Study of two promising MOFs, MIL-91(Ti) and MIL-160(Al), for CO_2 capture from flue gas

N. Heymans[1], A. Henrotin[1], S. Nandi[2], G. Mouchaham[2], F. Nouar[2], N. Garcia-Moncada[3], M. Wahiduzzaman[4], M. Daturi[3], G. Maurin[4], C. Serre[2] and G. De Weireld[1]

[1] Thermodynamics Department, University of Mons, 20 Place du Parc, 7000 Mons, Belgium

[2] Institut des Matériaux Poreux de Paris, FRE 2000 CNRS, Ecole Normale Supérieure, Ecole Supérieure de Physique et de Chimie Industrielles de Paris, PSL Research University 75005 Paris, France

[3] Laboratoire de Catalyse et Spectrochimie, ENSICAEN, Université de Caen, 14050 Caen, France

[4] Institut Charles Gerhardt Montpellier, Université de Montpellier, CNRS UMR 5253, ENSCM, 34095 Montpellier, France

e-mail: nicolas.heymans@umons.ac.be or guy.deweireld@umons.ac.be https://www.mof4air.eu/

Global overview

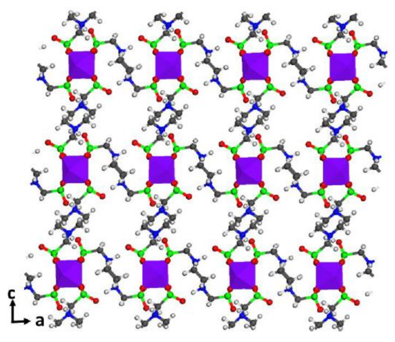
General Context

For two decades, the reduction of anthropogenic CO_2 emissions from industries has become one of the most crucial issue to combat global warming. Shifting towards a low-carbon economy needs cost-effective novel carbon capture utilization or sequestration (CCUS) solutions. Current benchmark technique, absorption-regeneration amine-based process, suffers from high energy penalties due to solvent regeneration and high environmental impacts. So, **adsorption process** is widely considered as a promising alternative. In this regard, **MOFs** as adsorbent offer tremendous potential, owing to their large CO_2 adsorption capacity and high CO_2 affinity. However, the performances of these materials have rarely been fully evaluated in real industrial conditions. In this context, this study focuses on the determination of performances on two promising MOFs, **MIL-91(Ti)**[1] and **MIL-160 (Al)**[2,3] in conditions close to real industrial conditions (presence of water, NOx, SOx…) for the purpose of being used in a **post-combustion capture process** based on a Vacuum Pressure Swing Adsorption (**VPSA**) process.

Selected adsorbents

MIL-91(Ti)

$TiO(O_3PCH_2NHC_4H_8NHCH_2PO_3)$

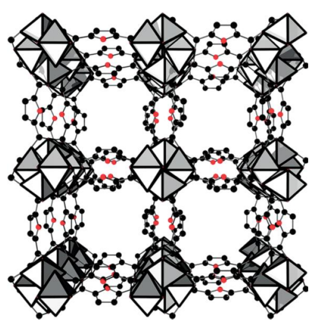


Chains of Ti octahedrons – Ligands phosponate (PMDP)

S_{BET} = 415 m²/g
Narrow pores (4.5 Å)
High degree of confinement
Flexible ligand
Highly hydrophilic

MIL-160(Al)

$Al(OH)[C_4H_2O\text{-}(CO_2)_2]$



Chains of Al octahedrons – Ligands 2,5-furan dicarboxylate (FDC)

S_{BET} = 1220 m²/g
Larger pores (6 Å)
Rigid ligand
Relatively less hydrophilic

Measurements and Methods

1) Pure CO_2 and N_2 adsorption isotherm measurements performed with a homemade apparatus using a Magnetic Suspension Balance Rubotherm GmbH[4] at several temperatures.

