Captage et transport du CO_2 : les progrès de la recherche

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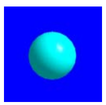
Metal-Organic-Frameworks (MOFs)

Strong bonds (ionocovalent) :

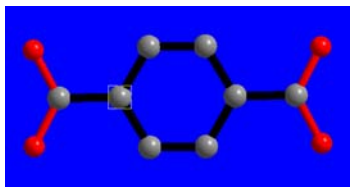
Inorganic moieties (cluster, chaîne, plan) + organic linker (carboxylate, phosphonate..)

MOF-5 or $Zn_4O(1,4\ BDC)_3$

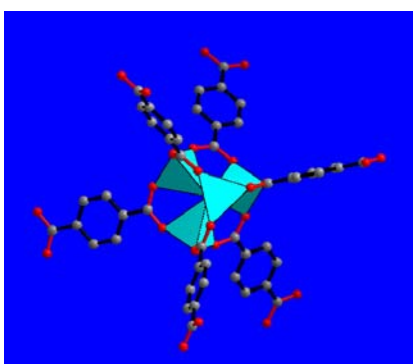


Zn(II)

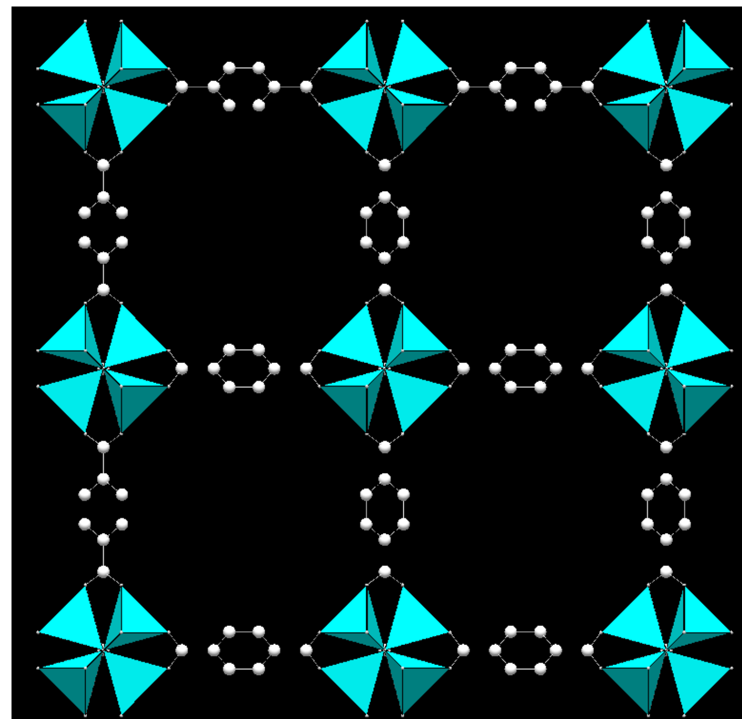
+



1,4-benzenedicarboxylic Acid



Yaghi *et al. Nature*, **402**, 277 (1999)



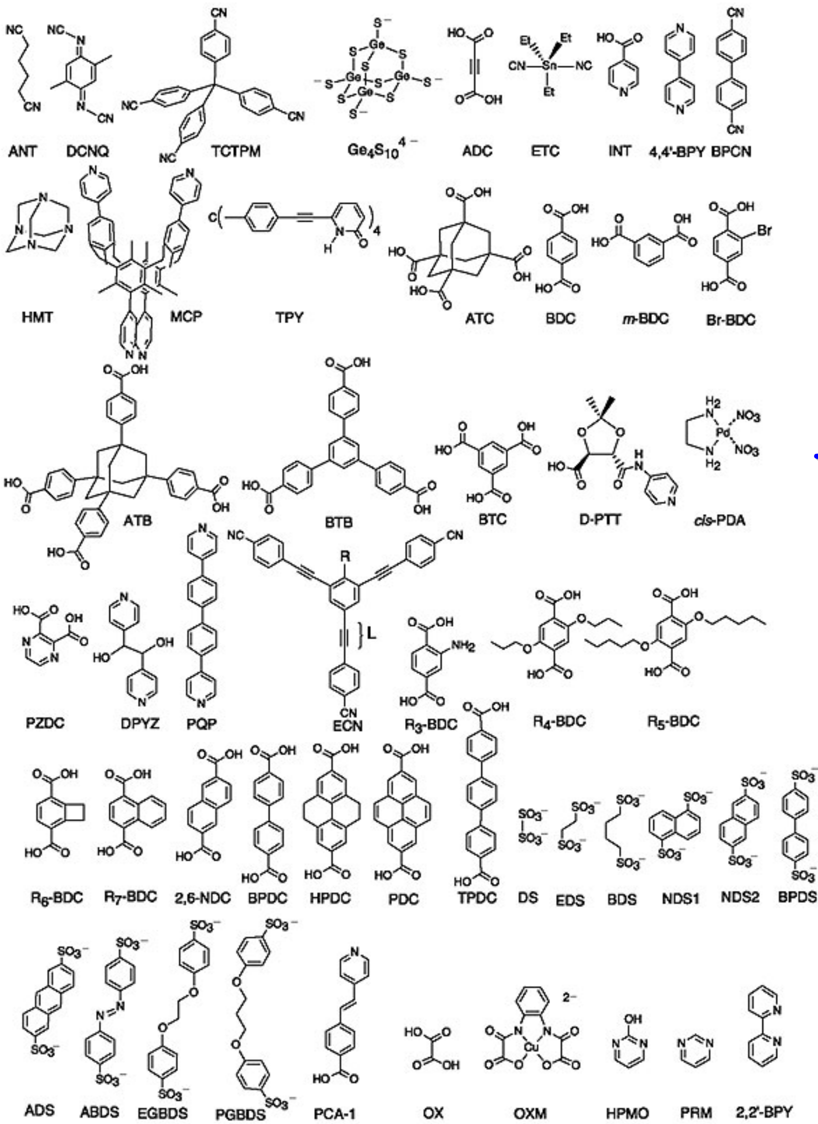
3D porous Structure

Large specific surface areas : 500-4500 m^2/g

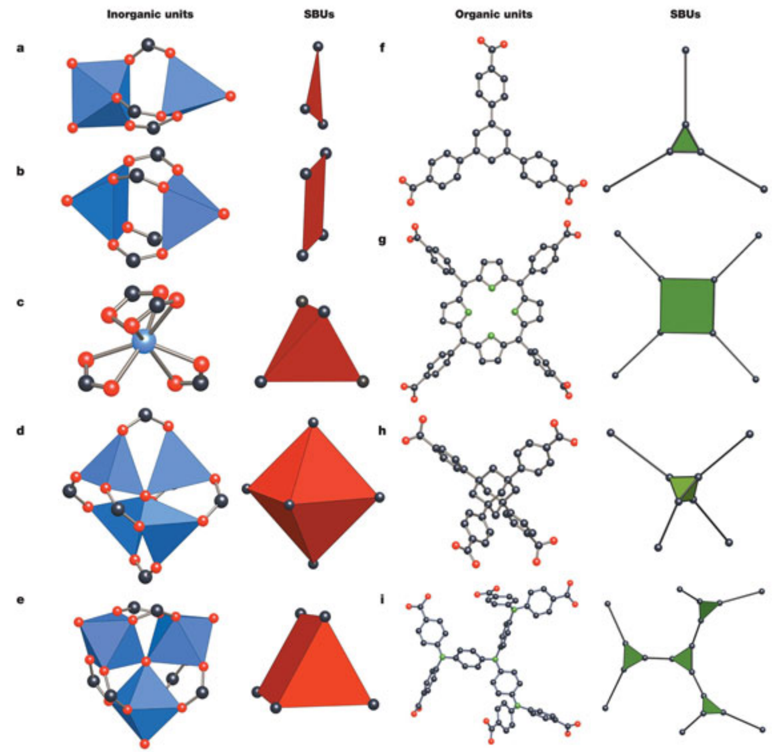
Excellent adsorbants

MOFs: a versatile class of porous solids

Rigid Linkers



+ Metal →



Secondary Building Units

Yaghi *et al. Nature* **423** 708 (2003)

