



Characterization and trends in CO₂ adsorption of 3D structured Hofmann clathrate

Rizwan Minhas, Laurent Perrier, N Brefuel, Christelle Miqueu

► To cite this version:

Rizwan Minhas, Laurent Perrier, N Brefuel, Christelle Miqueu. Characterization and trends in CO₂ adsorption of 3D structured Hofmann clathrate. 1st Mediterranean Conference, May 2023, Crete island, greece, Greece. hal-04387585

HAL Id: hal-04387585

<https://univ-pau.hal.science/hal-04387585>

Submitted on 11 Jan 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License

Characterization and trends in CO₂ adsorption of 3D structured Hofmann clathrate

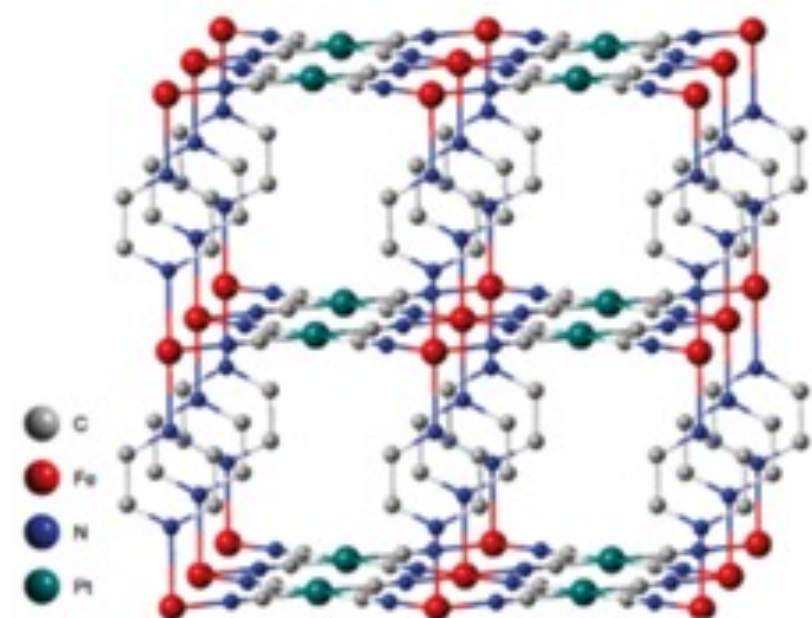
R. Minhas¹, L. Perrier¹, N. Brefuel², C. Miqueu¹

¹ Université de Pau et des pays de l'Adour, E2S UPPA, CNRS, LFCR, Anglet, France

² CEMES CNRS, Toulouse, France

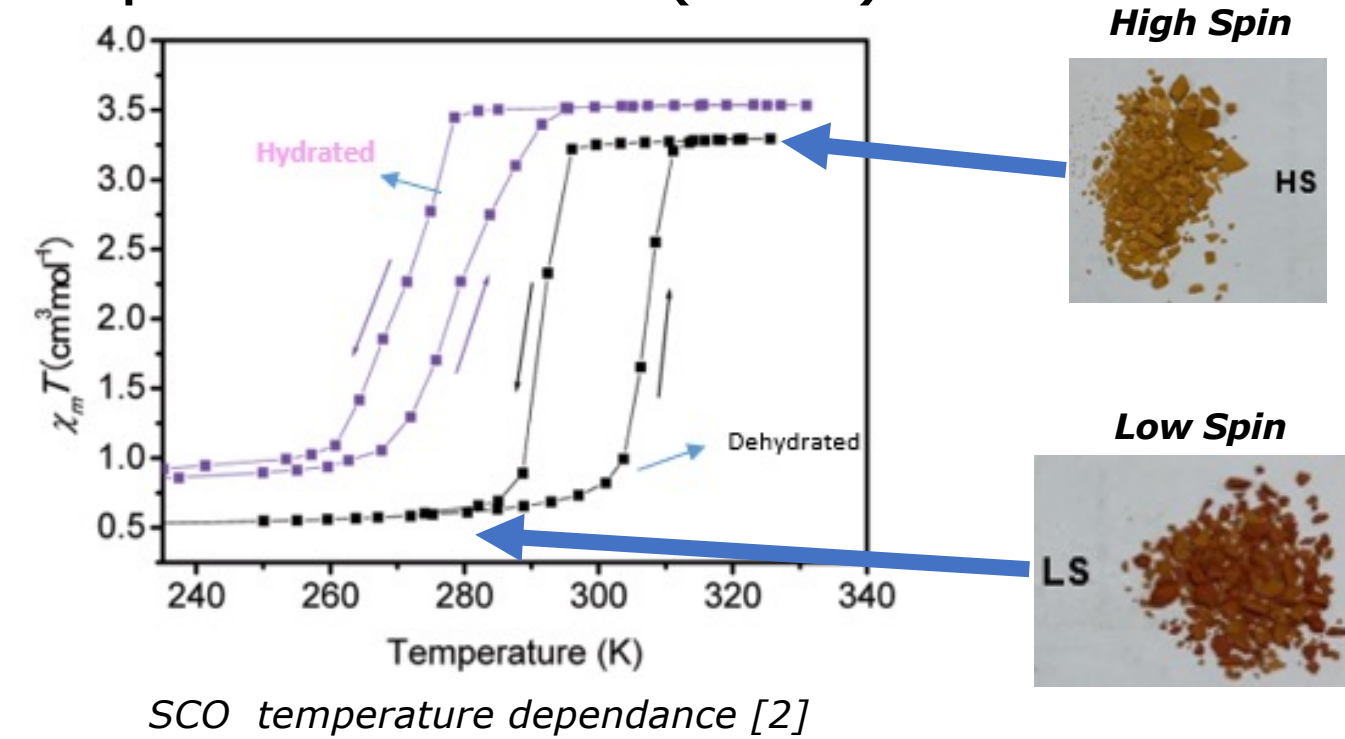
3D Hofmann Clathrate

Structure



Schematic Structure of 3D FeNi(CN)₄Pyrazine [1]

