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Evaluation of physical adsorbents for post-combustion CO2 capture

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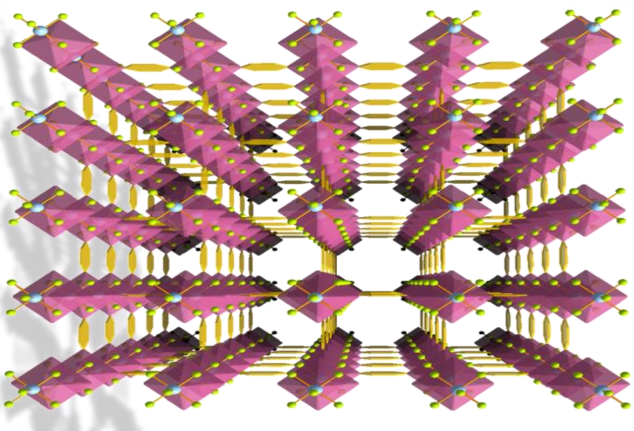
Low CO_2 Concentration Capture Using Physical Adsorbents. Are Metal-Organic Frameworks Becoming the New Benchmark Materials?



Nugent, P, Belmabkhout, Y et al (2013) Nature 494 (7439) ,80-84
Shekhah, O, Belmabkhout, Y et al (2014) Nature Commun.
DOI: 10.1038/ncomms5228

Youssef Belmabkhout

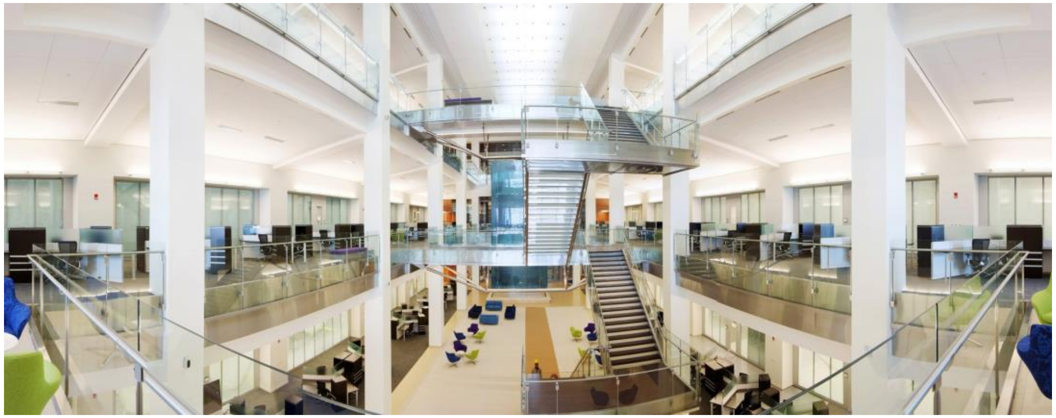
Functional Materials Design, Discovery and Development (FMD^3),
Advanced membranes and porous materials (AMPM)
King Abdullah University of Science and Technology KAUST (KSA)

CO_2 Summit II: Technologies and Opportunities 2016,
Albuquerque - NM, Santa Ana Pueblo, USA, 13th April 2016

King Abdullah University of Science and Technology

Location

Part of the campus and Library



Inside one of the buildings

Beginning of construction in 2007

Research structure/strategy at KAUST

3 academic Divisions

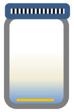
- Biological and Environmental Science and Engineering Division (BESE)
- Computer, Electrical and Mathematical Science and Engineering Division (CEMSE)
- Physical Science and Engineering Division (PSE)

11 Research Centers

- Advanced Membranes and Porous Materials Center (AMPMC)
- Catalysis (KCC)
- Clean Combustion (CCRC)
- Computational Bioscience (CBRC)
- Center for Desert Agriculture (CDA)
- Extreme Computing Research Center (ECRC)
- Red Sea Research Center (RSRC)
- Solar and Photovoltaics Engineering Research Center (SPERC)
- Upstream Petroleum Engineering Research Center (UPERC) (Not yet inaugurated)
- Visual Computing Center (VCC)
- Water Desalination and Reuse (WDRC)

Quest of innovative advanced materials in collaboration with Industry (Aramco)

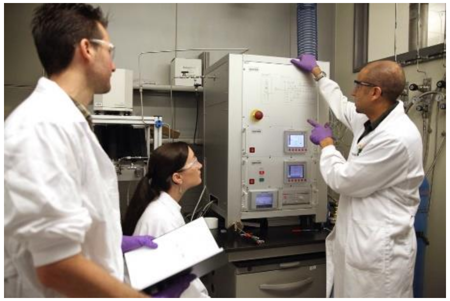
أرامكو السعودية
Saudi Aramco



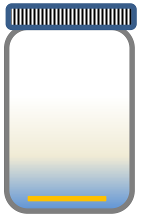
Synthesis of Materials

Evaluation of porosity at the small scale

Evaluation of Separation Properties at the small scale



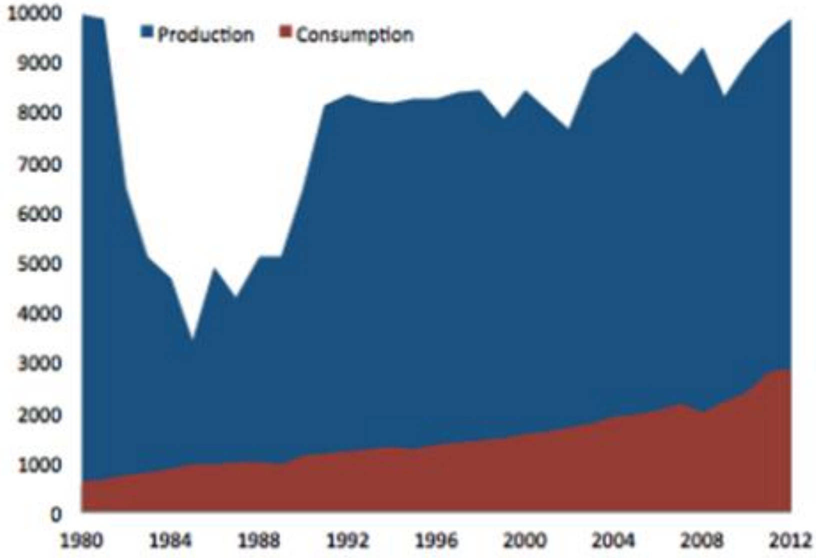
Scale-up of Materials



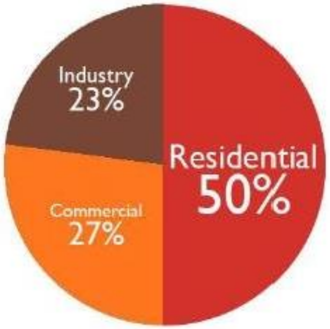
2nd stage evaluation at large scale

Motivation

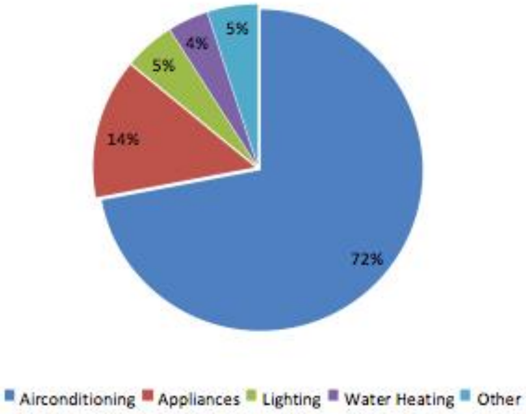
Saudi Arabian Oil Production vs Consumption (thousand bbl/day)



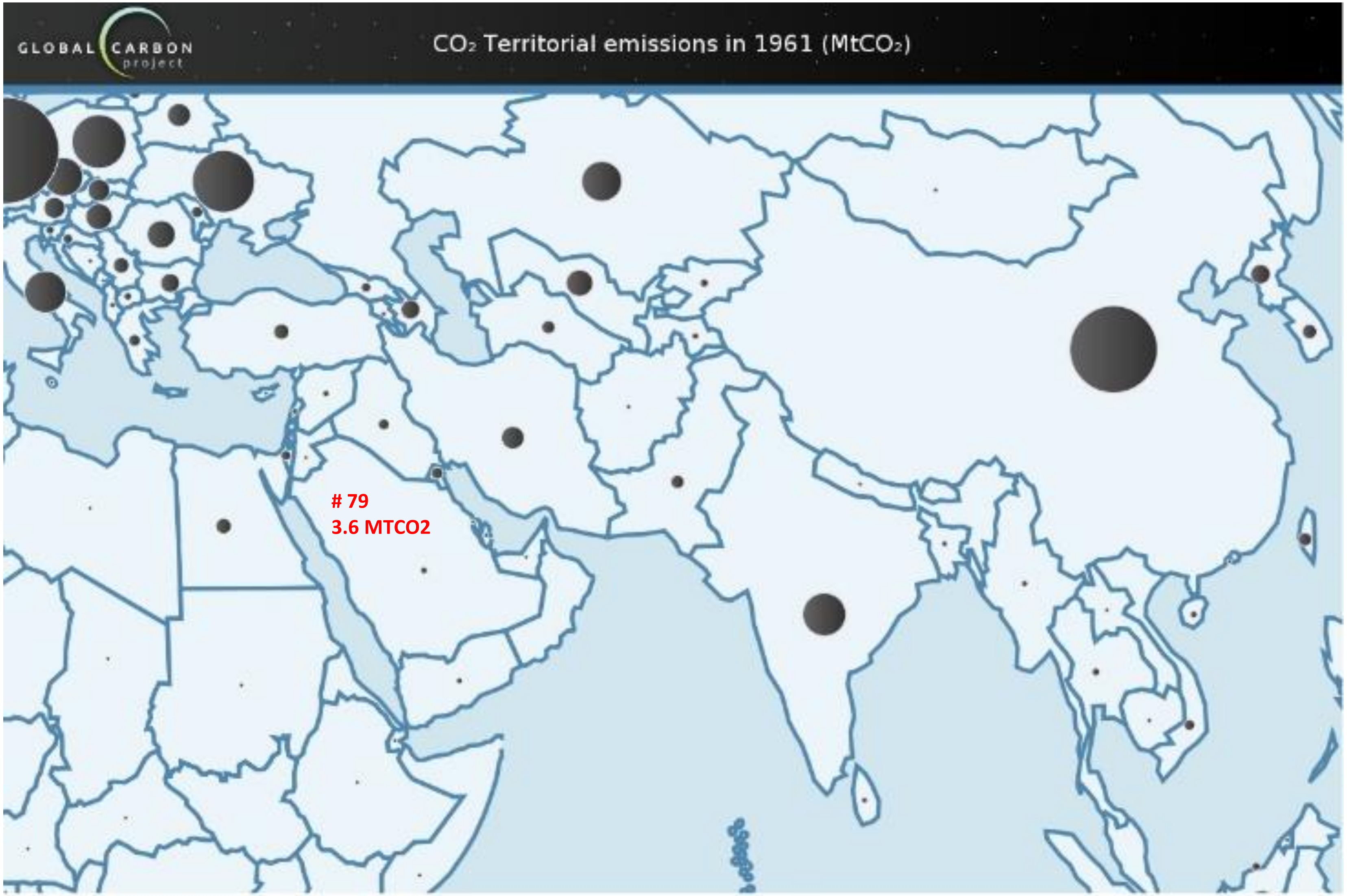
Energy Consumption by sectors in Saudi Arabia