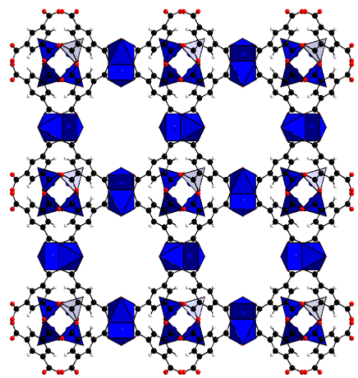
The most common types of porous MOFs

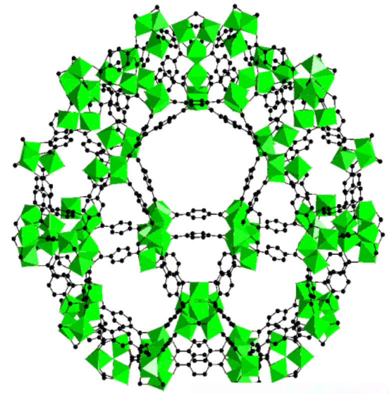
HKUST-1

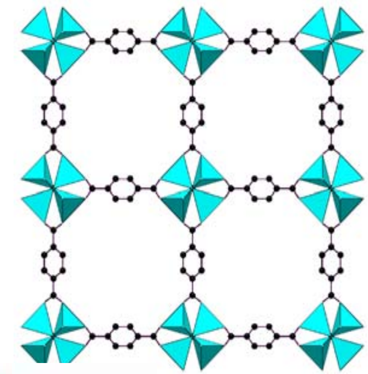
MIL-101

MOF-5

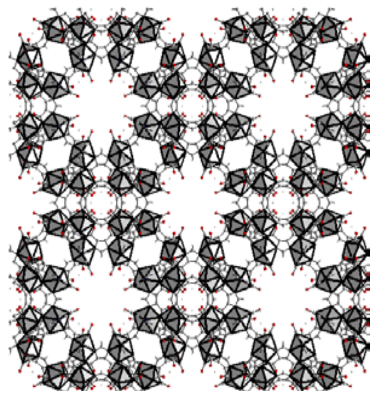
Metal Carboxylates





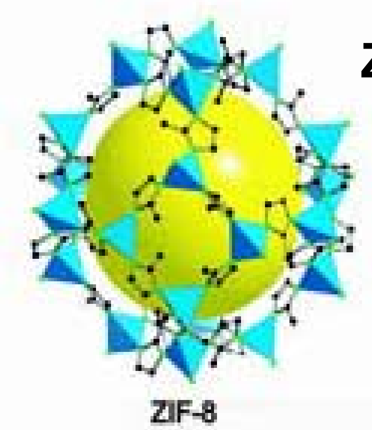


Metal Imidazolates

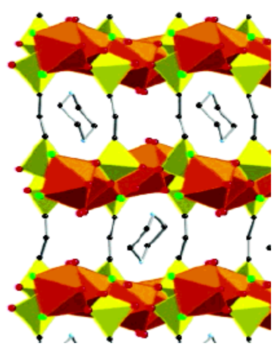


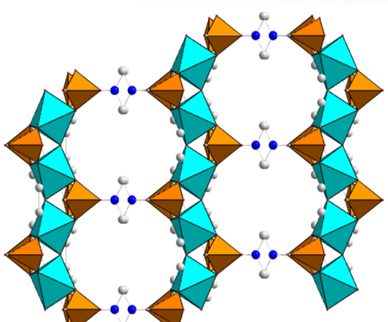
ZMOFs

ZIFs

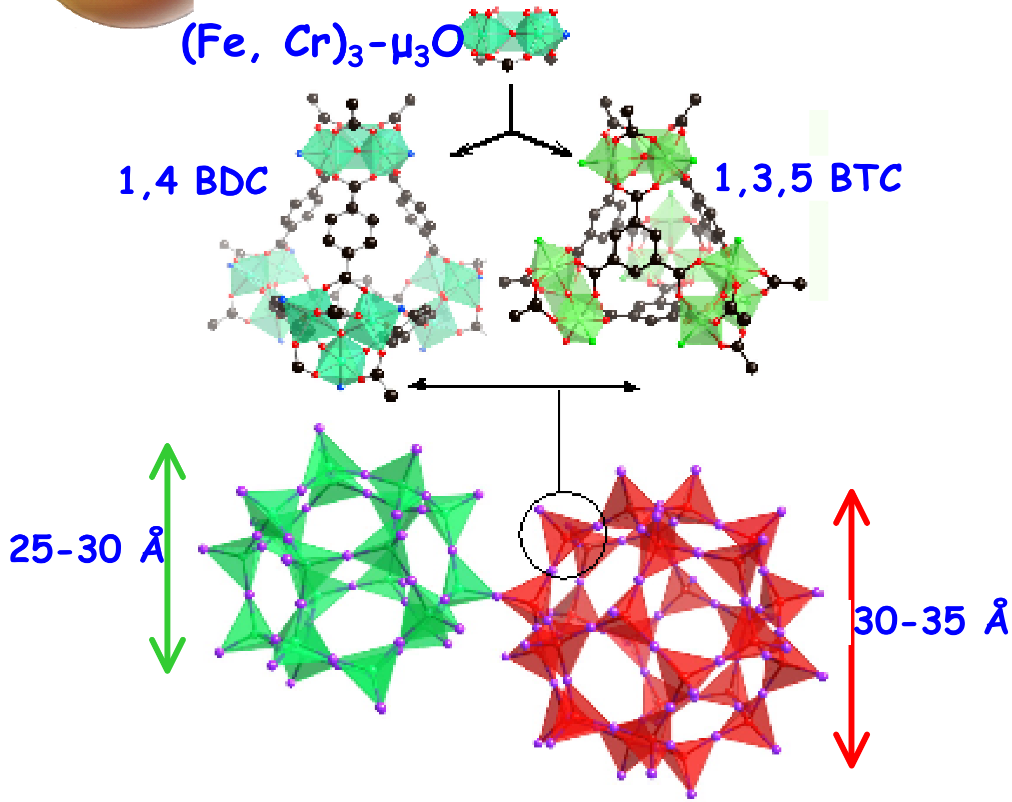


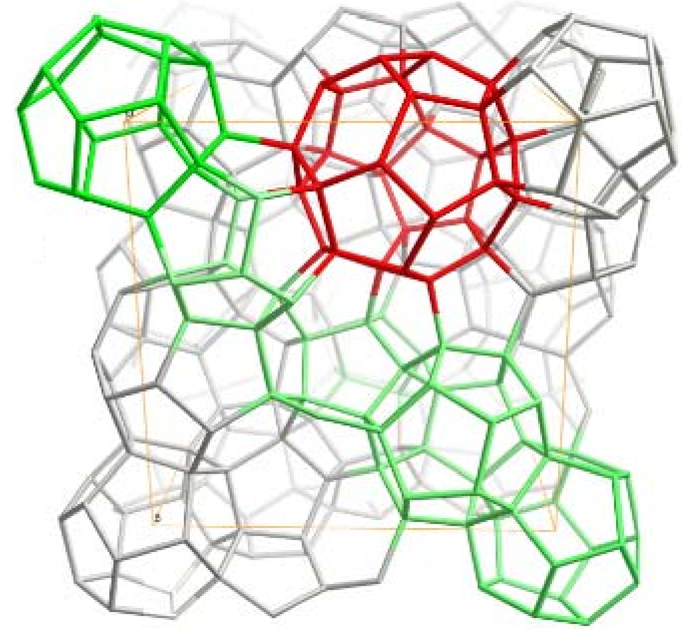
Metal Phosphonates





MIL-100 and MIL-101: mesoporous cristallised carboxylates



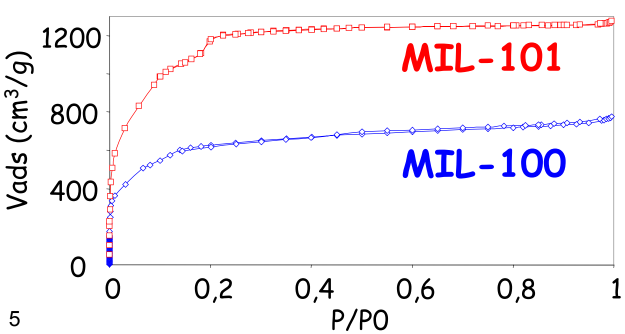


zeolitic topology

- MTN (cubic, a=19.9 Å, V=7900 Å^3)

Scale Chemistry

- MIL-100 (1,3,5 BTC): a=72.9 Å V=380000 Å^3)
- MIL-101 (1,4 BDC): a=89.9 Å, **V=706000 Å^3**)