→ Working capacities, heat of adsorption (Clausius-Clapeyron), CO_2/N_2 co-adsorption prediction (IAST[5])

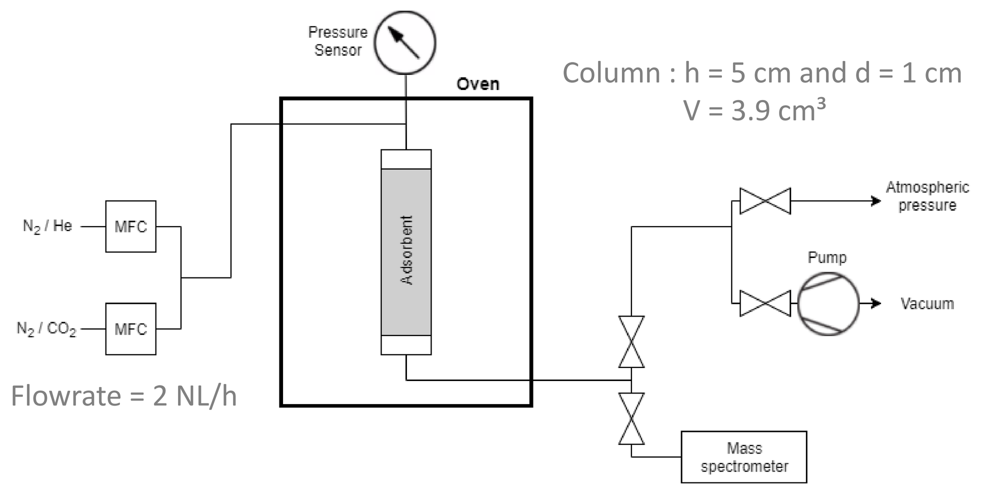
2) Breakthrough curves measurements

a) CO_2/N_2 (15/85) breakthrough curves after He pressurization at 1 bar

→ CO_2/N_2 selectivity and co-adsorption uptakes

b) CO_2/N_2 (15/85) adsorption/desorption breakthrough curve cycles at 30°C and 1.1 bar under dry and humid (p_w=0.02 bar) conditions

→ Regenerability, CO_2 adsorbed amounts



3) Water adsorption isotherm and CO_2 adsorption isotherm measurements after water pre-adsorption performed with DVS Vacuum provided by Surface Measurement Systems

→ Influence of water on CO_2 adsorption capacities

4) Operando analyses performed by coupling IR analysis of the gas phase in parallel with MS analysis under a flow containing contaminants (H_2O, SO_2, NOx, CO)

→ Evaluation of the MOF stability and performance under real conditions

5) GCMC simulation performed to provide an *in-depth* microscopic understanding of CO_2 and N_2 co-adsorption behavior under dry and variable humidity conditions.

→ Influence of water on CO_2 adsorption capacities

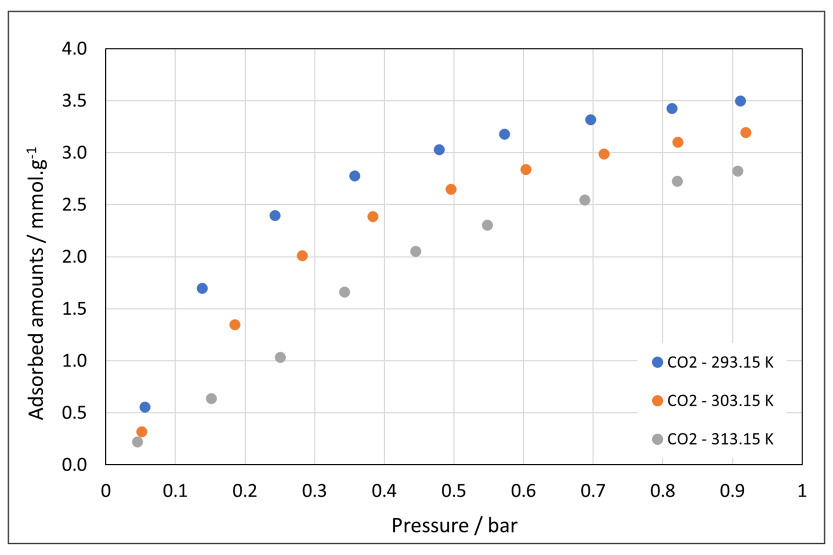
→ CO_2/N_2 selectivity under dry and humid conditions

These 5 steps constitute the complete procedure set up within the framework of the MOF4AIR project for the selection of the best MOF candidates in powder form before the scaling and shaping steps for their use in VPSA process. The results section will focus on the results obtained during the first 3 steps.

