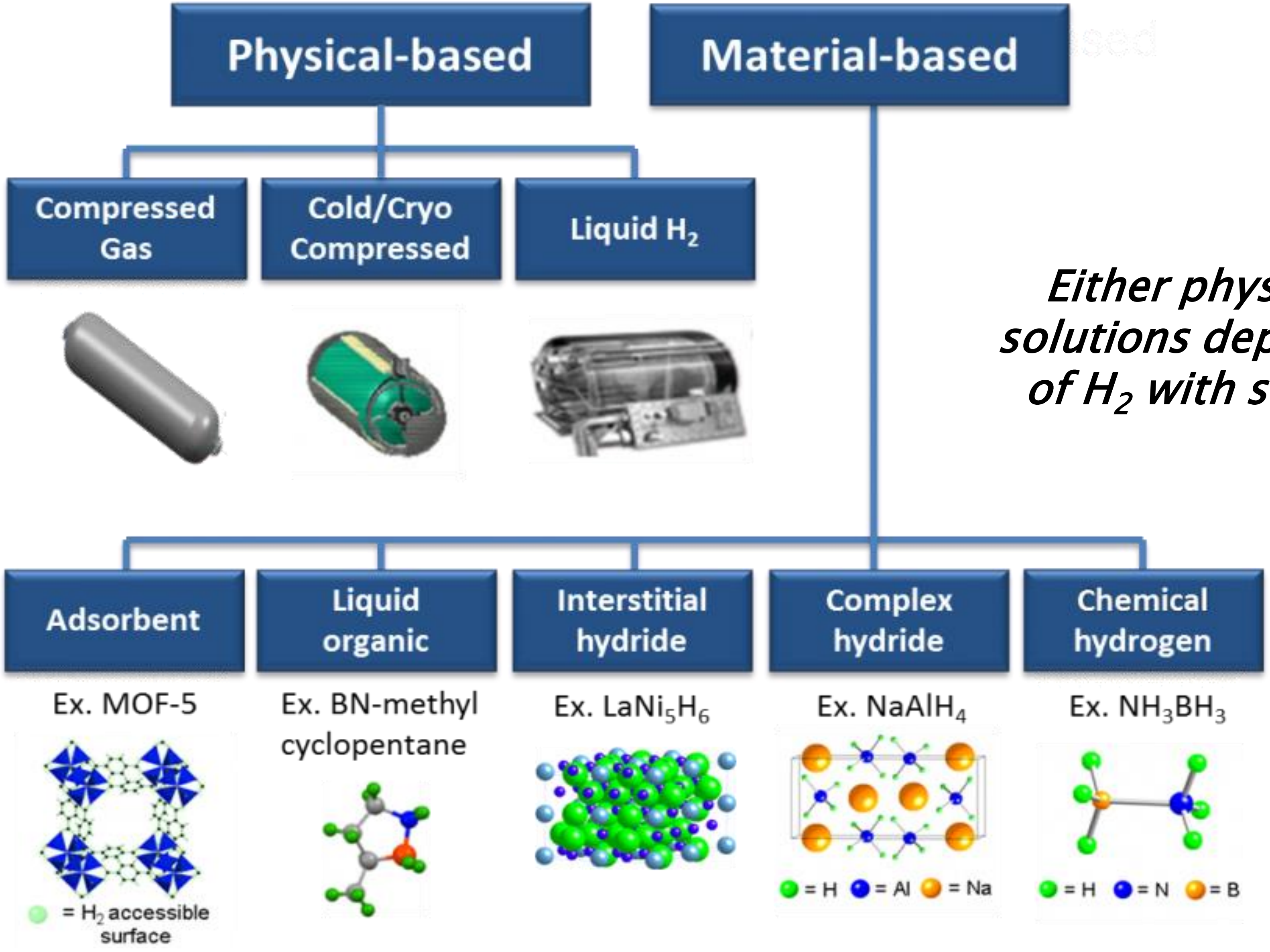




Christian SERRE – Rencontres CNC – 7 décembre 2023

Institute des Matériaux Poreux de Paris, ENS, ESPCI Paris , université PSL, CNRS, France

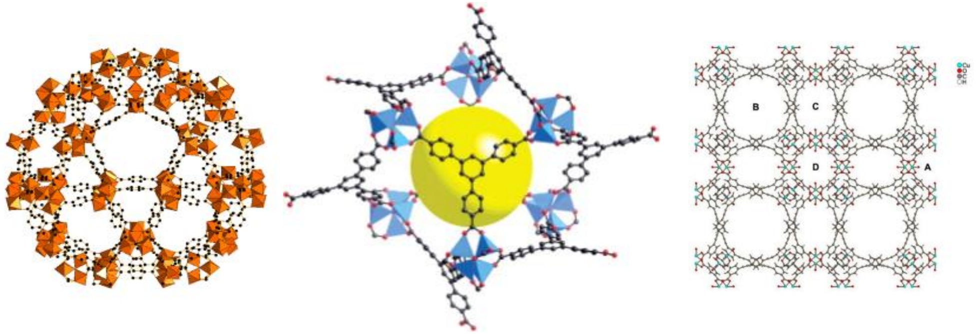
Physical *vs.* material-based solutions for hydrogen storage

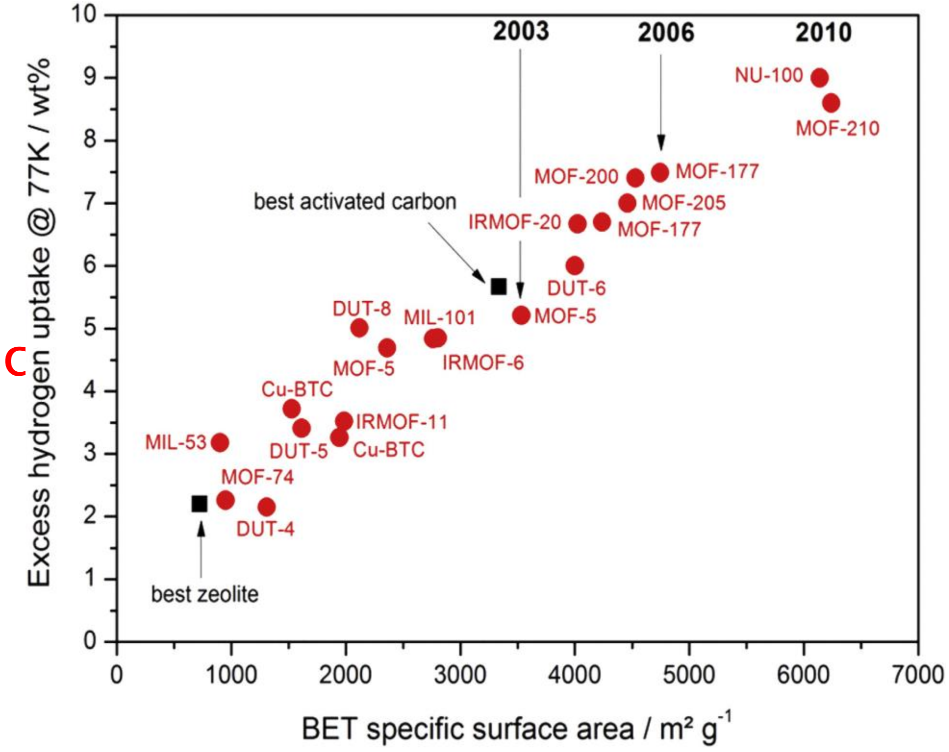


Either physical or materials–based solutions depending on the interaction of H_2 with surrounding environment

Hydrogen storage in MOFs

- **Advantages**
  - High porous volume and specific surface
  - Highly tunable chemistry and porosity
  - High adsorption capacities at 77 K
- **Disadvantages**
  - Limited volumetric capacity (small density 0,1–1 g/c
  - Weak capacities at RT ⬄ low heat of adsorption
  - Limited number of scalable, cheap materials