Saudi Residential power demand split

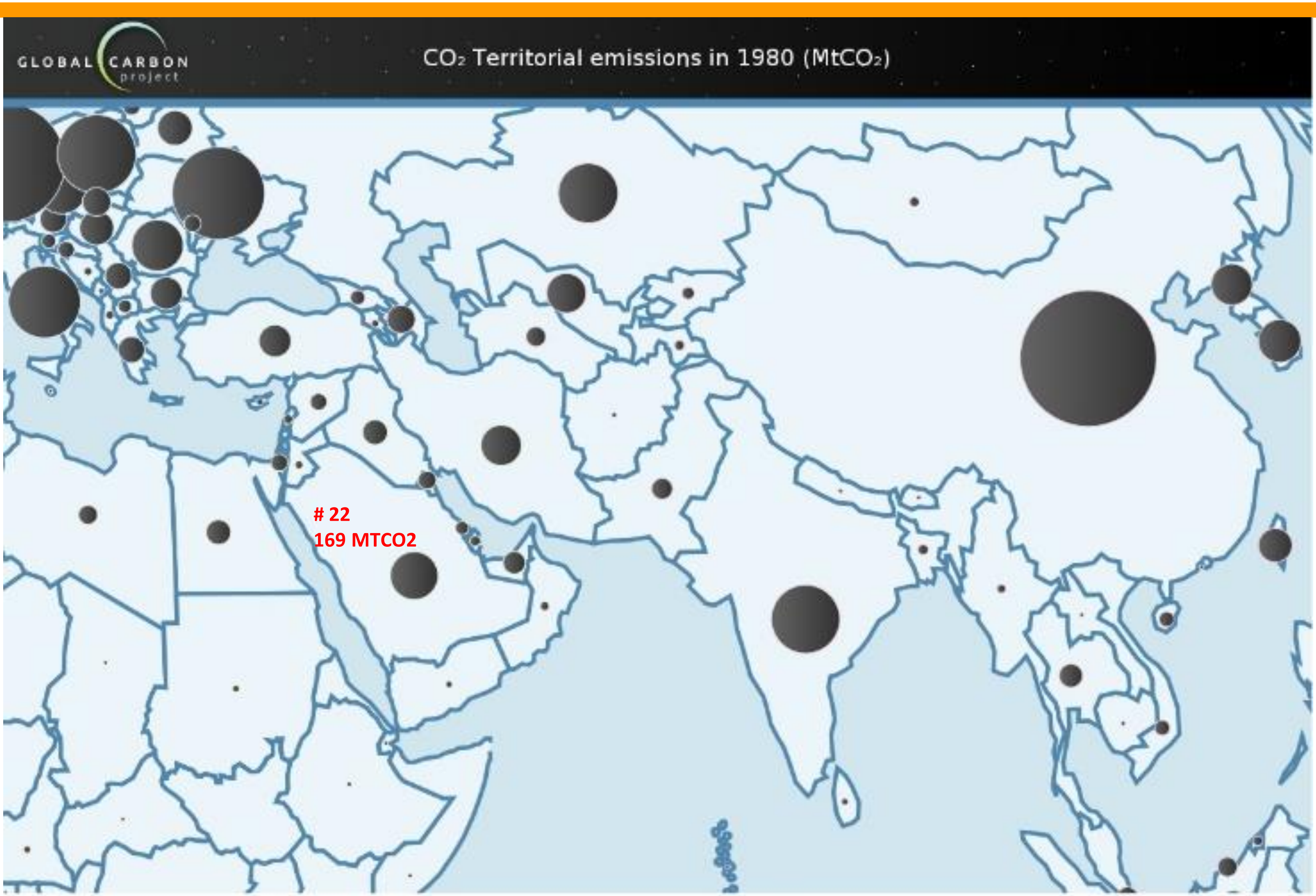


Evolution of CO_2 Emissions in the Middle East-Asia



Source: http://www.globalcarbonatlas.org/?q=en/emissions

Evolution of CO_2 Emissions in the Middle East-Asia



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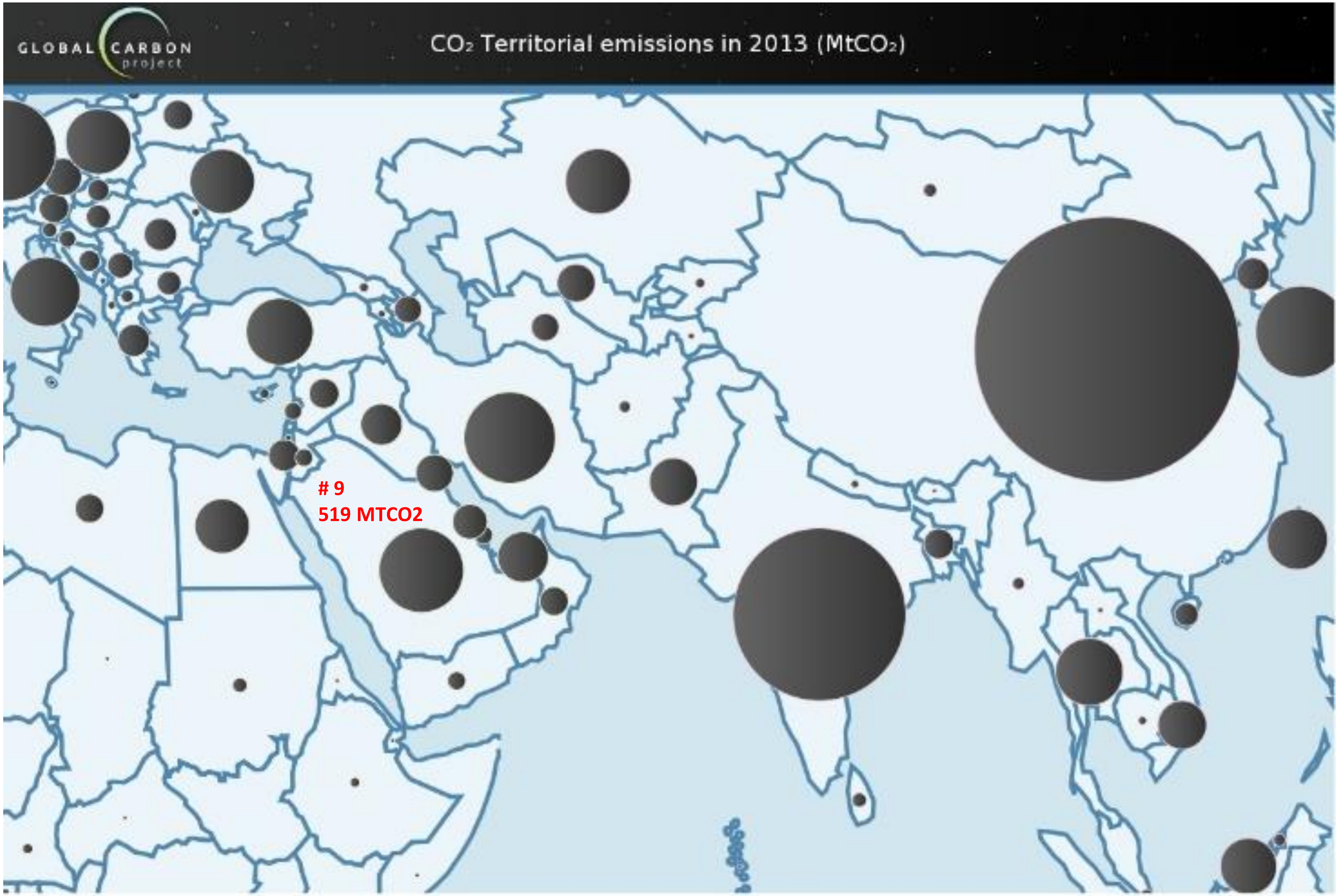
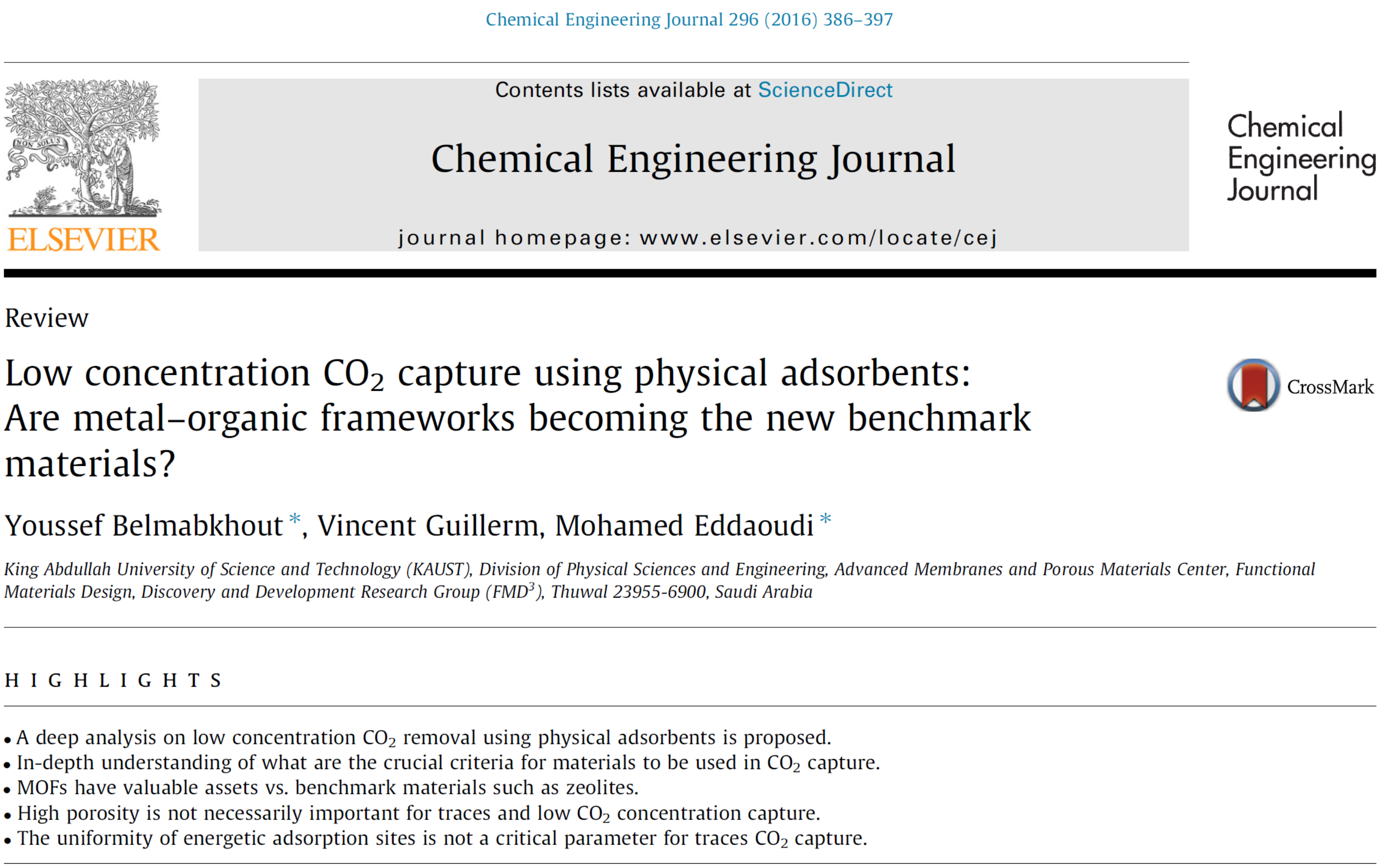


Source: http://www.globalcarbonatlas.org/?q=en/emissions



Chemical Engineering Journal 296 (2016) 386–397

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journal homepage: www.elsevier.com/locate/cej

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Review

Low concentration CO_2 capture using physical adsorbents: Are metal–organic frameworks becoming the new benchmark materials?

Youssef Belmabkhout *, Vincent Guillerm, Mohamed Eddaoudi *

King Abdullah University of Science and Technology (KAUST), Division of Physical Sciences and Engineering, Advanced Membranes and Porous Materials Center, Functional Materials Design, Discovery and Development Research Group (FMD^3), Thuwal 23955-6900, Saudi Arabia

HIGHLIGHTS

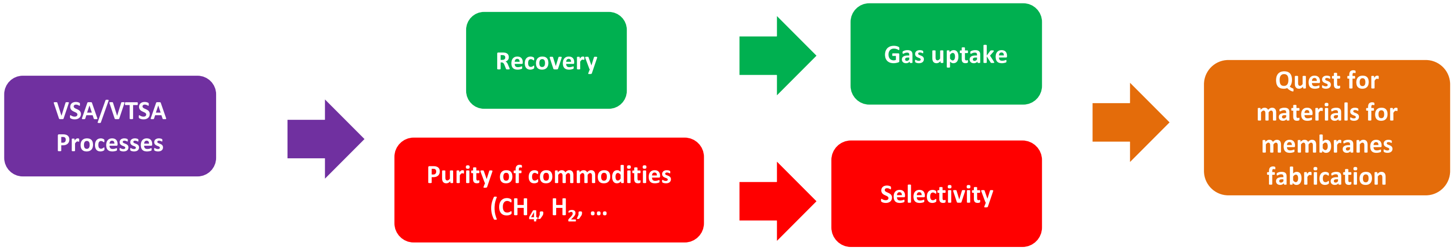
- A deep analysis on low concentration CO_2 removal using physical adsorbents is proposed.
- In-depth understanding of what are the crucial criteria for materials to be used in CO_2 capture.
- MOFs have valuable assets vs. benchmark materials such as zeolites.
- High porosity is not necessarily important for traces and low CO_2 concentration capture.
- The uniformity of energetic adsorption sites is not a critical parameter for traces CO_2 capture.

It is not about a specific material, it is about new concept of separation that lead to new generation of materials

Y.Belmabkhout et al. 2016, *Chemical Engineering Journal* 296, 386-397

Outline

- ✓ **Understanding of structural- CO_2 adsorption properties relationships → push the limit of gas separation with the lowest energy input using physical adsorbents**



VSA/VTSA Processes

Recovery

Purity of commodities (CH_4, H_2, …

Gas uptake

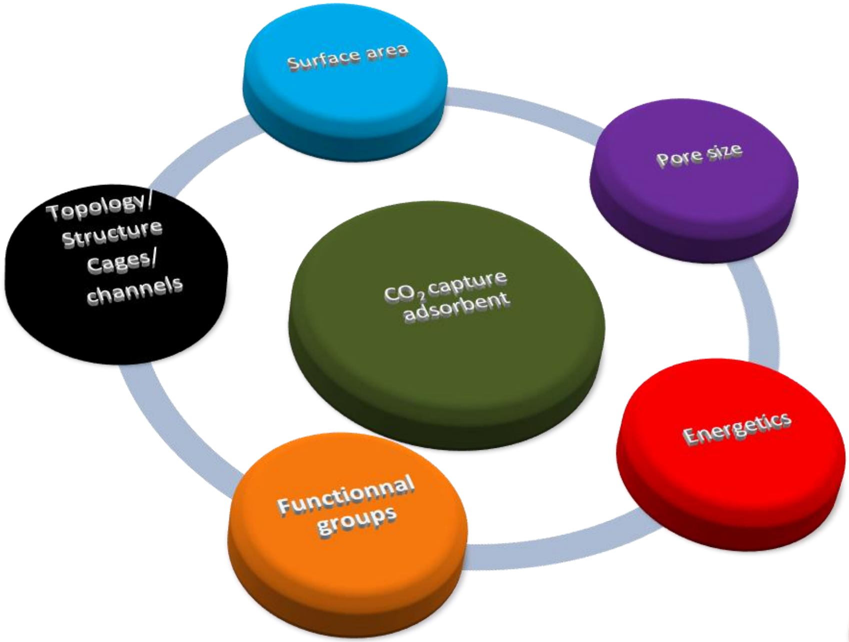
Selectivity

Quest for materials for membranes fabrication

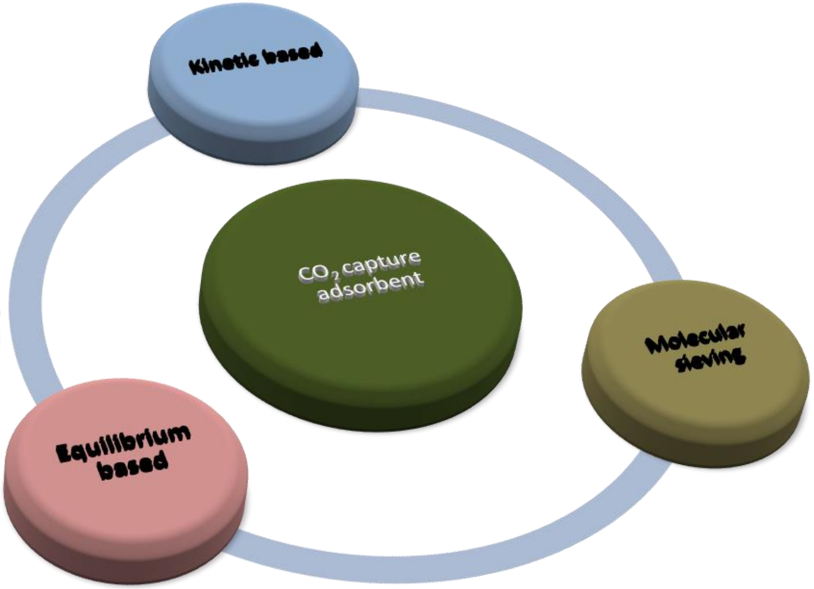
- ✓ **Conclusions from the past works (2012-2013)**
- ✓ **New finding.**
- ✓ **Shift to membrane technology.**
- ✓ **Conclusions**

Structural/chemical properties and adsorption properties relationships

- What is the key properties of an adsorbent to be suitable for CO_2 removal at different concentrations ?



- Which mechanism ?



CO_2 separation/capture in our life

CO_2 Separation

Energy

Health and Safety

Environment

Pre-purification before air Separation (PPU)

Alkaline Fuel Cells (AFC)

Syngas treatment (H_2 purification)

Natural gas upgrading (CH_4 purification)

Anesthesia Machine

Rebreather

Confined space (Space shuttles)

Confined space (submarine)

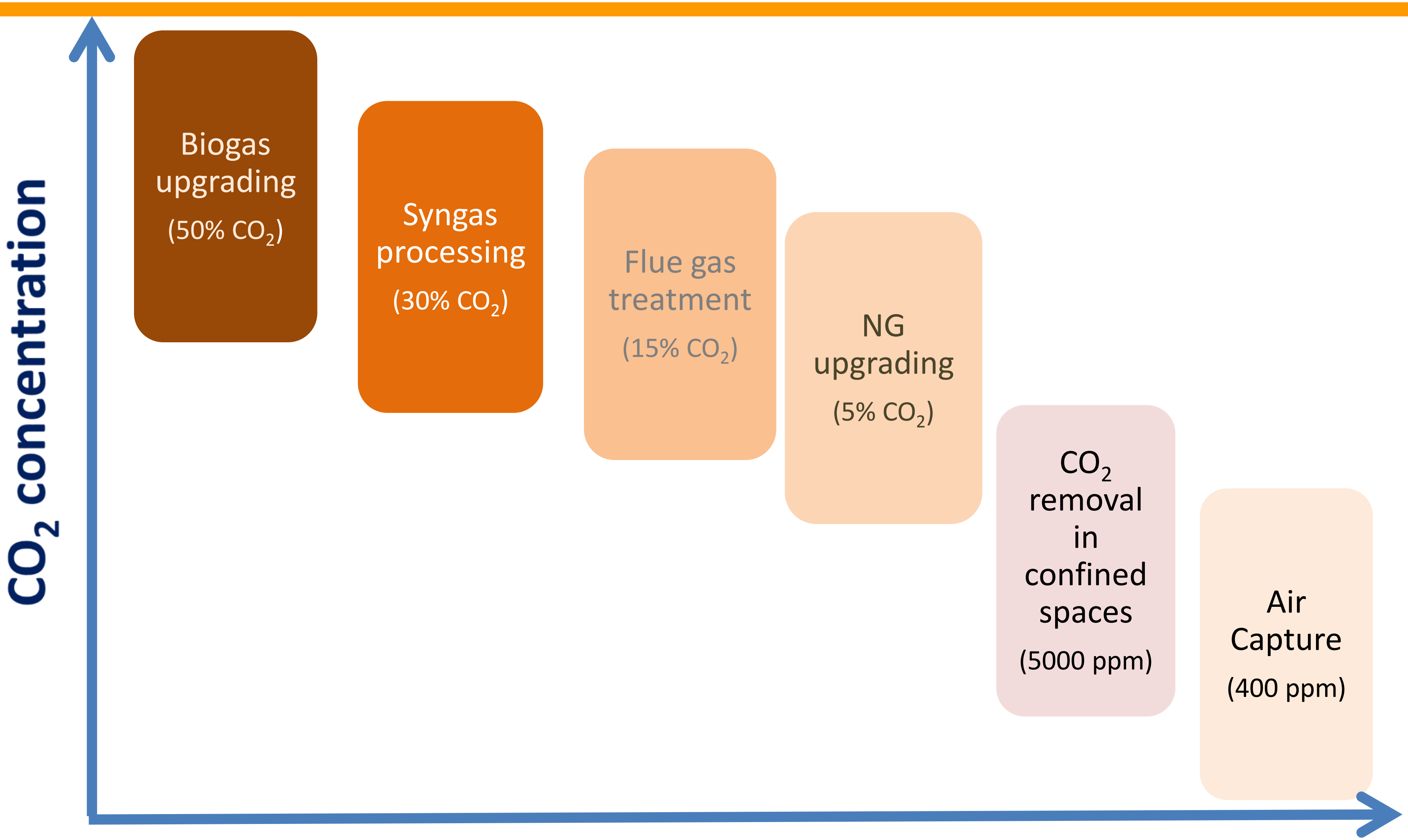
Air Capture

From the source

Stationary

On-Board

Important CO_2 removal applications at various concentrations



CO_2 concentration

Biogas upgrading
(50% CO_2)

Syngas processing
(30% CO_2)