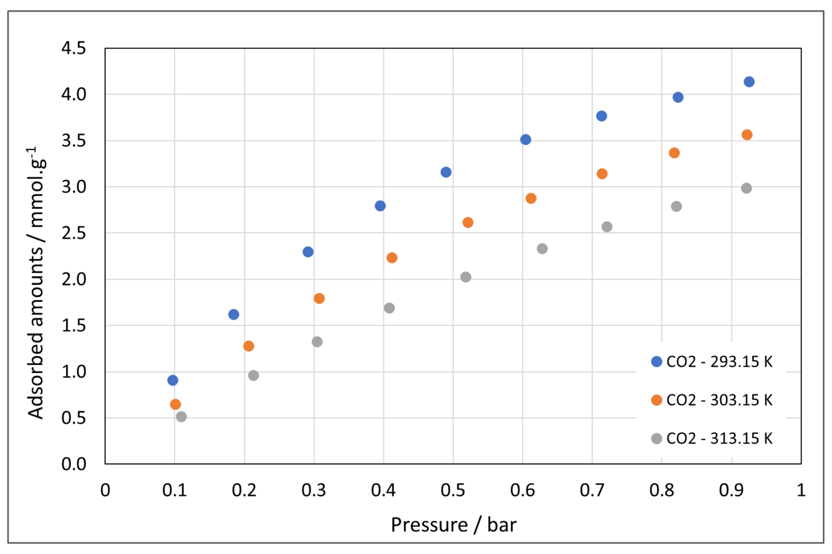
Results

Pure component adsorption isotherms

MIL-91(Ti)



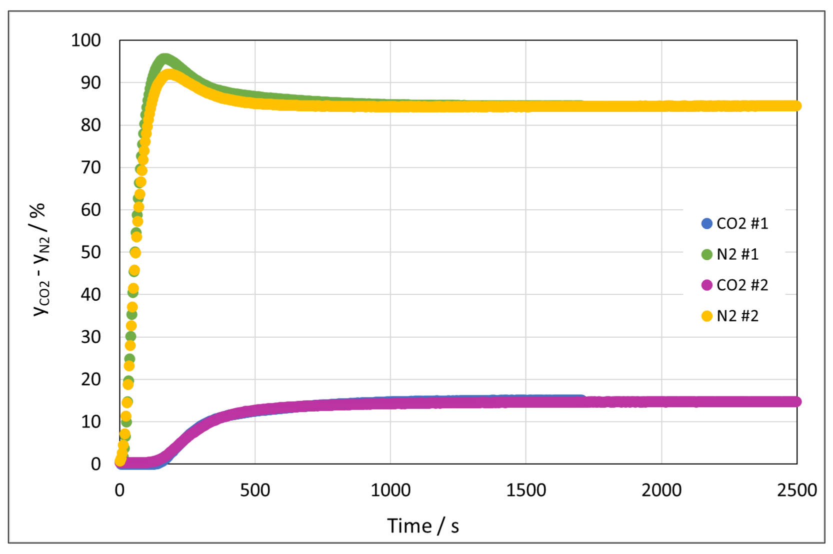
MIL-160(Al)