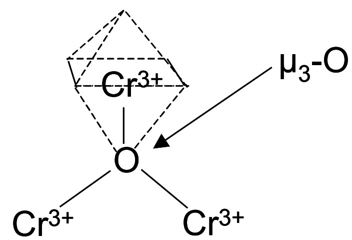


→ **micro- and mesoporosity**: exceptional surf. areas

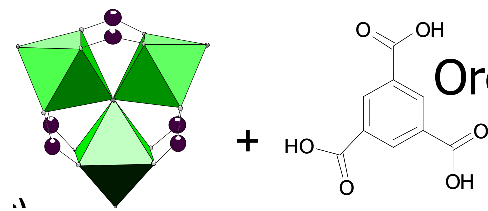
- MIL-100: 3100 m^2/g
- MIL-101: **5900 m^2/g**

G. Férey et al., Angew Chem 2004; Science 2005

IR detailed analysis of MOF-type structures

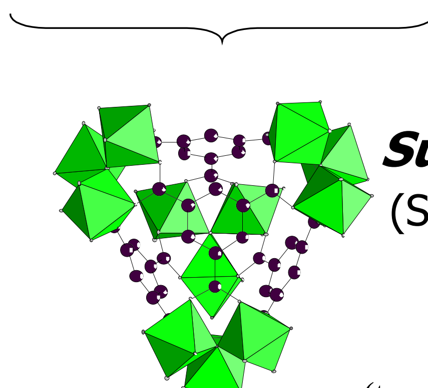


(A)



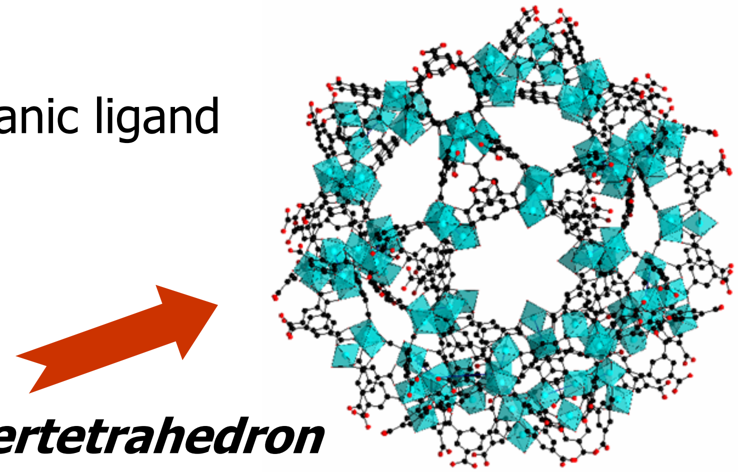
Organic ligand

inorganic blocks



Supertetrahedron

(Second Buildary Unit)

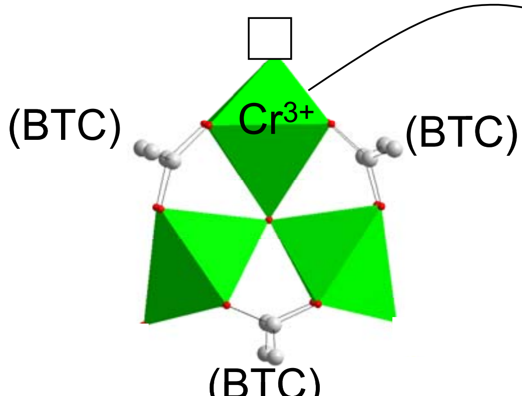


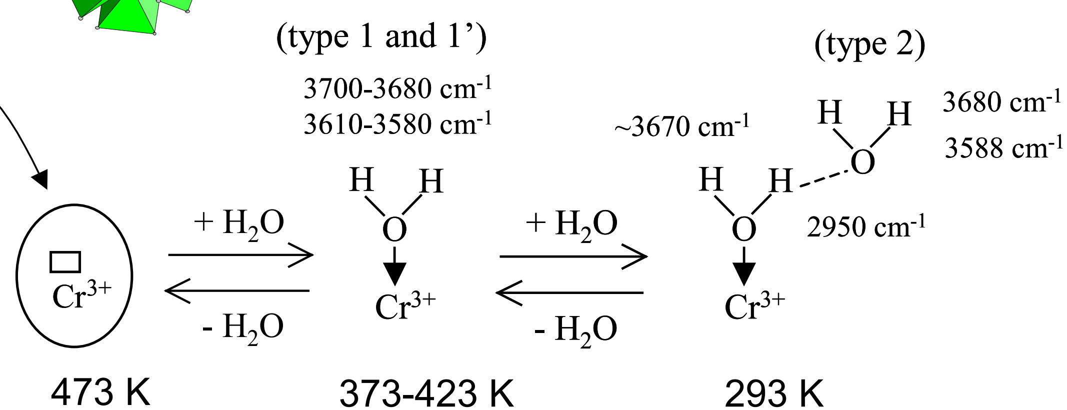
MIL-100

$Cr_3F(H_2O)_3O\ [C_6H_3\text{-}(CO_2)_3]_2$, n H_2O

chromium trimesate

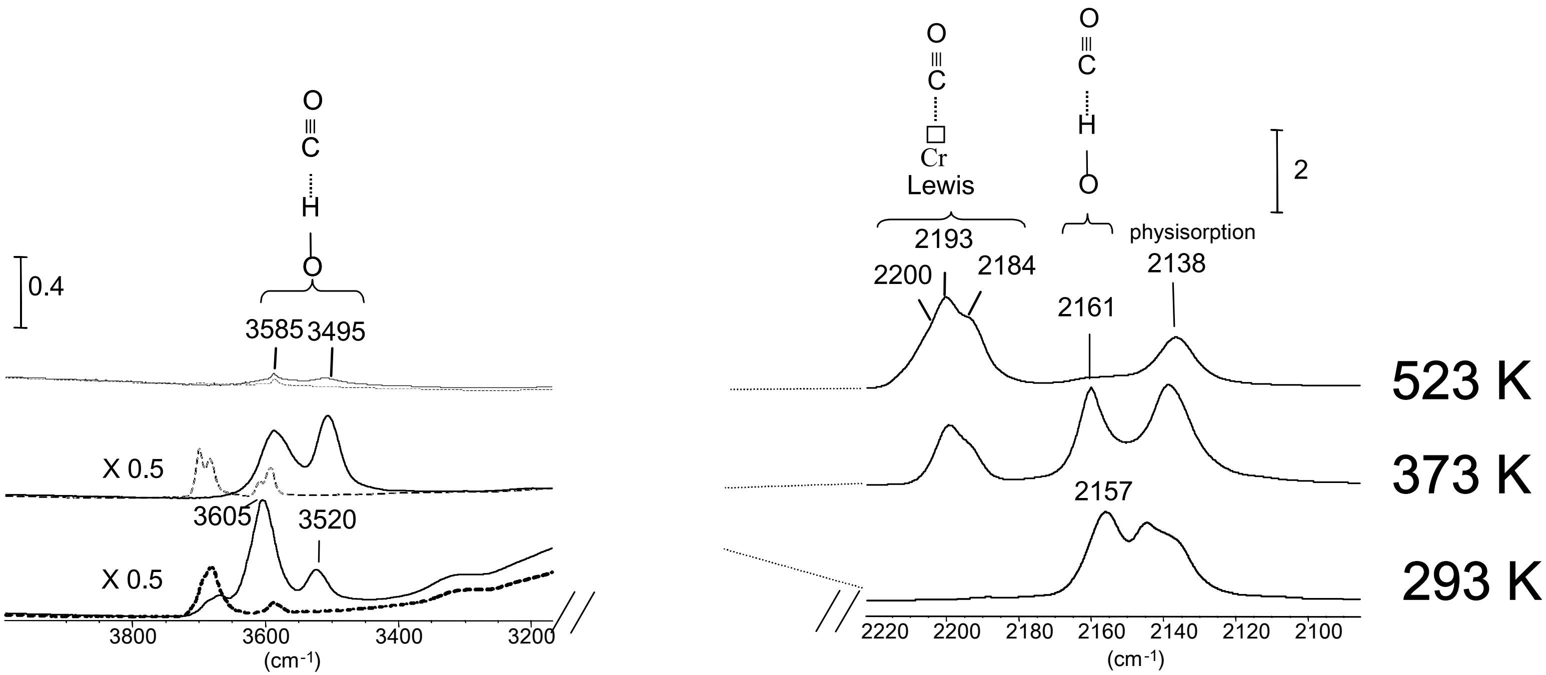
Identification of isolated sites and analysis of their acid-base properties