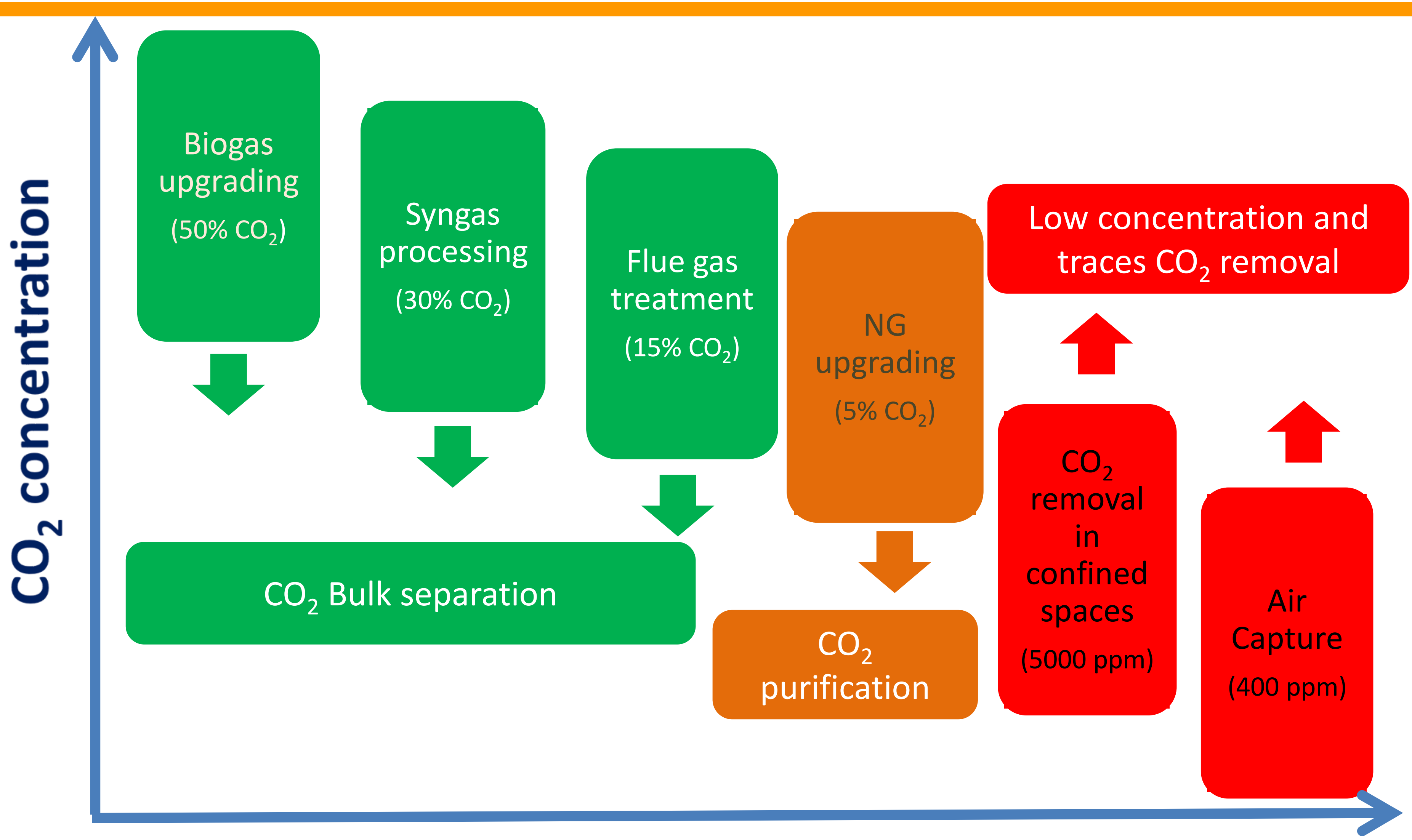
Flue gas treatment
(15% CO_2)

NG upgrading
(5% CO_2)

CO_2 removal in confined spaces
(5000 ppm)

Air Capture
(400 ppm)

Important CO_2 removal applications at various concentrations



CO_2 concentration

Biogas upgrading (50% CO_2)

Syngas processing (30% CO_2)

Flue gas treatment (15% CO_2)

NG upgrading (5% CO_2)

Low concentration and traces CO_2 removal

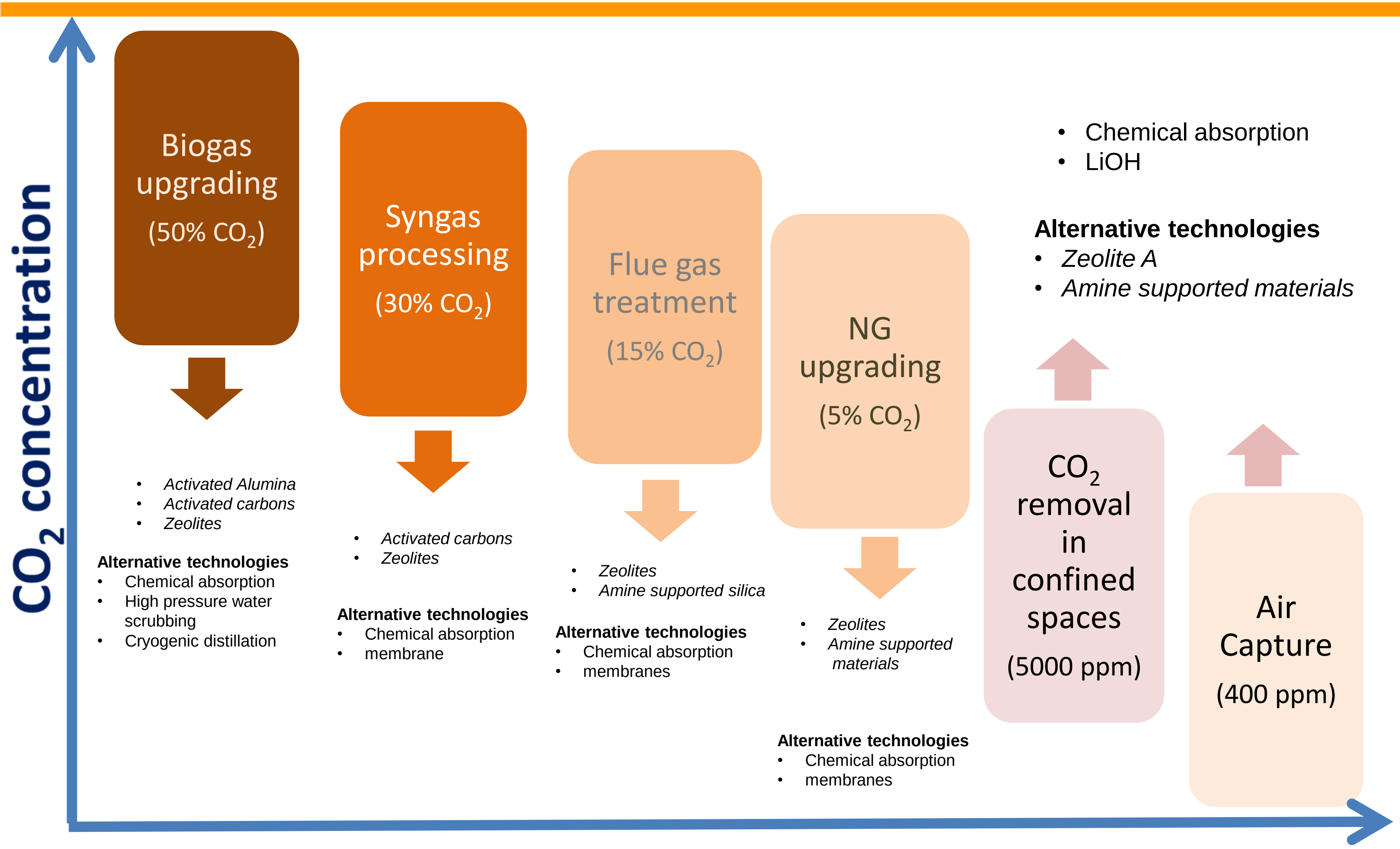
CO_2 Bulk separation

CO_2 purification

CO_2 removal in confined spaces (5000 ppm)

Air Capture (400 ppm)

Important CO_2 removal applications at various concentrations and adsorbents properties relationship



Biogas upgrading
(50% CO_2)

- *Activated Alumina*
- *Activated carbons*
- *Zeolites*

Alternative technologies
- Chemical absorption
- High pressure water scrubbing
- Cryogenic distillation

Syngas processing
(30% CO_2)

- *Activated carbons*
- *Zeolites*

Alternative technologies
- Chemical absorption
- membrane

Flue gas treatment
(15% CO_2)

- *Zeolites*
- *Amine supported silica*

Alternative technologies
- Chemical absorption
- membranes

NG upgrading
(5% CO_2)

- *Zeolites*
- *Amine supported materials*

Alternative technologies
- Chemical absorption
- membranes

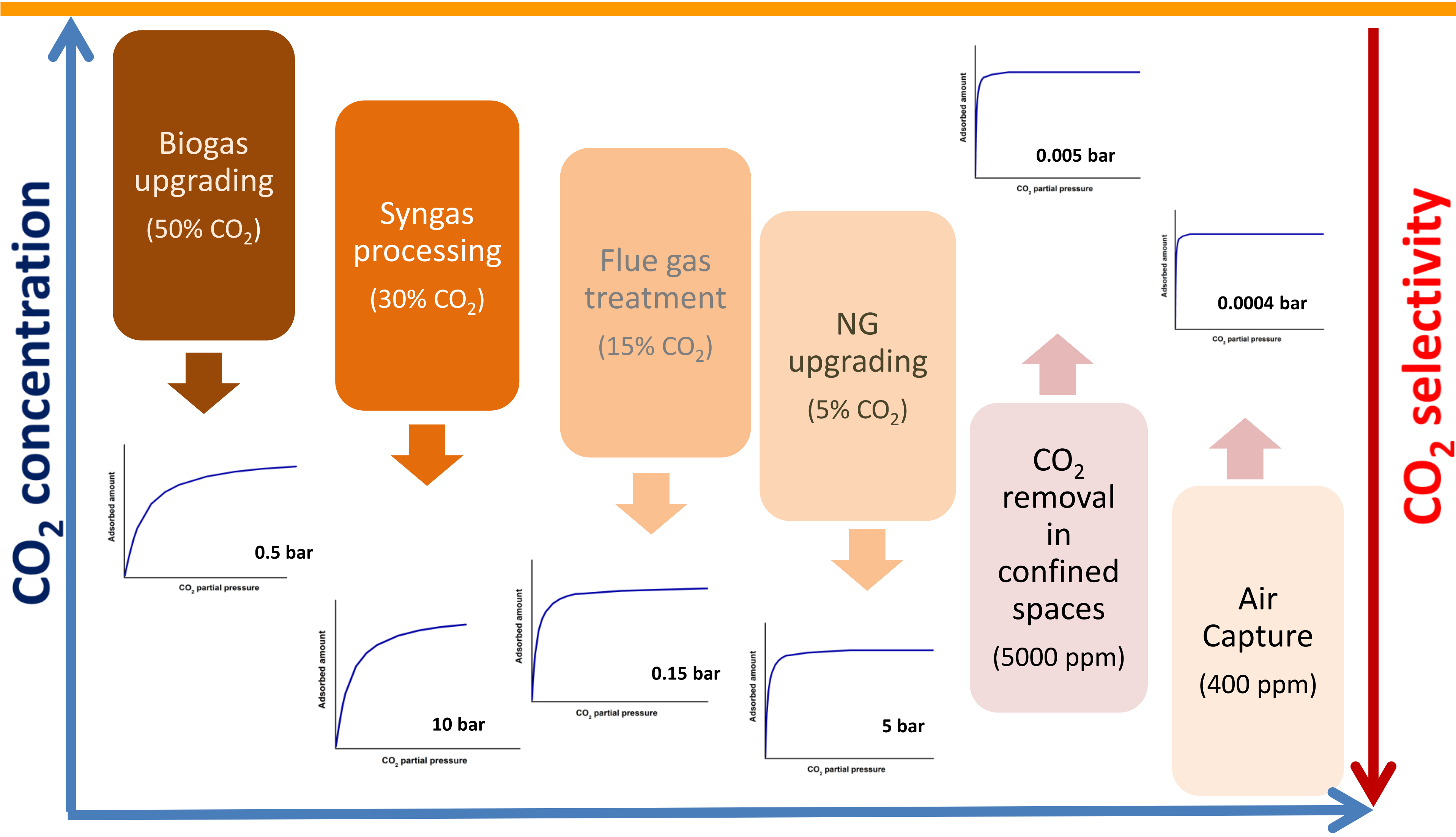
CO_2 removal in confined spaces
(5000 ppm)

Air Capture
(400 ppm)

- Chemical absorption
- LiOH

Alternative technologies
- *Zeolite A*
- *Amine supported materials*

Important CO_2 removal applications at various concentrations and adsorbents properties relationship



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Flue gas treatment
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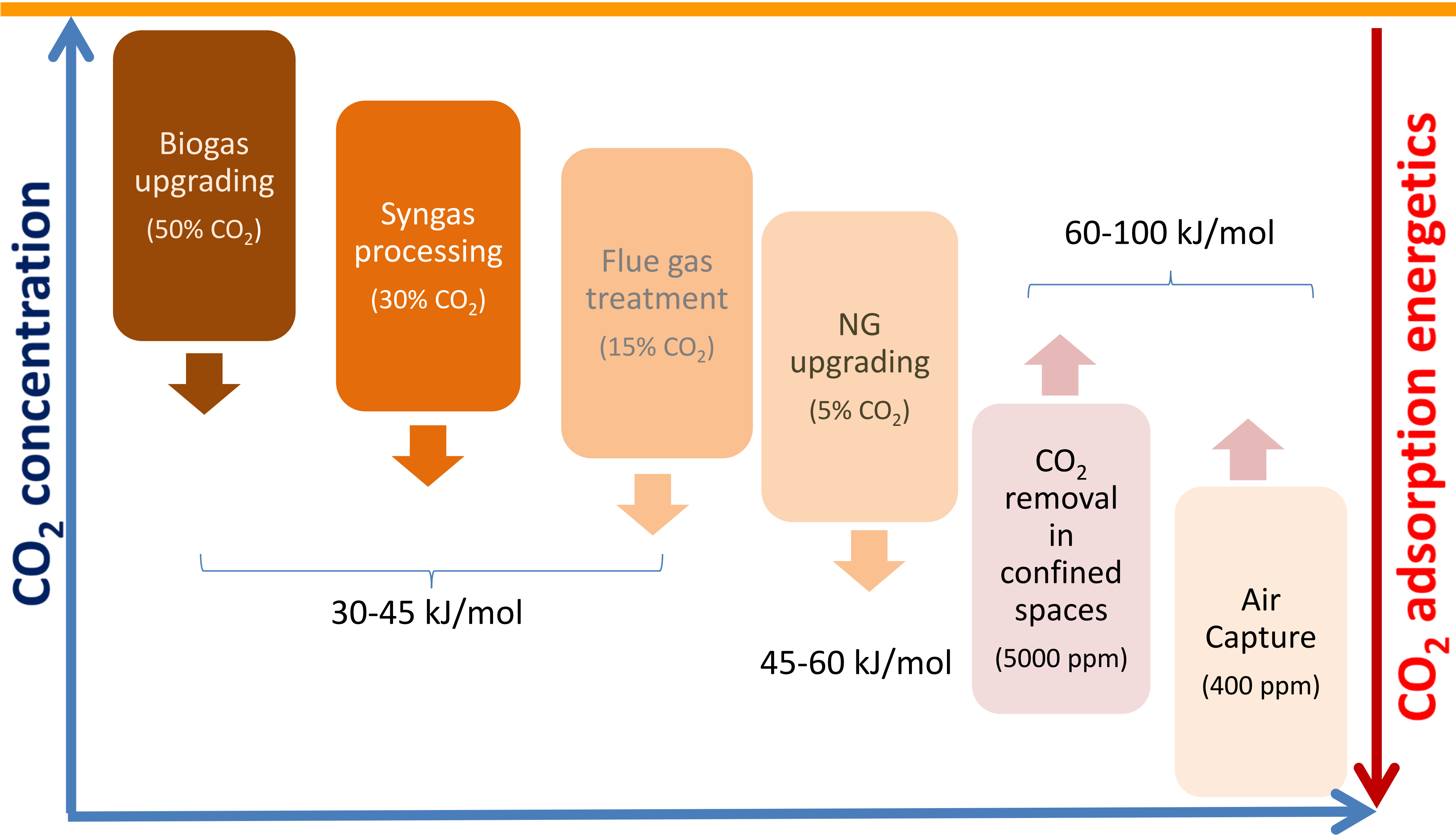
(5% CO_2)

CO_2 removal in confined spaces
(5000 ppm)