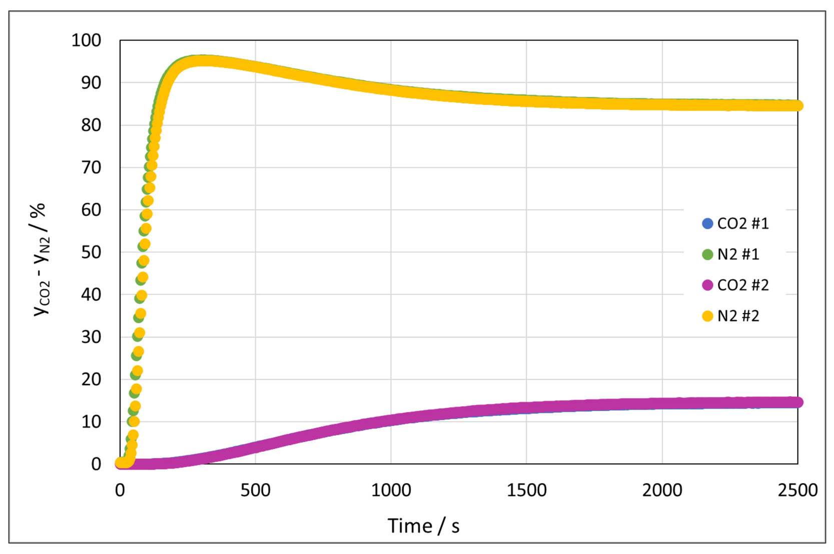
	CO_2 adsorbed amount (mmol/g) at 0.15 bar and 303.15 K	CO_2 working capacity (mmol/g) at 303.15 K	Δh_{ads}, CO_2 (kJ/mol)	Δh_{ads}, N_2 (kJ/mol)
MIL-91(Ti)	1.25	1.10	36	20
MIL-160(Al)	0.97	0.85	33	20

Breakthrough curves: CO_2/N_2 after He pressurisation

MIL-91(Ti)



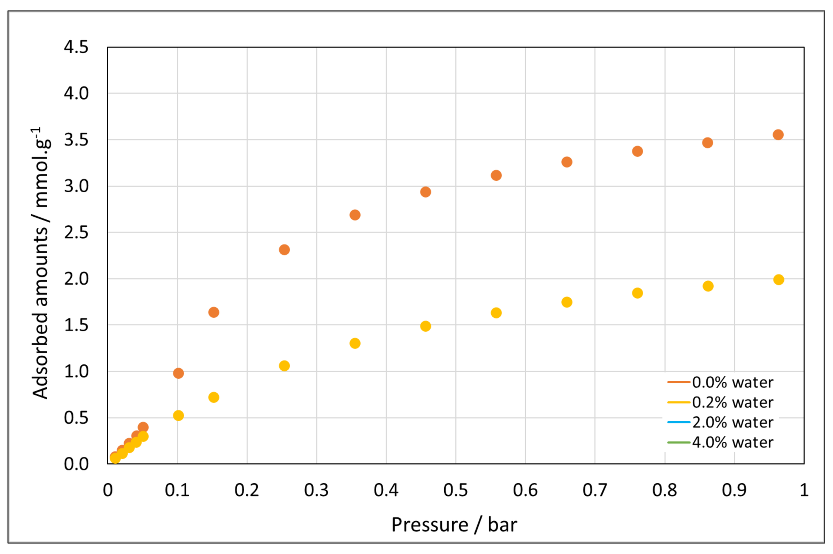
MIL-160(Al)



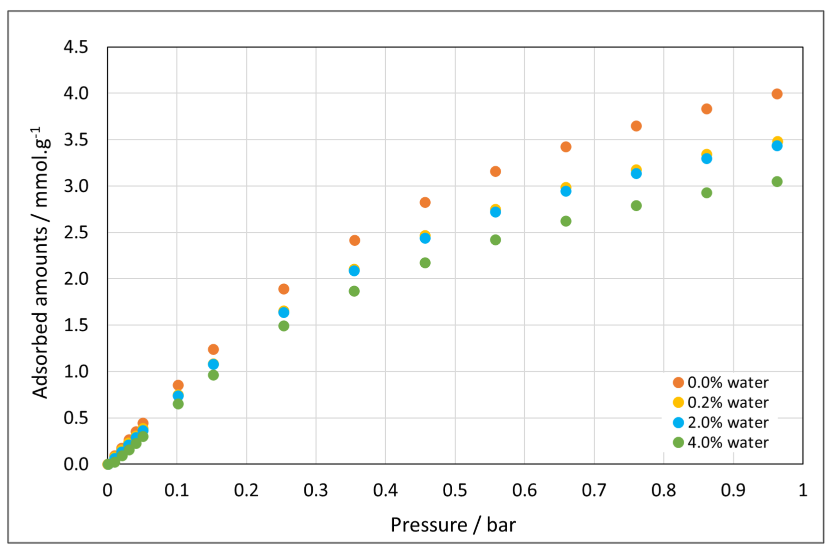
	CO_2 adsorbed amount (mmol/g)	N_2 adsorbed amount (mmol/g)	Exp CO_2/N_2 selectivity range	IAST CO_2/N_2 selectivity
MIL-91(Ti)	1.25 – 1.27	0.05 – 0.06	118 – 144	115
MIL-160(Al)	1.14 – 1.14	0.19 – 0.21	31 – 34	33