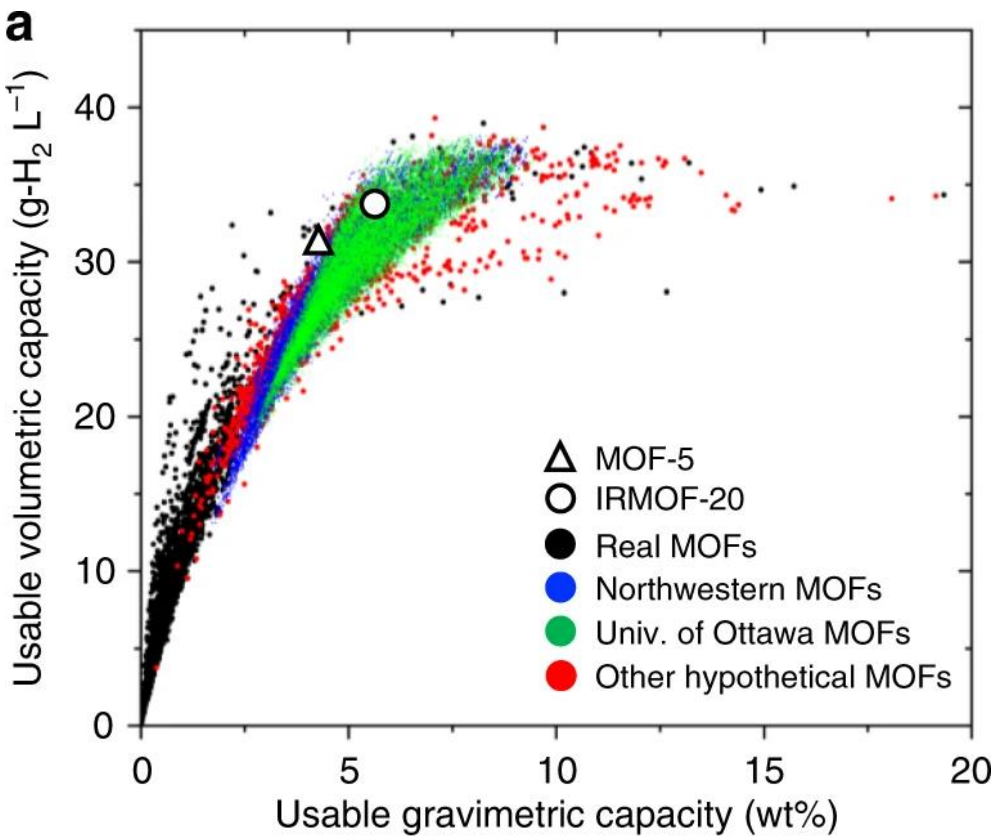




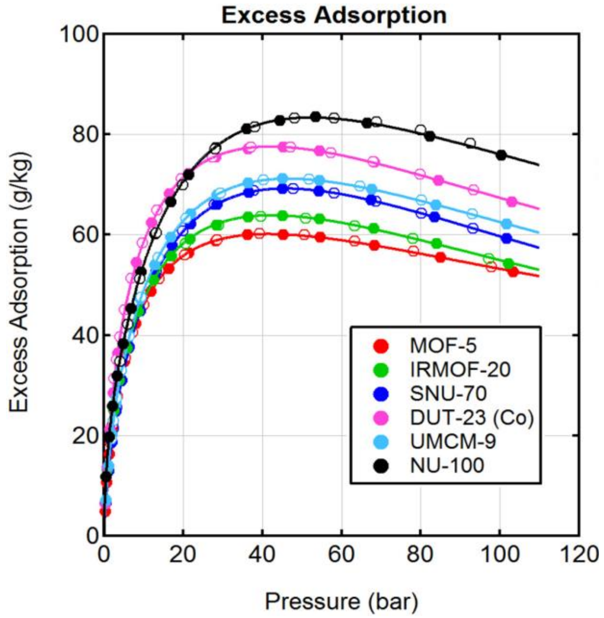
D. Broom et al, Inter. J. Hydrogen Energ, 2019, 44, 7768

High-throughput computational screening of MOFs – H_2

MOFs : crystalline solids
>25,000 exp. structures
⇔ Databases of experimental
And theoretical structures
(500,000)
⇔ Datamining, Machine Learning



Usable capacity = accessible uptake upon the pressure swing: 100 bar ↔ 2 bar at 77K



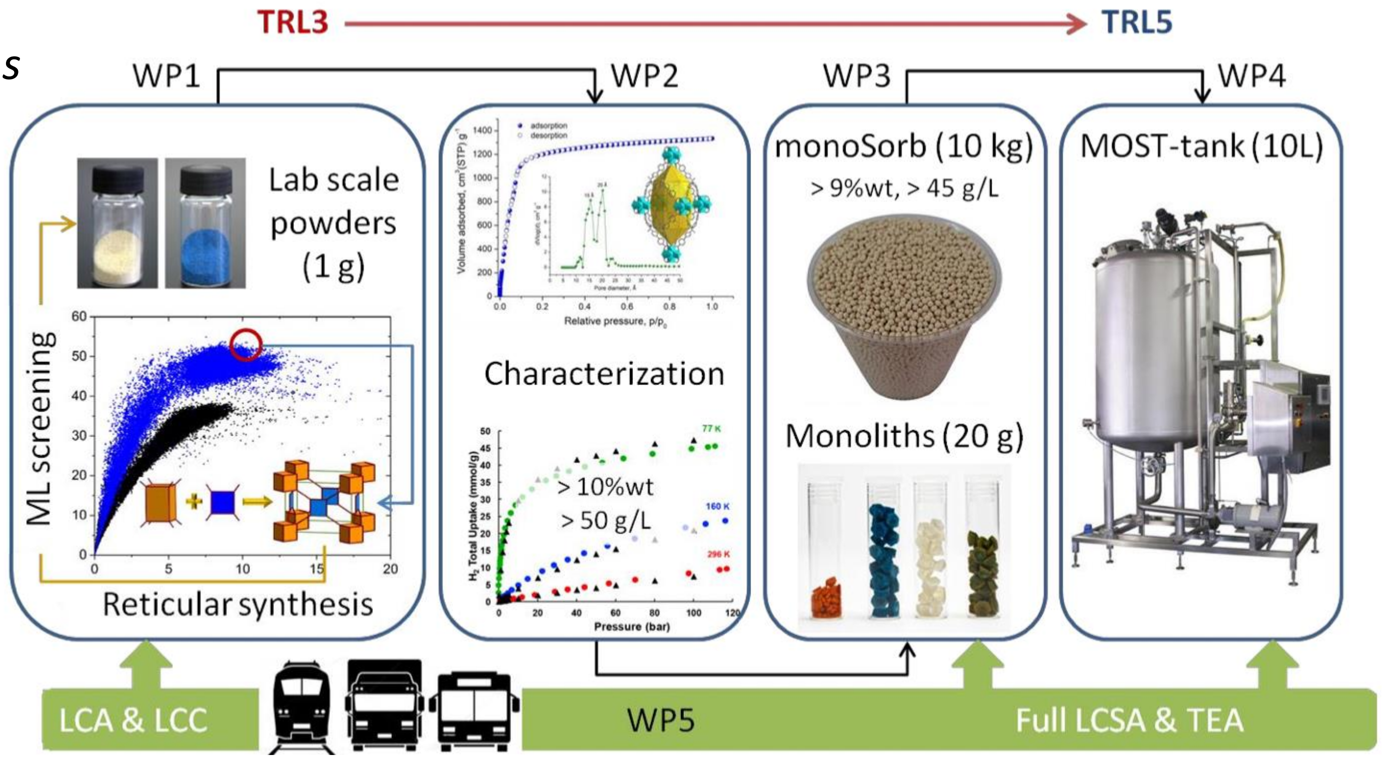
Farha et al. Nature Chem. 2012

- **Volumetric capacities increase with gravimetric capacity up to ~10 wt.%, with volumetric performance plateau ~40 g-H_2 L^{-1}**
- **Capacity can be maximized by increasing gravimetric surface area and porosity**

A. Ahmed *et al. Nat Commun* 10, 1568 (2019)

Optimising H_2 storage in MOFs : EU project MOST-H2

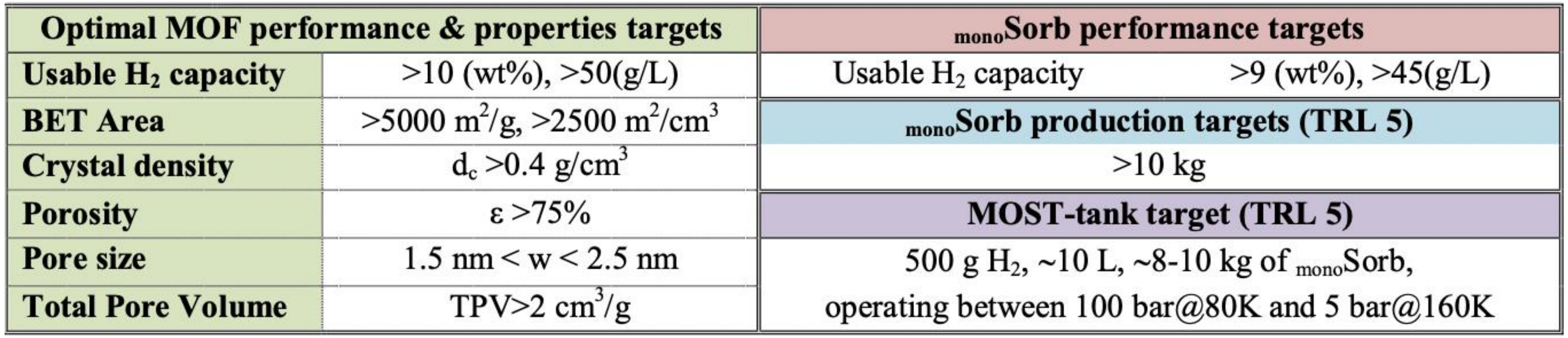
Dr Karim Adil
University Le Mans



Horizon-CL4-2021-Resilience-01-07: Advanced Materials for hydrogen storage

Multiscale lab-to-tank : Develop, validate and demonstrate innovative, low cost, cryo-adsorptive hydrogen storage

Monolithic MOFs with optimal volumetric and gravimetric capacity VTSA (80-160 K, 5-100 bar)



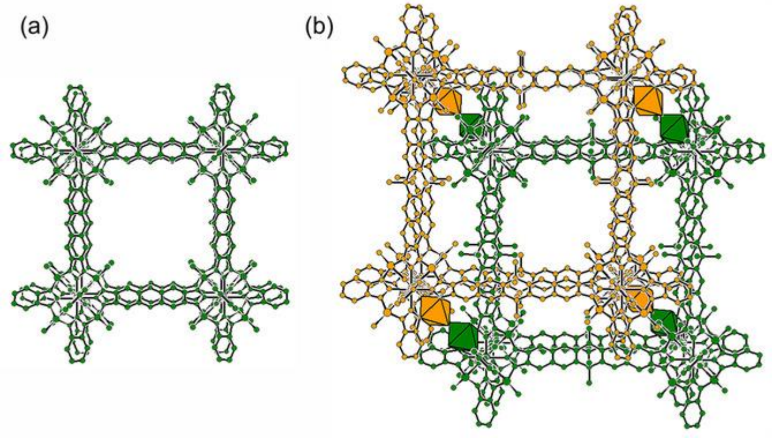
Optimal MOF performance & properties targets	
Usable H_2 capacity	>10 (wt%), >50(g/L)
BET Area	>5000 m^2/g, >2500 m^2/cm^3
Crystal density	d_c >0.4 g/cm^3
Porosity	ε >75%
Pore size	1.5 nm < w < 2.5 nm
Total Pore Volume	TPV>2 cm^3/g