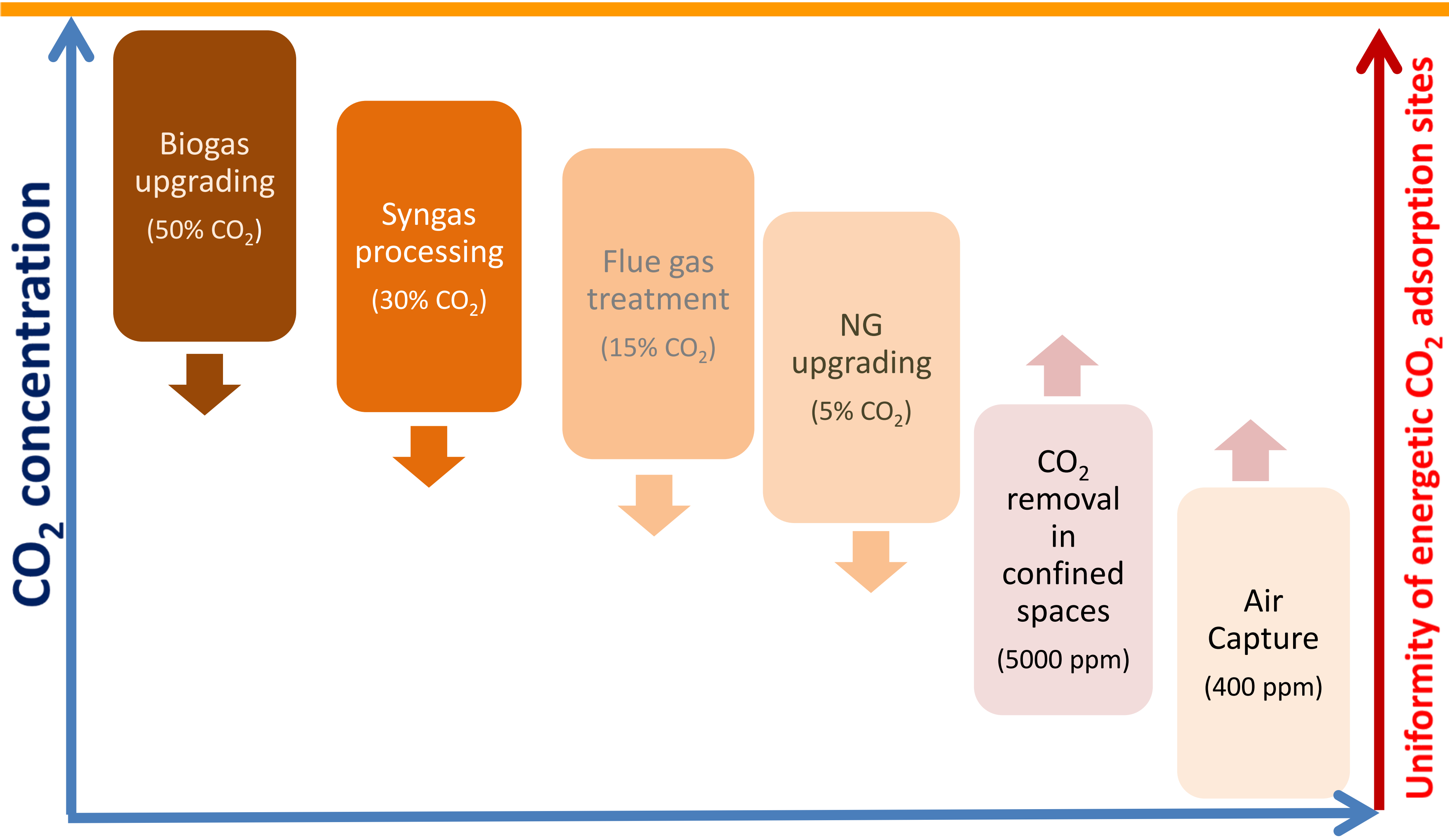
Air Capture
(400 ppm)

CO_2 selectivity

Important CO_2 removal applications at various concentrations and adsorbents properties relationship



Important CO_2 removal applications at various concentrations and adsorbents properties relationship



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(50% CO_2)

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Flue gas treatment

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NG upgrading

(5% CO_2)

CO_2 removal in confined spaces

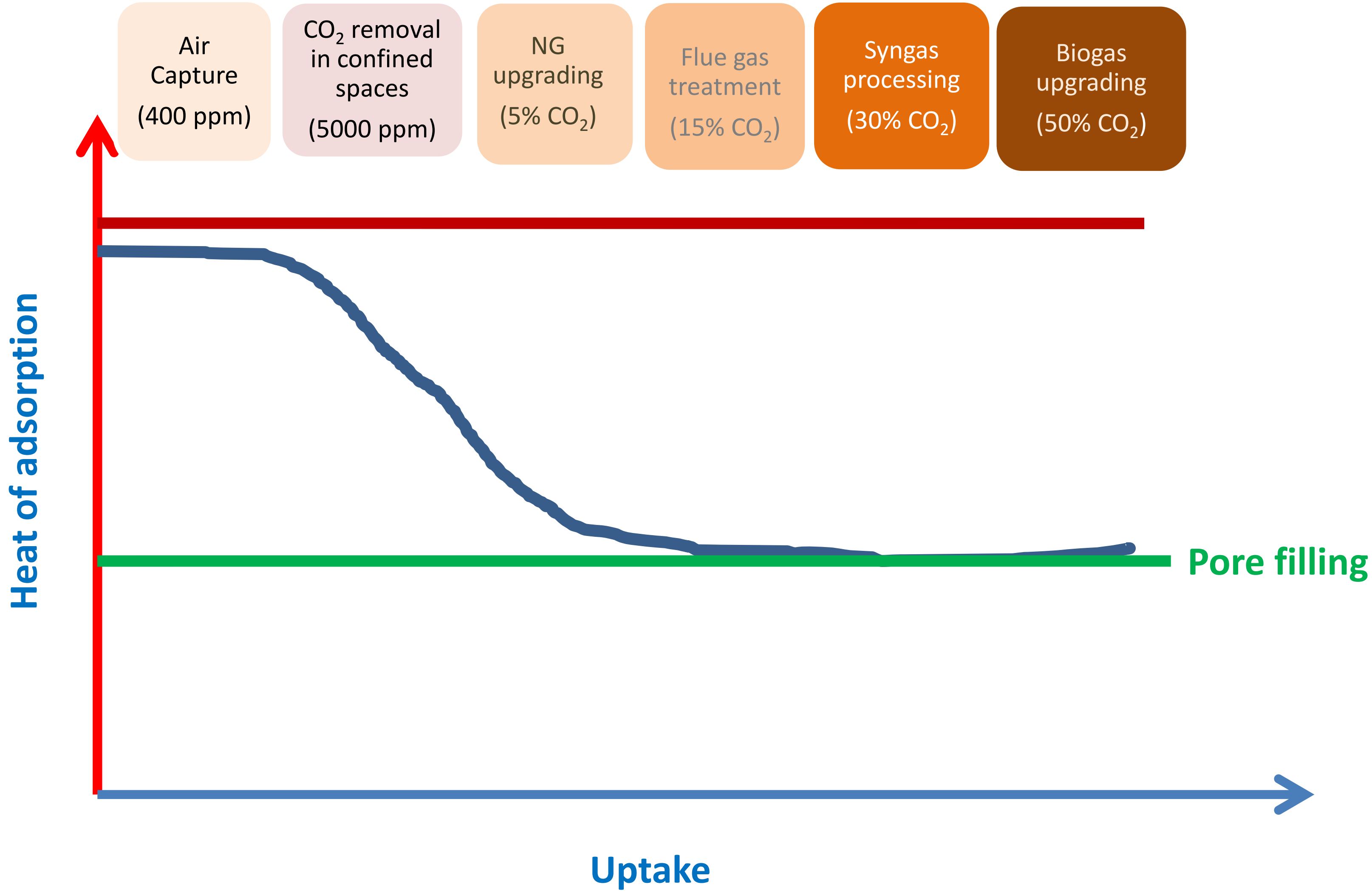
(5000 ppm)

Air Capture

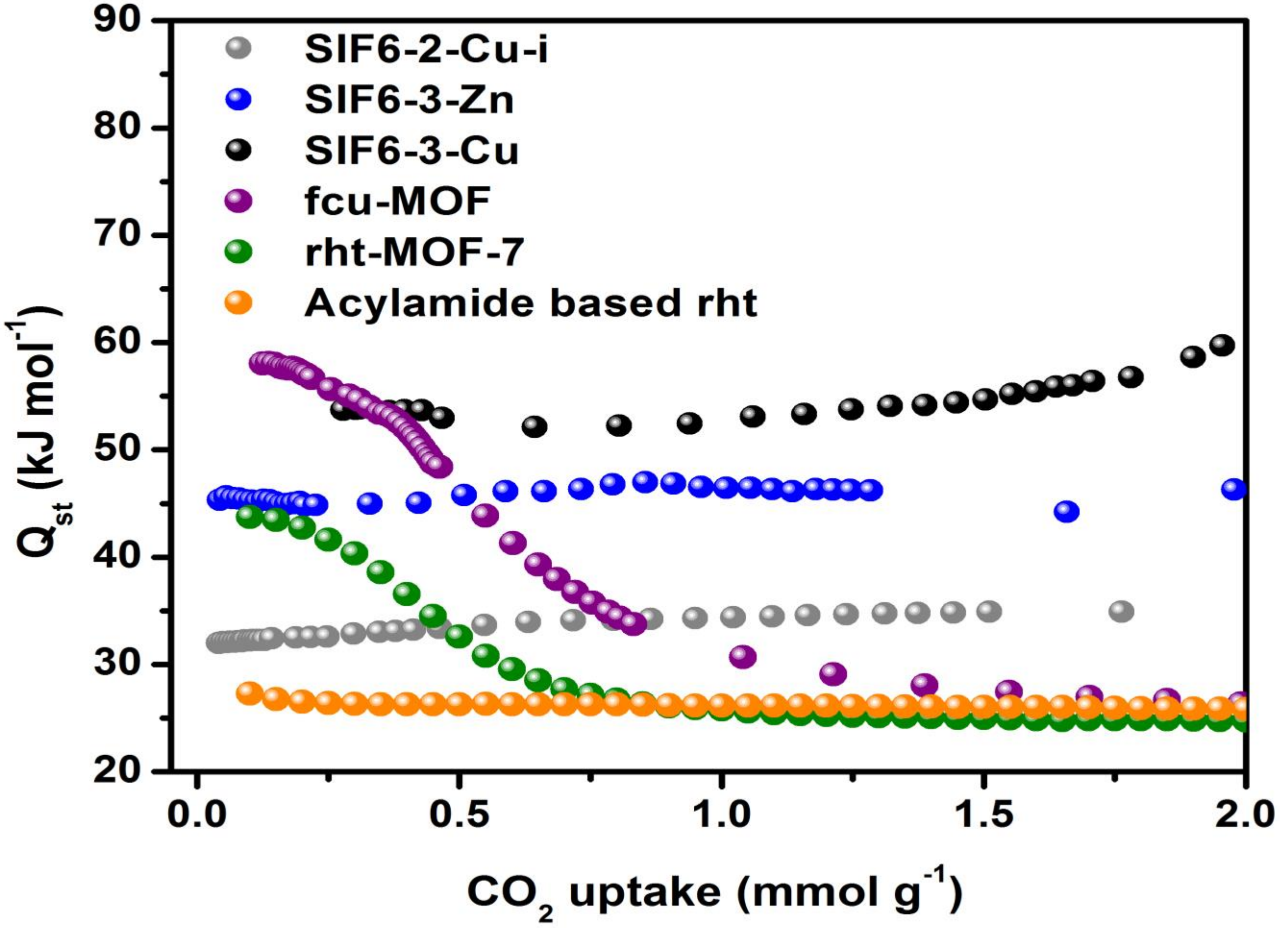
(400 ppm)

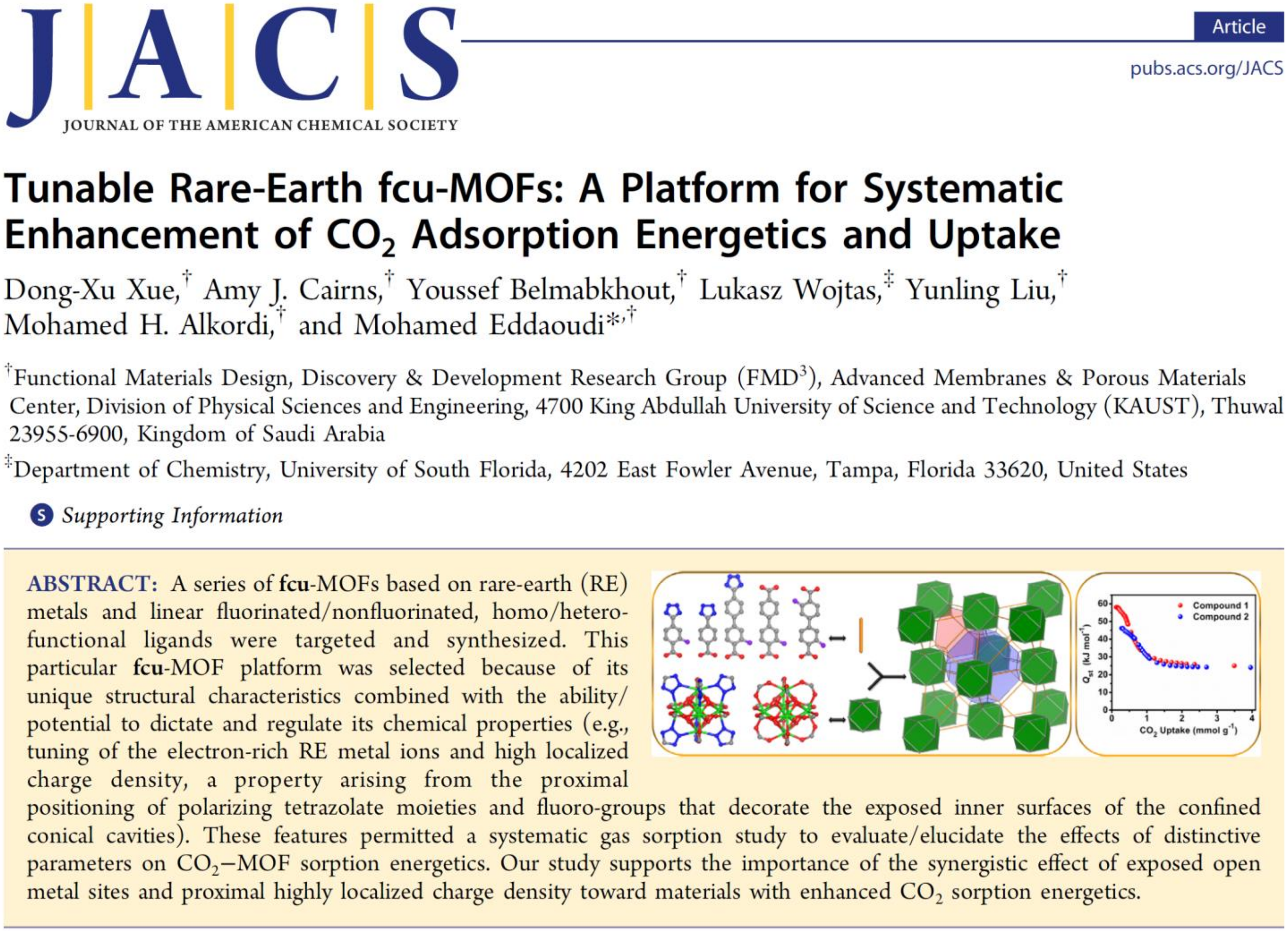
Uniformity of energetic CO_2 adsorption sites

Uniformity of energetic CO_2 adsorption sites in porous materials



Uniformity of energetic CO_2 adsorption sites





J|A|C|S JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Article
pubs.acs.org/JACS

Tunable Rare-Earth fcu-MOFs: A Platform for Systematic Enhancement of CO_2 Adsorption Energetics and Uptake

Dong-Xu Xue,[†] Amy J. Cairns,[†] Youssef Belmabkhout,[†] Lukasz Wojtas,[‡] Yunling Liu,[†] Mohamed H. Alkordi,[†] and Mohamed Eddaoudi*,[†]