Spin-Crossover (SCO)

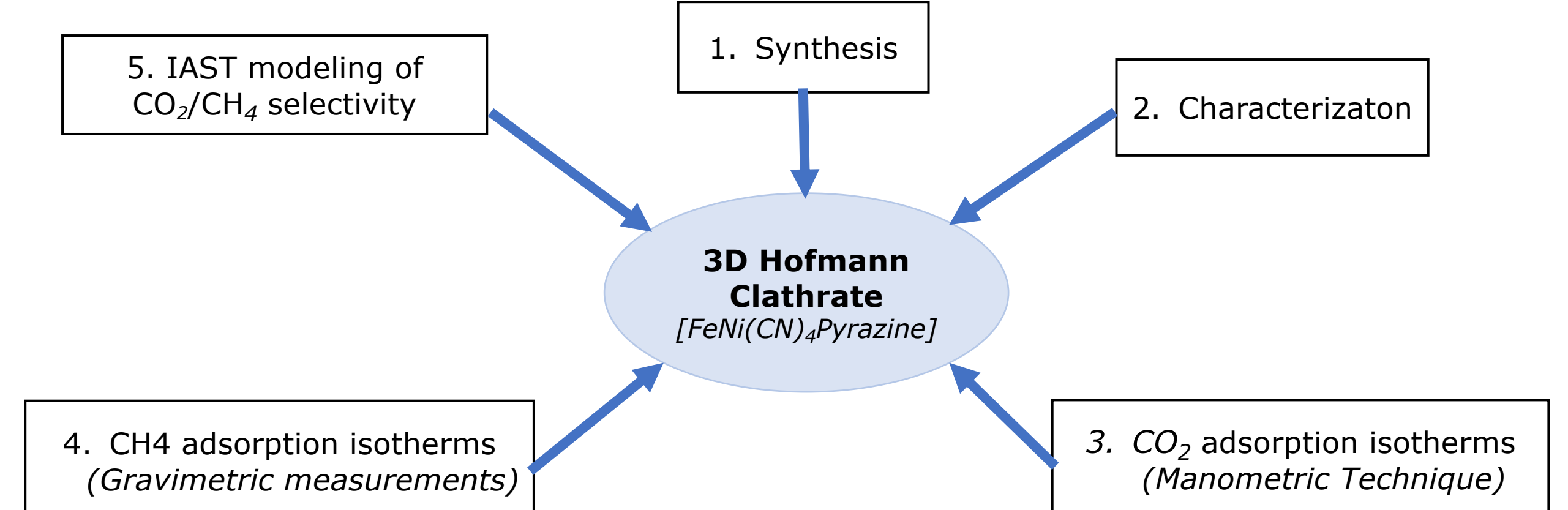


To address the increasing energy consumption and serious environmental problems, it is critical to develop efficient and clean energy conversion and storage devices. In this context, among various categories of materials, a 3D structured Spin Crossover (SCO) MOF, [FeNi(CN)₄Pyrazine] [2], in the family of materials known as Hofmann clathrates, has been synthesized, characterized and its CO₂ and CH₄ sorption capacities are measured and analyzed at several temperatures and pressures.

CONTEXT AND OBJECTIVE

Objective

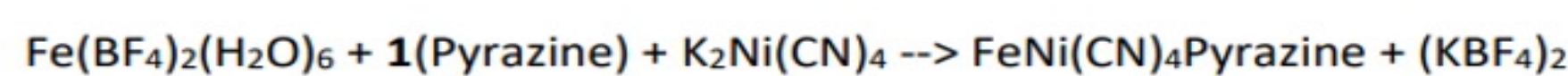
The aim of this work, is firstly to synthesize the 3D Hofmann clathrate and then characterize it to identify its porous as well as physical properties. Once completely characterized, the CO₂ and CH₄ sorption capacities are measured and analyzed using well developed manometric and gravimetric techniques (at high pressure and several temperatures) and finally to study CO₂/CH₄ selectivity of this MOF.



ADSORBENT SYNTHESIS

Chemical Reaction

The sample is synthesized using pyrazine ligands.