$_{mono}$Sorb performance targets	
Usable H_2 capacity	>9 (wt%), >45(g/L)
$_{mono}$Sorb production targets (TRL 5)	
>10 kg	
MOST-tank target (TRL 5)	
500 g H_2, ~10 L, ~8-10 kg of $_{mono}$Sorb, operating between 100 bar@80K and 5 bar@160K	

Strategies for improving H_2 storage in MOFs

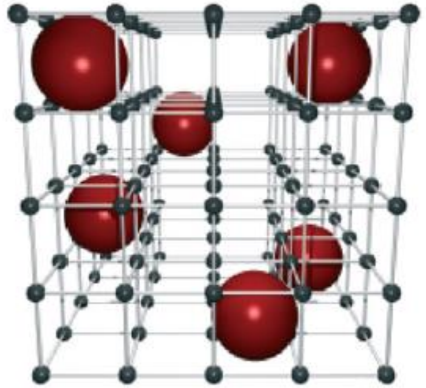
Interpenetration

Density doubled
Higher stability
Heat of adsorption increased



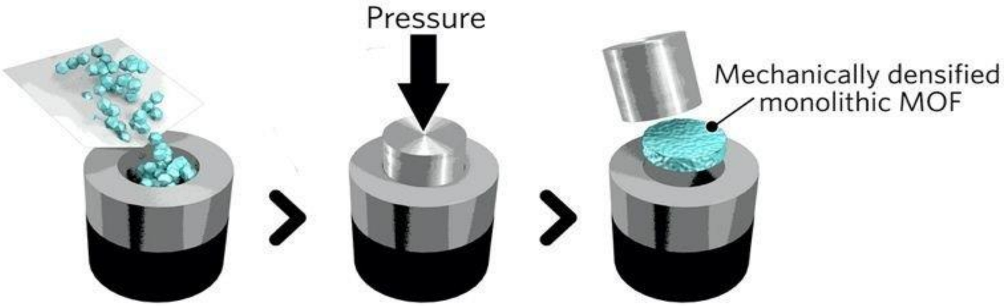
Active species loading (Pd°, hydrides…)

Heat of adsorption strongly increased
Spillover effect



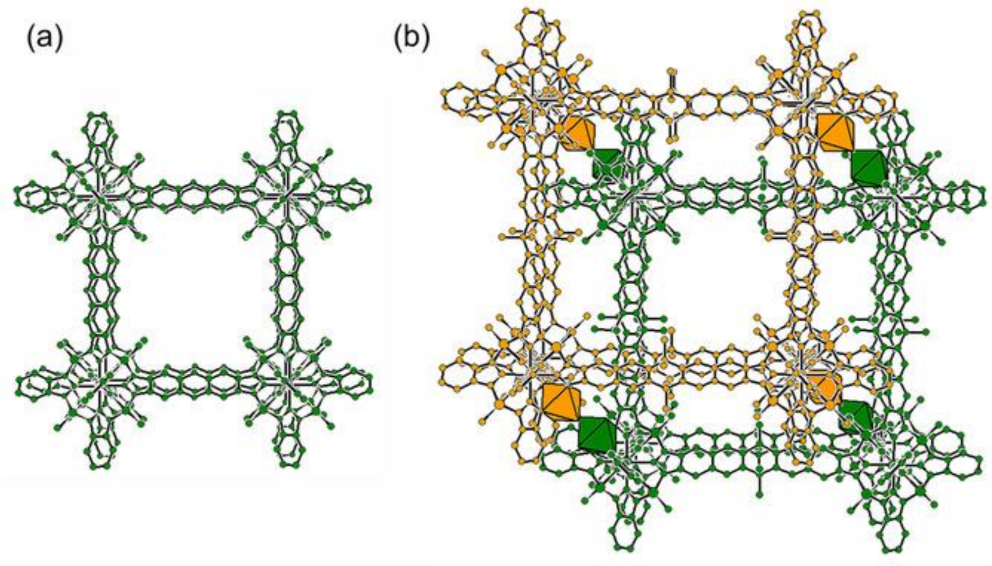
Densification

Density doubled
Higher stability
Heat of adsorption increased



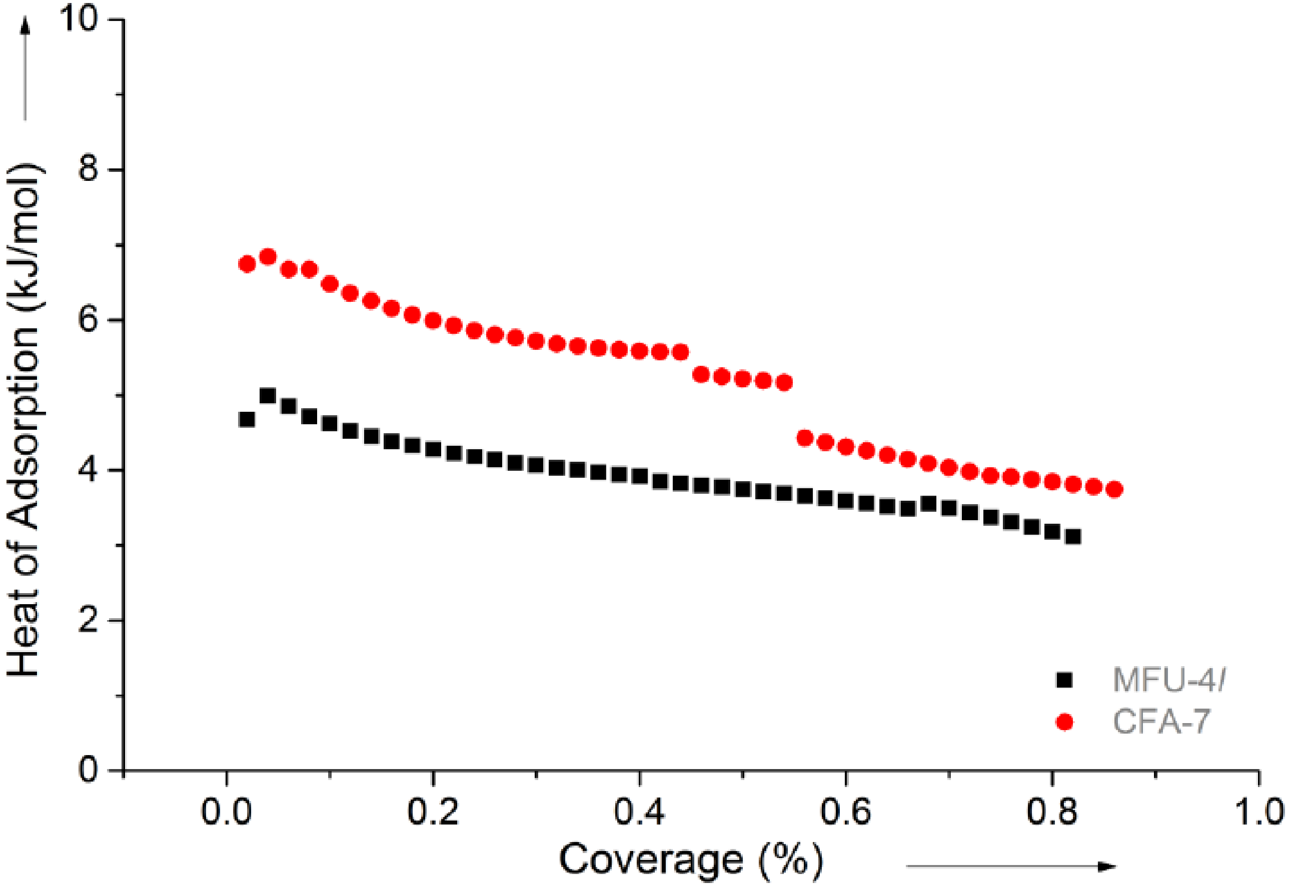
Interpenetration in MOFs for H_2 storage

Increasing the H_2 volumetric capacity through **interpenetration**



MFU-4*l*
~ 3000 m²/g
ρ = 0.5592 g/mL

CFA-7
~ 1700 m²/g
ρ = 1.570 g/mL

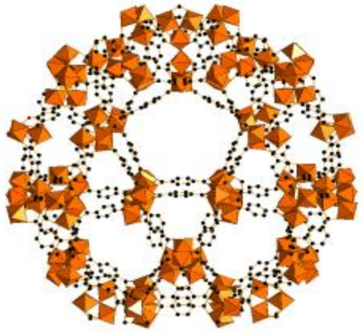


R. Balderas-Xicohténcatl et al. Energy Technol. 2018, 6, 510

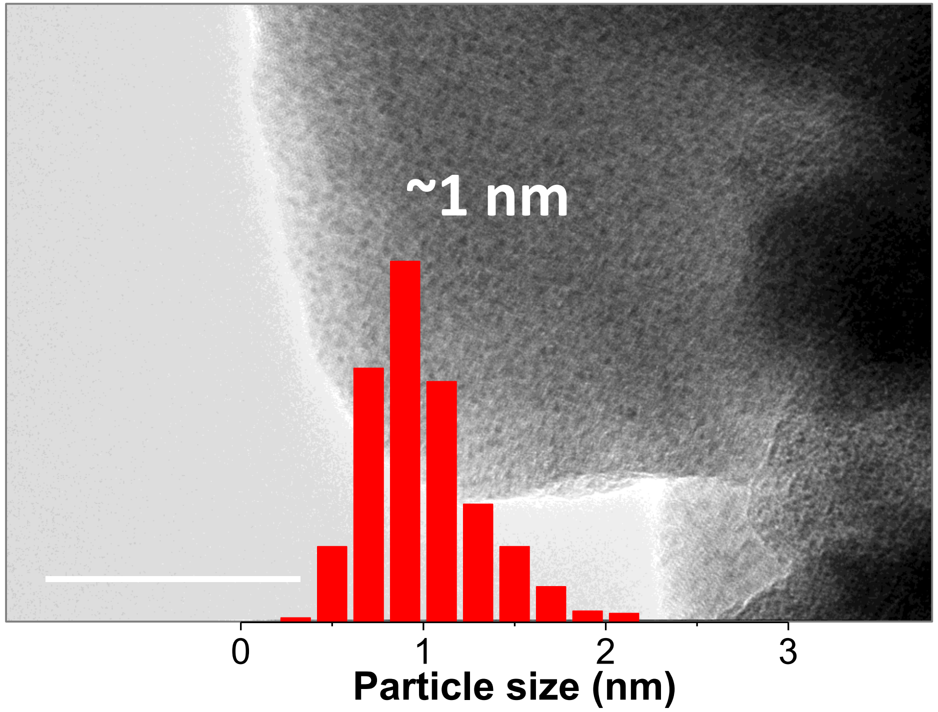
Loading active species to boost the H_2 storage