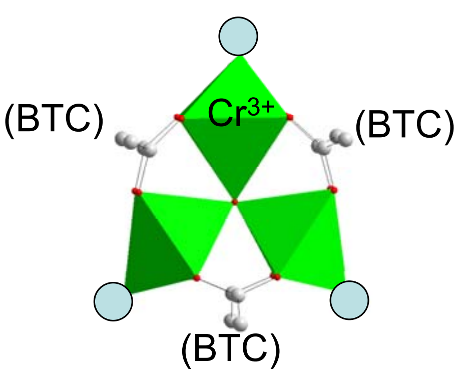


Vimont et al., *JACS 128 (2006) 3218*

Acidity: CO adsorption at 100 K on MIL-100 activated at 523 K



: anionic vacancy , F^-, $(OH)^-$, H_2O, $H_2O..H_2O$

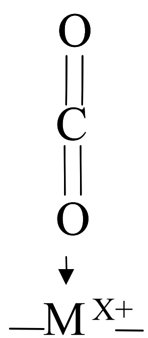


Quantification:

- about 2 *cus* Cr^{3+} per trimer (3500 µmol g^{-1})
- F and OH group localized on the top of the third Cr^{3+} octahedron

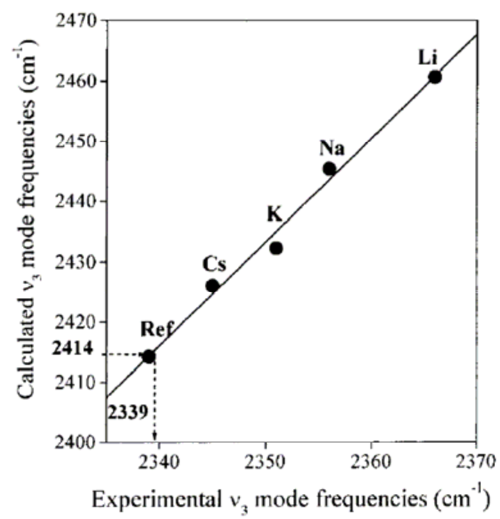
CO_2 as a probe for acidity

Coordination of CO_2 molecules on Lewis acid sites



(2340-2380 cm^{-1})

Linearly adsorbed



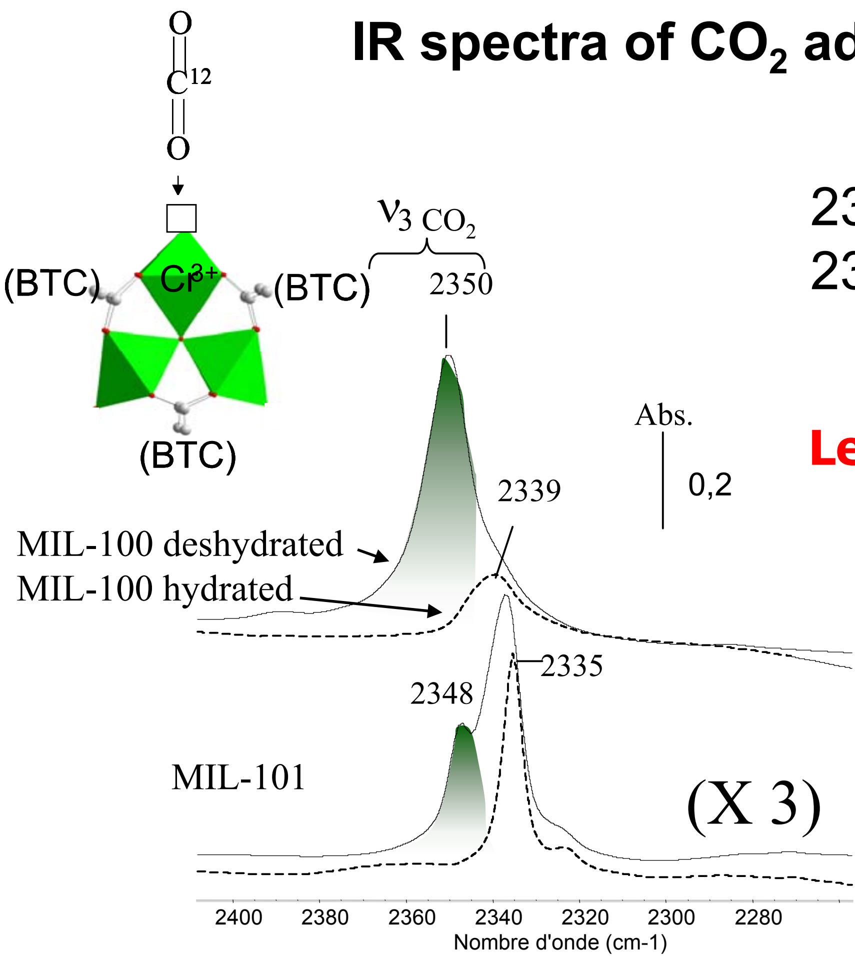
B. Bonelli,

J. Phys. Chem. B **2000**, *104*, 10978−10988

The higher the wavenumber the stronger the acidity

Preferential Adsorption modes of CO_2 on MIL 100 /101

IR spectra of CO_2 adsorbed on MIL-100/101 (low pressure)



2351 cm^{-1} on MIL-100
2348 cm^{-1} on MIL-101

The higher the frequency the stronger the acidity

Lewis acid sites measured by CO adsorption:

Concentration:

MIL-100 > MIL-101
(3.5 mmol g^{-1}) (1.5 mmol g^{-1})

Acid strength:

MIL100 > MIL-101
(ν(CO) 2200 cm^{-1}) (ν(CO) 2190 cm^{-1})

→ related to the CO_2 adsorption heat

A possible application: CO_2 sequestration …

P. L. Llewellyn et al., *Langmuir* (2008)

Adsorption of green house gases

Methane

DOE Target (2010)
180 v/v
35 bars

Best materials are to date :
Activated carbons
Adsorb at RT
Fast Kinetics
Cheap
Good volumetric
Capacities (<200 v/v)

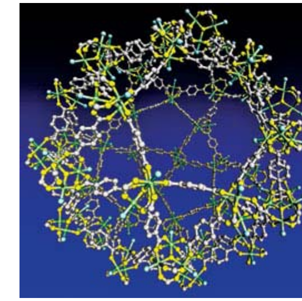
Capture of CO_2

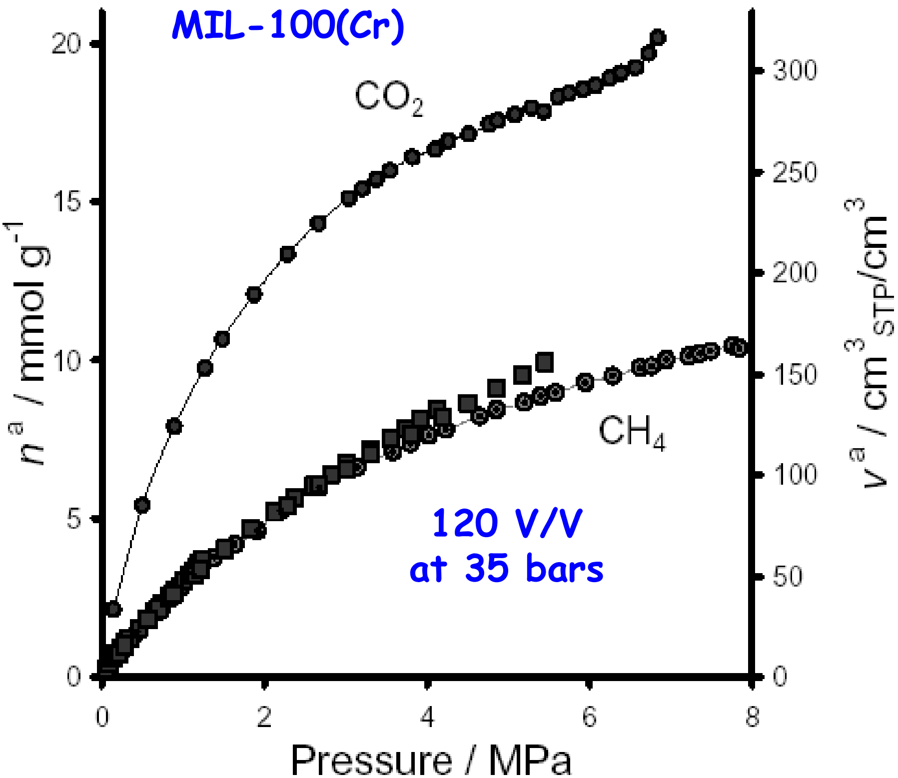
- Amines : very selective but not very cheap (regeneration)
- Zeolites (excellent selectivity but higher regeneration costs and limited capacity)
- Activated Carbons : moderate Selectivity and capacity

