How can MOFs save the world?

Breakthrough Post Combustion Capture Technologies workshop

March 25-26th 2015, Melbourne, Austalia

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CSIRO 'solar sponge' soaks up CO_2 emissions

CSIRO discovered a new photosensitive metal organic framework (MOF) that could

Most effective

Published on Mon, Jan 16,
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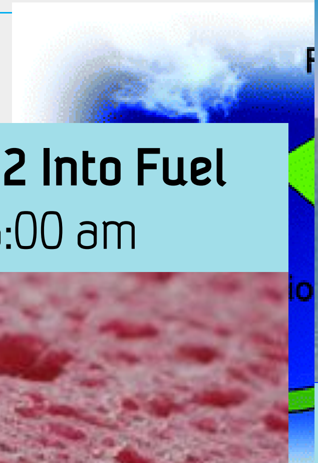
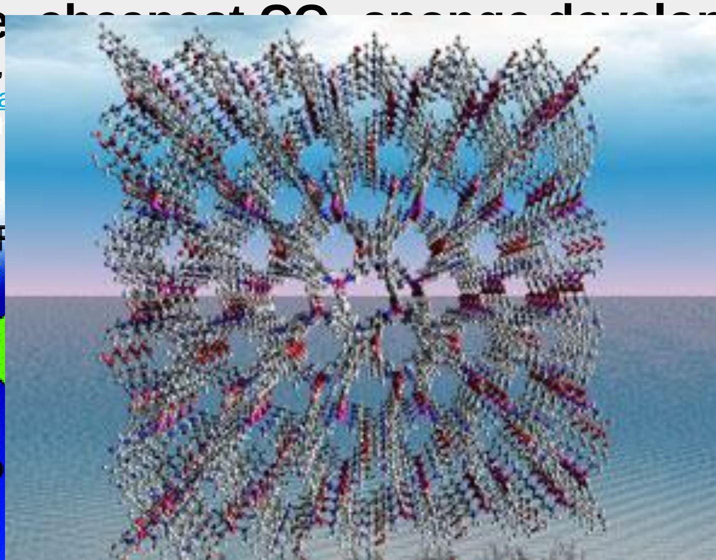
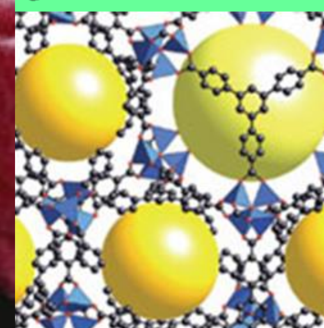


Cool New Sponges Can Recycle CO2 Into Fuel

by Beth Buczynski, March 6, 2013, 5:00 am



MOF gate opens selective CO2 gas storage door

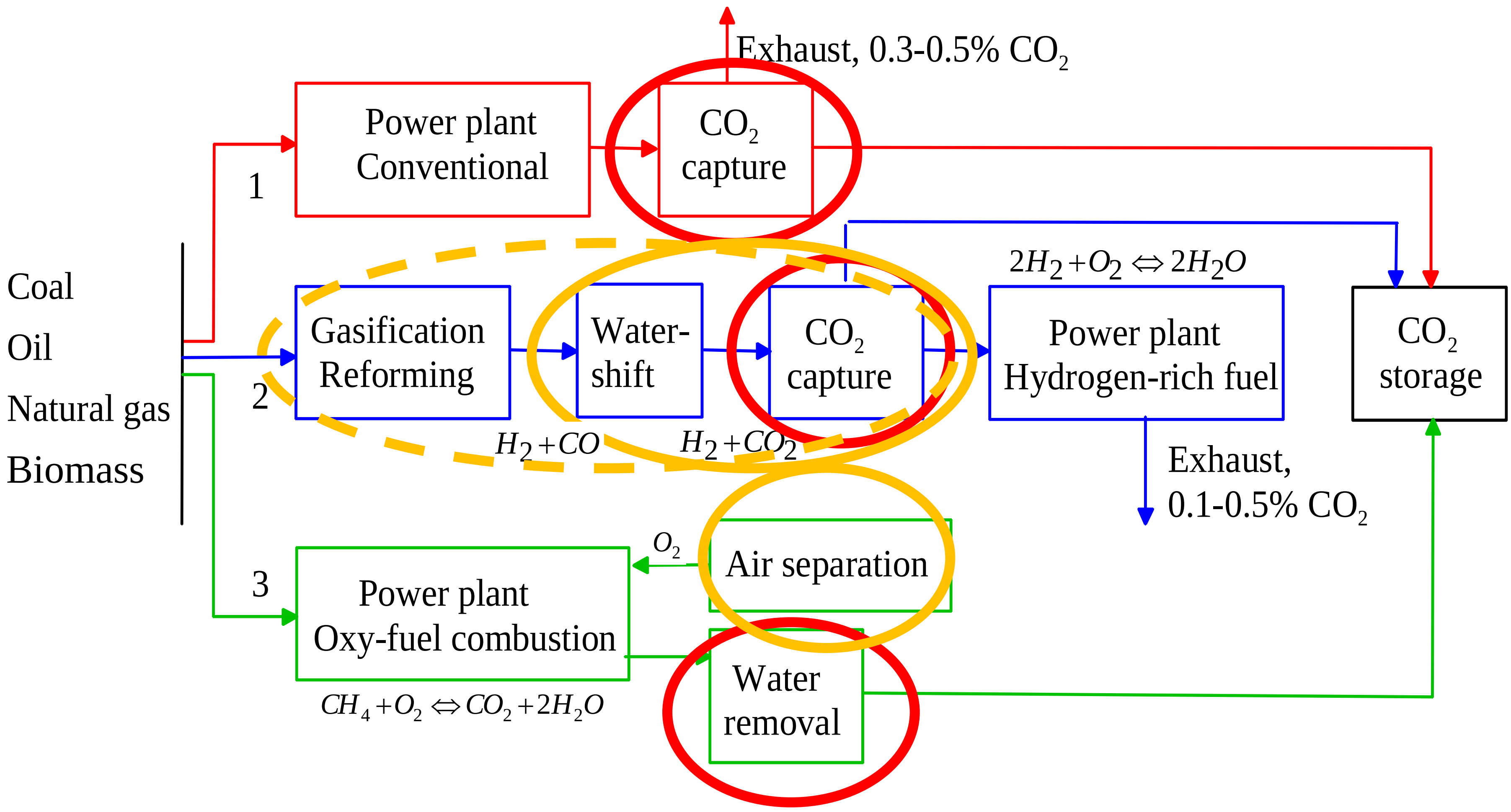


Pores a plenty Composed of 1,3,5-benzenetribenzoate units and zinc clusters (blue), MOF-177 can store exceptionally large quantities of CO_2 in its pores (yellow)