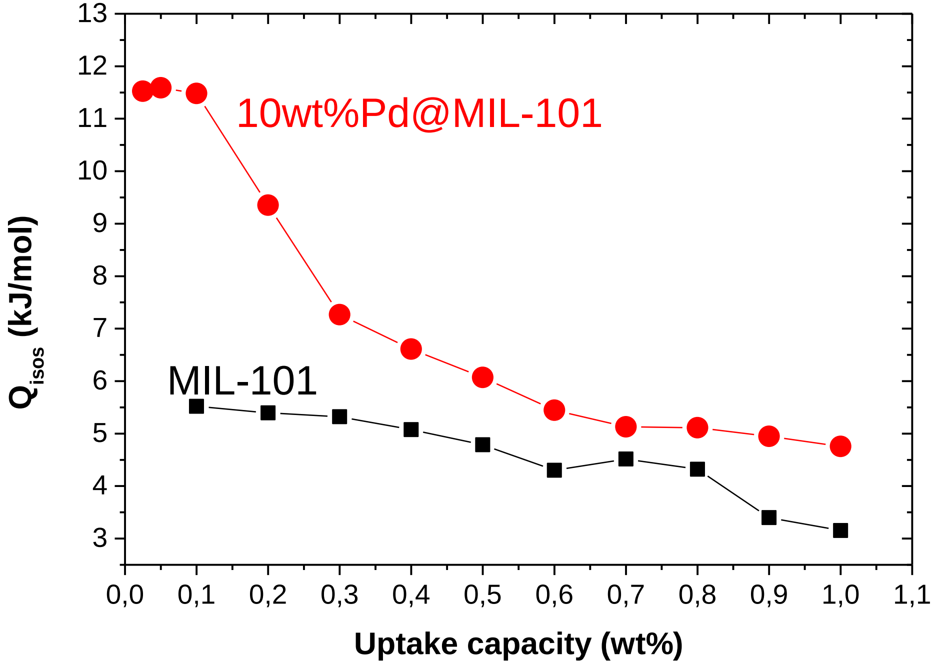
Dr Claudia Zlotea
ICMPE, CNRS

Increasing the H_2 volumetric capacity : **functionalization** of MOFs with metal nanoparticles (or metal hydrides)



Mesoporous MOFs
(MIL-101(Cr))





But at the expenses of gravimetric capacity at 77 K

A. Malouche et al., J. Mat. Chem. A, 2017, 5, 23043
C. Roesler and R. A. Fischer, Crystengcomm 2015, 17, 199

Hydrogen Storage in Metal Doped MOF Composites

ANR Project "PhotoStor2 ", Coordinator: Prof. Johnny Deschamps (UCP, ENSTA IP Paris),

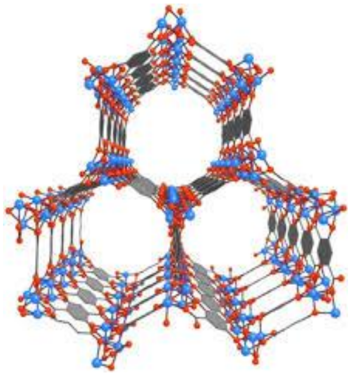
Partner: Dr Hynd Remita (ICP, Paris Saclay)

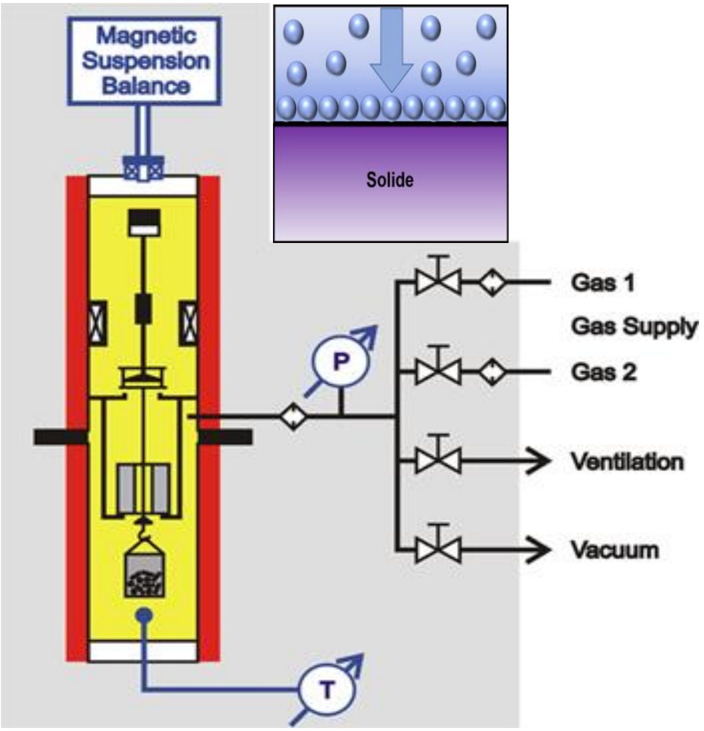
MOF Materials + Activated Coal (AC) + Metal or Bi-Metallic Nanoparticles

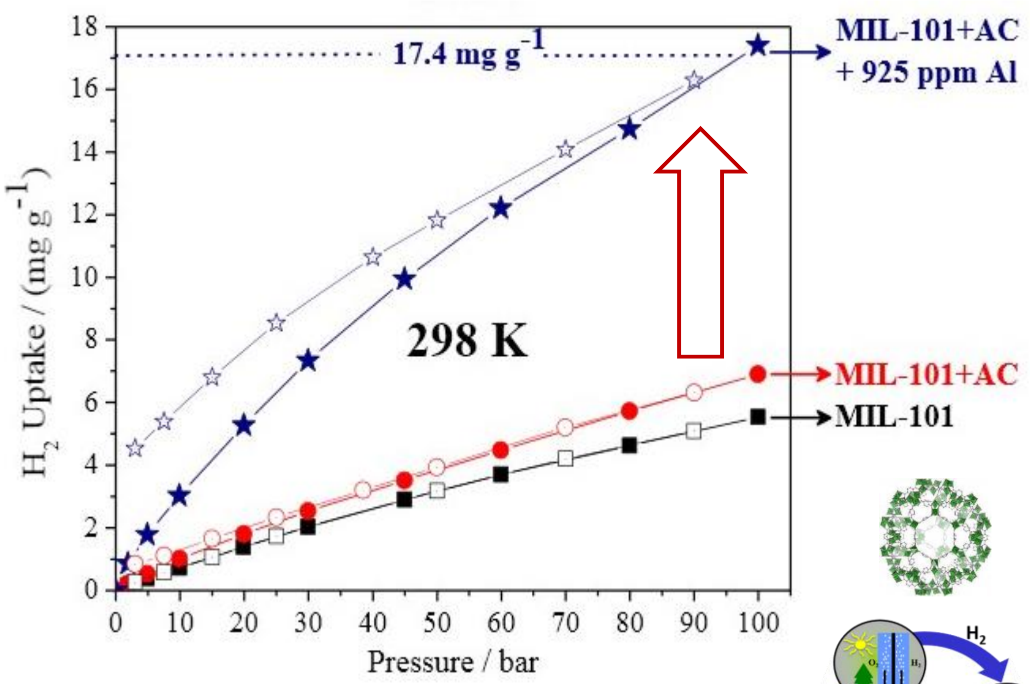
Hydro/solvo-thermal syntheses; Radiolysis; Doping by impregnation in solution or under pressure

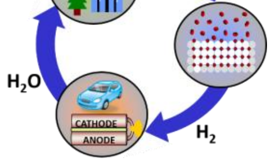
H_2 adsorption at RT

Moderate pressure (max. 100 bar)









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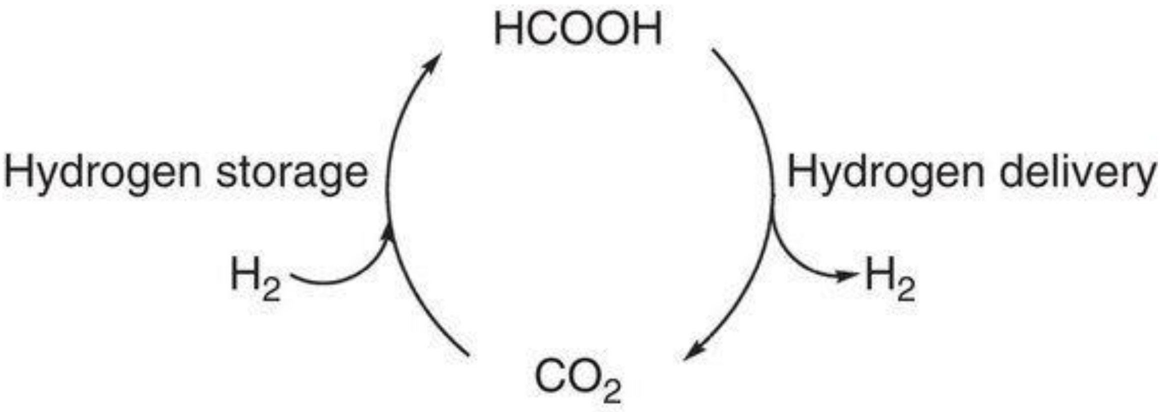
université PARIS-SACLAY

