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

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

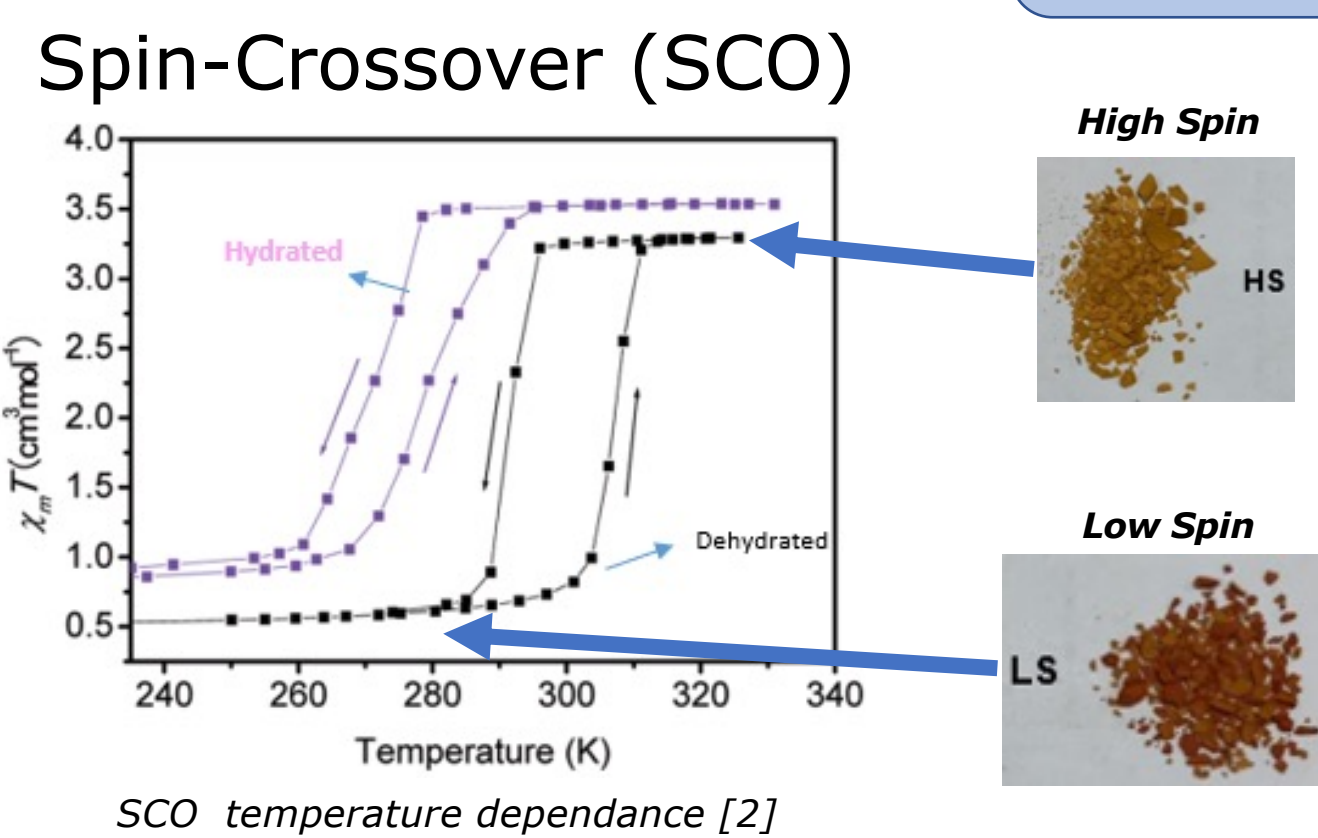