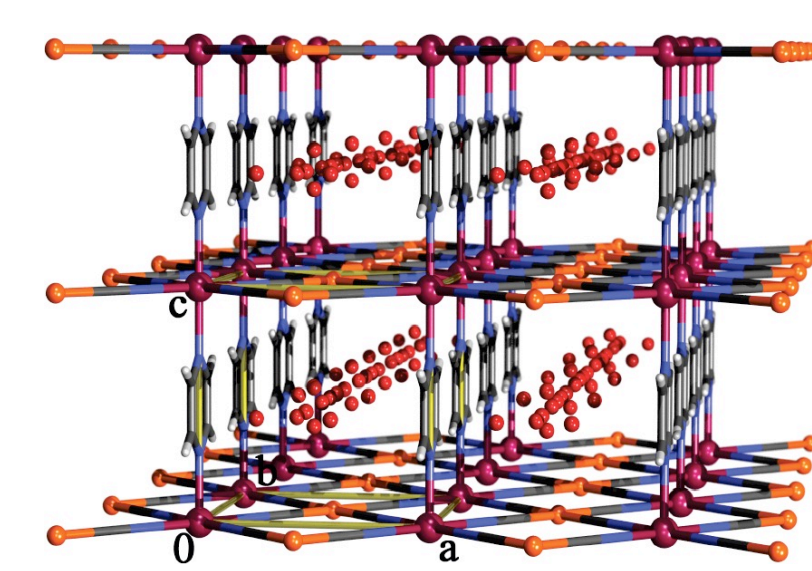
Immediately precipitates as orange powder

Removal of KBF₄ upon washing with pure water or using Centrifugator

Chemical composition of the adsorbent

Elemental composition of [FeNi(CN)₄](C₄H₄N₂)(H₂O)₂

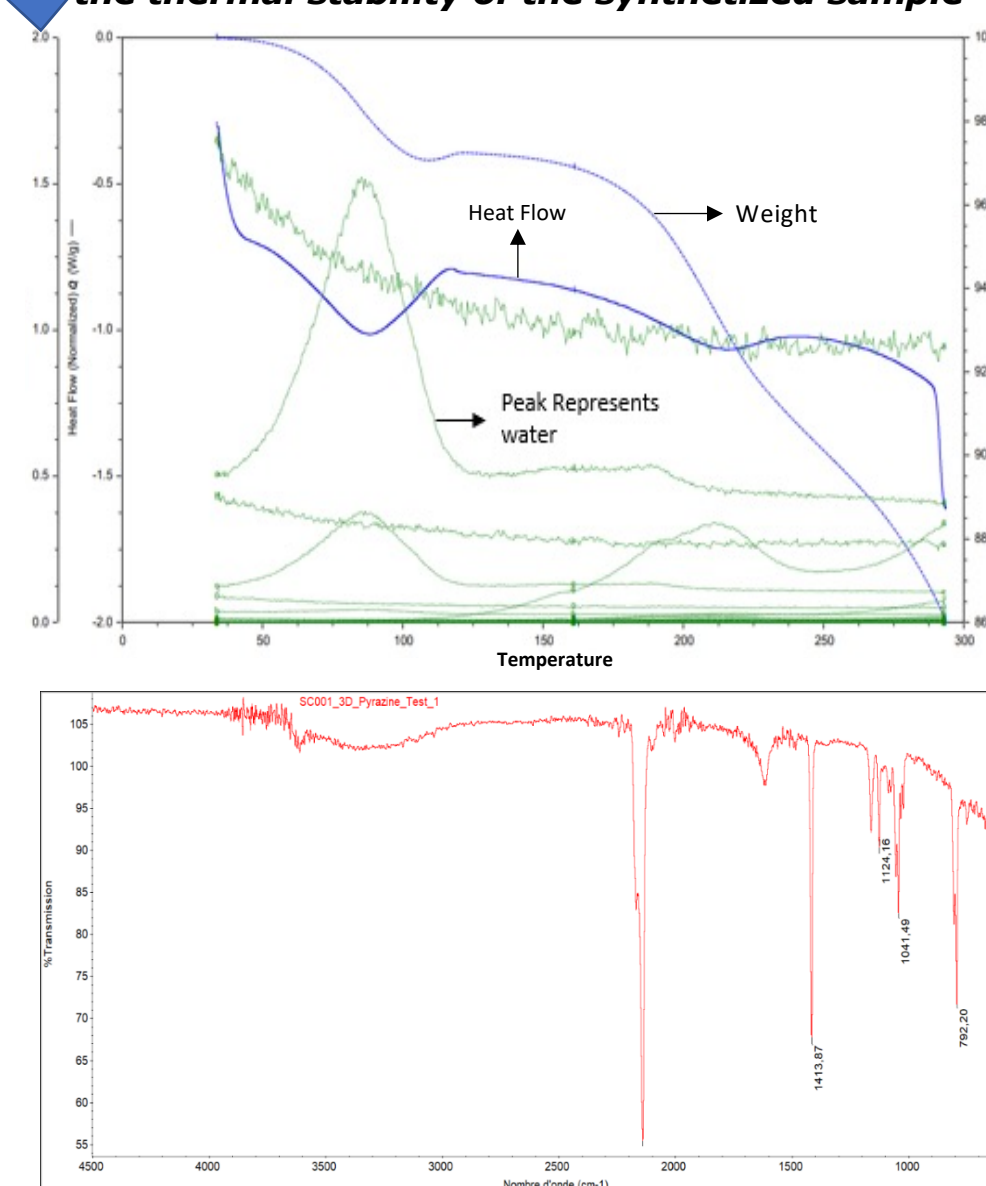
Element	Symbol	Atomic weight	Atoms	Mass percent
Hydrogen	H	1.00794	8	2.4090
Oxygen	O	15.9994	2	9.5597
Carbon	C	12.0107	8	28.7057
Nitrogen	N	14.0067	6	25.1071
Iron	Fe	55.845	1	16.6838
Nickel	Ni	58.6934	1	17.5347



Hydrated structure (as synthesized)