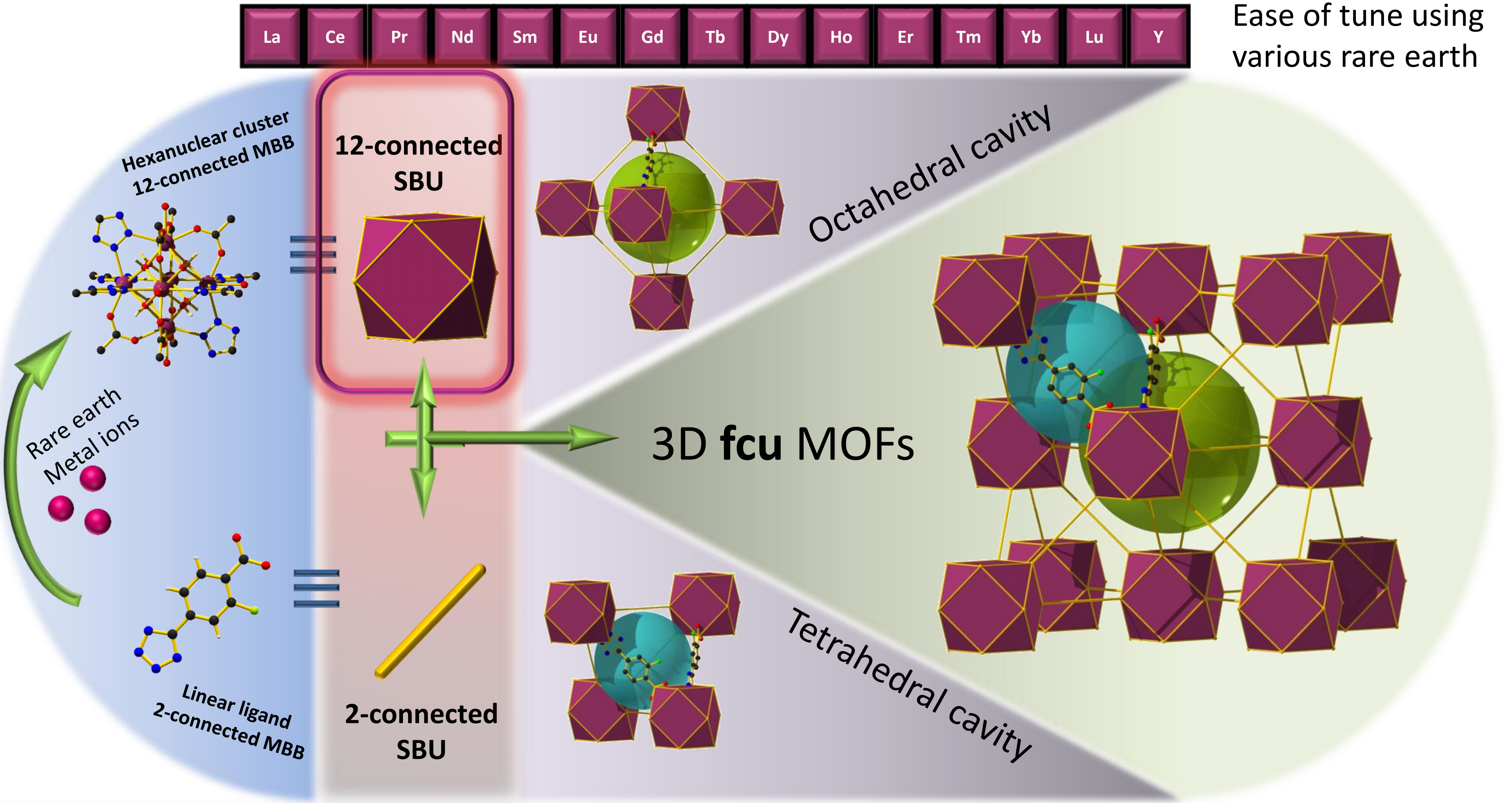
[†] Functional Materials Design, Discovery & Development Research Group (FMD³), Advanced Membranes & Porous Materials Center, Division of Physical Sciences and Engineering, 4700 King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Kingdom of Saudi Arabia

[‡] Department of Chemistry, University of South Florida, 4202 East Fowler Avenue, Tampa, Florida 33620, United States

S *Supporting Information*

ABSTRACT: A series of **fcu**-MOFs based on rare-earth (RE) metals and linear fluorinated/nonfluorinated, homo/hetero-functional ligands were targeted and synthesized. This particular **fcu**-MOF platform was selected because of its unique structural characteristics combined with the ability/potential to dictate and regulate its chemical properties (e.g., tuning of the electron-rich RE metal ions and high localized charge density, a property arising from the proximal positioning of polarizing tetrazolate moieties and fluoro-groups that decorate the exposed inner surfaces of the confined conical cavities). These features permitted a systematic gas sorption study to evaluate/elucidate the effects of distinctive parameters on CO_2–MOF sorption energetics. Our study supports the importance of the synergistic effect of exposed open metal sites and proximal highly localized charge density toward materials with enhanced CO_2 sorption energetics.

Tunable Rare-Earth fcu-MOFs Platform



La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Y

Ease of tune using various rare earth

Hexanuclear cluster
12-connected MBB

12-connected
SBU

Rare earth
Metal ions

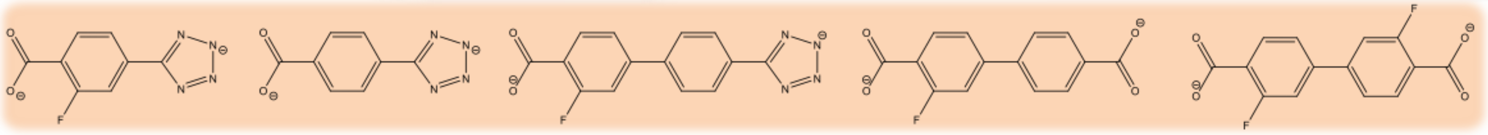
Linear ligand
2-connected MBB

2-connected
SBU

Octahedral cavity

3D **fcu** MOFs

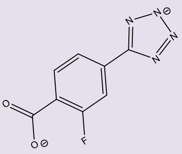
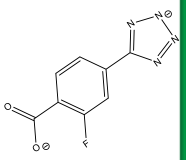
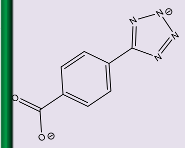
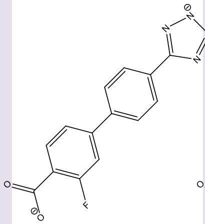
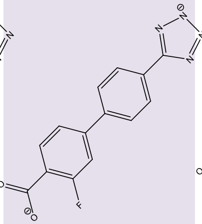
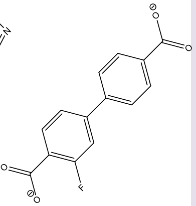
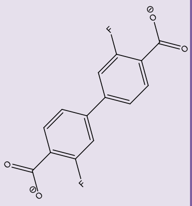
Tetrahedral cavity

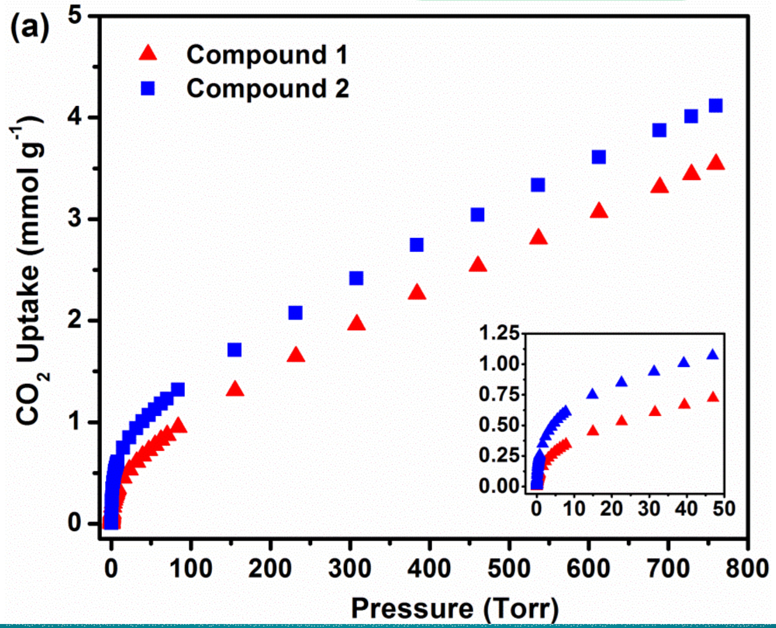


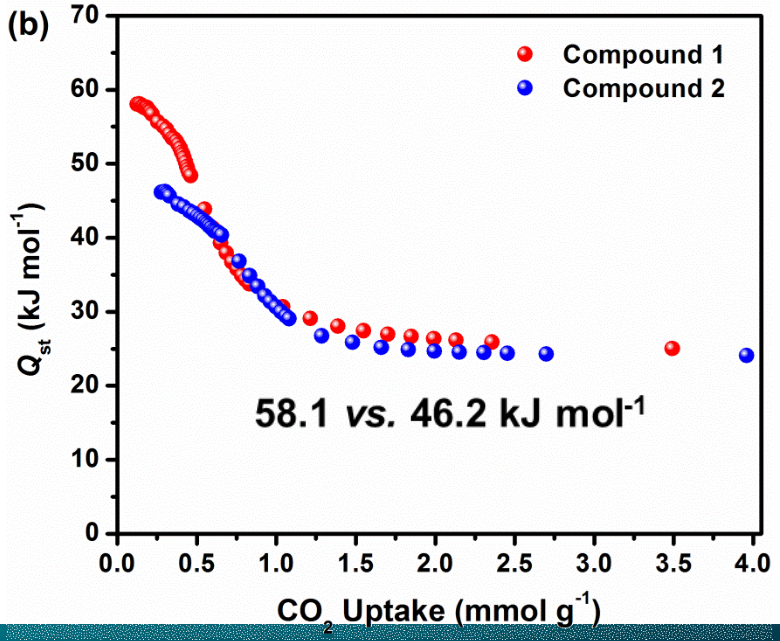
Ease of tune using various ligands

Xue, D. –X. et. al. *J. Am. Chem. Soc.* 2013, *135*, 7660-7667.

Porosity and CO_2 Adsorptions

Compound (Metal)	1 (Tb)	2 (Y)	3 (Tb)	4 (Tb)	5 (Y)	6 (Tb)	7 (Tb)
Ligand							
BET (m^2 g^{-1})	1220	1310	904	2200	**2410**	1940	1854
P.V. (cm^3 g^{-1})	0.51	0.56	0.39	0.86	0.94	0.78	0.72
CO_2 Uptake (mmol g^{-1})	7.53, 5.86 and 3.54	8.33, 6.46 and 4.12	5.96, 4.53 and 2.50	3.93, 2.75 and 1.64	4.01, 2.81 and 1.59	3.50, 2.40 and 1.37	3.91, 2.63 and 1.36
Q_{st} for CO_2 (kJ mol^{-1})	**58.1**-25.0	46.1-24.0	46.6-23.8	36.7-20.3	27.2-19.5	39.1-18.5	41.6-20.7

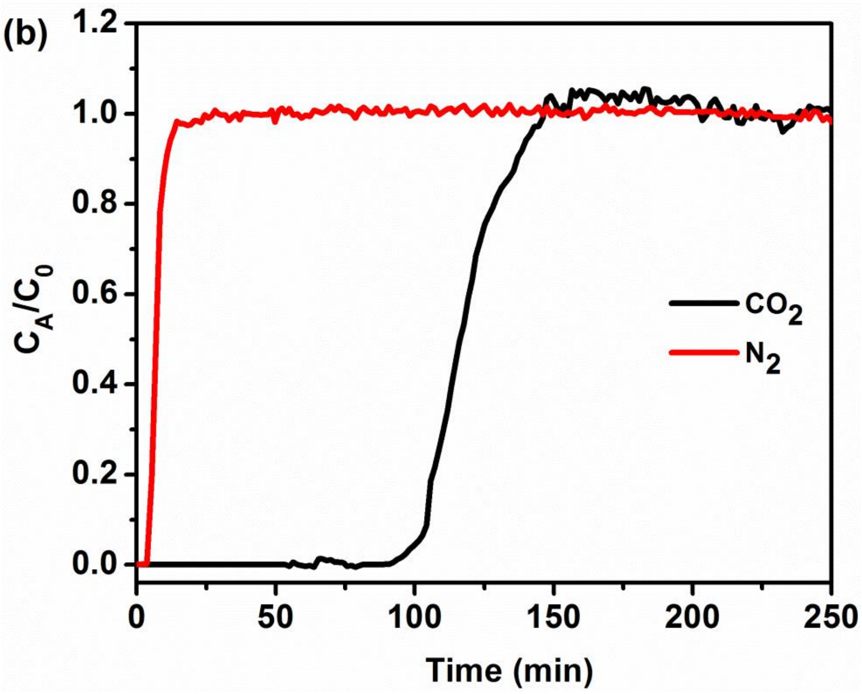




Xue, D. –X. et. al. *J. Am. Chem. Soc.* **2013**, *135*, 7660-7667.

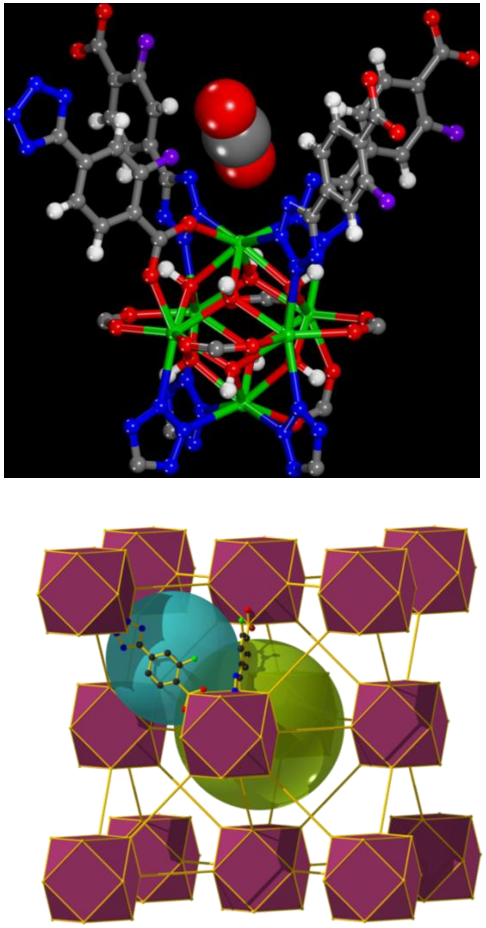
Traces and Low CO_2 concentration removal. Column Breakthrough

Column breakthrough tests using CO_2/N_2: 0.1/99.9% mixture



CO_2/N_2 (0.1/99.9%): ca. 1051

Conical pockets decorated with –F, -OH moieties and tetrazolate groups (proximal to Oms)



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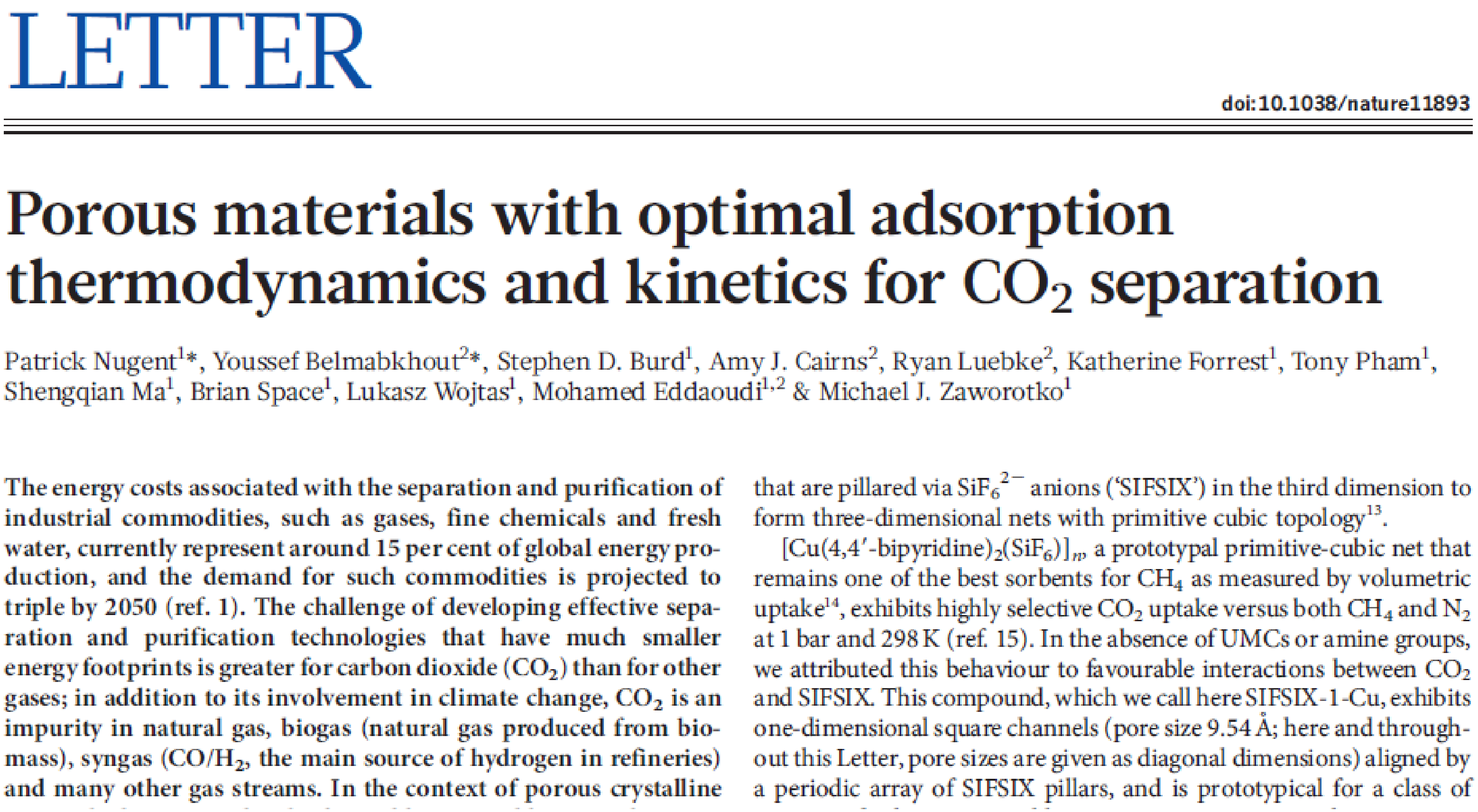
SiF$_6$ MOF Platform