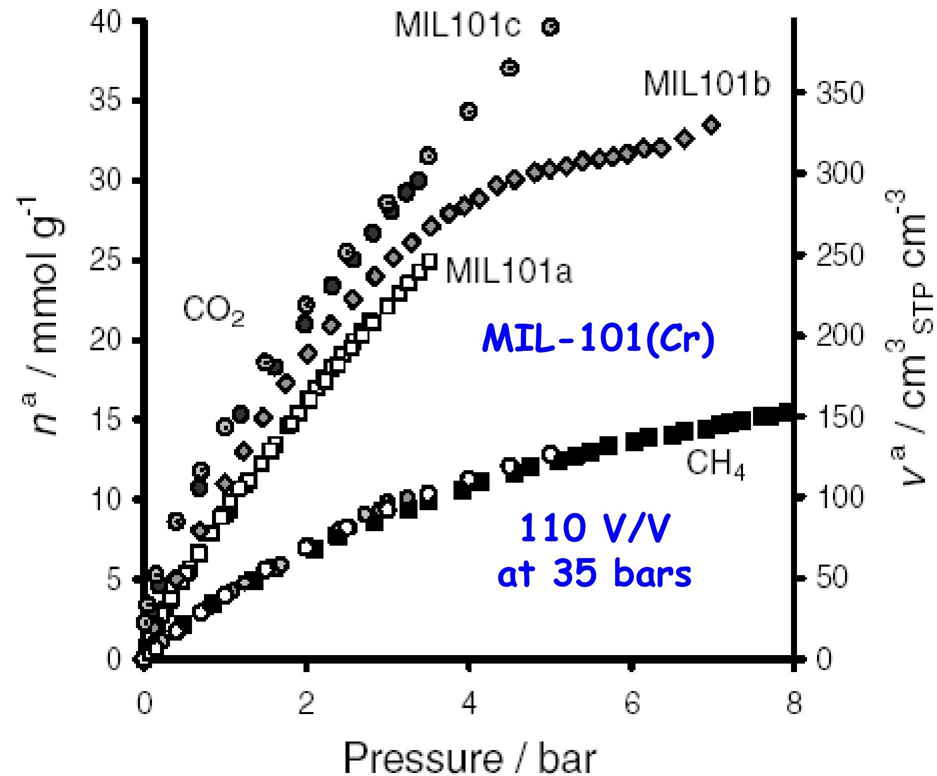
Metal-Organic-Frameworks ?

Rigid MOFs for adsorption of green house gases

Mesoporous Cages
Microporous windows







Moderate methane capacity but huge adsorption of 300-400 V/V at high Pressure of CO_2

S. Bourrelly et al., Langmuir 2008

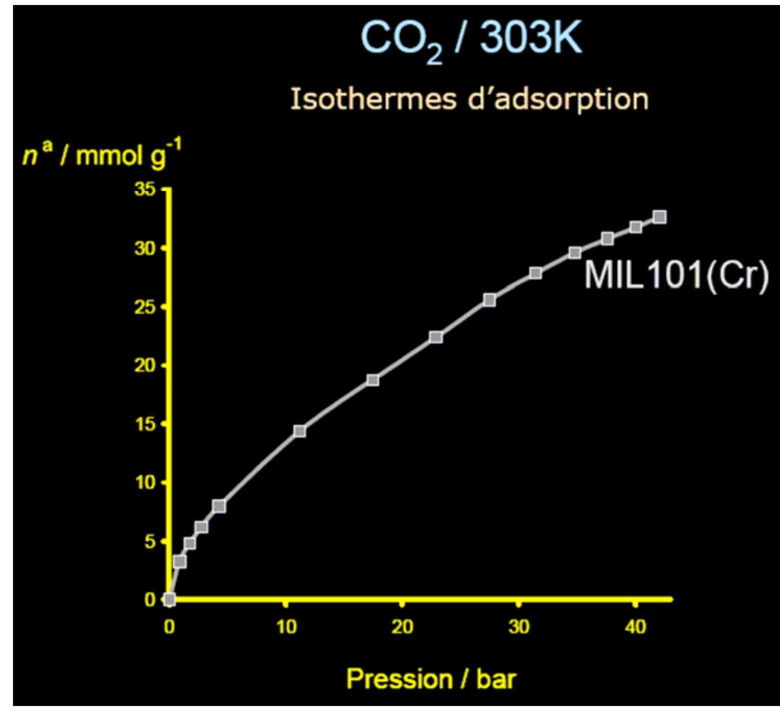
MIL-101 capacity for CO_2 storage

Table 2. Carbon Dioxide Adsorption Capacities for Various Adsorbents

adsorbent	conditions	max loading ($mmol\ g^{-1}$)	max loading ($cm^3\ cm^{-}$
silicalite[35]	302 K/3.0 MPa	2.5	123
zeolite NaX[36]	302 K/3.0 MPa	7.8	147
SBA-16[31]	300 K/3 MPa	nongrafted 6	na
		grafted 3−4	na
active carbon NORIT R1[6]	298 K/3.0 MPa	10	96
active carbon − Maxsorb[6]	298 K/3.5 MPa	25	162
$Cu(bpy)(BF_4)_2$[13]	273 K/3.0 MPa	4	153
MIL53(Al, Cr)[14]	302 K/2.5 MPa	10	225
HKUST-1[15,25]	298 K/4.2 MPa	10.7	210
MIL-47(V)[14]	302 K/2.0 MPa	11	250
IRMOF-1[15]	298 K/3.5 MPa	21.7	290
MOF-177[15]	298 K/4.2 MPa	33.5	320
MIL-100(Cr)	304 K/5.0 MPa	18	280
MIL-101c(Cr)[a]	304 K/5.0 MPa	40	390

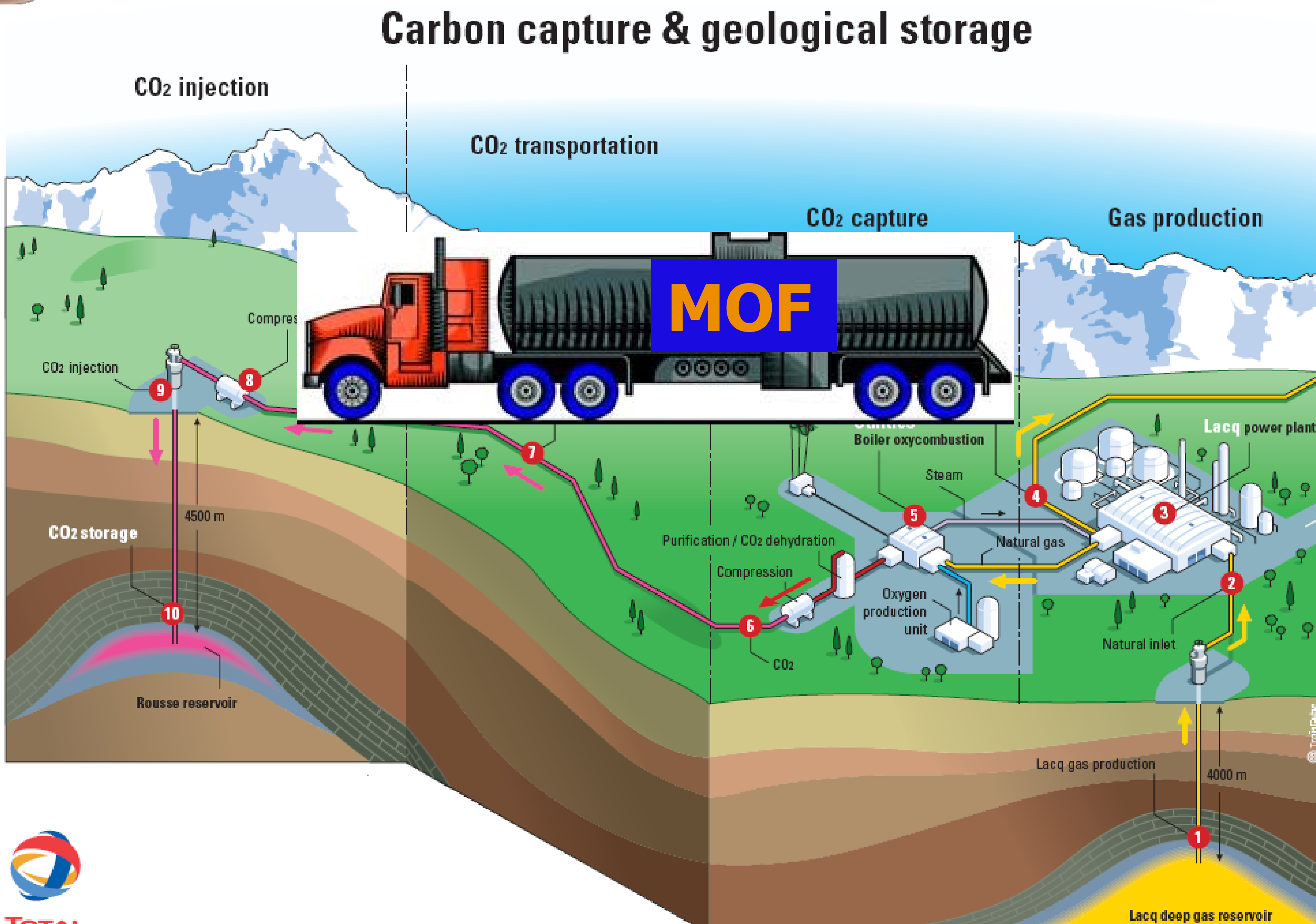
[a] Sample MIL-101 activated by EtOH + NH_4F treatments.