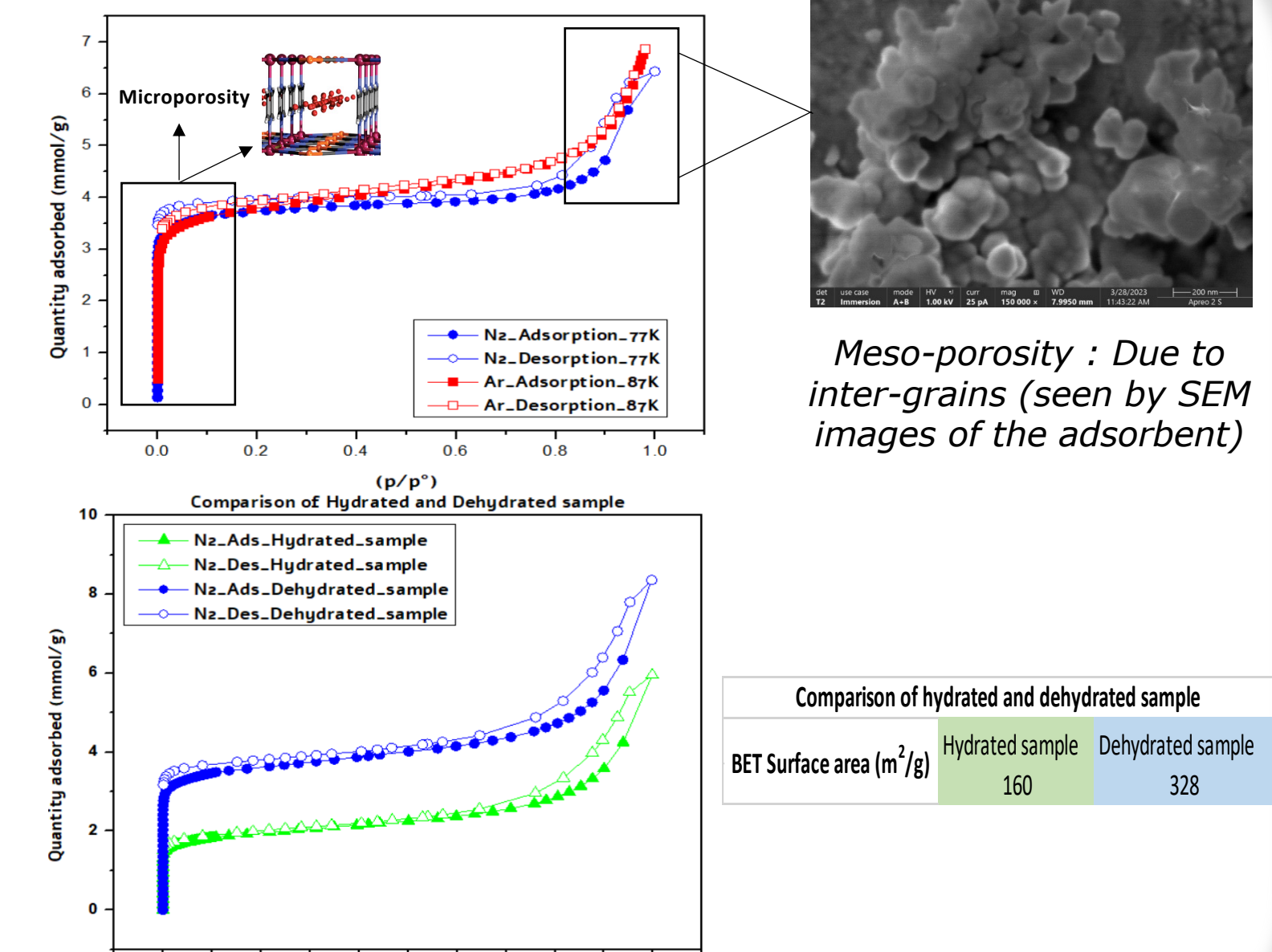
ADSORBENT CHARACTERIZATION

TGA/MS analysis to check the synthesis and the thermal stability of the synthesized sample