H_2 production from formic acid (1)



Formic acid : short cycle, highly promising for H_2 storage/transportation

Current catalysts : NPs of Palladium in mesoporous solids (water, 60°C, formic acid / formates)

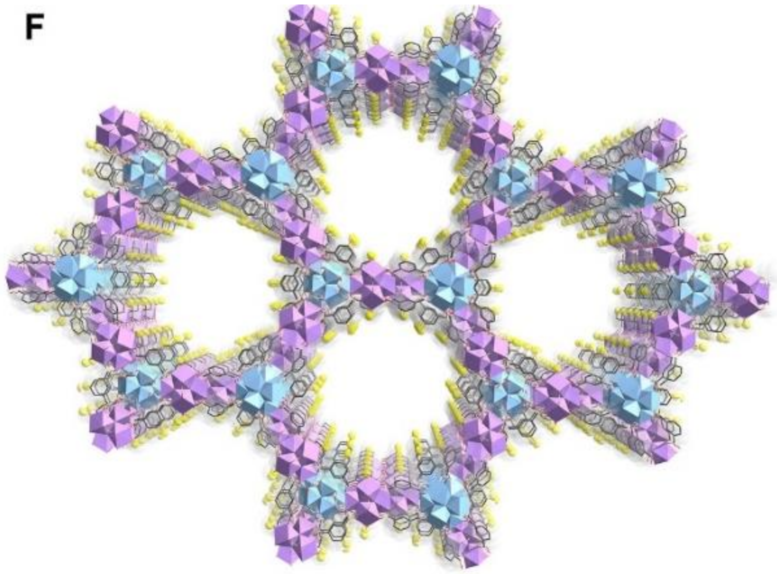
BUT desactivation, degradation thus limiting the practical use

www.futura-sciences.com/planete/actualites/environnement-co2-transforme-acide-formique-stocker-energie-renouvelable

H_2 production from formic acid (2)

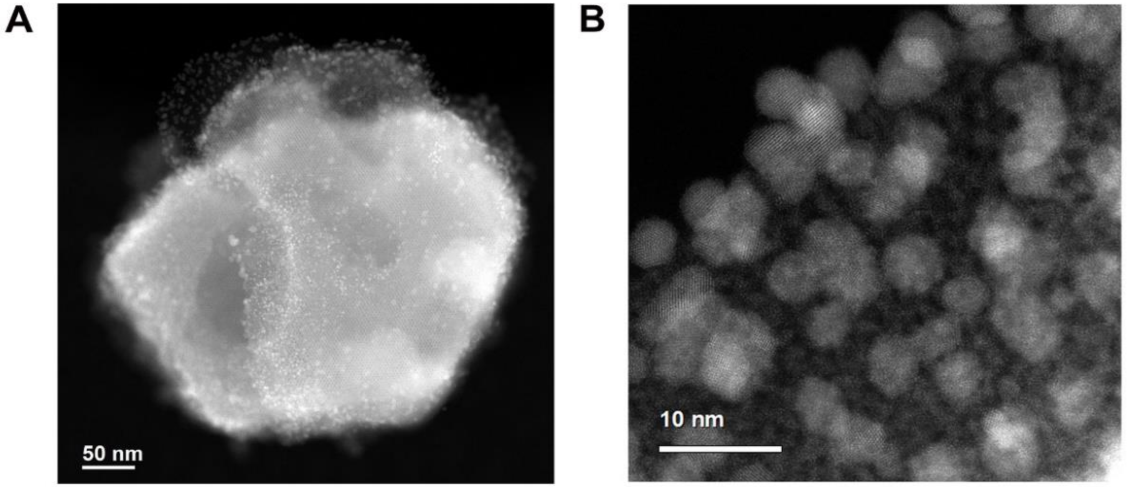
Mesoporous Zr-MOFs loaded with Pd NPs ($NaBH_4$) for production of H_2 from formic acid

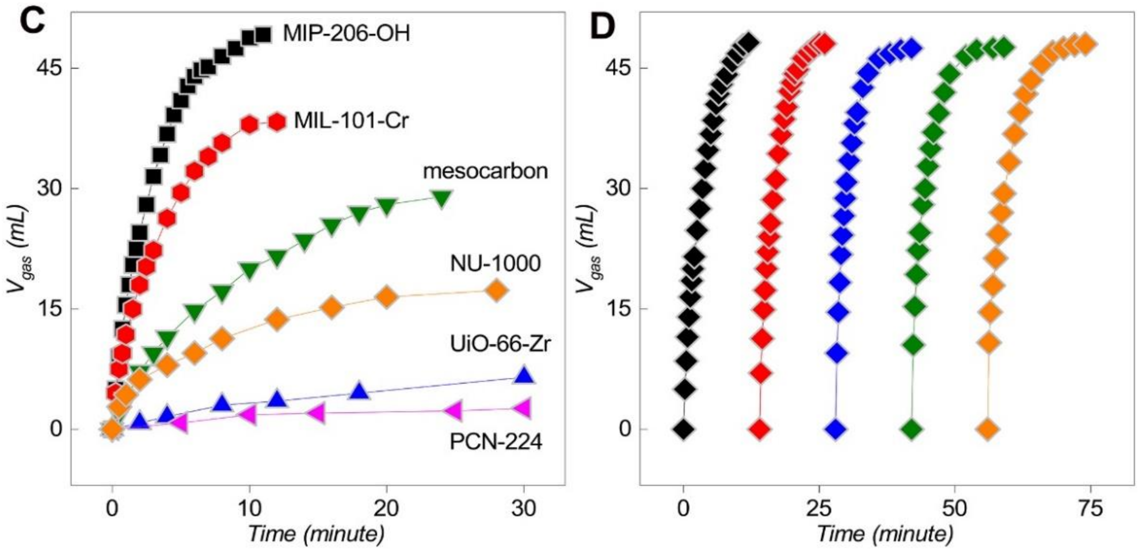
Sujing Wang



MIP-206 : Zr-1,3 BDC
Mesoporous (2.6 nm)
Highly stable, tunable

Among the best composite for the chemical reduction of formic acid !
Reusable !





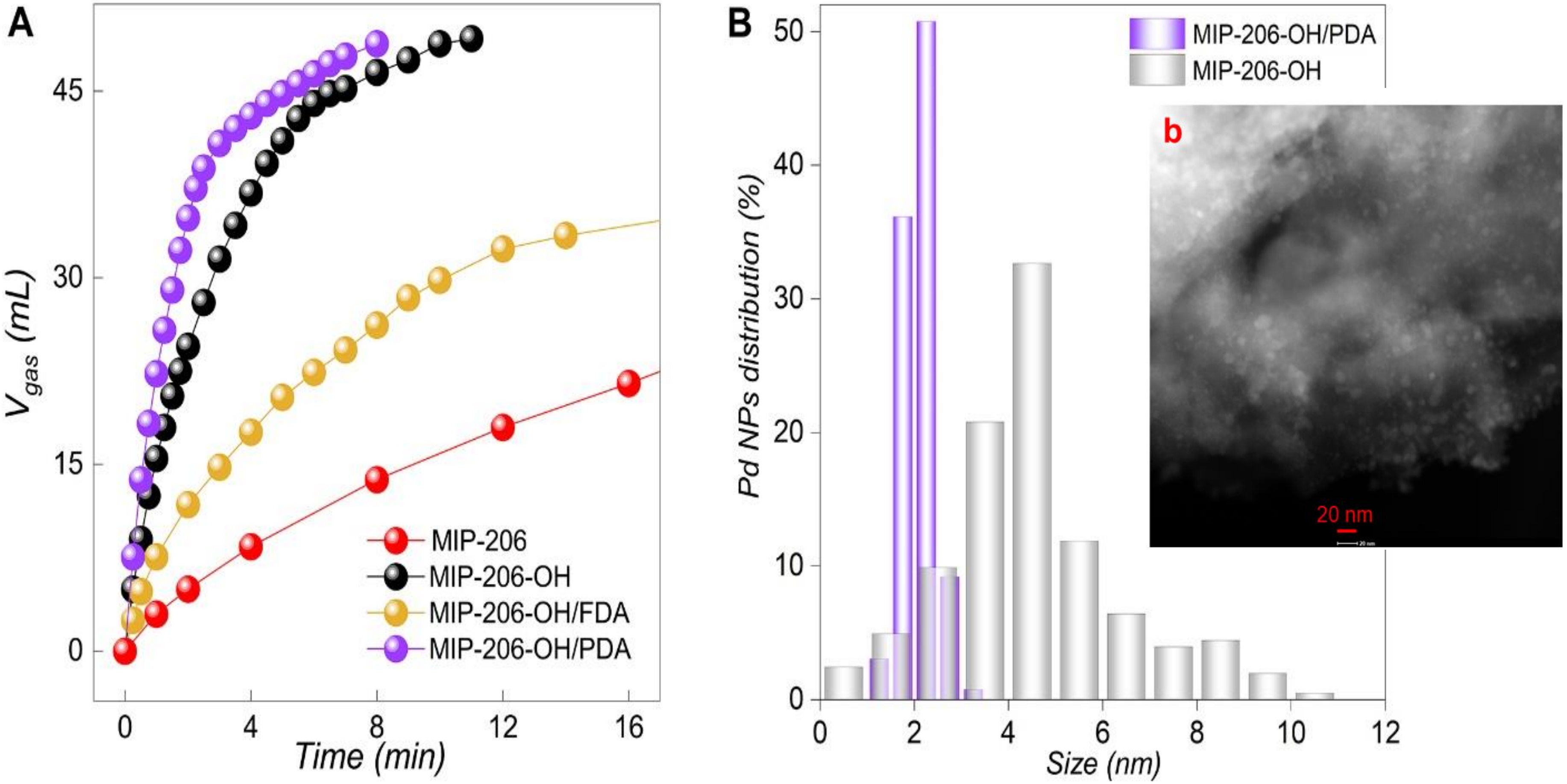
Collaboration
Qianq Xu / Liyu Chen
(Osaka /
Shenzen)