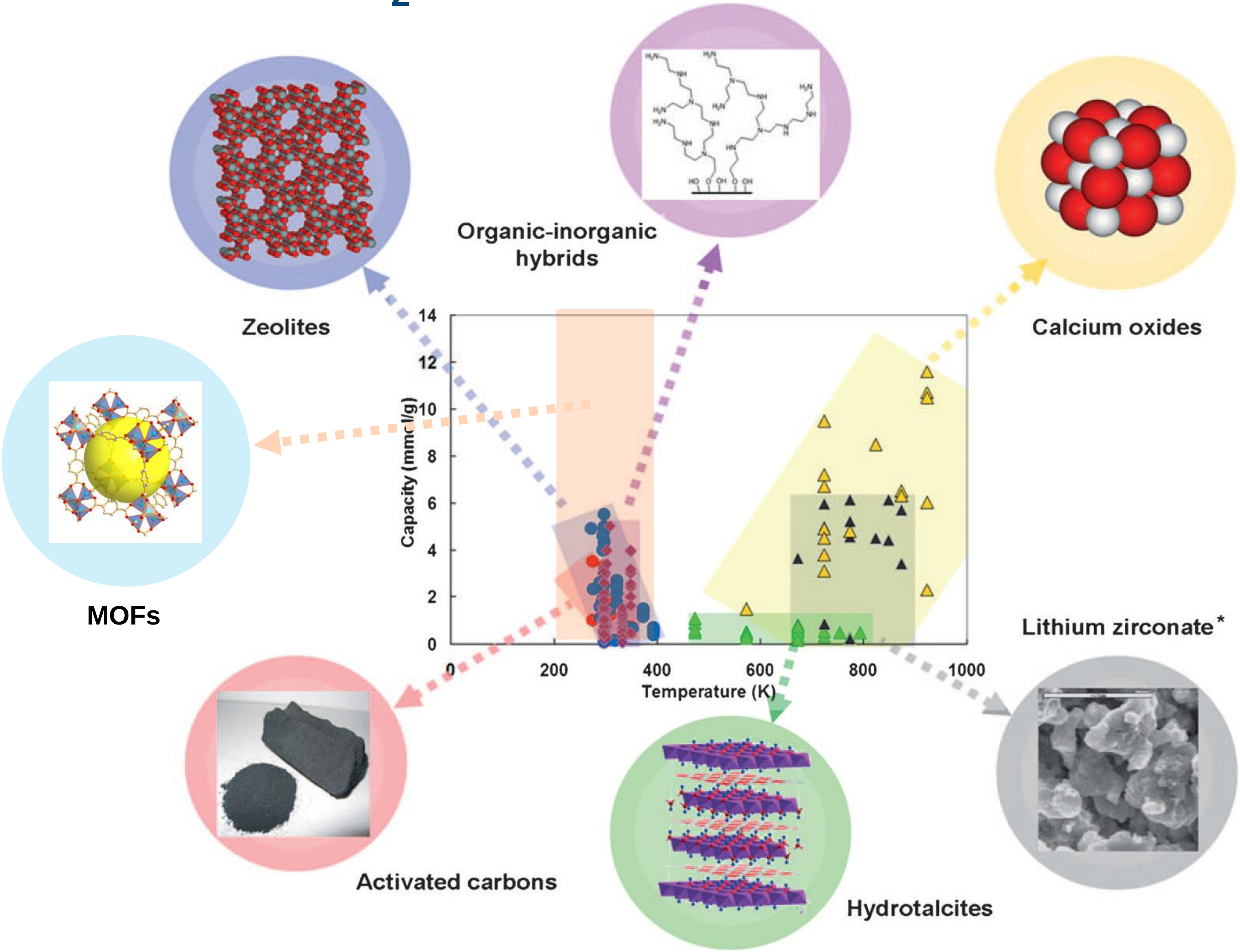
Outline

- CO_2 capture schemes
- Various sorbents - What are MOFs?
- MOFs in CO_2 capture
  - Requirements for use in CO_2 capture
    - Post-combustion adsorption
    - Pre-combustion adsorption
  - MOF formulation
- Conclusions

CO_2 capture technologies – possible use of MOF based sorbents



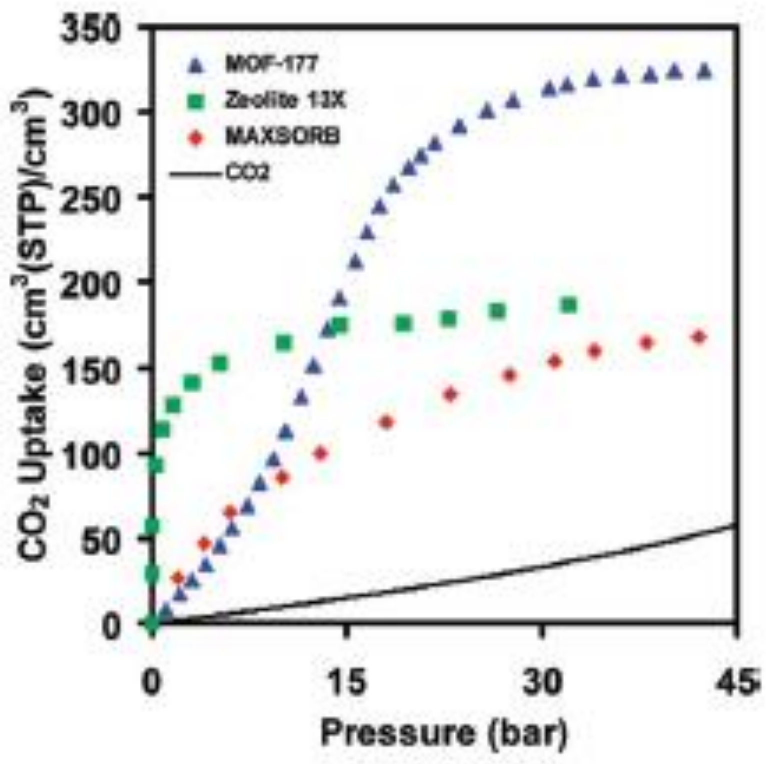
Various families of CO_2 sorbents:



Partly taken from: Choi et al, *ChemSusChem*, 2009

What determines the applicability of a certain adsorbent?

- The shape of the isotherm relative to boundary conditions of the adsorption process.
  - T, p & composition of inlet gas
  - T, p & composition demand of outlet gas(es)
  - For TSA processes you need a sorbent having large capacity difference between sorption and desorption temperatures
  - For a PVSA process you need a sorbent having large capacity different between the sorption and desorption pressures



Milward & Yaghi, *J. Am. Chem. Soc*, 2005

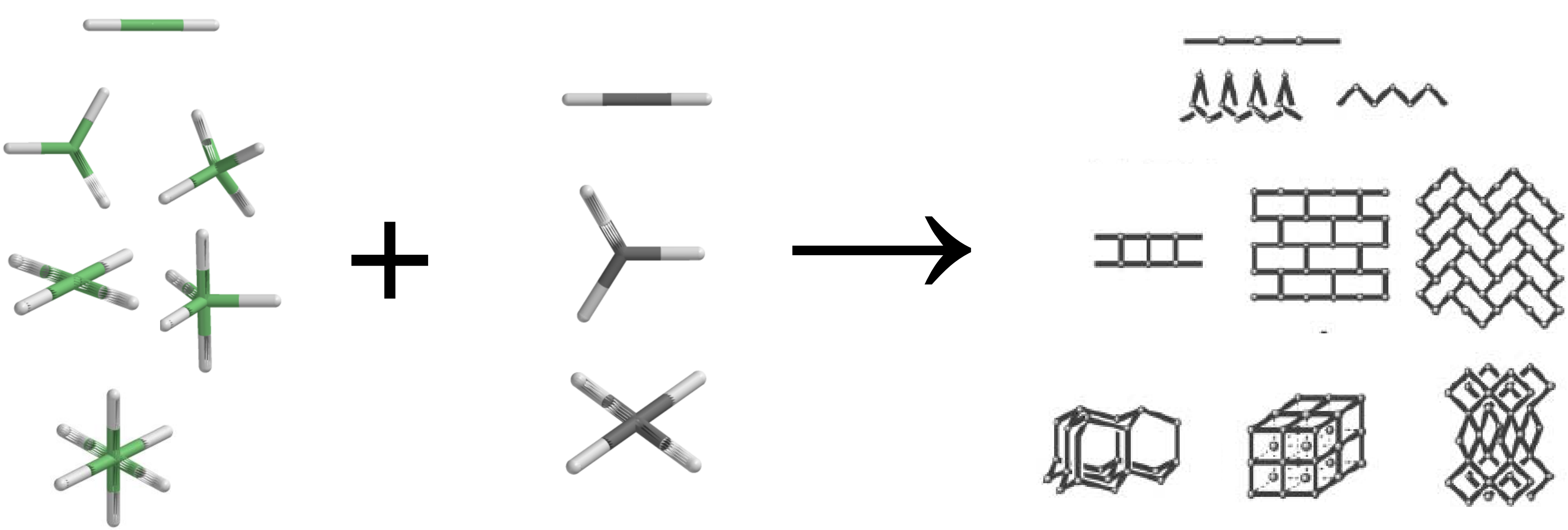
- And kinetics!
- And certainly; selectivity is an issue…….
- And so is the physical stability of the sorbent….

What are MOFs?

Metal centre or cluster (inorganic part)