CO_2 adsorption isotherms under dry and diverse humidity conditions

MIL-91(Ti)



MIL-160(Al)

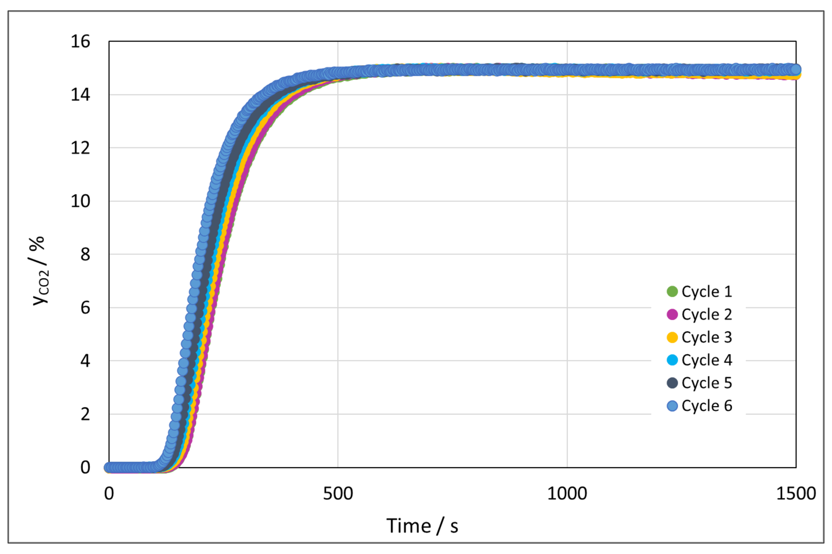


CO_2 adsorbed amount (mmol/g) at 0.15 bar and 298.15 K	Dry	0.2% RH	2% RH	4% RH
MIL-91(Ti)	1.64	0.72	-	-
MIL-160(Al)	1.24	1.09	1.08	0.97

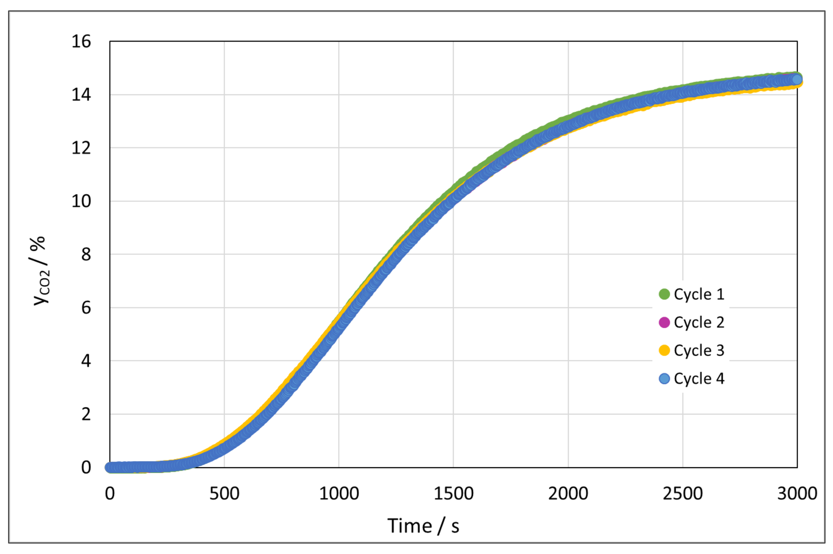
Breakthrough curves: CO_2/N_2 adsorption/desorption - Cyclability