LETTER

doi:10.1038/nature11893

Porous materials with optimal adsorption thermodynamics and kinetics for CO_2 separation

Patrick Nugent[1]*, Youssef Belmabkhout[2]*, Stephen D. Burd[1], Amy J. Cairns[2], Ryan Luebke[2], Katherine Forrest[1], Tony Pham[1], Shengqian Ma[1], Brian Space[1], Lukasz Wojtas[1], Mohamed Eddaoudi[1,2] & Michael J. Zaworotko[1]

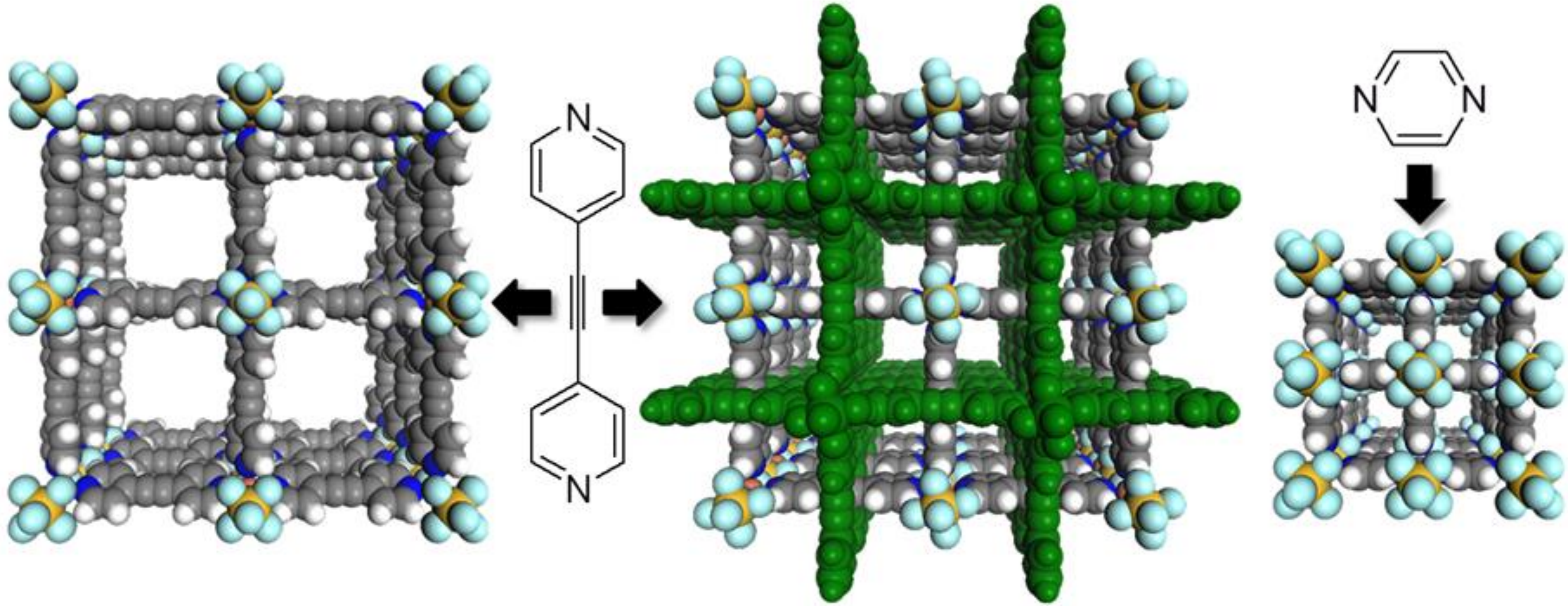
The energy costs associated with the separation and purification of industrial commodities, such as gases, fine chemicals and fresh water, currently represent around 15 per cent of global energy production, and the demand for such commodities is projected to triple by 2050 (ref. 1). The challenge of developing effective separation and purification technologies that have much smaller energy footprints is greater for carbon dioxide (CO_2) than for other gases; in addition to its involvement in climate change, CO_2 is an impurity in natural gas, biogas (natural gas produced from biomass), syngas (CO/H_2, the main source of hydrogen in refineries) and many other gas streams. In the context of porous crystalline

that are pillared via SiF_6^{2-} anions ('SIFSIX') in the third dimension to form three-dimensional nets with primitive cubic topology[13].

$[Cu(4,4'\text{-bipyridine})_2(SiF_6)]_n$, a prototypal primitive-cubic net that remains one of the best sorbents for CH_4 as measured by volumetric uptake[14], exhibits highly selective CO_2 uptake versus both CH_4 and N_2 at 1 bar and 298 K (ref. 15). In the absence of UMCs or amine groups, we attributed this behaviour to favourable interactions between CO_2 and SIFSIX. This compound, which we call here SIFSIX-1-Cu, exhibits one-dimensional square channels (pore size 9.54 Å; here and throughout this Letter, pore sizes are given as diagonal dimensions) aligned by a periodic array of SIFSIX pillars, and is prototypical for a class of

Nugent, P, Belmabkhout, Y et al (2013) Nature 494 (7439) ,80-84

pyrazine/Zn 2-D periodic 4^4 square grids pillared by SiF_6 anions

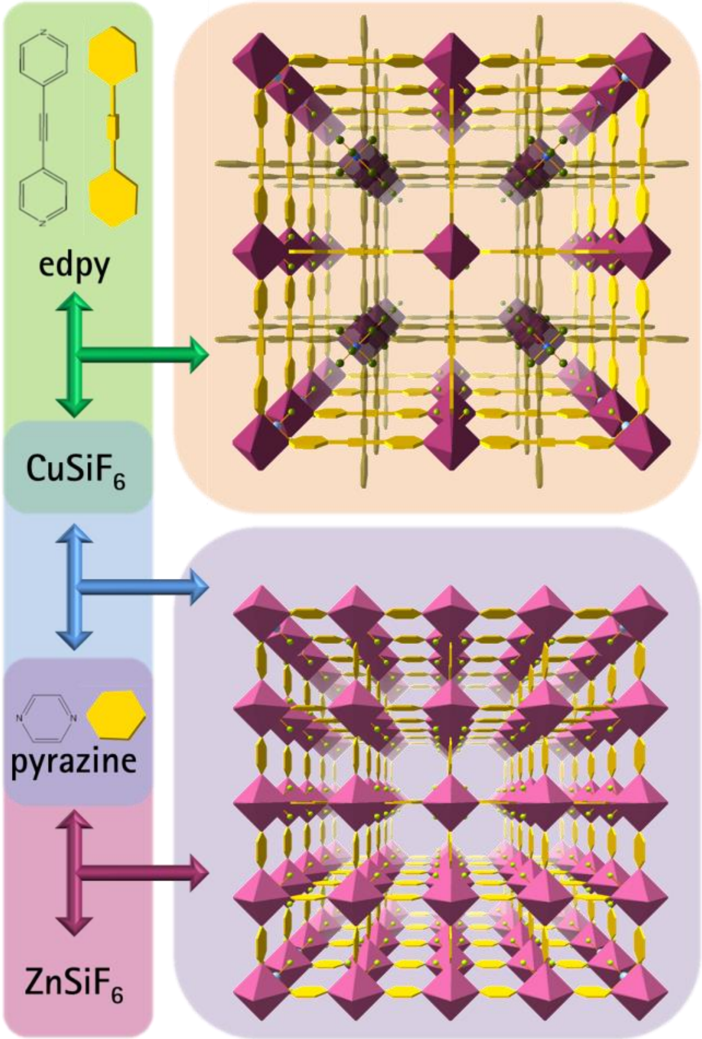


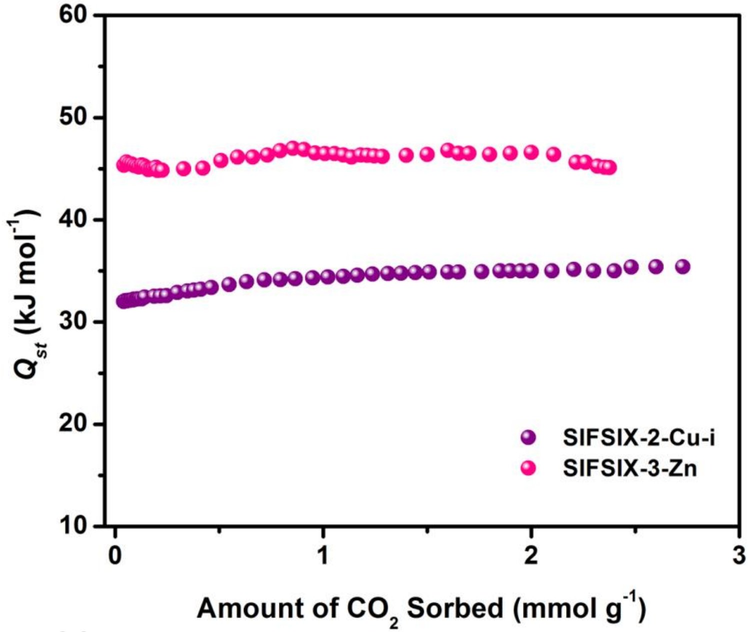
SIFSIX-2-Cu
10.5 Å pore
3140 m^2/g (N_2)

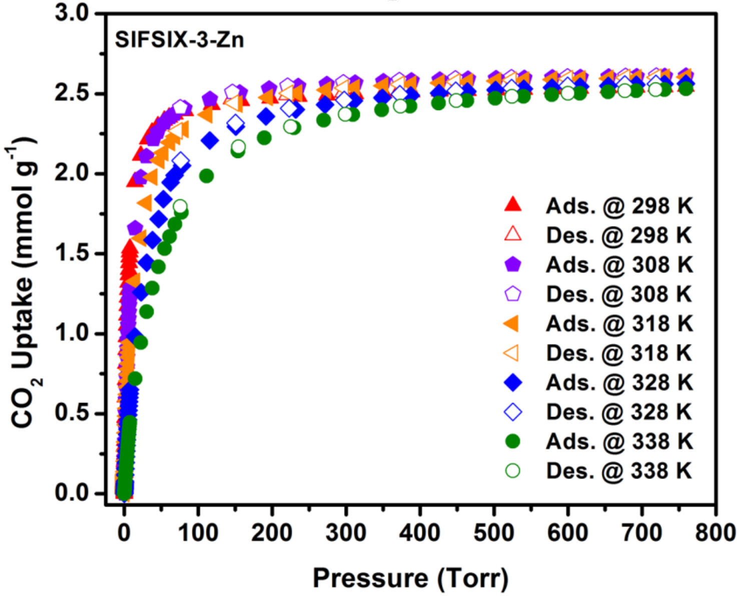
SIFSIX-2-Cu-i
4.9 Å pore
735 m^2/g (N_2)

SIFSIX-3-Zn
3.9 Å pore
250 m^2/g (CO_2)

Nugent, P, Belmabkhout, Y et al (2013) Nature 494 (7439) ,80-84, Patent Pending



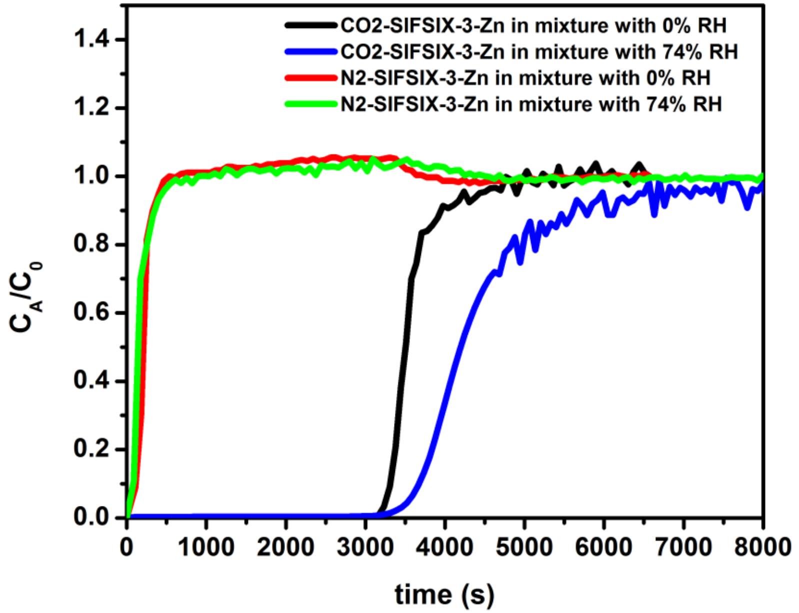


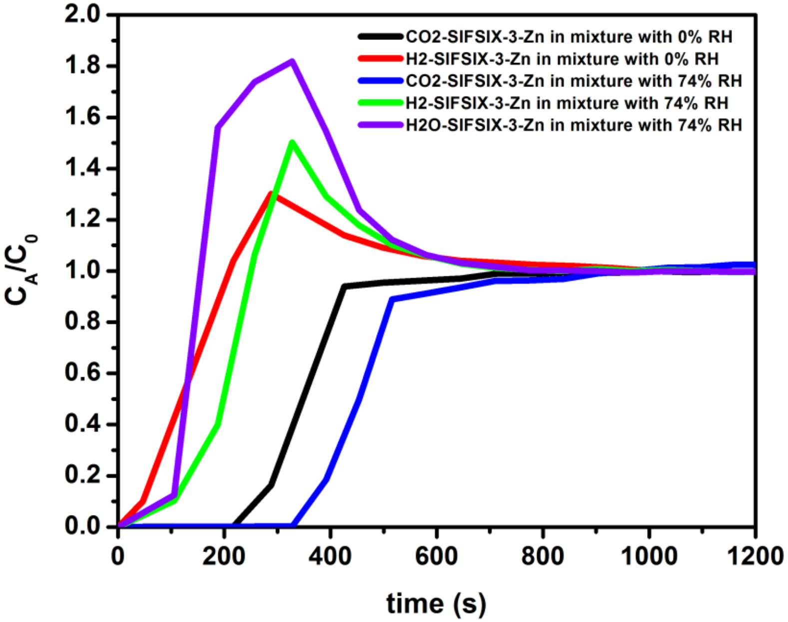


Nugent, P, Belmabkhout, Y et al (2013) Nature 494 (7439) ,80-84, Patent Pending

CO_2/N_2 and CO_2/H_2 separation using SIFSIX-3-Zn MOFs- Effect of humidity

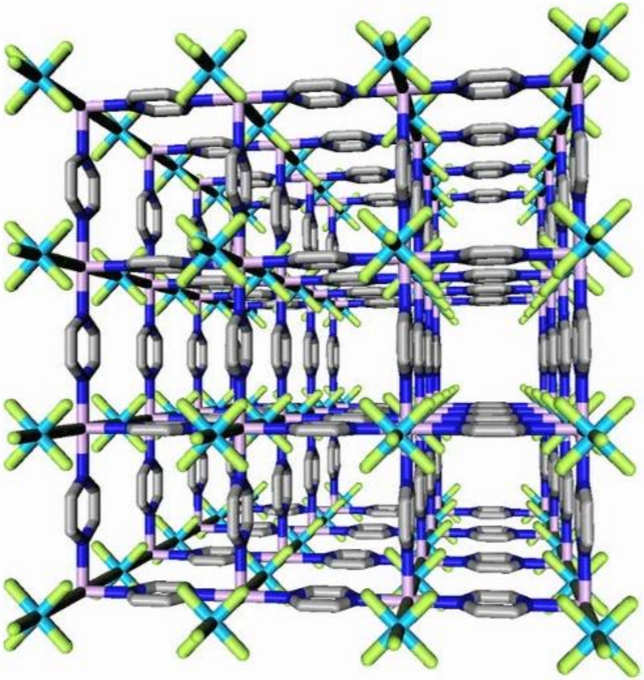
CO_2/N_2 (flue gas)and CO_2/H_2 (syngas) mixtures adsorption - column breakthrough
adsorption tests in humid conditions