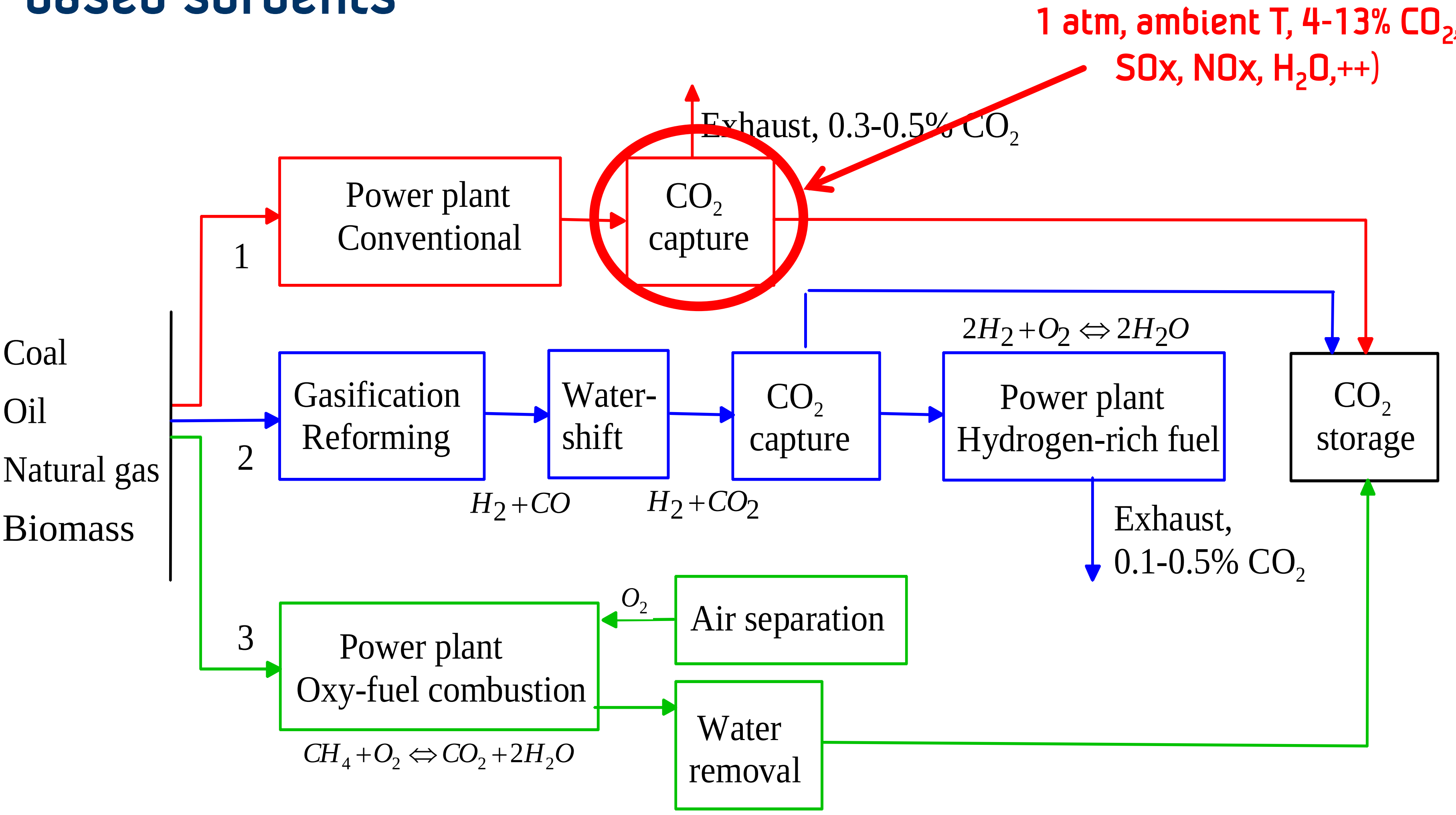
[Linker (organic part)]

Metal Organic Framework (coordination polymer)



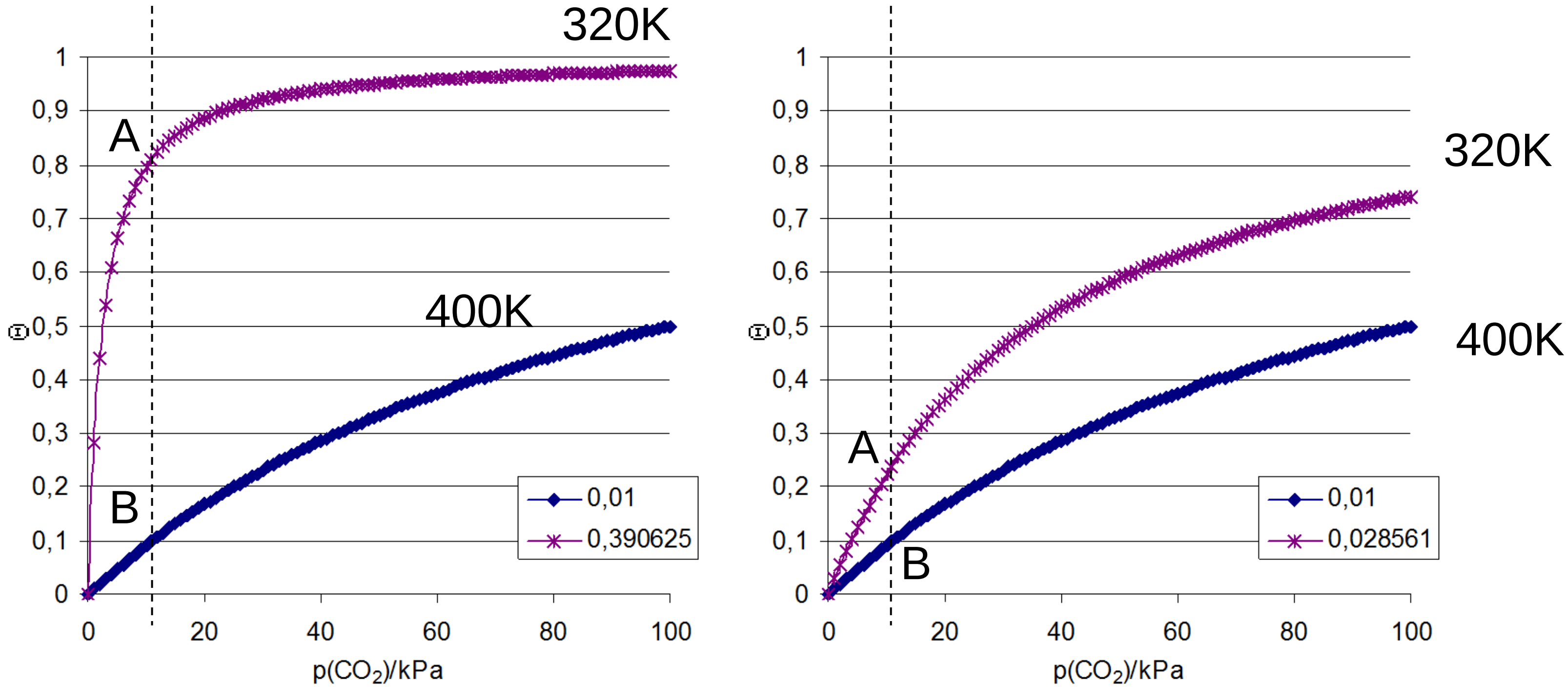
- **Combining the whole inorganic chemistry with the whole organic chemistry give a close to infinite number of possible diverse structures !**

Post-combustion CO_2 capture – possible use of MOF based sorbents



Langmuir: $\theta = \frac{y}{y_{\max}} = \frac{bp}{1+bp}$

Temperature swing adsorption (TSA):

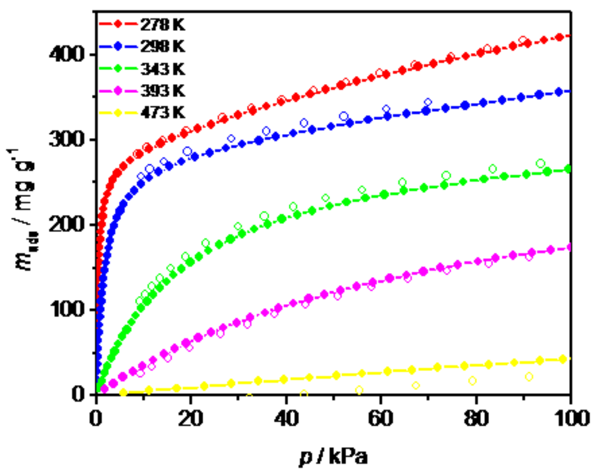


E_{ads} = 46 kJ/mole

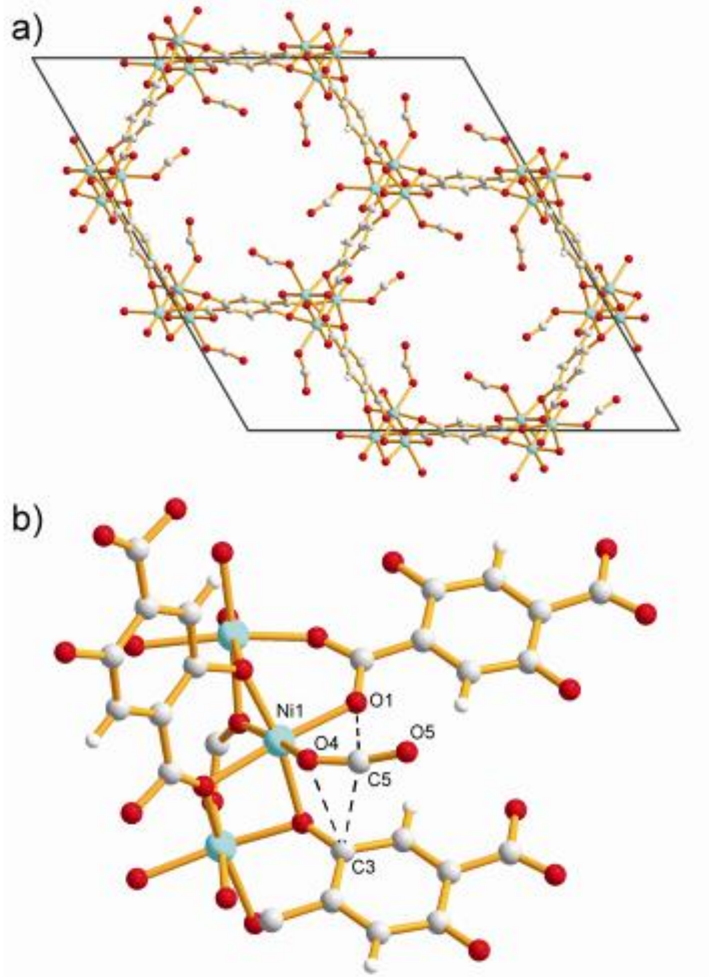
E_{ads}= 16 kJ/mole

The CPO-27-M family:

- Relatively high adsorption energies are needed to selectively adsorb CO_2 from dilute flue gas
- High potential cyclic CO_2 capacities
- Synthetic gas mixtures (also H_2O) seems to give stable and good results
- Ongoing work on cyclic capacity using realistic gas composition



The best adsorbent can adsorb as much as 25 wt% CO_2 at room temperatures and 10 kPa CO_2 pressure (0.1 atm)

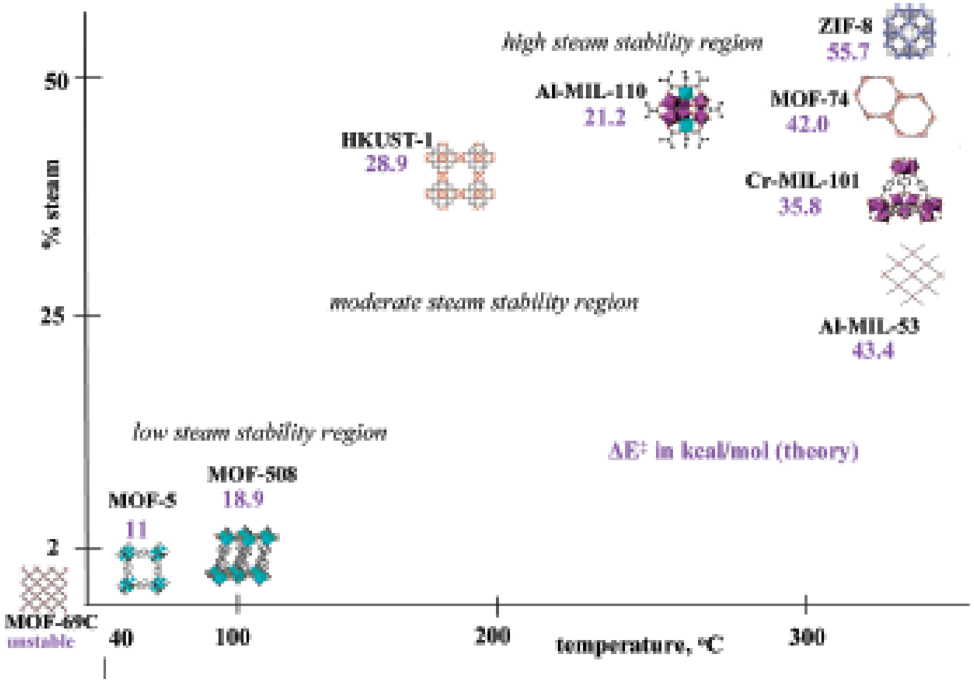


Structural analyses show that CO_2 bonds directly to the open metal center on CPO-27-Ni

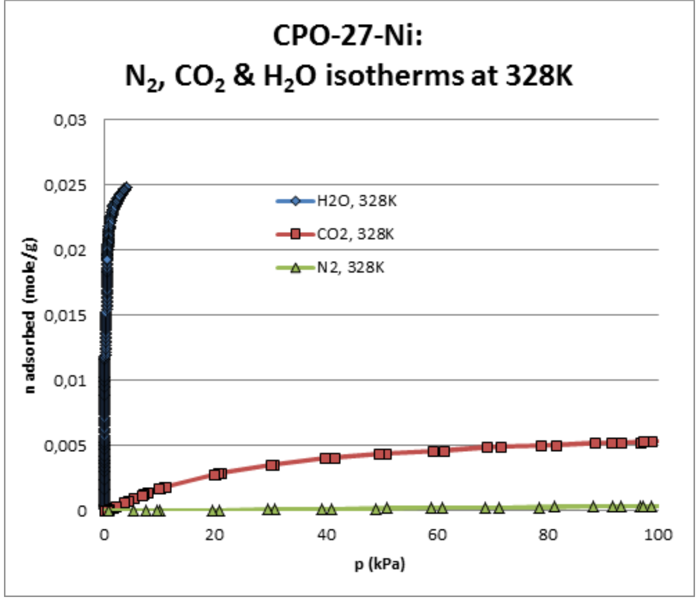
Dietzel, Johnsen, Fjellvåg, Bordiga, Groppo, Chavan & Blom, *Chem. Commun.*, 2008

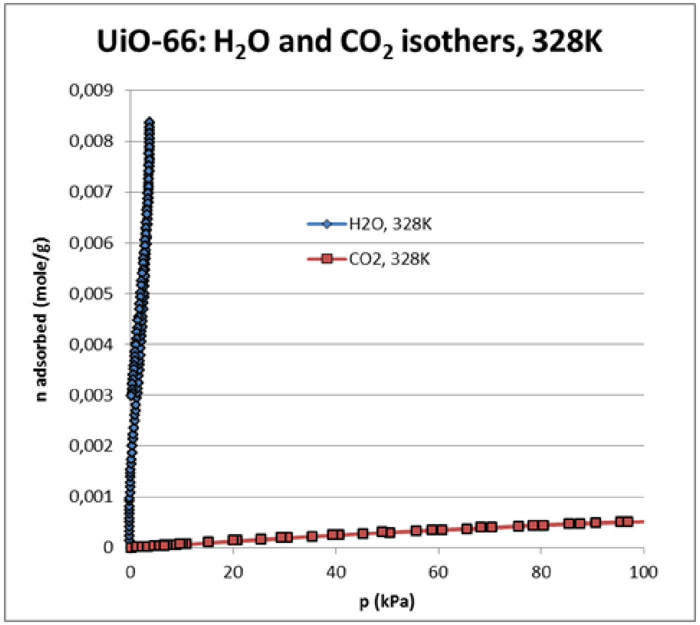
MOF challenges: Water stability and selectivity….