← 400 X its volume in CO_2



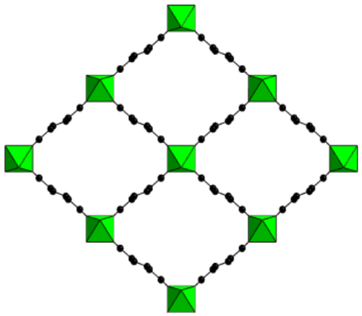
P. L. Llewellyn, S. Bourrelly, C. Serre , A. Vimont , M. Daturi ,L. Hamon, G. De Weireld , J-S Chang, D-Y. Hong, Y. K. Hwang, S. H. Jhung, G. Férey *' High uptakes of CO_2 and CH_4 in the mesoporous Metal-Organic-Frameworks MIL100 and MIL101'*, ***Langmuir* , 2008**

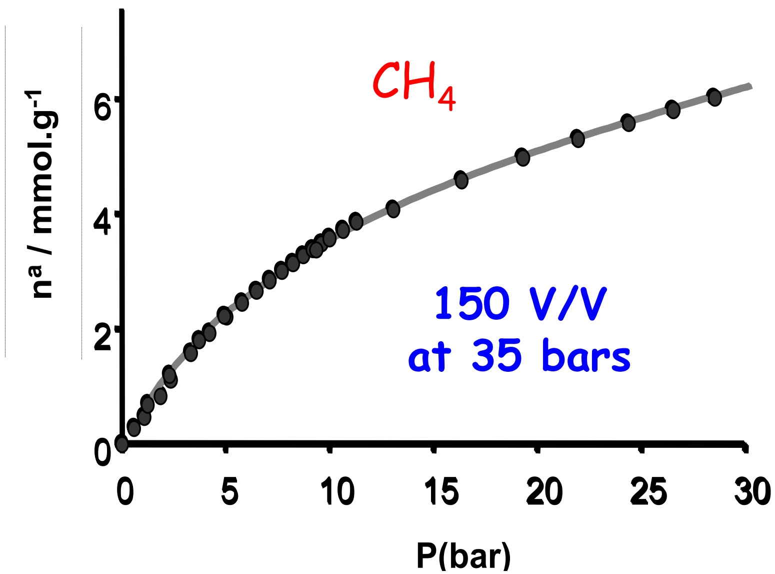
Possible application of MIL-CO2 affinity

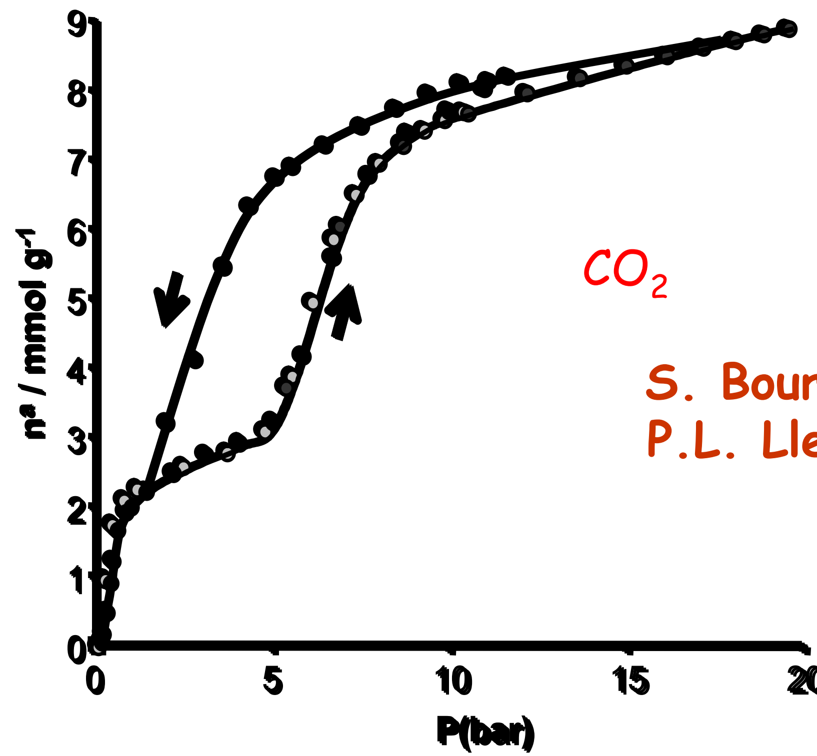


Flexible MOFs for adsorption of green house gases

Flexibles MOFs MIL-53(Cr, Al) (T=298 K)