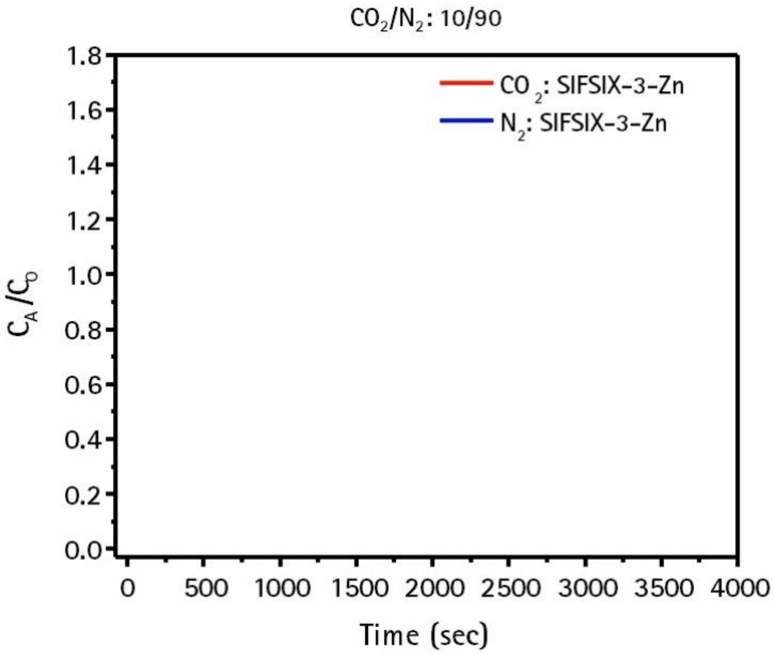




Nugent, P, Belmabkhout, Y et al (2013) Nature 494 (7439) ,80-84, Patent Pending

Column breakthrough test: CO_2/N_2: 10/90 mixture

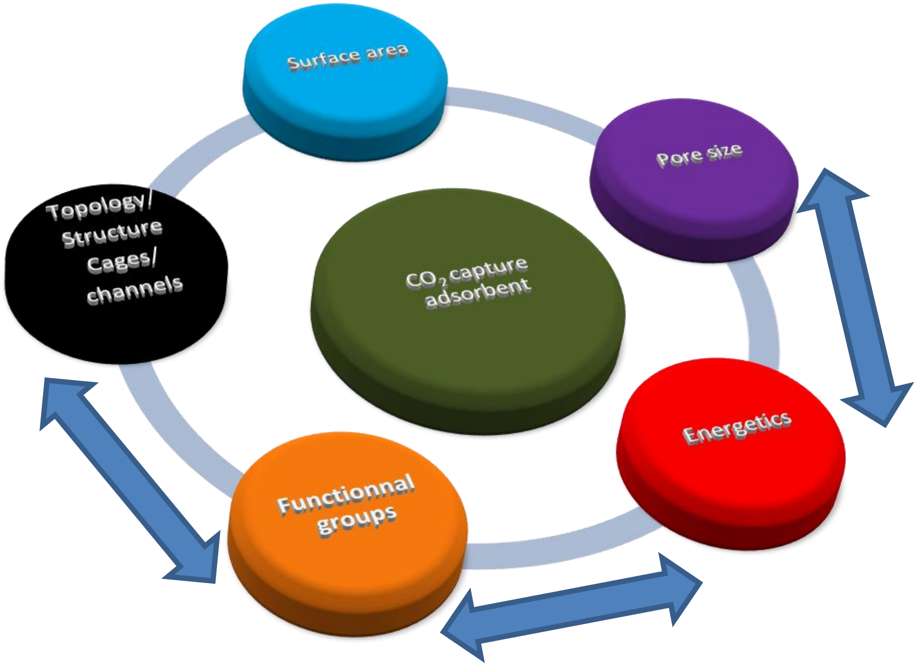




Nugent, P, Belmabkhout, Y et al (2013) Nature 494 (7439) ,80-84, Patent Pending

What we have learned so far ?

- ○ What is the key properties of an adsorbent to be suitable for CO_2 removal at different concentrations ?



CO_2 capture adsorbent

Surface area

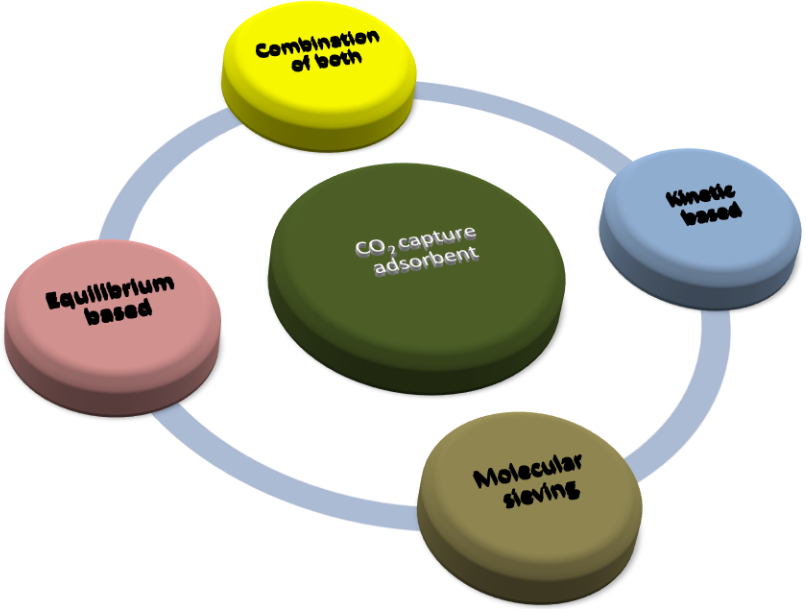
Pore size

Energetics

Functionnal groups

Topology/ Structure Cages/ channels

- ○ Which mechanism ?



CO_2 capture adsorbent

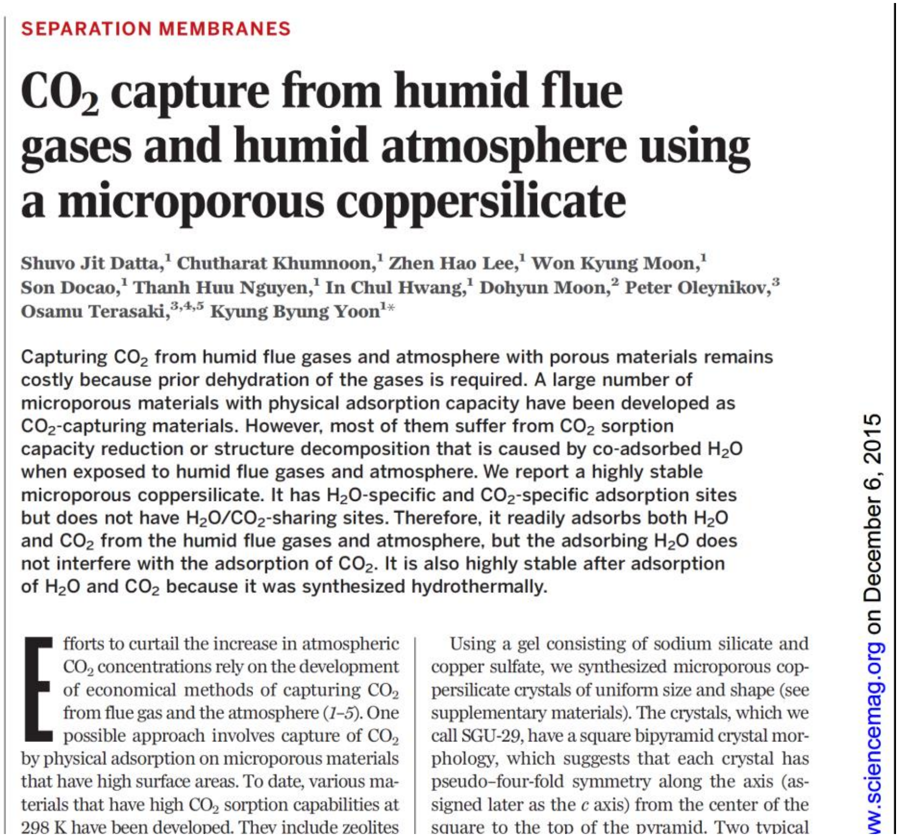
Combination of both

Kinetic based

Molecular sieving

Equilibrium based

Same concept with other materials



SEPARATION MEMBRANES

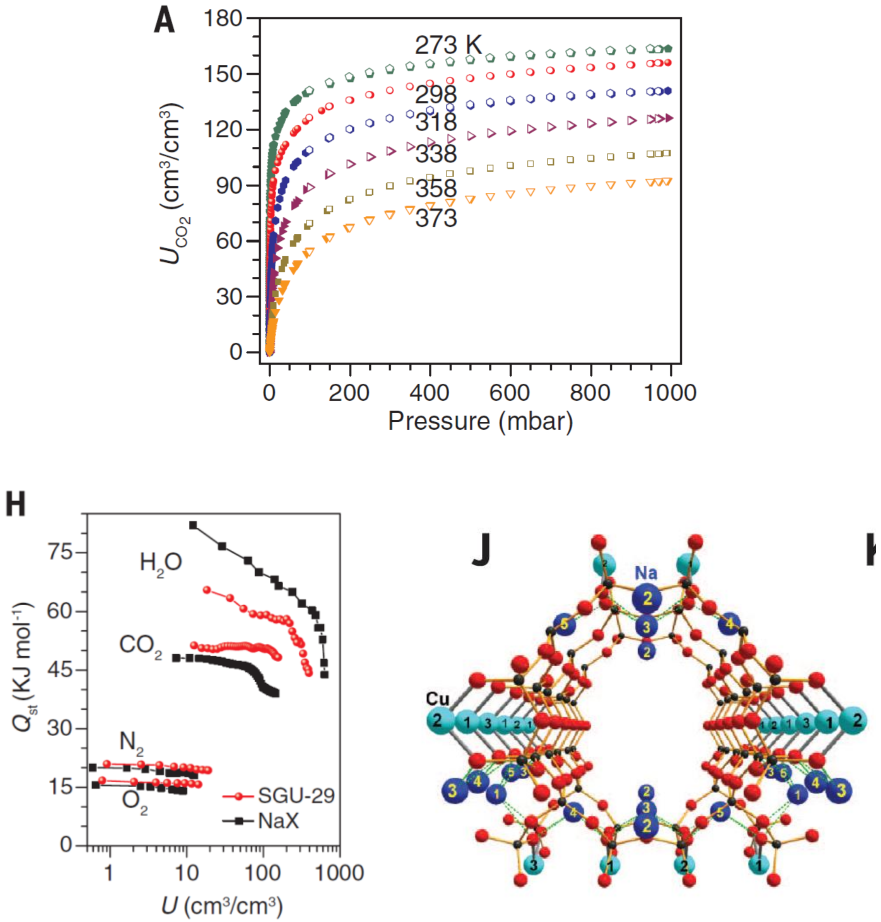
CO_2 capture from humid flue gases and humid atmosphere using a microporous coppersilicate

Shuvo Jit Datta,[1] Chutharat Khumnoon,[1] Zhen Hao Lee,[1] Won Kyung Moon,[1] Son Docao,[1] Thanh Huu Nguyen,[1] In Chul Hwang,[1] Dohyun Moon,[2] Peter Oleynikov,[3] Osamu Terasaki,[3,4,5] Kyung Byung Yoon[1]*

Capturing CO_2 from humid flue gases and atmosphere with porous materials remains costly because prior dehydration of the gases is required. A large number of microporous materials with physical adsorption capacity have been developed as CO_2-capturing materials. However, most of them suffer from CO_2 sorption capacity reduction or structure decomposition that is caused by co-adsorbed H_2O when exposed to humid flue gases and atmosphere. We report a highly stable microporous coppersilicate. It has H_2O-specific and CO_2-specific adsorption sites but does not have H_2O/CO_2-sharing sites. Therefore, it readily adsorbs both H_2O and CO_2 from the humid flue gases and atmosphere, but the adsorbing H_2O does not interfere with the adsorption of CO_2. It is also highly stable after adsorption of H_2O and CO_2 because it was synthesized hydrothermally.

Efforts to curtail the increase in atmospheric CO_2 concentrations rely on the development of economical methods of capturing CO_2 from flue gas and the atmosphere (*1*–*5*). One possible approach involves capture of CO_2 by physical adsorption on microporous materials that have high surface areas. To date, various materials that have high CO_2 sorption capabilities at 298 K have been developed. They include zeolites

Using a gel consisting of sodium silicate and copper sulfate, we synthesized microporous coppersilicate crystals of uniform size and shape (see supplementary materials). The crystals, which we call SGU-29, have a square bipyramid crystal morphology, which suggests that each crystal has pseudo-four-fold symmetry along the axis (assigned later as the *c* axis) from the center of the square to the top of the pyramid. Two typical



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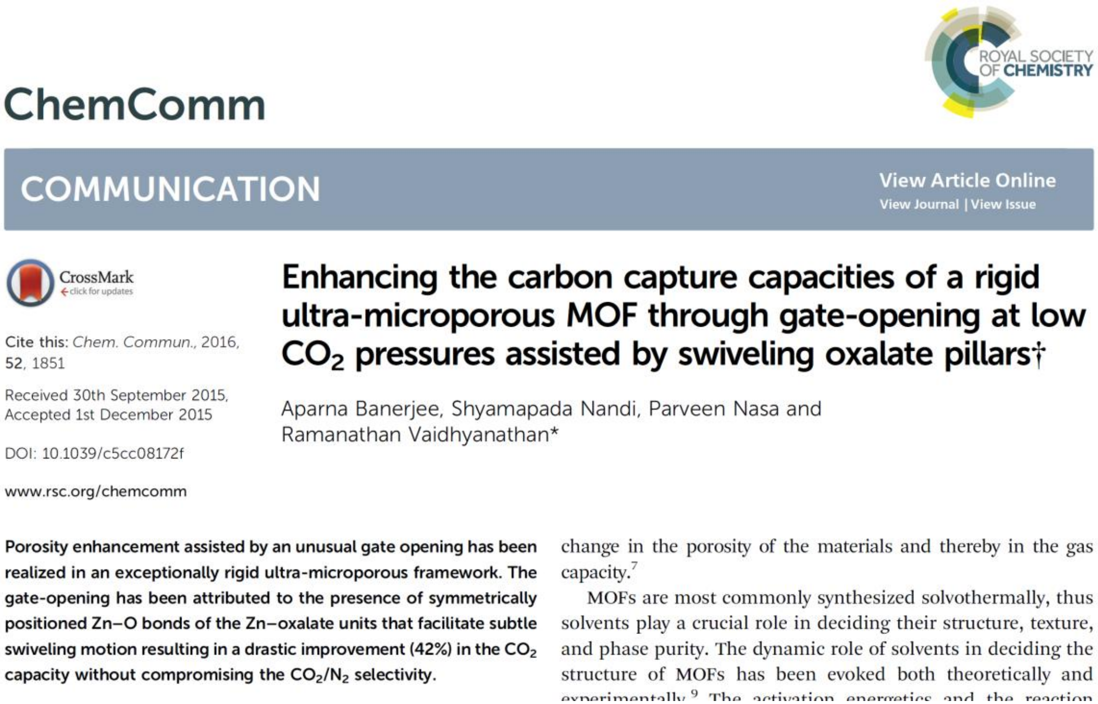
Same concept with other materials



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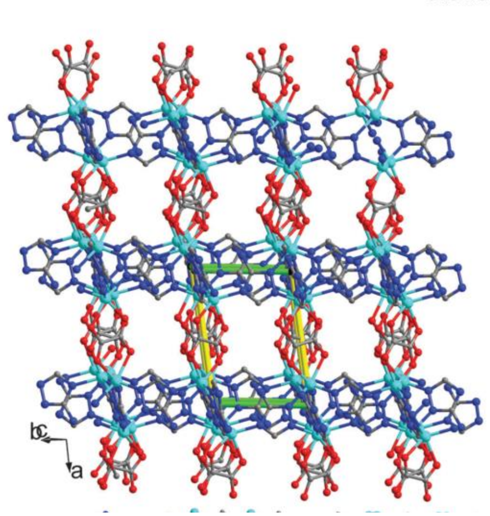
Enhancing the carbon capture capacities of a rigid ultra-microporous MOF through gate-opening at low CO_2 pressures assisted by swiveling oxalate pillars†

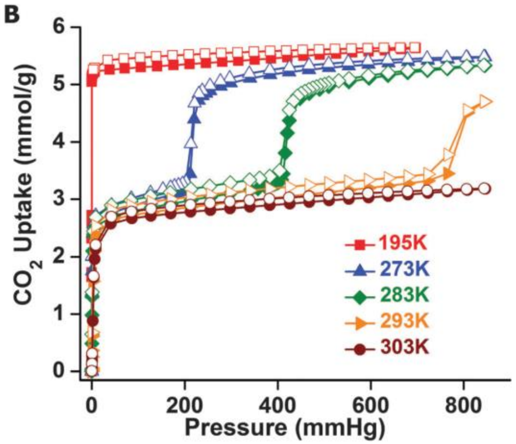
Aparna Banerjee, Shyamapada Nandi, Parveen Nasa and Ramanathan Vaidhyanathan*

Porosity enhancement assisted by an unusual gate opening has been realized in an exceptionally rigid ultra-microporous framework. The gate-opening has been attributed to the presence of symmetrically positioned Zn–O bonds of the Zn–oxalate units that facilitate subtle swiveling motion resulting in a drastic improvement (42%) in the CO_2 capacity without compromising the CO_2/N_2 selectivity.