- Hydrothermal stability……
- If stable… what is the moisture limit?
- Kinetics……



Low, Benin, Jakubczak, Abrahamiam, Faheem & Willis, *J. Am. Chem. Soc.* 2009

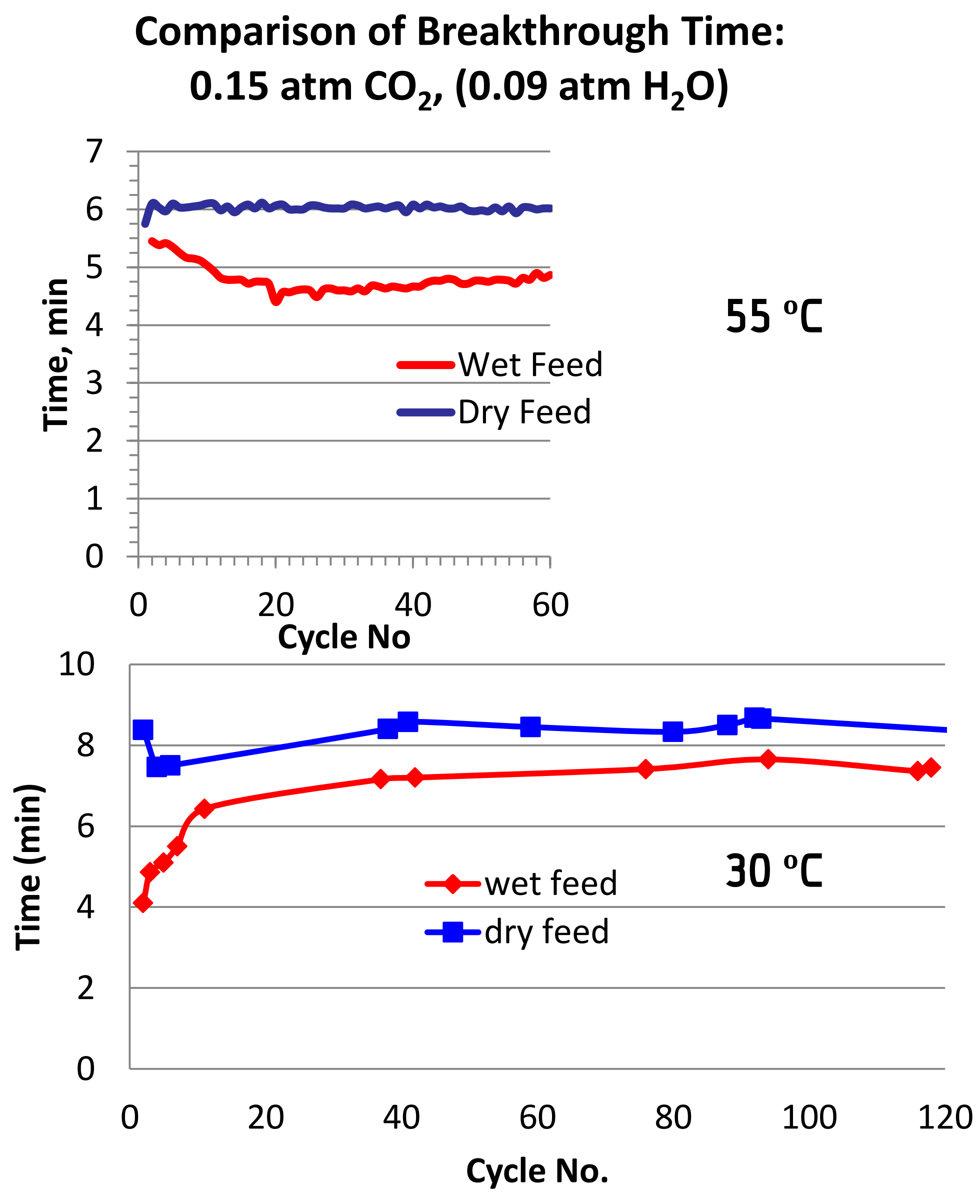




Grande & Blom, 2013

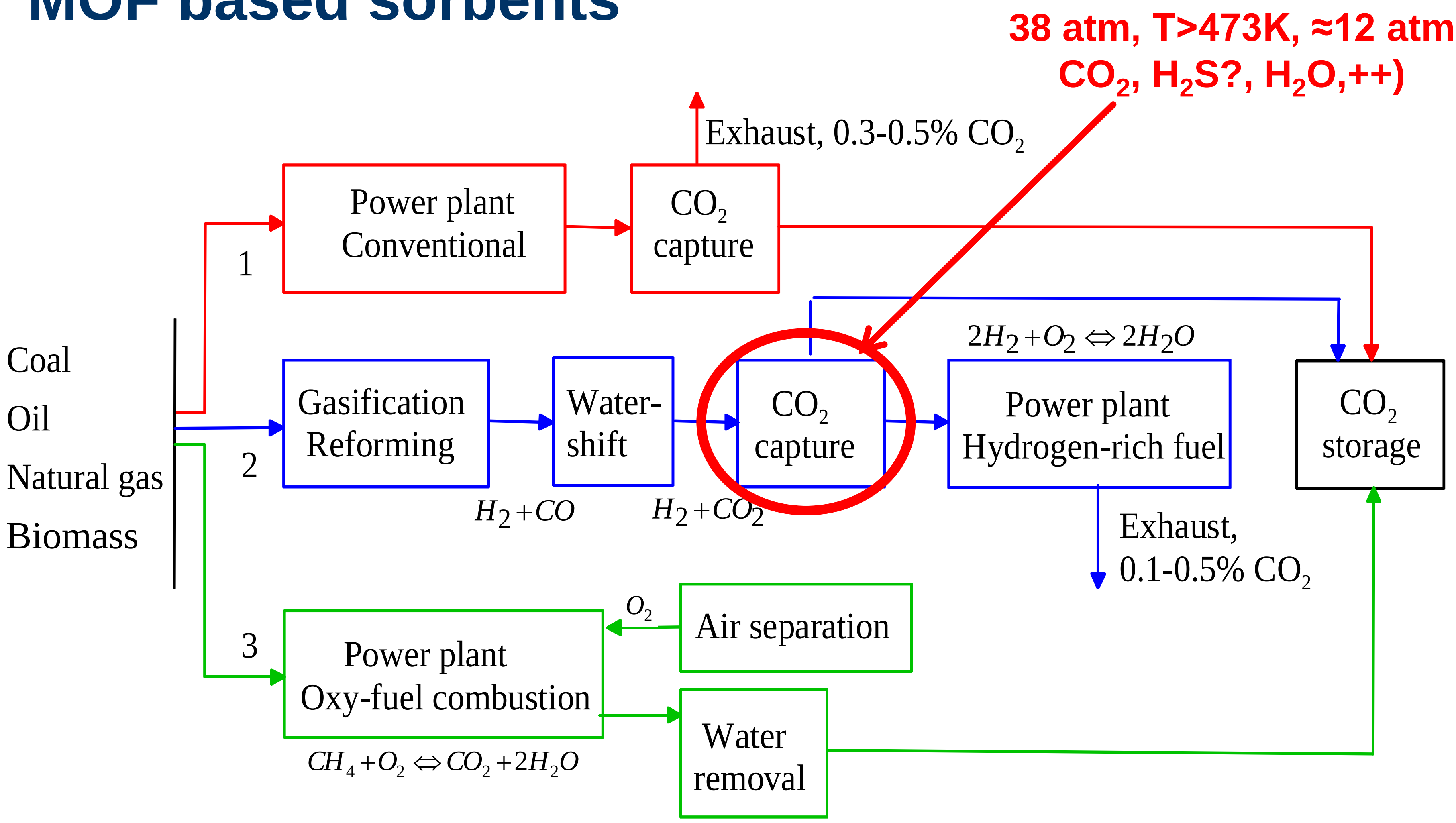
VSA using CPO-27-Ni beads:

- Steady cyclic CO_2 capacity is achieved also in the presence of moisture
- At wet conditions, under counter-current regeneration, the cyclic CO_2 capacity reaches a steady state level of about 80% of the cyclic CO_2 capacity at dry conditions.



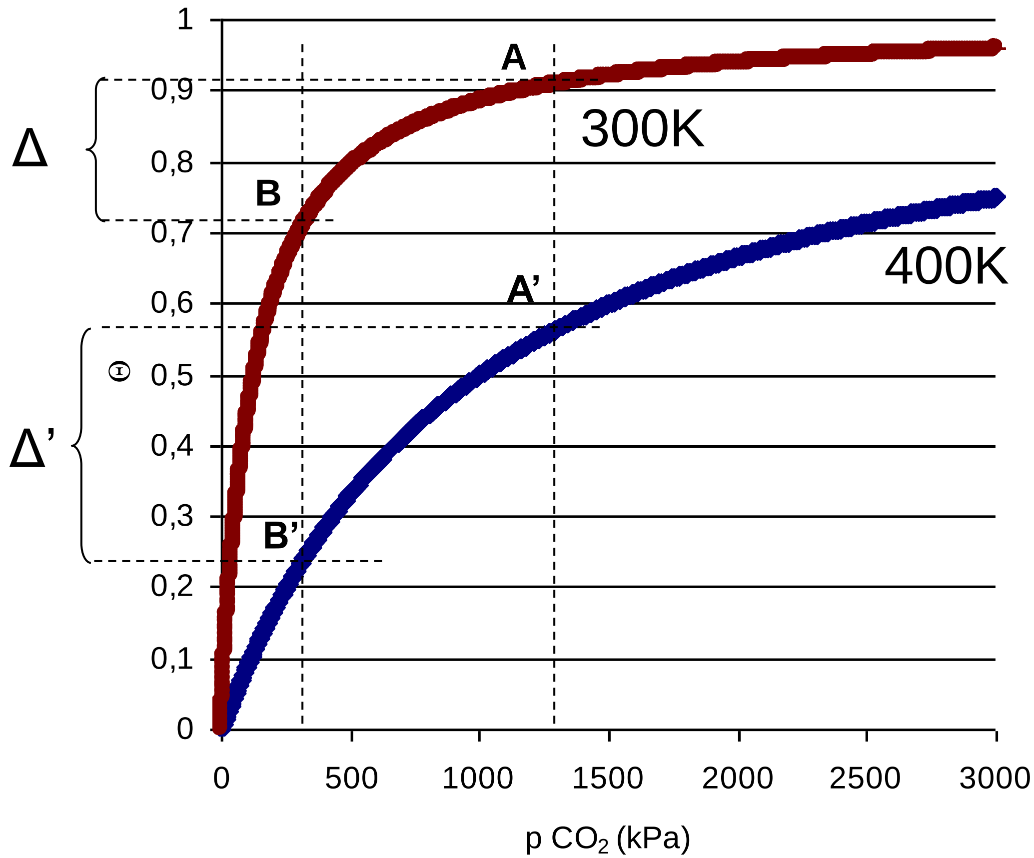
Nanoti & Blom, 2014.