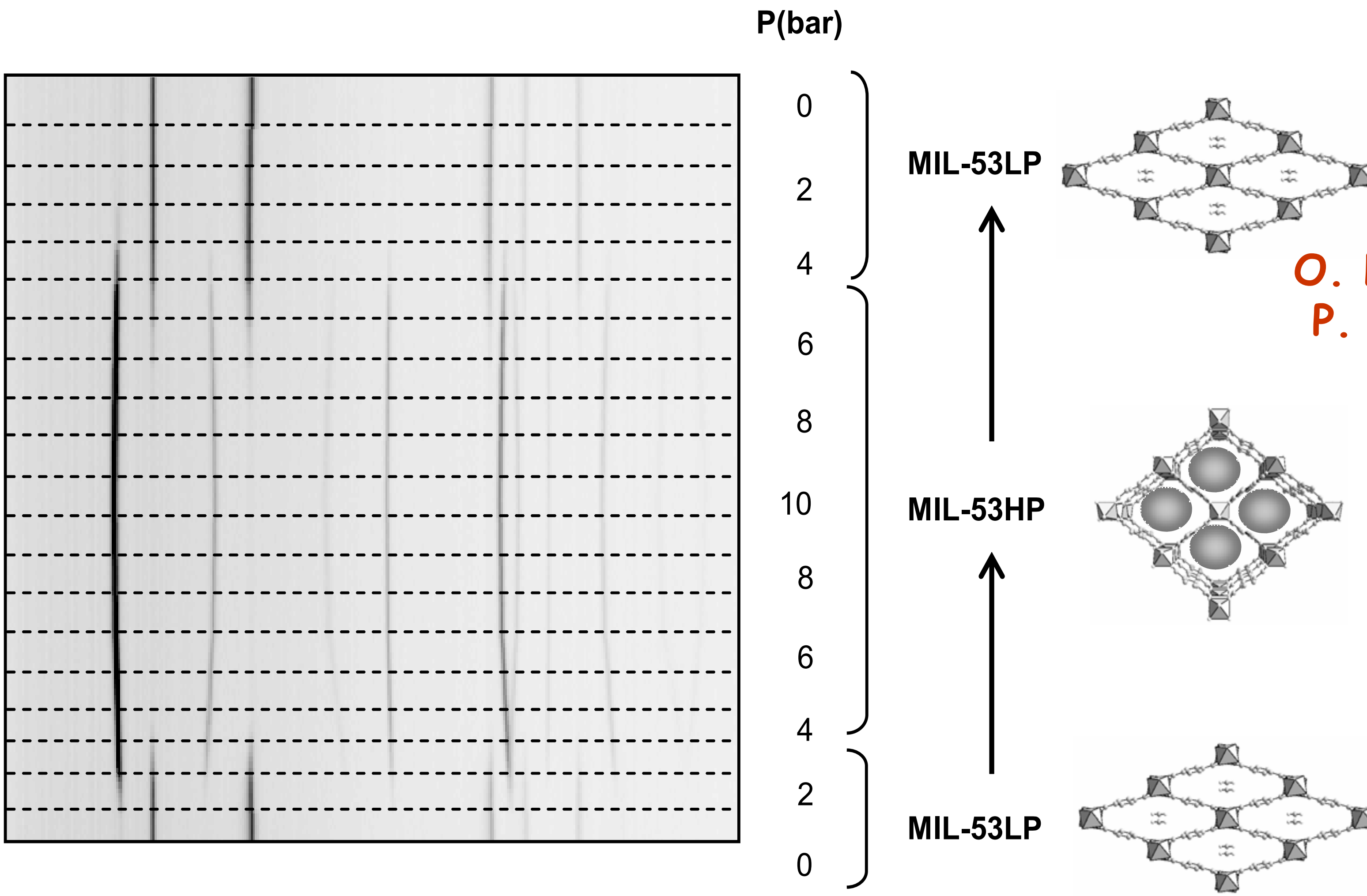


Type I (rigid phase)

Steps (flexible phase)

S. Bourrelly et al., J. Am. Chem. Soc. 2005; P.L. Llewellyn et al., Angew. Chem. 2006
C. Serre et al., Adv. Mater. 2007

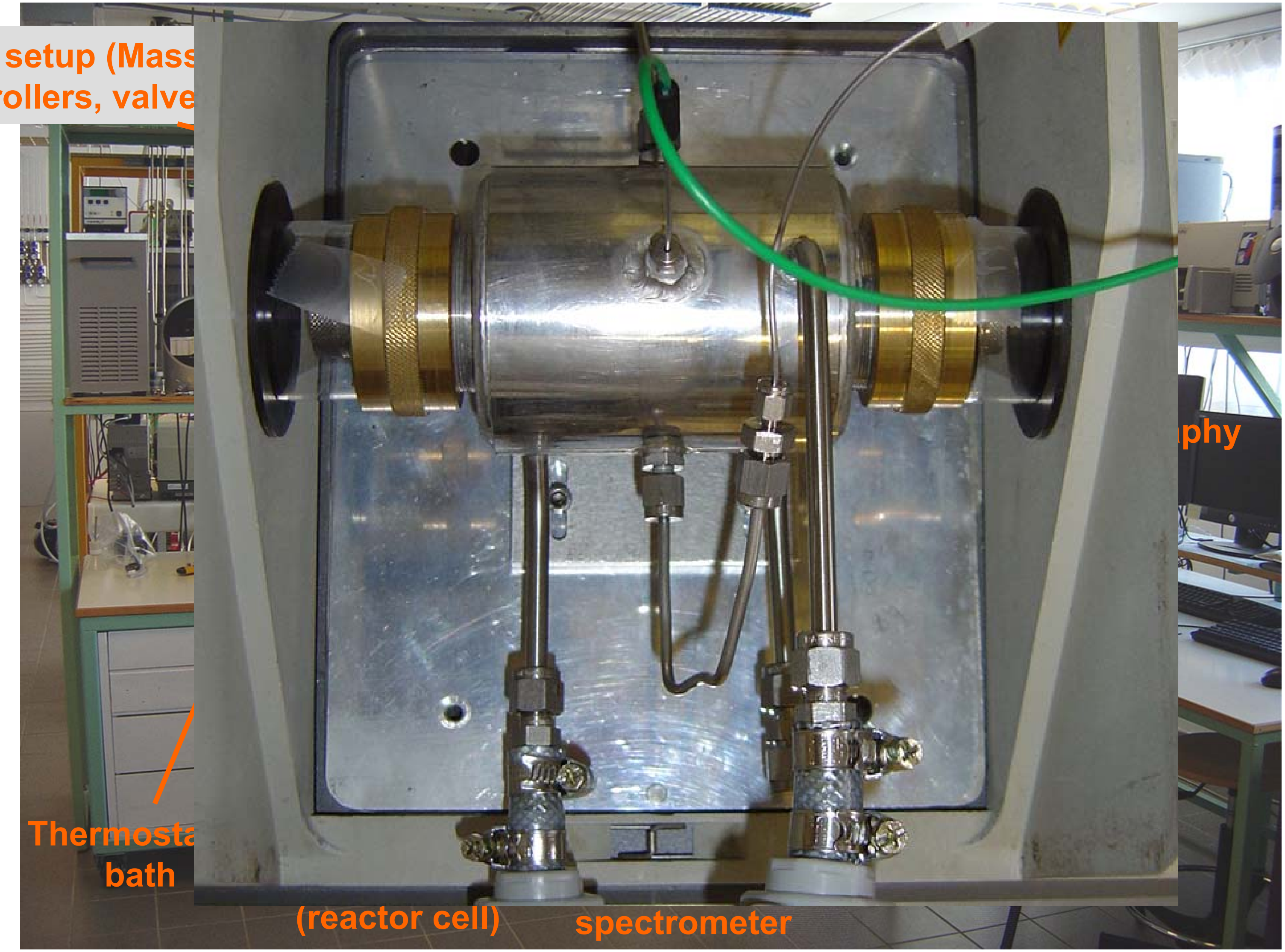
XRD in situ analysis of the breathing of MIL-53 under pressure of CO_2



O. Leynaud
P. Barnes

C. Serre et al., Adv. Mater., 2007

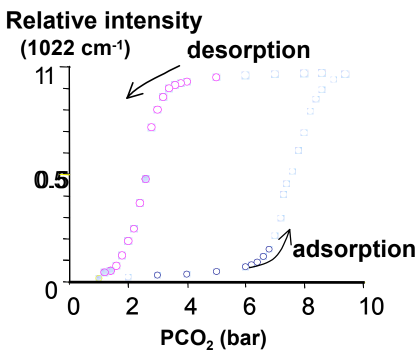
FT-IR in situ analysis of MIL-53 breathing under pressure of CO_2



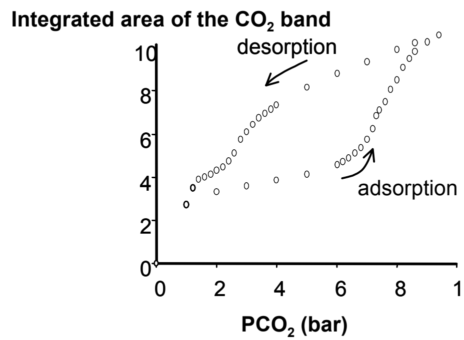
Properties of “breathing” MOF structures MIL-53 (Cr)