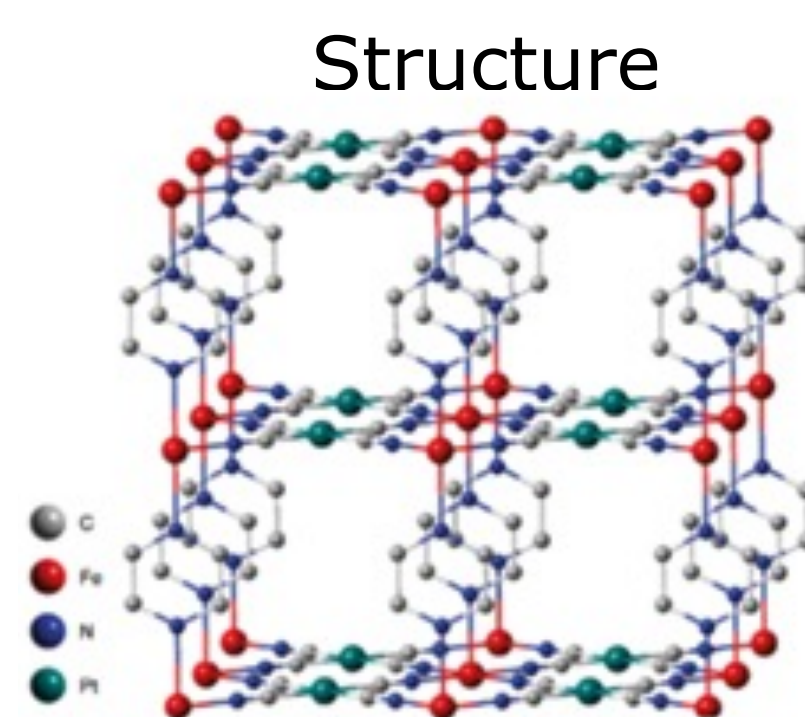
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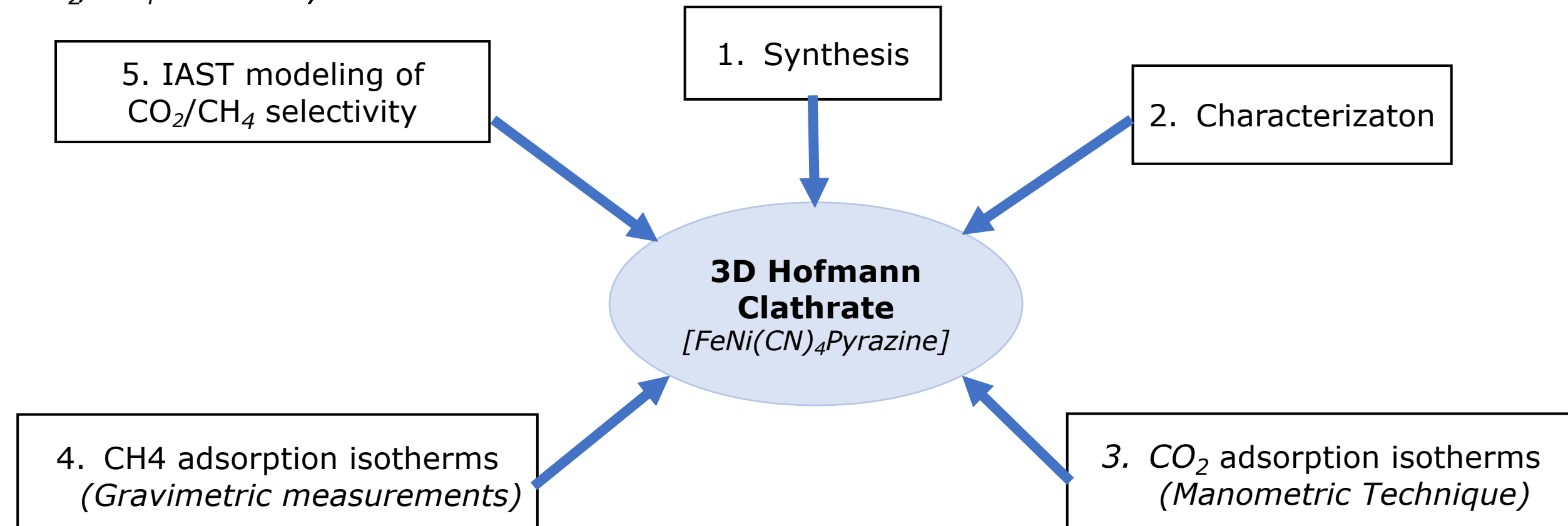
3D Hofmann Clathrate