Pre-combustion CO_2 capture – possible use of MOF based sorbents



Pre-combustion

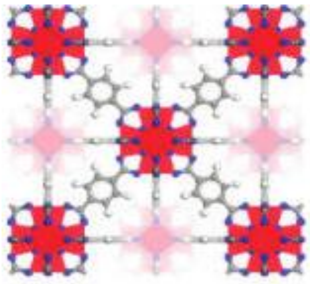
Pressure/Vacuum swing adsorption (PVSA)



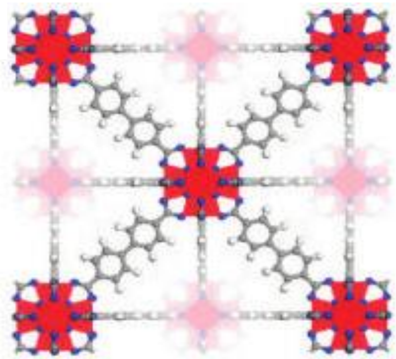
E_{ads} = 20 kJ/mol.

Vertical dotted lines at 13 and 3 atm.

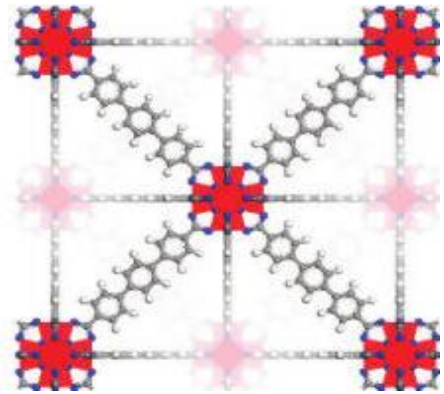
Systematic increment of pore size: UiO-6X system



UiO-66
BET=1100-1350 m^2/g

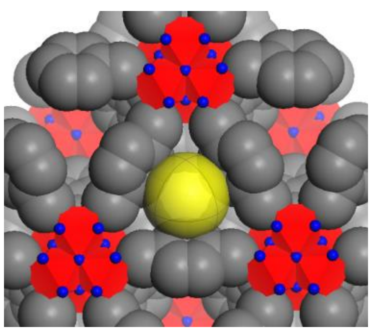


UiO-67
BET=2200-2450 m^2/g

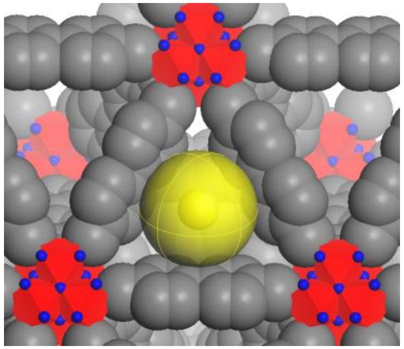


UiO-68
BET≈ 4000 m^2/g

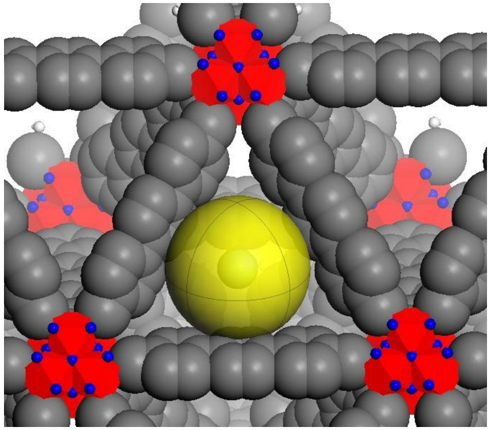
Increasing the length of the linker results in materials with lager pore size and higher surface area.



UiO-66; Probe 6 Å diameter.



UiO-67; Probe 8 Å diameter.



UiO-68; Probe 10 Å diameter.

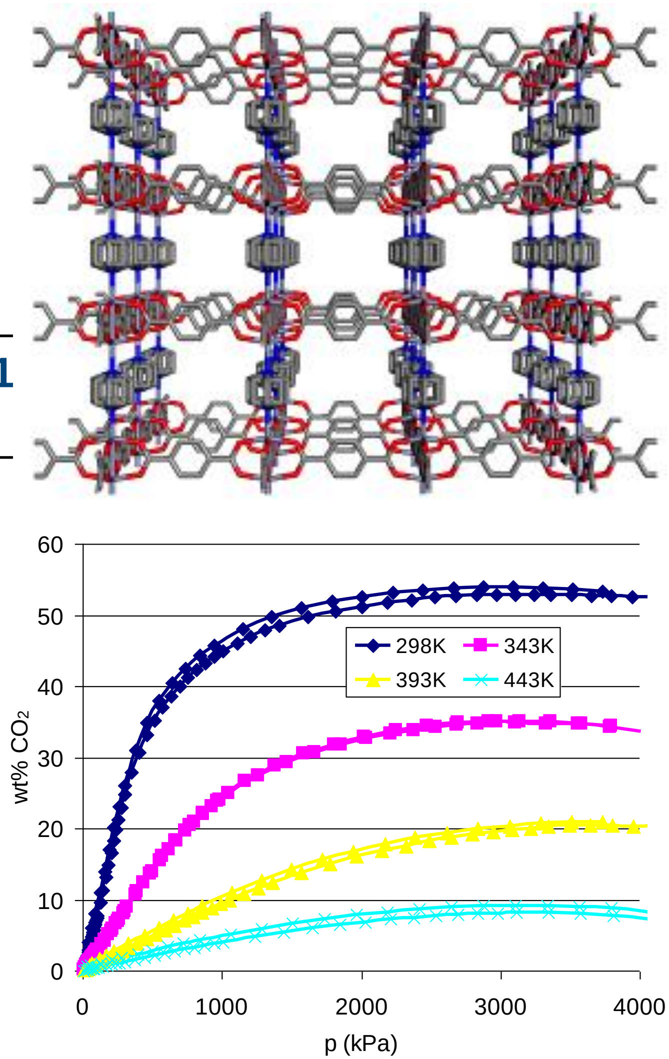
The pore openings are also increasing as a function of linker length.

Cavka, Jakobsen, Olsbye, Guillou, Lamberti, Bordiga & Lillerud, *J. Am. Chem. Soc.*, 2008

Pre-combustion

Physical properties of the different adsorbents: state-of-art vs. novel MOF adsorbents

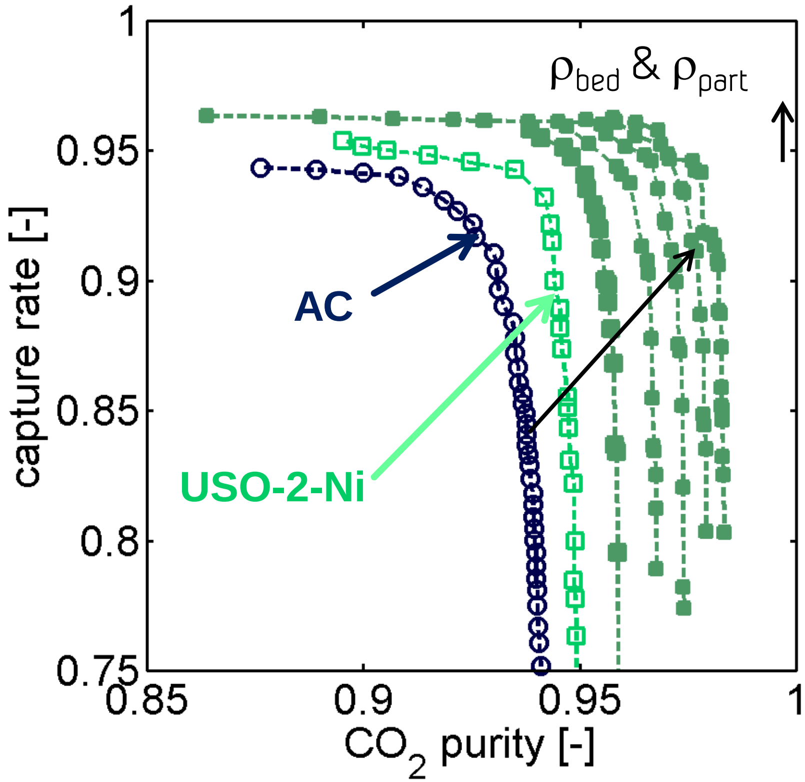
	Activated Carbon	USO-2-Ni	UiO-67/MCM-41
d_p [mm]	3	1-2	0.2-0.5
r_{mat} [kg/m3]	1970	1700	1570
r_{part} [kg/m3]	850	531	557
r_{bed} [kg/m3]	507	300	320
Cs [J/K kg]	1000	1160	1250



Structure and CO_2 isotherms of USO-2-Ni

Casas, Schell, Blom, Mazzotti, *Sep. Purif. Techn.* 2013

Comparison assuming higher densities for the MOFs
- modeling of 6-column PSA separation process based on breakthrough experiments



Density	Porosity	
original	ε_{bed}	0.435
	ε_{tot}	0.823
+ 10%	ε_{tot}	0.805
+ 20%	ε_{tot}	0.788
+ 30%	ε_{tot}	0.771
+ 40%	ε_{tot}	0.7529
+ 50%	ε_{tot}	0.735

$$\varepsilon_{bed} = 1 - \frac{\rho_{bed}}{\rho_{part}}$$

$$\varepsilon_{tot} = 1 - \frac{\rho_{bed}}{\rho_{mat}}$$

Casas, Schell, Blom, Mazzotti, *Sep. Purif. Techn.* 2013

So formulation is important !