Dry conditions

MIL-91(Ti)



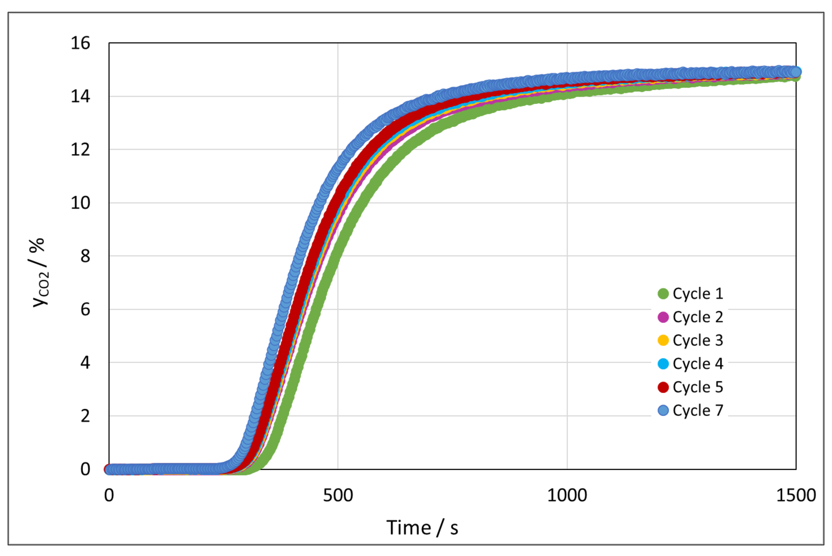
MIL-160(Al)



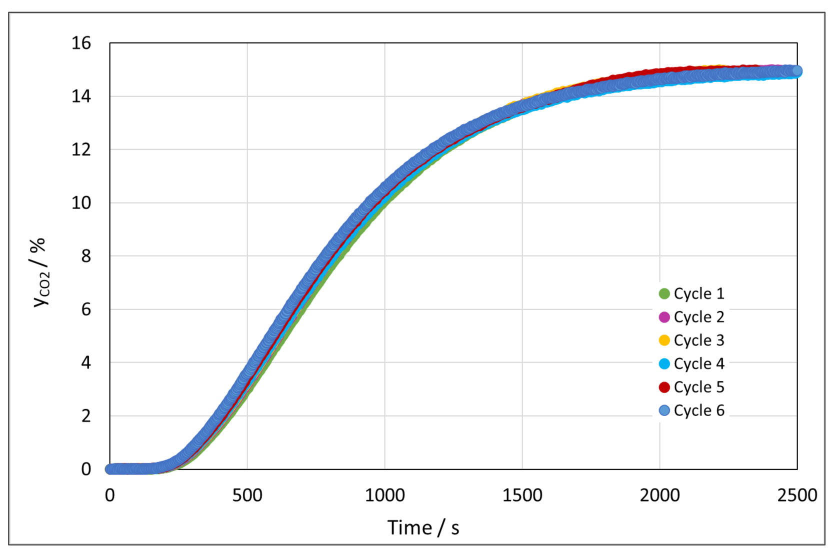
Observation of a 11% loss of adsorbed amounts for MIL-91(Ti) → Vacuum and/or heat required
Complete regeneration for MIL-160(Al) without heat or vacuum

Humid conditions

MIL-91(Ti)



MIL-160(Al)



Observation of a 20% loss of adsorbed amounts for MIL-91(Ti) → Vacuum and/or heat required
Still complete regeneration for MIL-160(Al) without heat or vacuum

Conclusions & Prospects

These measurements highlight that MIL-91(Ti) has better performances than MIL-160(Al) in terms of working capacity and selectivity in dry conditions, however, MIL-160(Al) is less impacted by water and impurities maintaining these CO_2 adsorption properties under dynamic conditions. Moreover, MIL-160(Al) can be regenerated easily under humid conditions. These results highlight the need of measurements close to real conditions to properly select an adsorbent. MIL-160(Al) is therefore the first MOF selected in MOF4AIR project to be scaled-up and shaped for testing in VPSA process.

References

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