IR Spectroscopy to check the contaminants in the sample

Gas Porosimetry : Nitrogen & Argon Adsorption

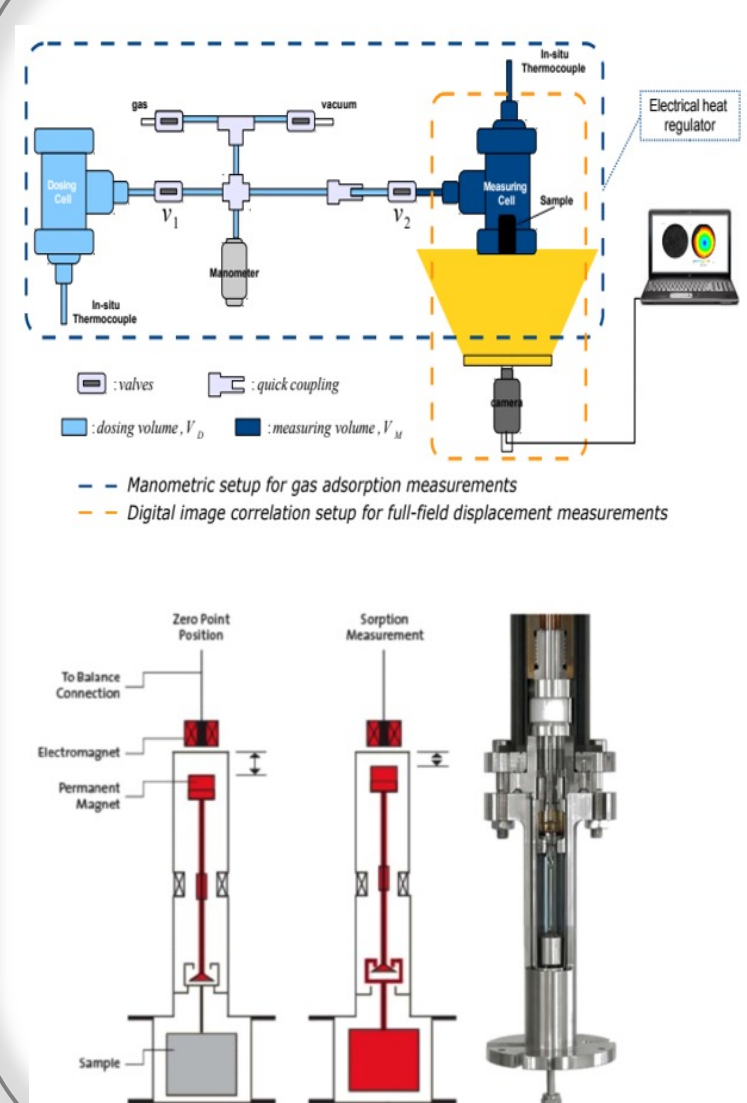


Meso-porosity : Due to inter-grains (seen by SEM images of the adsorbent)

Comparison of hydrated and dehydrated sample		
BET Surface area (m ² /g)	Hydrated sample	Dehydrated sample
	160	328

HIGH PRESSURE CO₂ and CH₄ ISOTHERMS : Measurements and Modelling

Apparatus



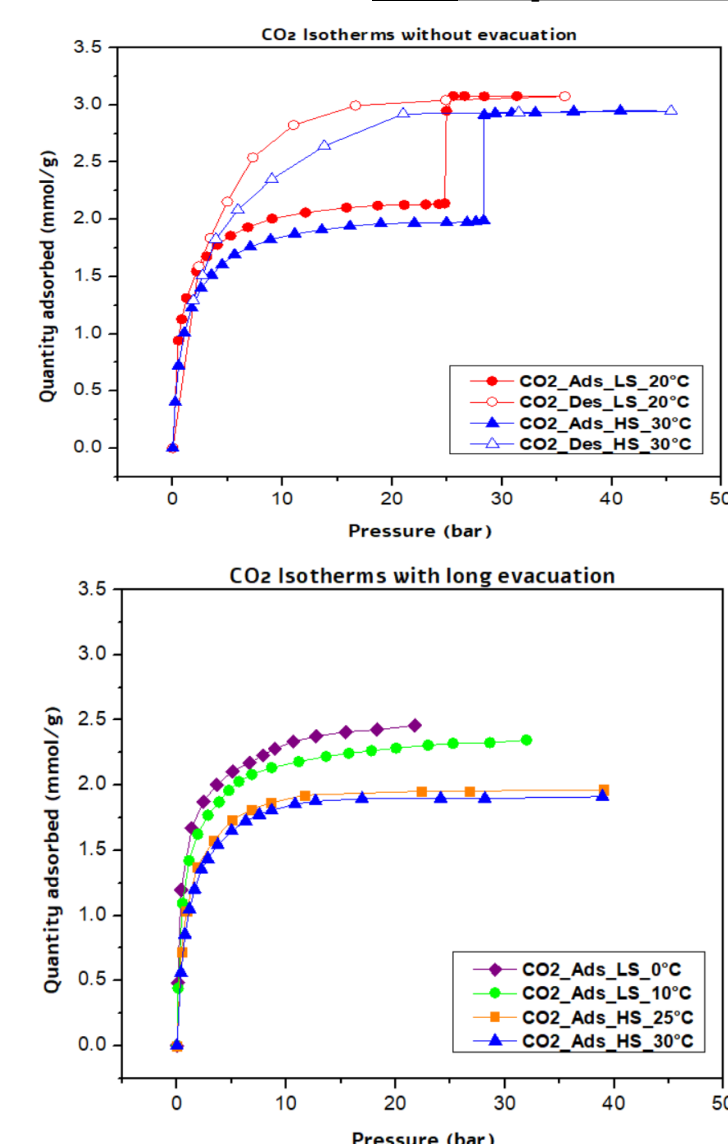
High pressure isotherms (0-60 bar)

➤ *Homemade Manometric setup coupled with DIC [3]*

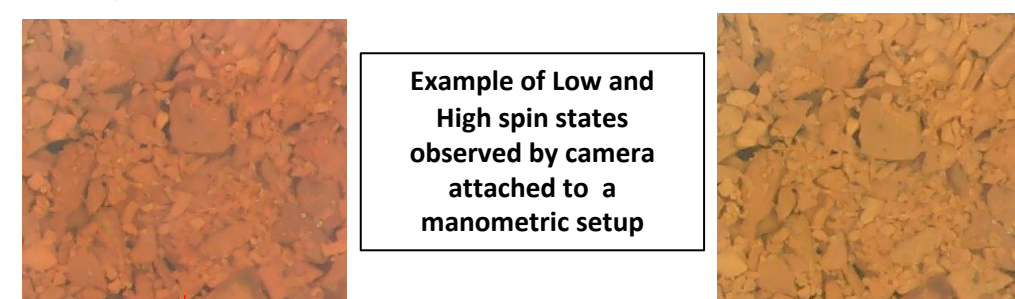
High pressure isotherms (0-150 bar)

➤ *Magnetic Suspension Balance (MSB)*

CO₂ experimental adsorption isotherms



- High pressure CO₂ isotherms are measured for the first time for this material and a sudden "jump" is observed at pressures higher than 20 bar (temperature dependent).
- The "jump" does not correspond to a LS -> HS change as evidenced by no color change in the sample (example of LS -> HS change shown below).
- It is related to the sample as no jump observed when the sample is submitted to a long evacuation under primary vacuum.