Firstly, because a chemical engineer will never put a fluffy powder into their reactor……..

Secondly, because it really improve the process performance!

But – important to keep the properties of the virgin (nano)-powder throughout the formulation process

MOF formulation: Can a general method be developed?

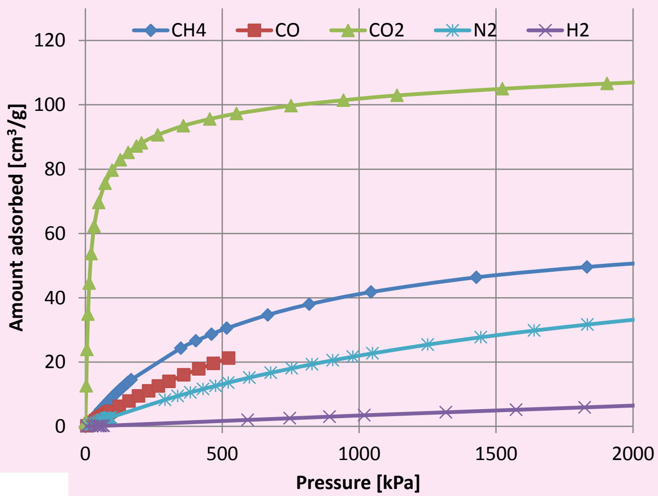
- ***Pelletizing***: The fine powder is blended with a binder (e.g. polyvinylalco (PVA), graphite or silica) and pressed at a certain pressure to give pell can be crushed and fractionized by sieving.
- ***Cake crushing****:* The fine powder is mixed with a certain amount of a bind r, typically PVA, dissolved in a solvent. Enough binder/solvent solution is to make a paste that is dried, then crushed and sieved into the wanted p size fraction.
- ***Mixing/extrusion/Spheronizing***: Using this method the fine powder is mixed with a binder (e.g. cellulose, PVA, etc.) and a solvent (e.g. water, alcoho to give a paste. The paste is extruded to give “spaghetti” which is then ma into spheres in a “spheronizer” (a fast circulating plate)
- ***The alginate method***: A slurry of the fine powder is made in a solution of an alginate dissolved in water. The homogeneous slurry is dropwise added water solution of Ca^{2+} ions where a spontaneous cross-binding of the al slurry droplets occur.

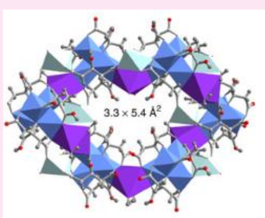
Formulation of metal-organic frameworks - Extrusion

Focus on utilization of organic linkers that remain in the structure but provide hardness and porosity.

UTSA-16

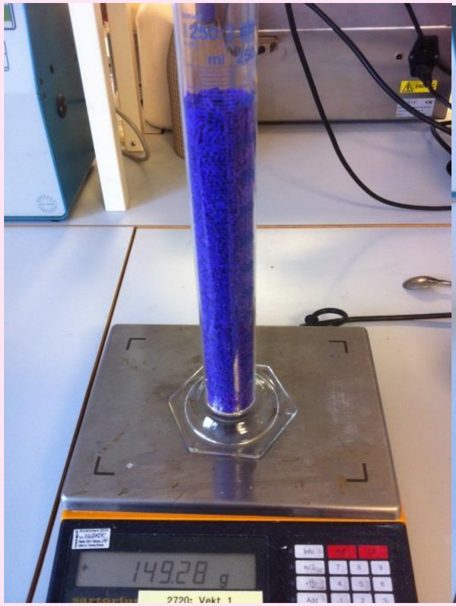
- Adsorbent presents low surface area loss after extrusion. High CO_2 loading remains.
- No significant mass transfer resistance added after extrusion.





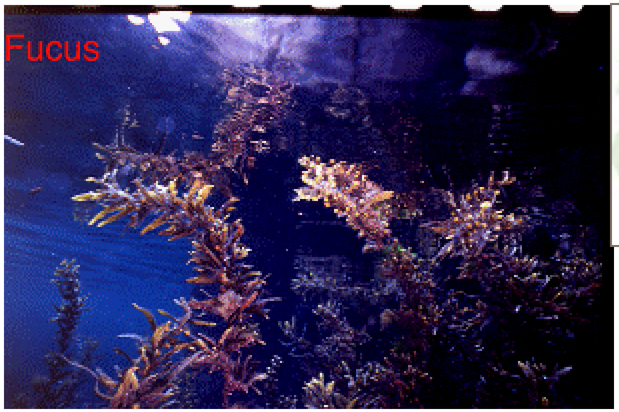
Scale

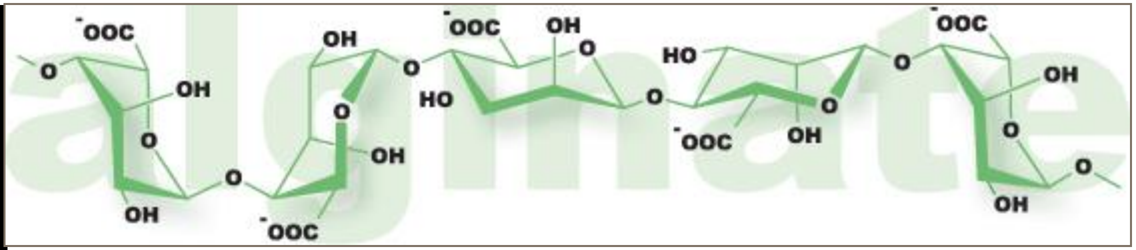
- We have obtained around 200 grams of extruded UTSA-16 with: very low surface area loss, good adsorption properties, narrow pore distribution and with density comparable to zeolite materials.

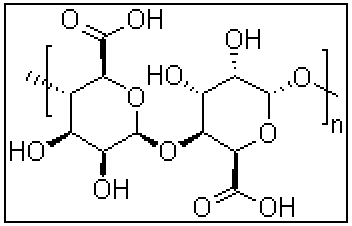


Agueda, et al. *Chem. Eng. Sci.* 2015, *124*, 159; Grande, et al, *Chem. Eng. Sci.* 2015, *124*, 154.