Water, 60° C
Formic acid / Formates

S. Wang et al., Matter, 2020; patent application 2018

H_2 production from formic acid (3)

Control of the Pd NP formation through ligand mixing (MTV)



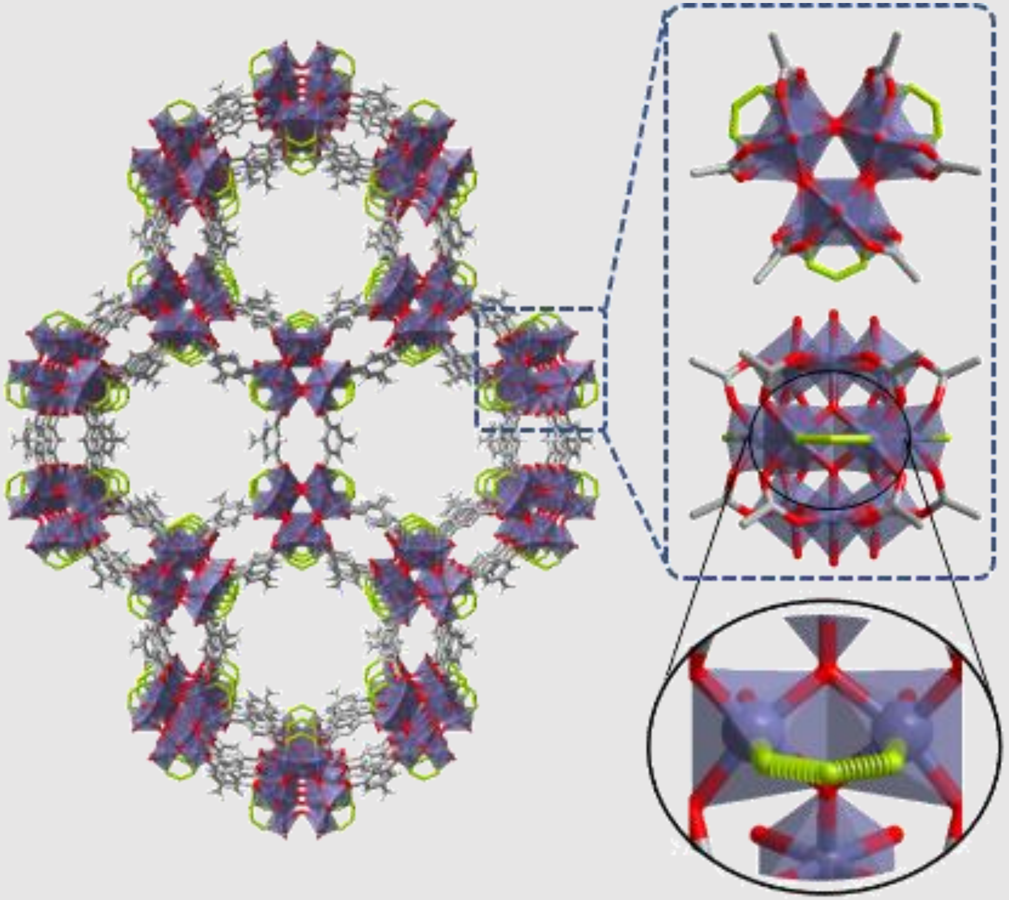
Pd@MTV-MIP-206-OH/PDA (33 % substituted PDA):
→ Smaller NP, lower PSD→ inside the pores → higher conversion achieved !!

S. Wang et al., Matter, 2020; patent application 2018

Photocatalytic H_2 production from formic acid (1)

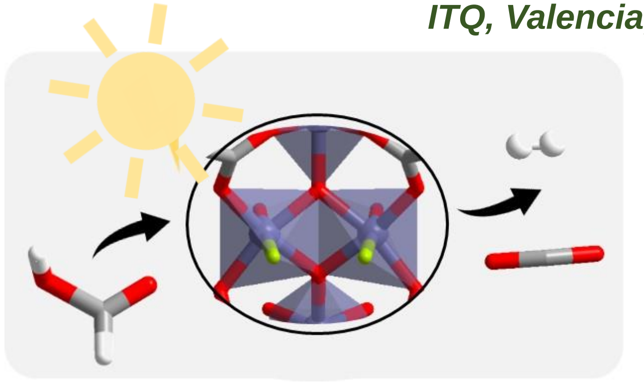
Sergio Navalon & Hermegildo Garcia
ITQ, Valencia, Spain

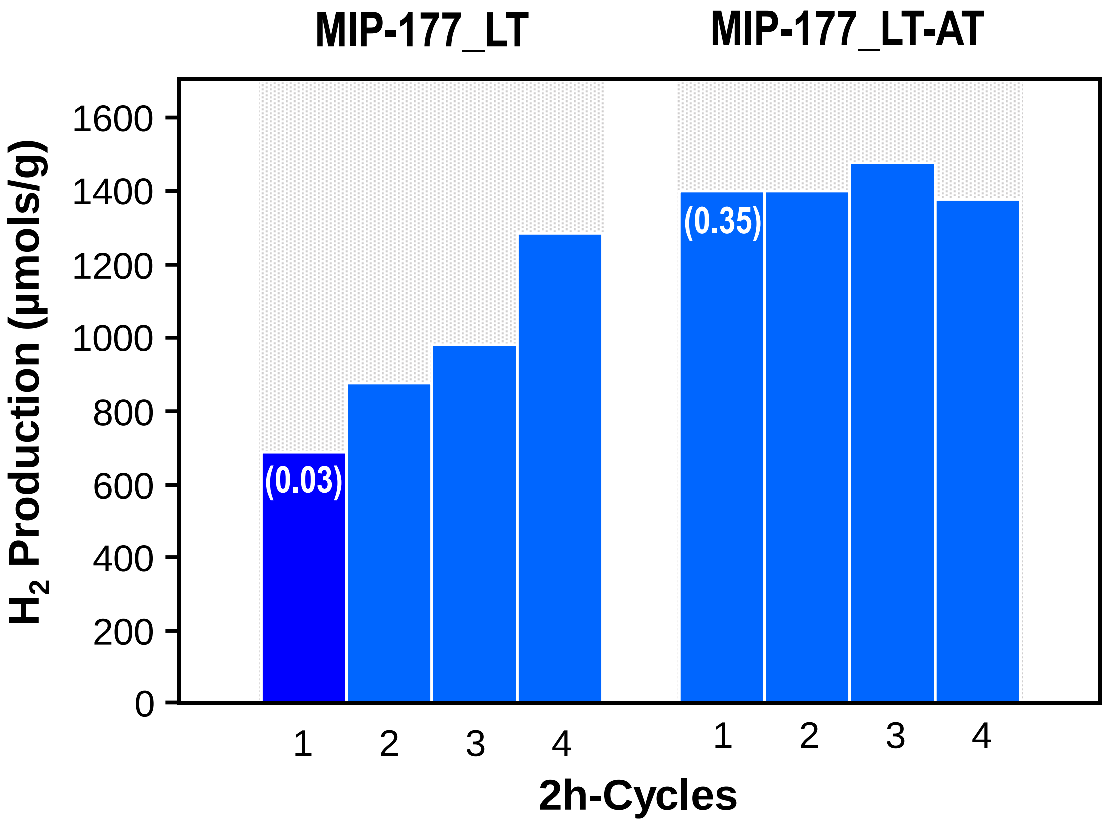
$Ti_{12}O_{15}$ oxocluster + accessible metal sites + porosity



S. Wang *et al., Nat. Commun.* **2018**, 1660

H. García-Baldoví *et al.*, *Energy Environ. Sci.* **2023**, 167





Photocatalytic H_2 production from formic acid (2)