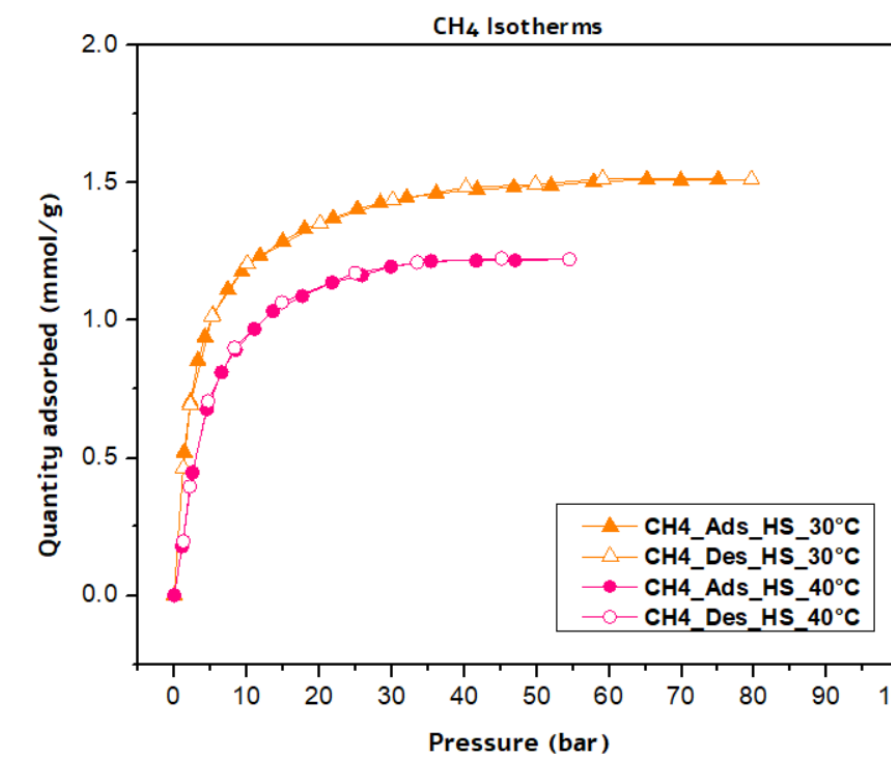


Low spin Mean = 189.35 STD = 17.38

High spin Mean = 192.34 STD = 18.57

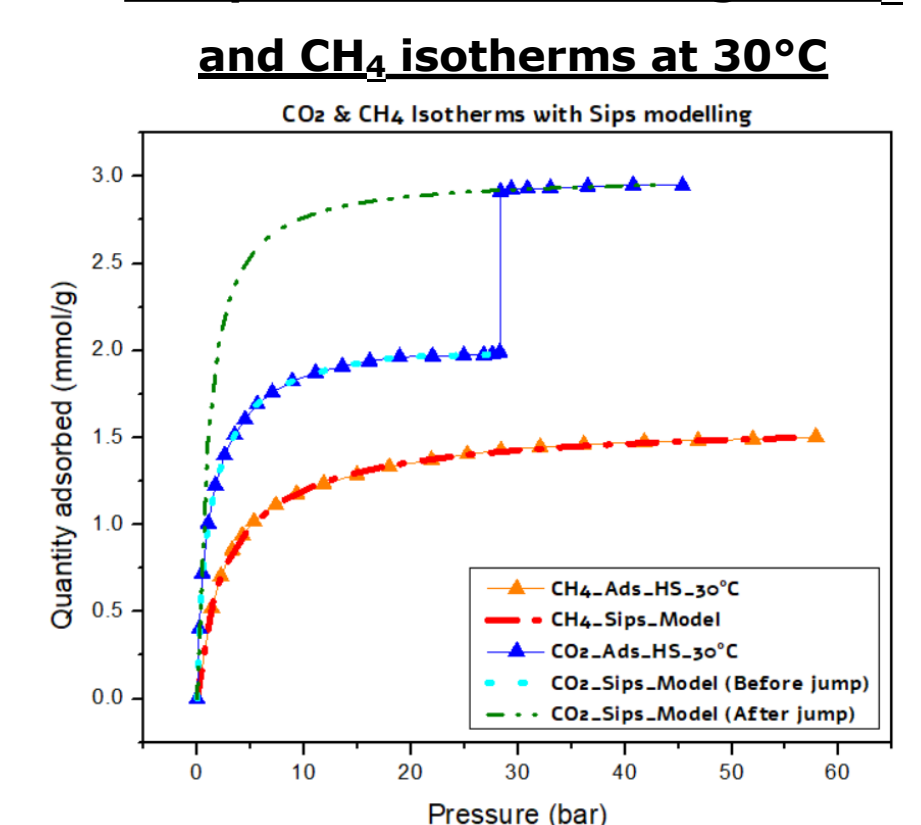
Color Histogram

CH₄ experimental adsorption isotherms



- No "jump" observed whatever the evacuation of the sample.
- Unlike CO₂, adsorption is reversible.