Diaporama
crosoft PowerPo

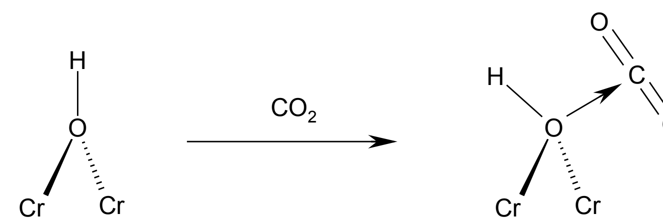
Fraction of MIL-53HP

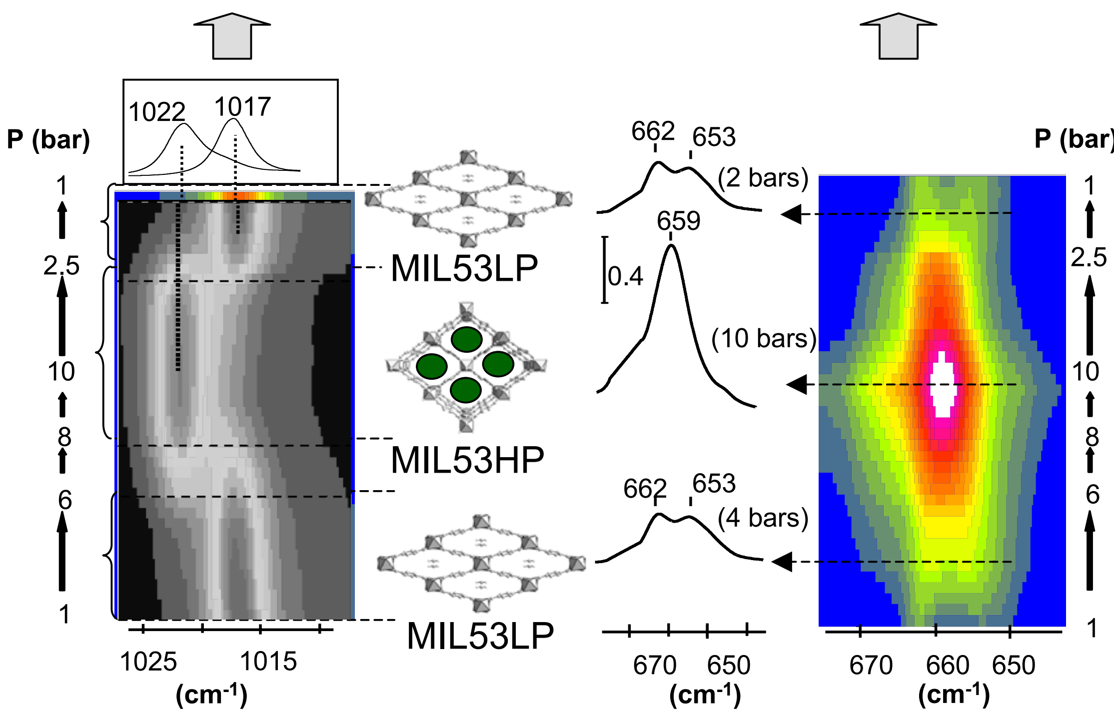


Quantity of adsorbed CO_2



Hysteresis phenomenon observed during the adsorption-desorption cycle (curves obtained from the quantitative analysis of the IR spectra)





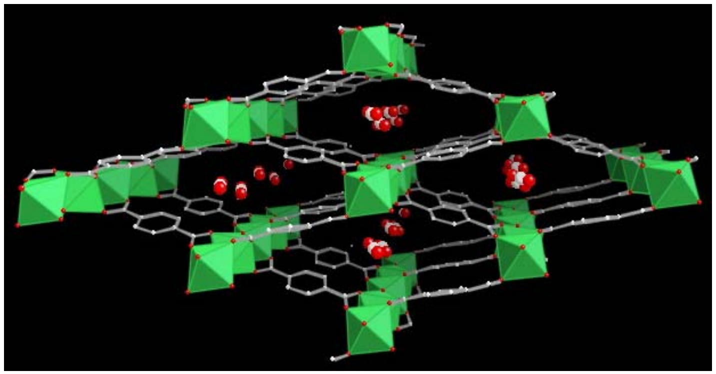
Variation of the intensity of the MIL53LP structural band (1017 cm^{-1}) and MIL53HP (1022 cm^{-1}), and that of the ν_2 mode of CO_2 (653, 662 cm^{-1} MIL53LP; 659 cm^{-1} MIL53HP) versus CO_2 pressure.

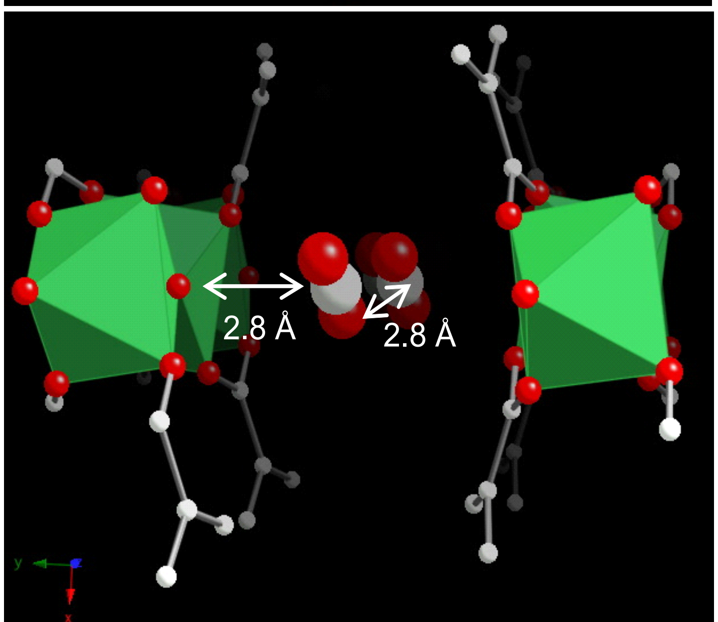
Vimont et al., ***Chem. Commun.*** **(2007) 3291**
C. Serre et al., ***Adv. Mater.*** **19 (2007) 2246**

Modelling of framework- CO_2 interactions in MIL-53

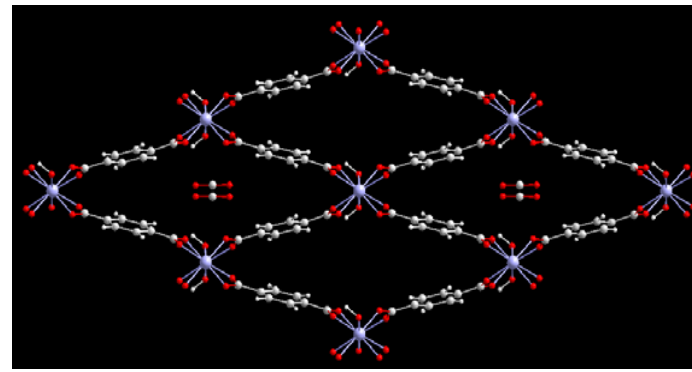
N. Ramsahye,
G. Maurin

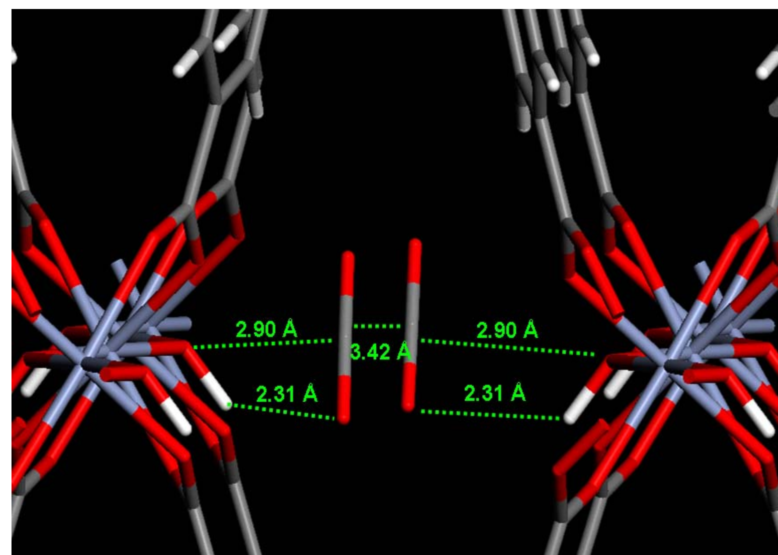
Structure from XRPD





Simulated structure





C. Serre et al., *Adv. Mater.*, 2007; N. Ramsahye, *Chem. Comm.*, 2007

Conclusion

MOFs for adsorption :

- ✓ A large range of compositions, structures and pore sizes
- ✓ Can be cheap and water stable
- ✓ Low regeneration costs
- ✓ Flexibility leads to new sorption behaviors
- ✓ Functionnalisation (metal, linker) to design sorption ?

Possible Applications in adsorption, separation :

- ✓ Gas storage (methane, hydrogen ?)
- ✓ Capture and transfert of CO_2 (Biogas…)
- ✓ Separation (propane/propene, gasoline…)
- ✓ Purification (removal of sulfurs, H_2…)

Future Research (adsorption) :

- ✓ New MOFs + understanding
- ✓ Stability (moisture, cyclability…)
- ✓ Large scale (pilot) tests using pelletized samples