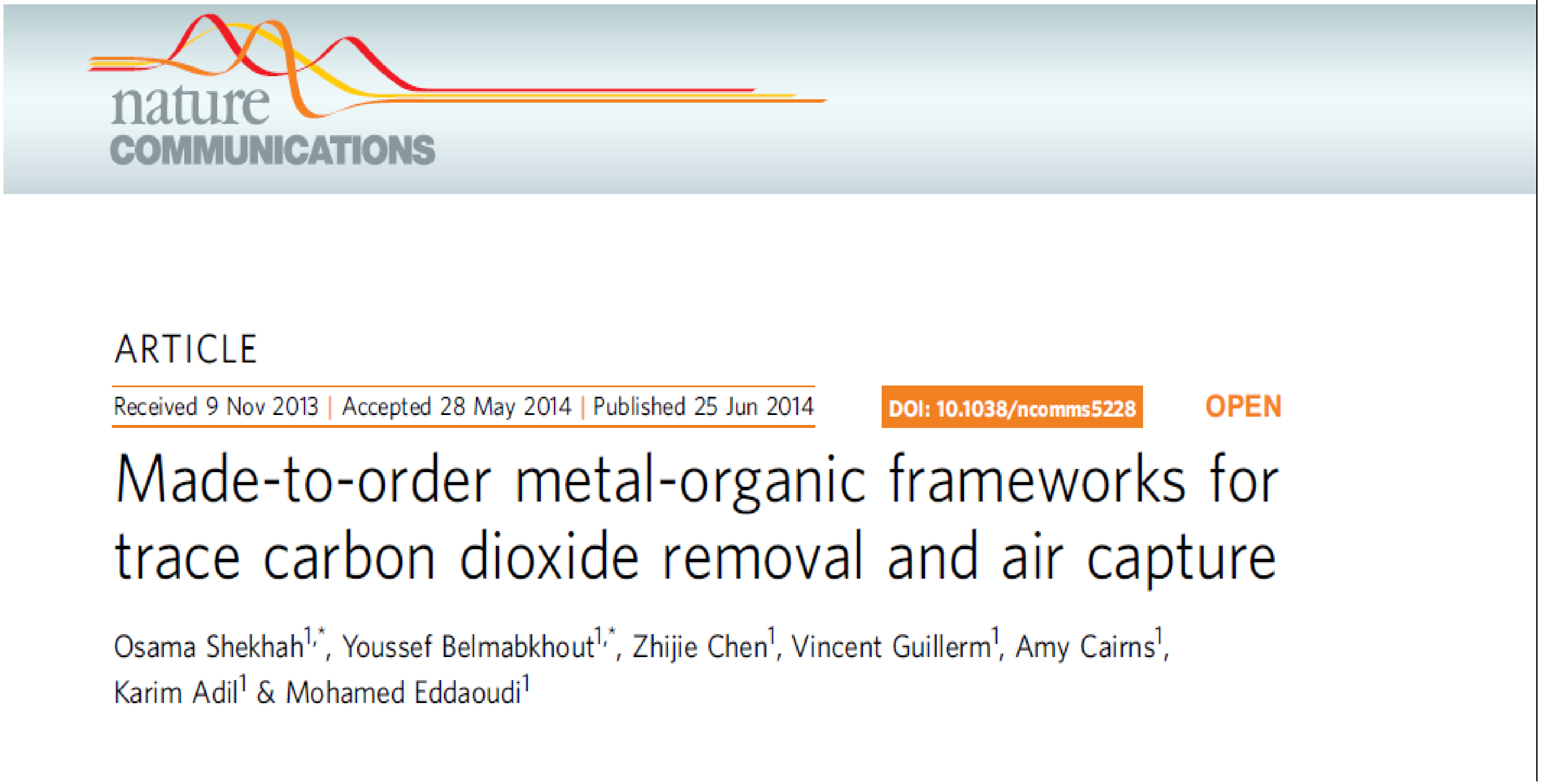
change in the porosity of the materials and thereby in the gas capacity.[7]

MOFs are most commonly synthesized solvothermally, thus solvents play a crucial role in deciding their structure, texture, and phase purity. The dynamic role of solvents in deciding the structure of MOFs has been evoked both theoretically and experimentally.[9] The activation energetics and the reaction





Recent finding (2014)



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ARTICLE

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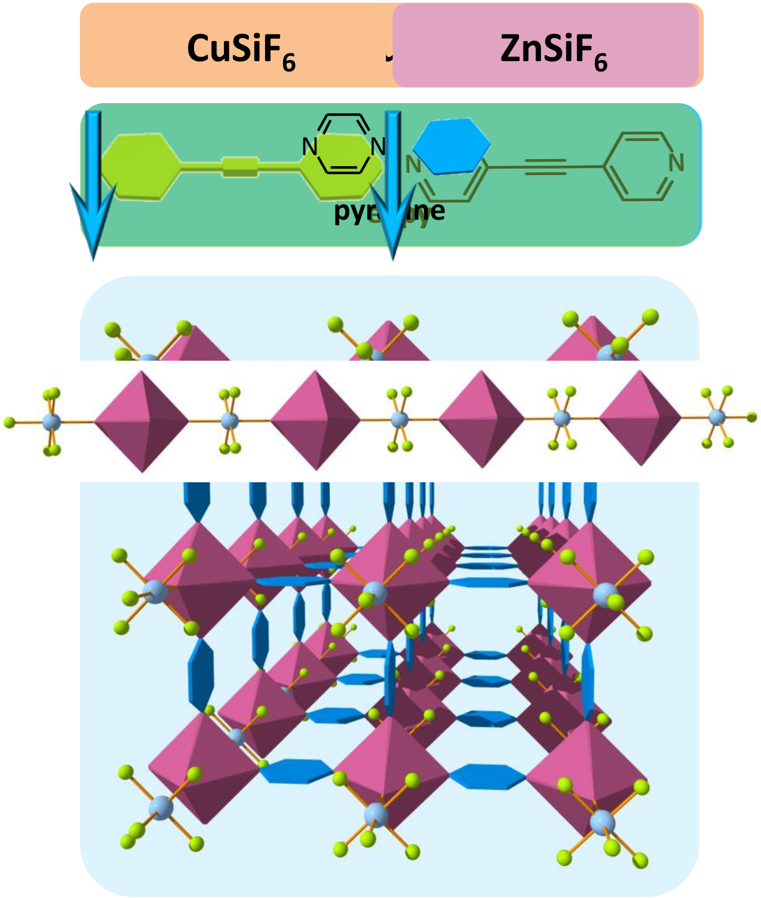
Made-to-order metal-organic frameworks for trace carbon dioxide removal and air capture

Osama Shekhah[1,*], Youssef Belmabkhout[1,*], Zhijie Chen[1], Vincent Guillerm[1], Amy Cairns[1],
Karim Adil[1] & Mohamed Eddaoudi[1]

SIFSIX based MOFs



M-SIF$_6$ pillars

SIFSIX-2-Cu

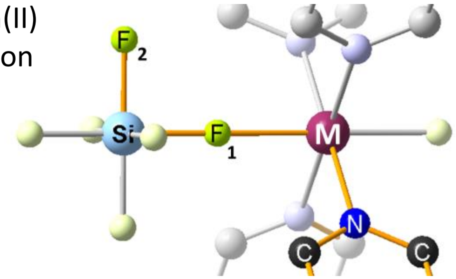
SIFSIX-3-Cu/Zn

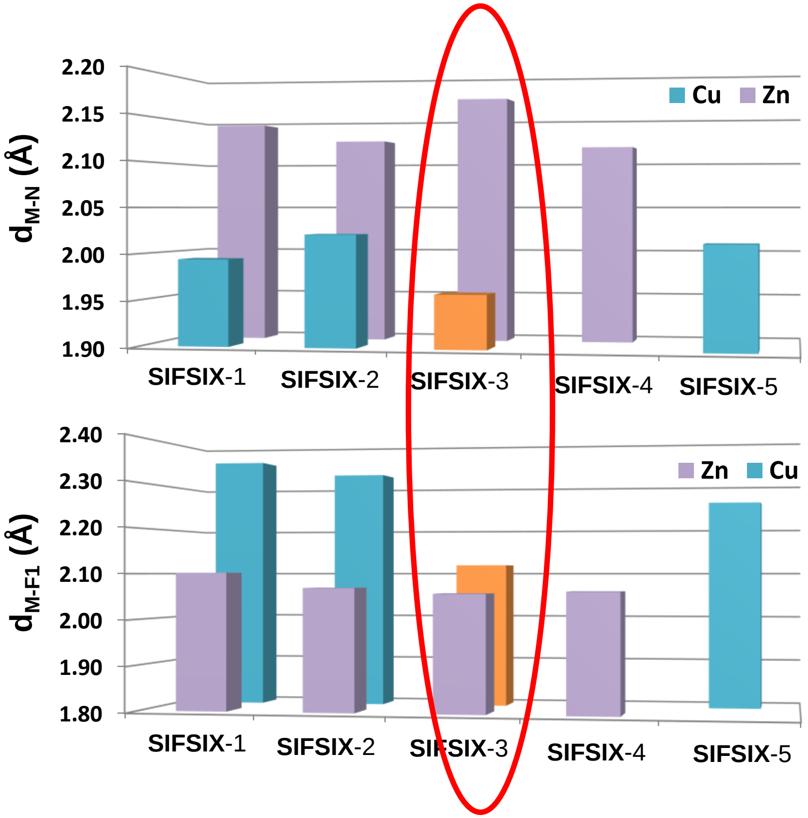
SIFSIX-2-Cu-i

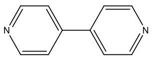
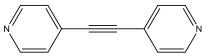
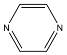
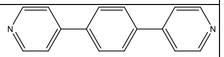
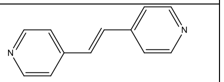
Shekhah, O, Belmabkhout, Y et al (2013). Nature Commun 2014, 5, 4228

SIFSIX-3-Cu MOFs. Interatomic distances in SIFSIX based MOFs.

The rational is based on conventional coordination chemistry suggesting that replacement of Zn(II) by Cu(II) to form an iso-structural **SIFSIX**-3-Cu will potentially induce an additional pore contraction due to Jahn-Teller distortions of the octahedral coordination geometry of Cu(II), CuN_4F_2.





MOF	d_{M-N} (Å)	d_{M-F1} (Å)	D_{Si-F1} (Å)	D_{Si-F2} (Å)†	reference	Ligand
SIFSIX-1-Zn	2.157	2.082	1.757	1.600	[38]	
	2.131	2.122	1.720	1.650	[39]	
SIFSIX-1-Cu	2.007	2.379	1.703	1.672	[40]	
	2.009	2.357	1.698	1.609	[41]	
	1.966	2.336	1.692	1.685	[42]	
SIFSIX-2-Zn	2.125	2.069	1.698	1.668	[39]	
SIFSIX-2-Cu	2.027	2.300	1.684	1.684	[43]	
SIFSIX-2i-Cu	2.015	2.353	1.693	1.679	[43]	
SIFSIX-3-Zn	2.172	2.057	1.747	1.657	[44]	
SIFSIX-3-Cu	1.958	2.119	1.834	1.651	this work	
SIFSIX-2D-Cu	2.061*	2.402	1.727	1.688	[44]	
SIFSIX-2D-H_2O-Cu	2.031	2.412	1.695	1.675	[42]	
SIFSIX-4-Zn	2.117	2.062	1.712	1.653	[39]	
SIFSIX-5-Cu	2.012	2.258	1.727	1.681	[40]	

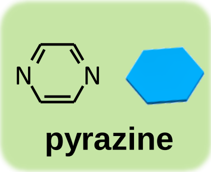
Shekhah, O, Belmabkhout, Y et al (2013). Nature Commun 2014, 5, 4228

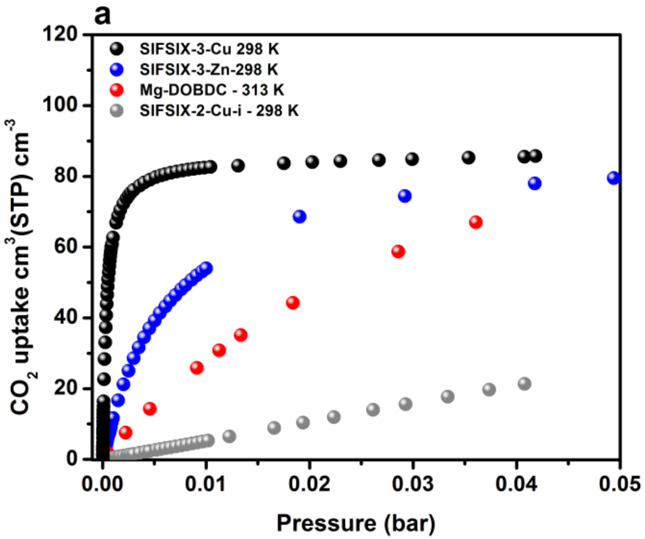
Enhanced charge density by slight pore contraction

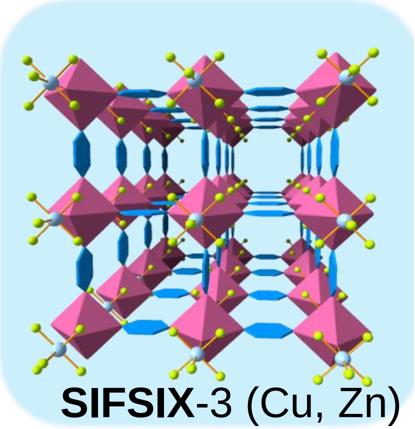
Uptake at 1300 ppm

SIFSIX-3-Cu	**43 cm³ STP/g**
Sr^{2+} SAPO-34	15 cm³ STP/g
Ca^{2+} LTA (**5A**)	9 cm³ STP/g

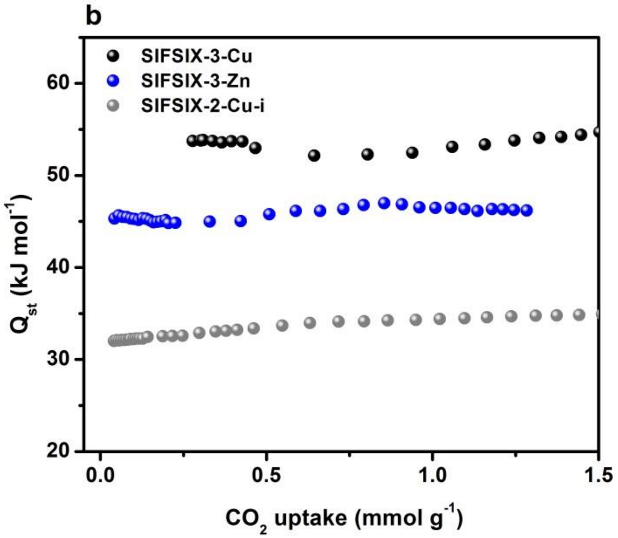
SIFSIX-3-M







SIFSIX-3 (Cu, Zn)



- ➢**High charge density + suitable pore size**
- ➢**Enhanced charge density by pore contraction**

Shekhah, O, Belmabkhout, Y et al (2013). Nature Commun 2014, 5, 4228, Patent Pending

CO_2 separation/capture in our life

CO_2 Separation

Energy

Health and Safety

Environment

Pre-purification before air Separation (PPU)

Alkaline Fuel Cells (AFC)

Syngas treatment (H_2 purification)

Natural gas upgrading (CH_4 purification)

Anesthesia Machine

Rebreather

Confined space (Space shuttles)

Confined space (submarine)

Air Capture

From the source

Stationary

On-Board

Conclusion

- ○ In-depth understanding of what are crucial measures for physical adsorbents to be used in CO_2 capture
- ○ Because of the high degree of tunability of MOFs we confirmed the discovery of new separation concept involving the combination of thermodynamics and Kinetics
- ○ Synergetic effect between the presence of uniform charge density and suitable pore size allow to unveil physical adsorbents with high selectivity and uptake for CO_2 (similar to MEA) but with much Lower heat and temperature for regeneration.
- ○ Porosity
  - - Channel based adsorbents are more suitable for separation in general and CO_2 in particular
  - - Suitable pore size is critical for gas separation in CO_2 capture in particular
  - - Surface area is not crucial parameter to develop materials for CO_2 capture

Acknowledgment

Thank you

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