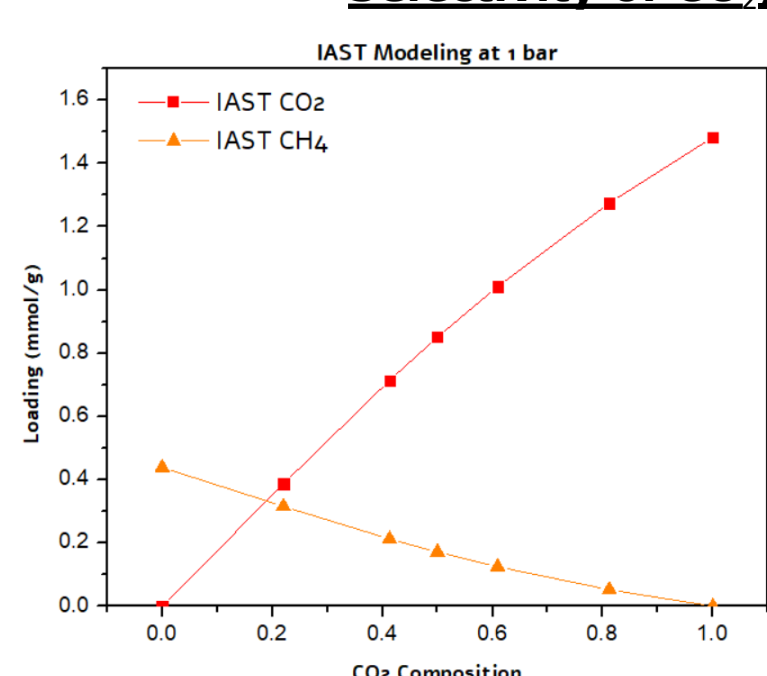
Comparison and modeling of CO₂ and CH₄ isotherms at 30°C



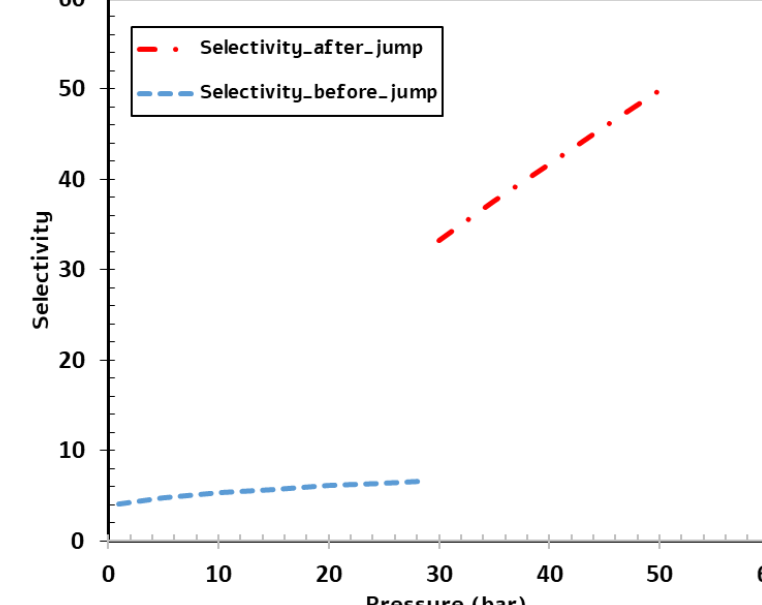
Sips Modeling Parameters			
	CH4 at 30°C	CO2 at 30°C (Before Jump)	CO2 at 30°C (After Jump)
q _m (mmol/g)	1.61	2.13	3.00
b (bar) ⁻¹	0.33	0.84	0.98
n	1.12	1.17	0.93

IAST MODELLING FOR CO₂/CH₄ SEPARATION

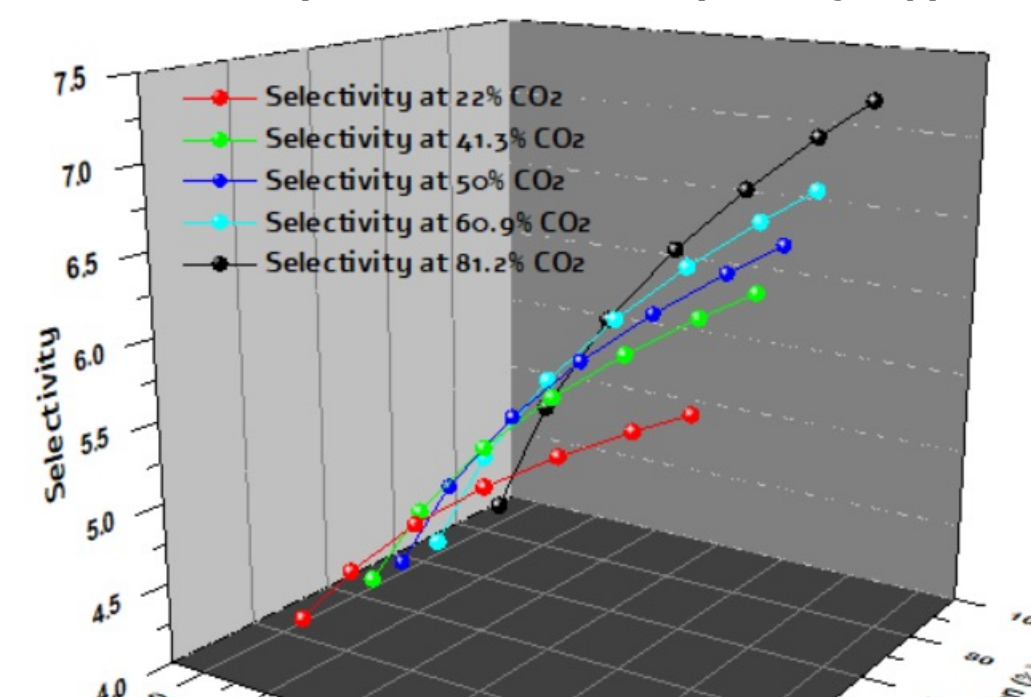
Selectivity of CO₂/CH₄ at 1 bar and 30°C