MOF Formulation: The alginate method





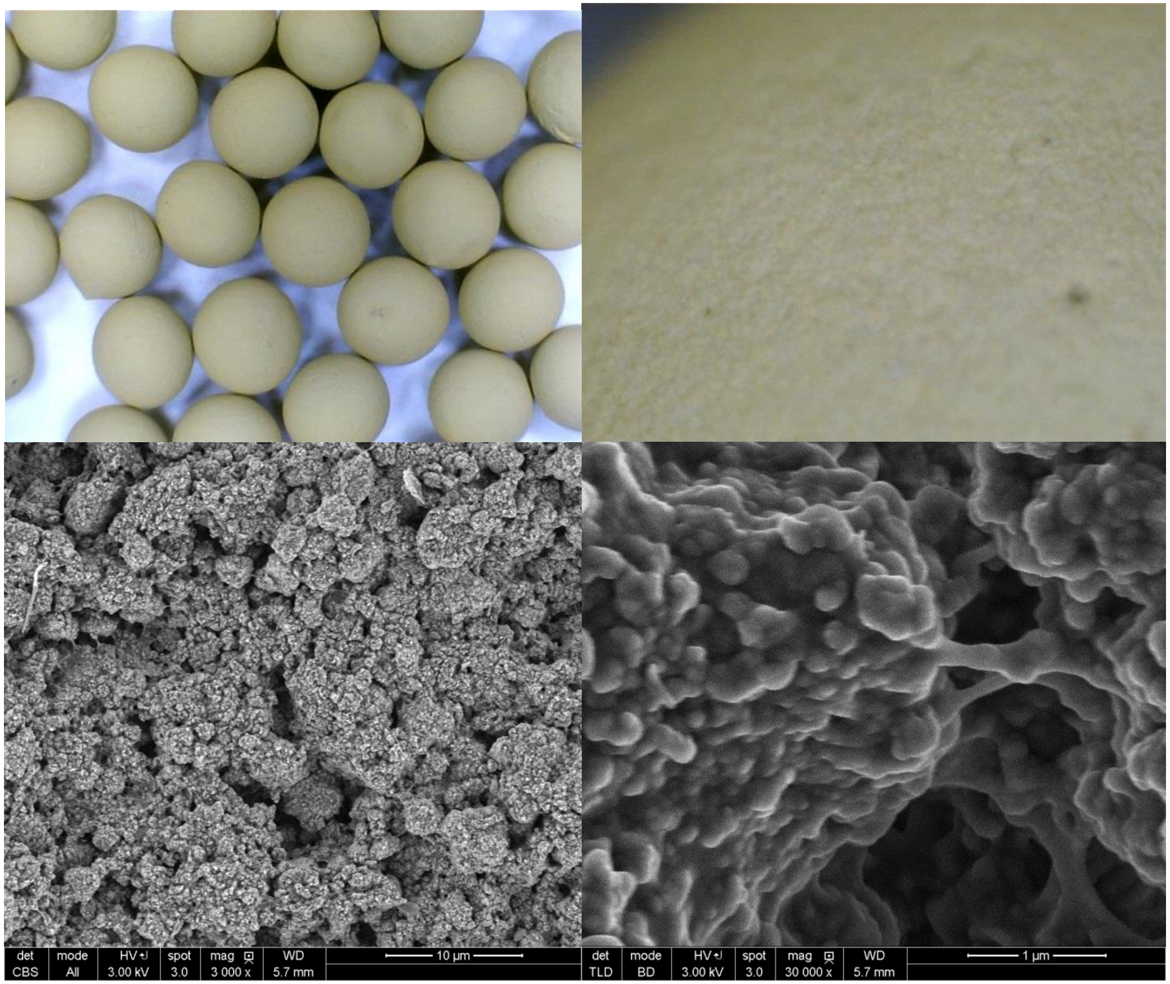


Molecular Formula:
$(C_6H_8O_6)_n$

- **Discovery of alginates were done by Edward Stanford in 1883**
- **Polymerizes into a three dimentional metal-bioorganic network in the presence of cations such as Ca^{2+}**
- **Used in molecular gastronomy for ages…..**

MOF formulation by molecular gastronomy methods……

Looking into the spheres: CPO-27-Ni/alginate



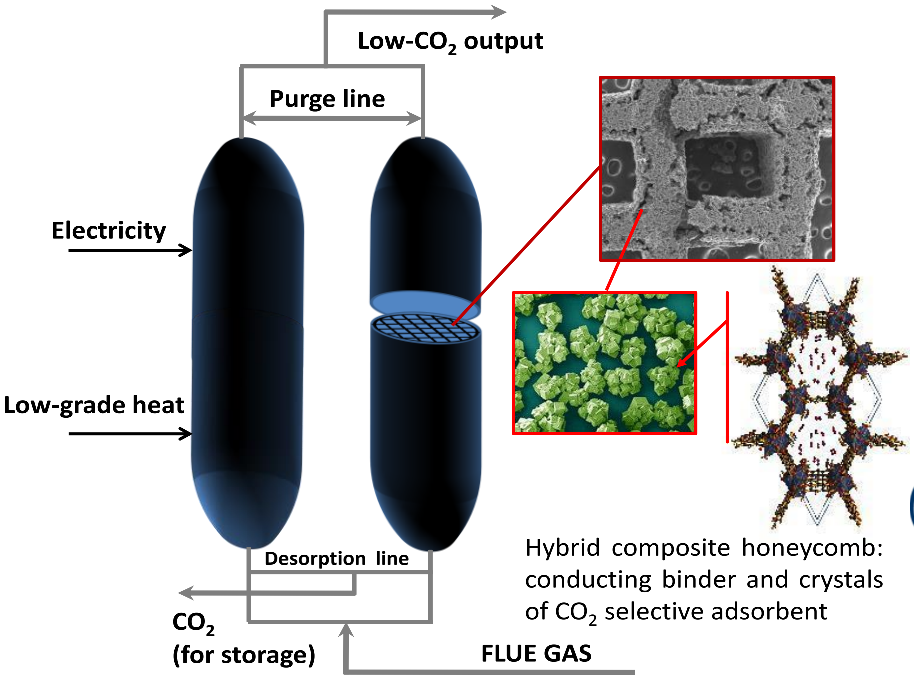
- **The interior has macro-pores that give fast gas diffusion**
- **The alginate matrix seems evenly distributed and glue to MOF crystallites together**
- **Still, there is a lot to gain on increasing the particle density through optimisation of the procedure**

Spjelkavik, Didriksen, Aarti, Divekar, Blom. *Chem. Eur. J.* 2014

But formulation is not only preparation of well defined particulates…..

Advanced Materials and Electric Swing Adsorption Process for CO_2 Capture (MATESA)

The objective of MATESA is to make a "**proof of concept**" of a cutting-edge adsorption technique termed Electric Swing Adsorption (ESA) as a **new-generation high-efficiency** post-combustion CO_2 capture process**.**



Main benefits for Europe

- Novel energy-efficient technology for CCS
- Improved hybrid materials for improved adsorption processes
- High CO_2 loading adsorbents for CCS.
- Promote R&D cooperation with Australia

→ Develop an innovative CO_2 capture technique with better environmental fingerprint.

Total budget = 5.709 K€
Total EU funding = 2.966 K€
Coordinator: Carlos A. Grande

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THE LINDE GROUP Linde
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MONASH
Fraunhofer IKTS
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UNIVERSITÀ DEGLI STUDI DI TORINO
ALMA UNIVERSITAS TAURINENSIS
Biokol
MELBOURNE SCHOOL OF ENGINEERING
CYCLeco
PSE

Concluding comments:

- Several MOFs have adsorption properties superior to state-of-art adsorbents like Zeolites and Activated Carbon both for post- and pre-combustion CO_2 capture.

- However, the MOF field is still in its infancy, and certain issues needs more attention:
  - Hydrothermal stability
  - Stability in the presence of contaminants (SOx, NOx, etc.)
  - Water selectivity (?)
  - Still black box synthesis (?)
  - Price (?)

- Developing good formulation techniques that maintain the good properties of the MOF at high volumetric capacities are needed before real application takes place

Thanks to:

- Coworkers through the last years:
  - Prof. Pascal D. C. Dietzel, UiB (NO)
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  - Prof. Marco Mazotti, Dr. Johanna K. Schell, Dr. Natalie Casas, ETHZ (CH)
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  - Prof. Stefano Brandani, Mr. Shreenath Krishnamurthy, University fo Edinburgh
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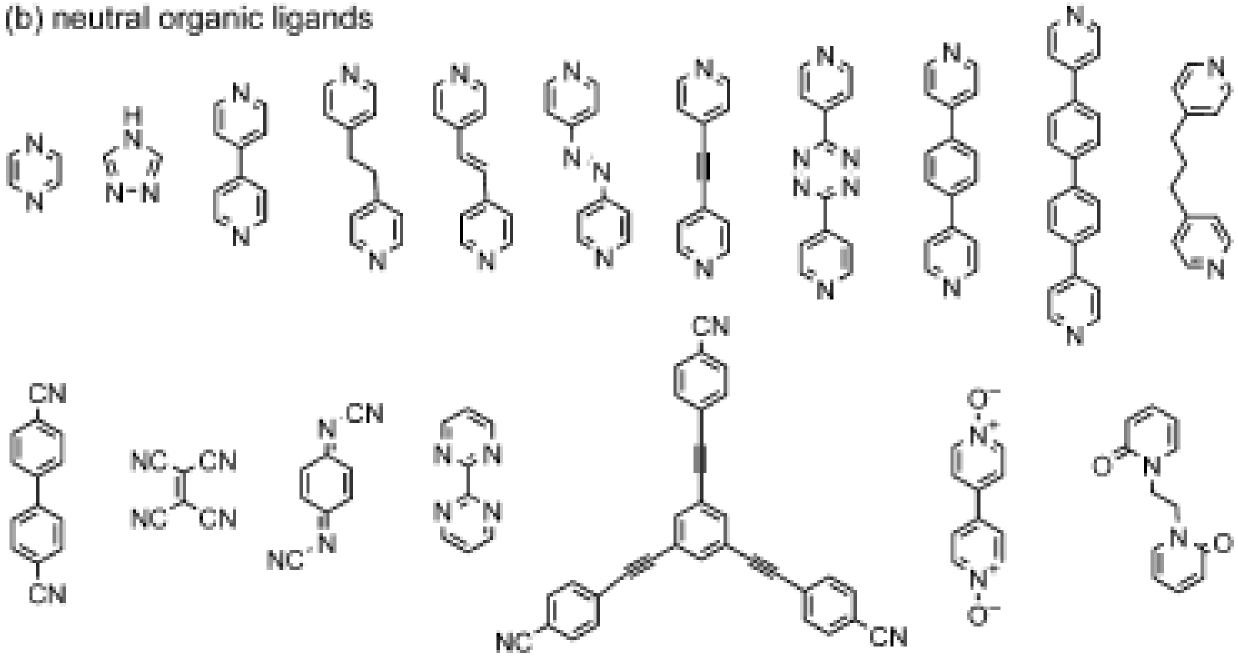
  - EU FP6 and FP7 (MOFCAT and NANOMOF through NMP program, DECARBIT through the ENERGY program)
  - The Norwegian Embassy in Delhi

For your kind attention !

(b) neutral organic ligands



(c) anionic organic ligands