Sergio Navalon & Hermegildo Garcia
ITQ, Valencia, Spain

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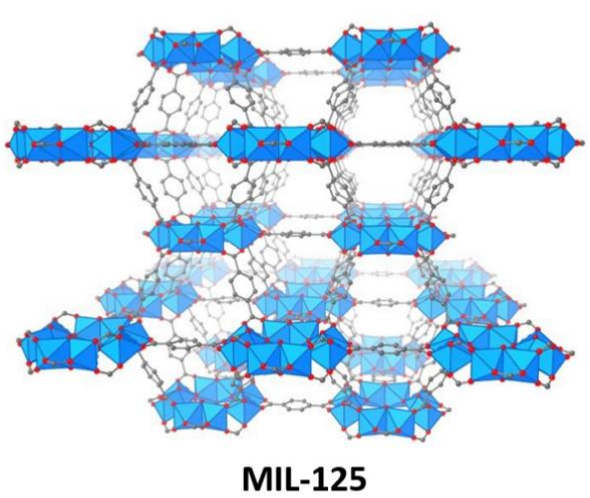
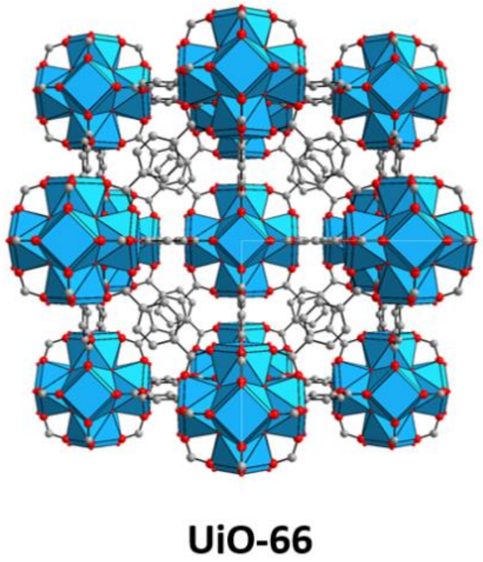
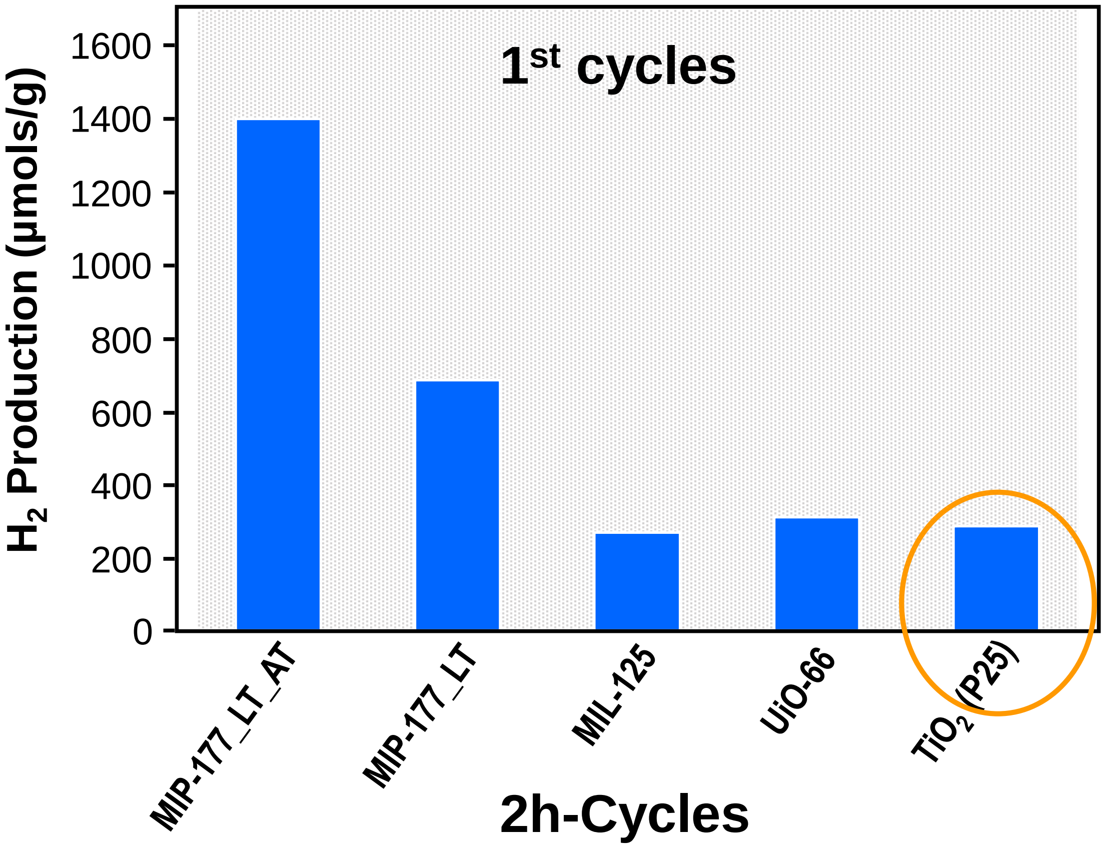
MIP-177_LT outperforms other MOFs and TiO_2

300 W arc Xe lamp
10 mg in 20 mL of 10^{-3} M FA/H_2O

Benchmarking

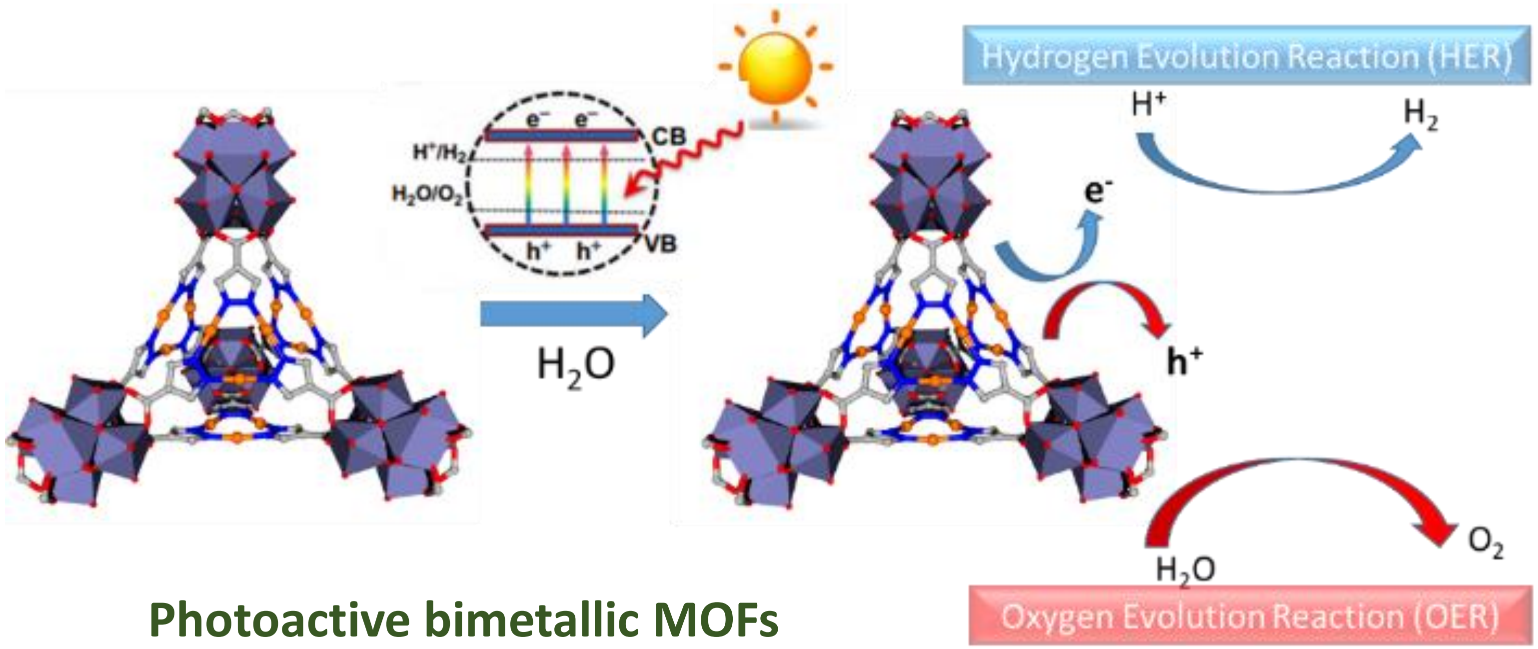

MIL-125


UiO-66



H. García-Baldoví *et al.*, Energy Environ. Sci. **2023**, 167

Photocatalytic H_2 production from Overall Water Splitting



Photoactive bimetallic MOFs

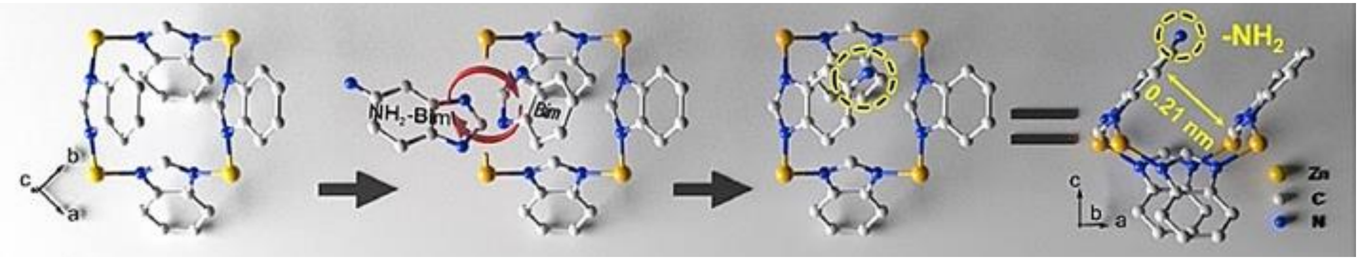
MOF2H2 ***:*** *Horizon-CL5-2021-D3-03: Sustainable, secure and competitive energy supply*

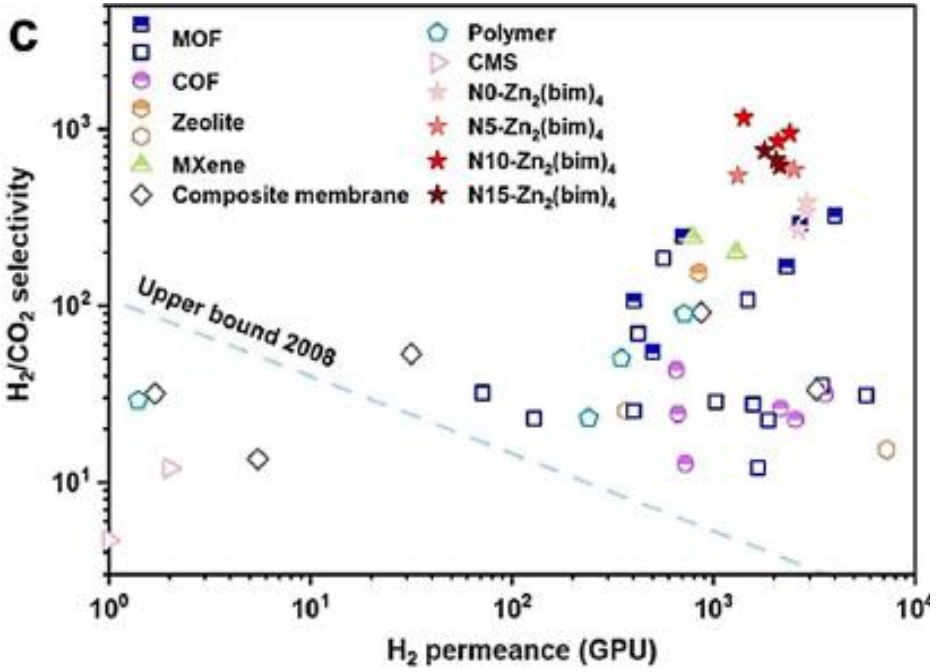
Coordinator:
ESPCI – Paris
(C. Serre)