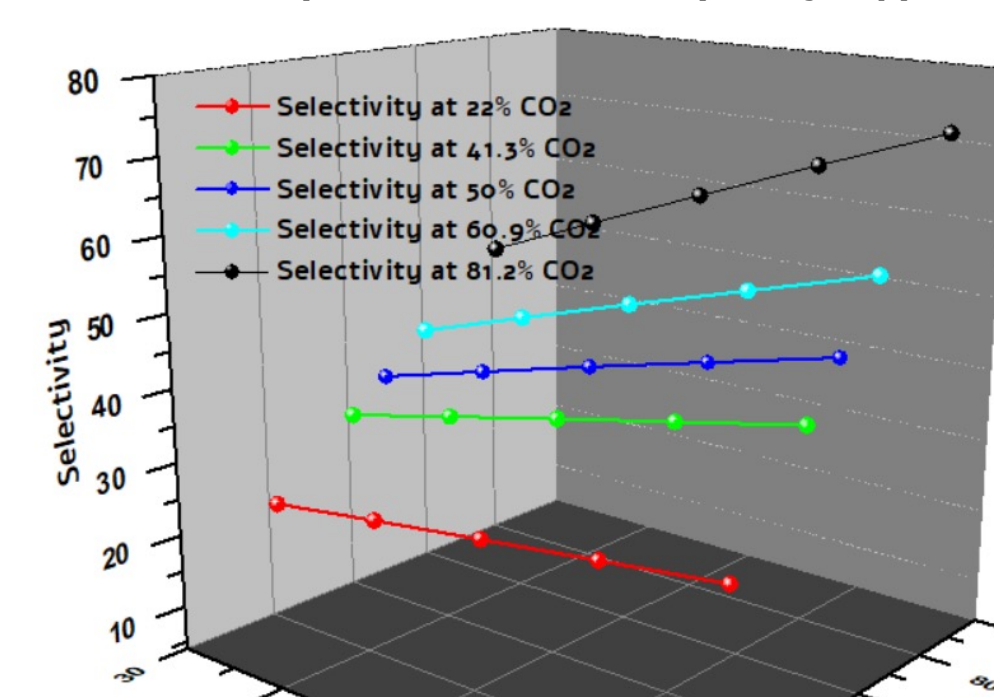
Comparison of CO₂/CH₄ Selectivity at 50% composition



Selectivity of CO₂/CH₄ at 30°C (before jump)



Selectivity of CO₂/CH₄ at 30°C (after jump)



CONCLUSIONS

- The success of [FeNi(CN)₄Pyrazine] synthesis is confirmed by the results of the characterization.
- The gas porosimetry results confirm the microporosity of the adsorbent while the irregular mesoporosity is merely due to the inter-grains (seen by the SEM images).
- The complete removal of water molecules (at a temperature of 120°C, confirmed by TGA analysis) from the cavities of the structure is necessary for the guest adsorption.
- A home-made manometric setup is built to analyze different gas adsorptions at high pressure and at several temperatures while simultaneously visualizing the sample by means of a camera placed near the sapphire window.
- A pronounced jump is observed for the first time for CO₂ capture at high pressure. It can be attributed to changes in the framework structure while not being a classical spin-state change. The pressure of this structure change depends on temperature.
- IAST modeling shows an impressive selectivity of CO₂ thanks to this change of structure.

REFERENCES

- V. Niel, J. M. Martinez-Aguado, M. C. Muñoz, A. B. Gaspar, and J. A. Real, "Cooperative Spin Crossover Behavior in Cyanide-Bridged Fe(II)-M(II) Bimetallic 3D Hofmann-like Networks (M = Ni, Pd, and Pt)," *Inorg. Chem.*, vol. 40, no. 16, pp. 3838-3839, Jul. 2001, doi: 10.1021/10010259y.
- P. D. Southon et al., "Dynamic Interplay between Spin-Crossover and Host-Guest Function in a Nanoporous Metal-Organic Framework Material," *J. Am. Chem. Soc.*, vol. 131, no. 31, pp. 10998-11009, Aug. 2009, doi: 10.1021/ja902187d.
- L. Perrier, F. Planter, and D. Grégoire, "A novel experimental setup for simultaneous adsorption and induced deformation measurements in microporous materials," *Rev. Sci. Instrum.*, vol. 88, no. 3, p. 035104, Mar. 2017, doi: 10.1063/1.4977595.

E2S UPPA hub Newpores supported by the "Investissements d'Avenir" French programme managed by ANR (ANR-16-IDEX-0002) is acknowledged for the funding of this project and R. Minhas PhD grant. TEOT is acknowledged for financial support.