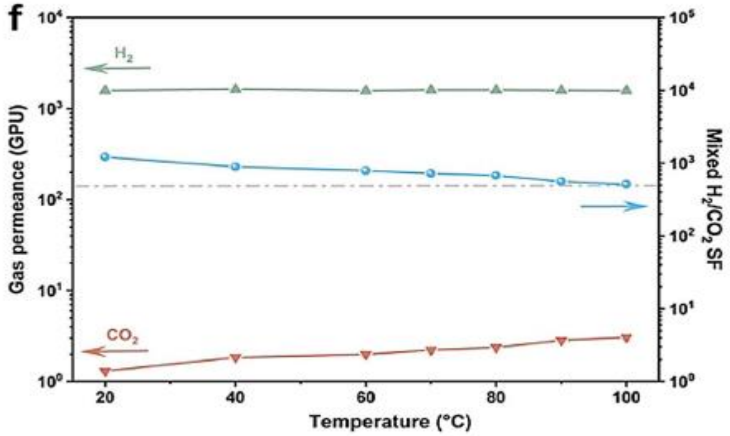
- Noble metal free MOFs record-breaking STH for Overall Water Splitting under visible light, with an STH of >2-5%
- Laboratory-scale photocatalytic system, based on an easily green, scalable MOF to efficiently perform the OWS using sunlight irradiation and with long-term stability

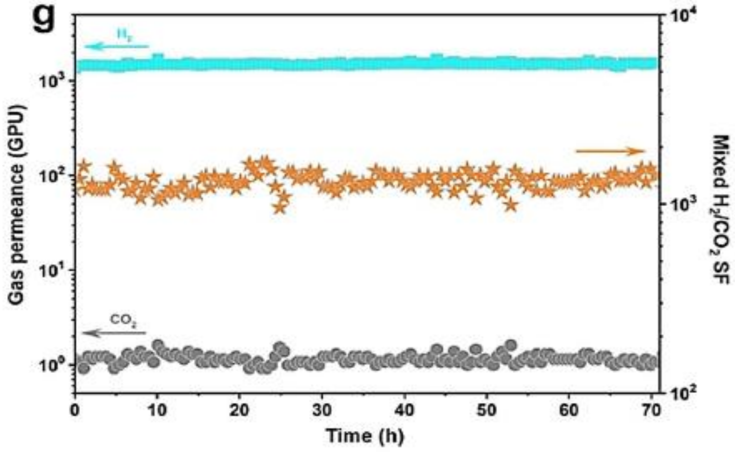
MOFs for the purification of hydrogen

Microporous Zn benzimidazole
Functionalised (amino groups) membrane







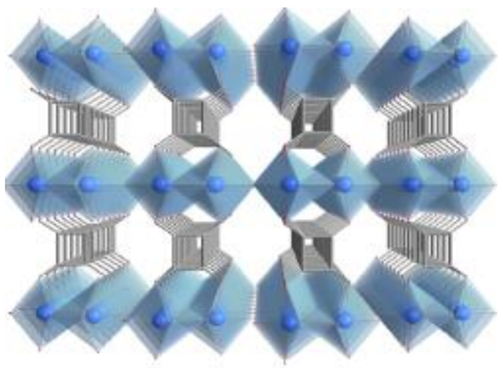


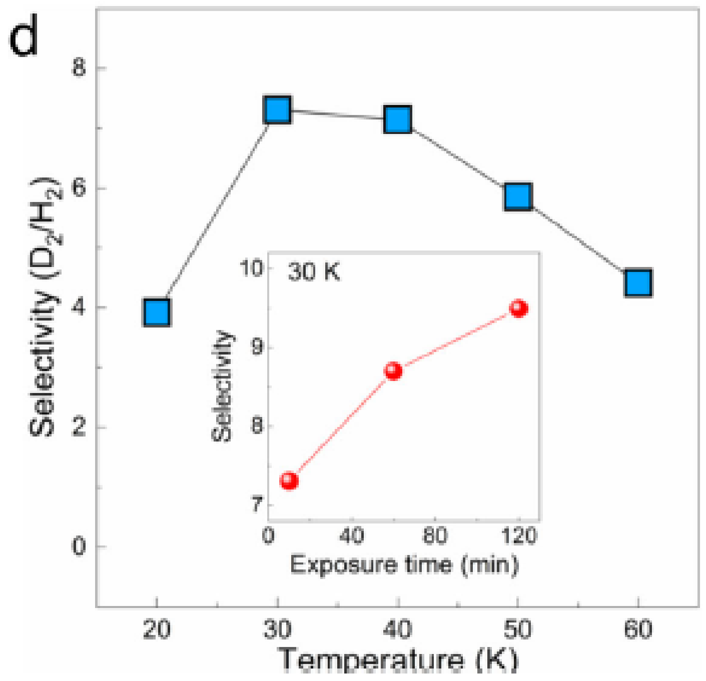
Exceptional H_2/CO_2 selectivity and permeability

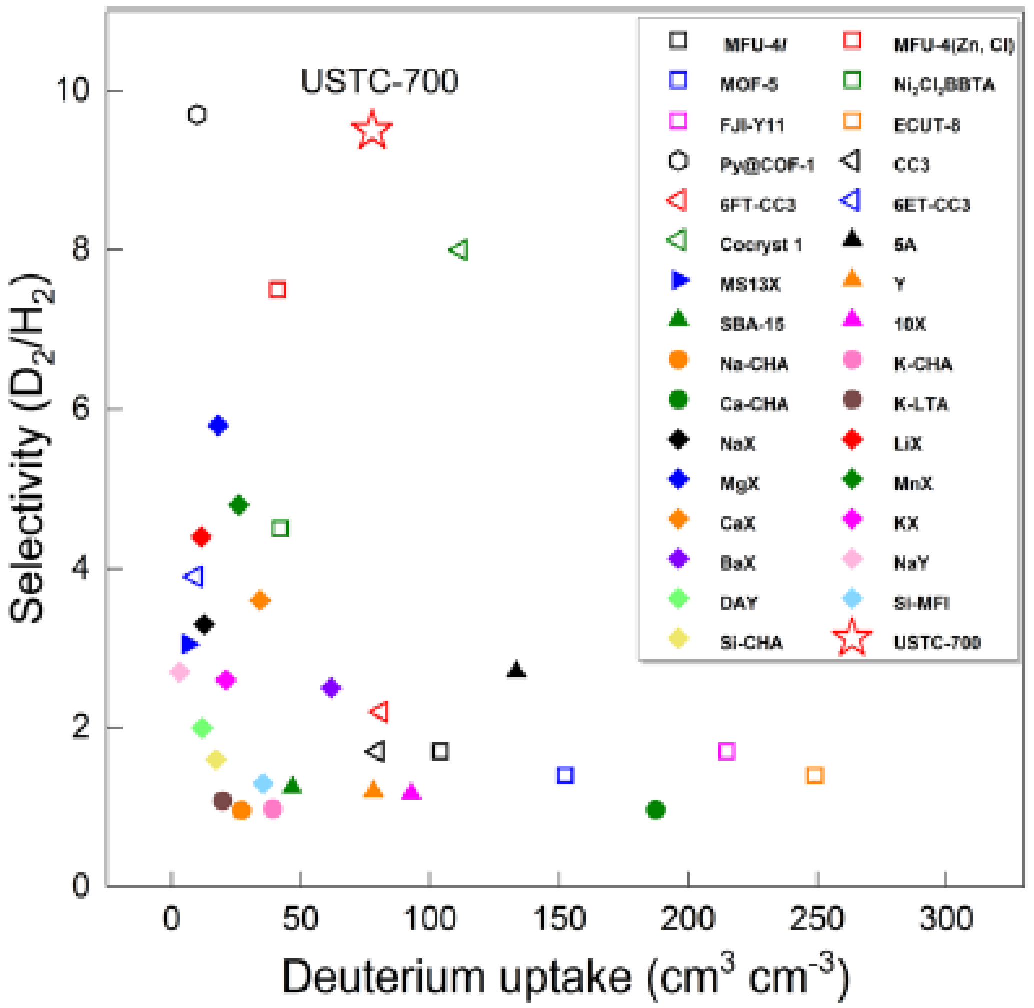
W. Yang et al, Angew. Chem. Int. Ed. 2023

MOFs for the H_2/D_2 (cryogenic) separation

Microporous Ti squarate







Exceptional H_2/CO_2 selectivity and capacity

G. Maurin, S. Yang et al, Nat. Comm. 2023

Acknowledgments

- **Post-docs/Students : Sujing Wang, Raquel Del Angel Montes**
- **Colleagues : George Mouchaham, Antoine Tissot, Iurii Dovgaliuk**

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- **Liyu Chen, Qiang Xu** ***(Osaka, Japon / Shenzen, Chine)***

- **Mohammad Wahiduzzaman, Dong Fan, Guillaume Maurin** ***(Montpellier, France)***

- **Eric Elkaim (*Cristal*), William Shepard *(PX2)* (*Soleil*, France)**

- **Claudia Zlotea** ***(ICMPE, Thiais, France)***

- **Karim Adil** ***(Le Mans, France)***

- **Johnny Deschamps,** ***(Ensta, France)***

- **Hynd Remita** ***(ICP, Saclay, France)***

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