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.



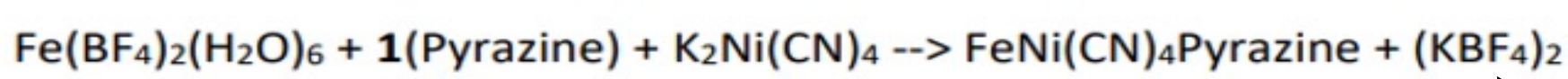
To address the increasing energy consumption and serious environmental problems, it is critical to develop efficient and clean energy conversion and storage devices. In this context, among various categories of materials, a 3D structured Spin Crossover (SCO) MOF, [FeNi(CN)₄Pyrazine] [2], in the family 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.

ADSORBENT SYNTHESIS

ADSORBENT CHARACTERIZATION

Chemical Reaction

The sample is synthesized using pyrazine ligands.



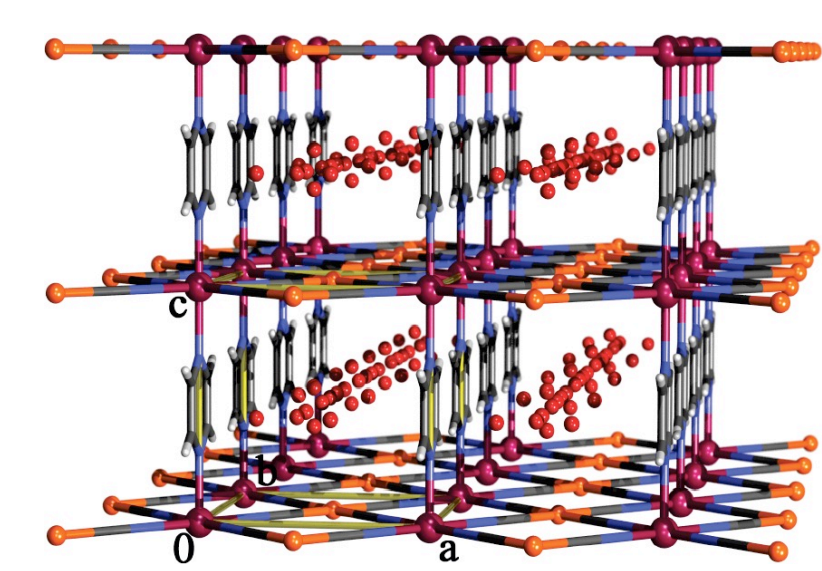
Immediately precipitates as orange powder

Removal of KBF₄ upon washing with pure water or using Centrifugator

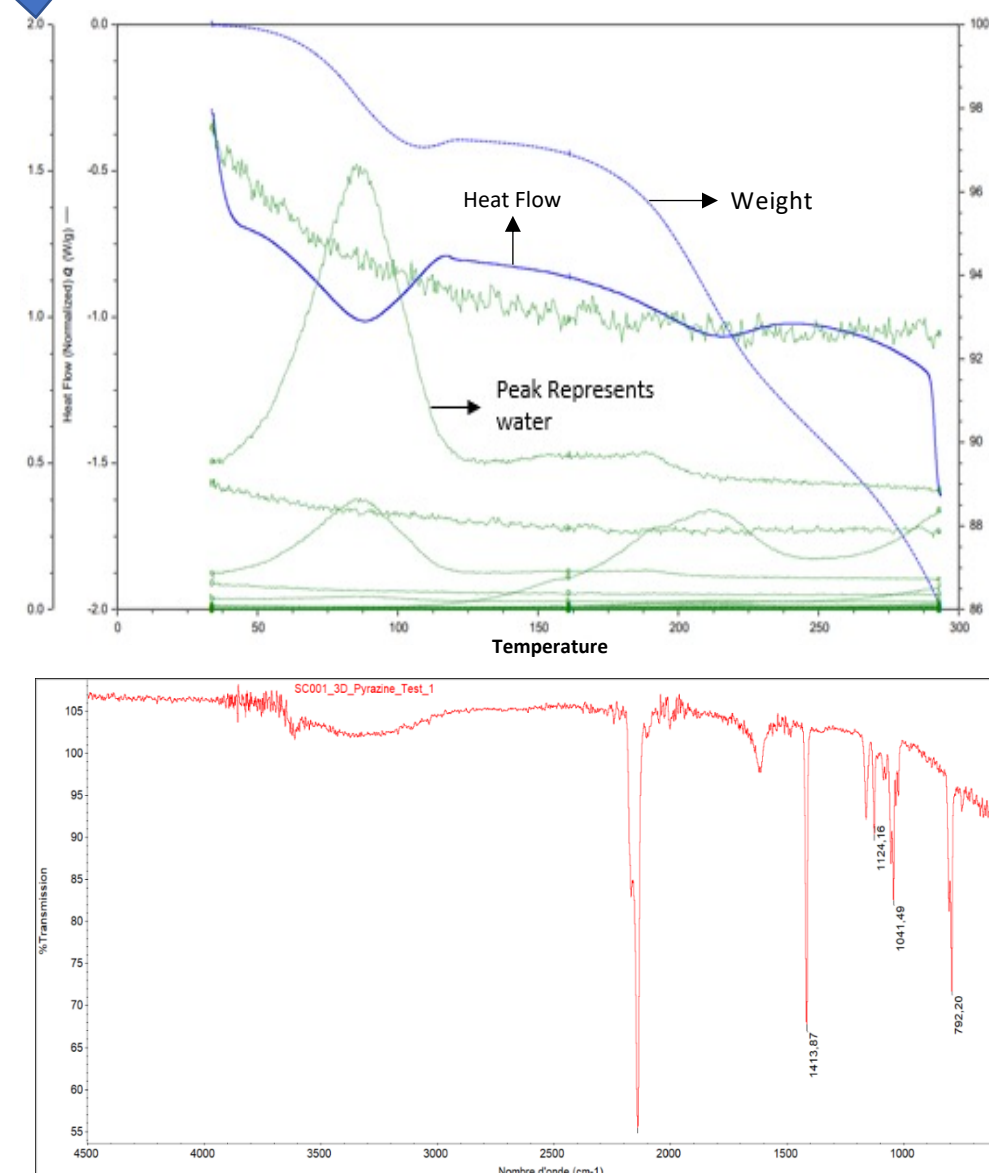
Chemical composition of the adsorbent

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

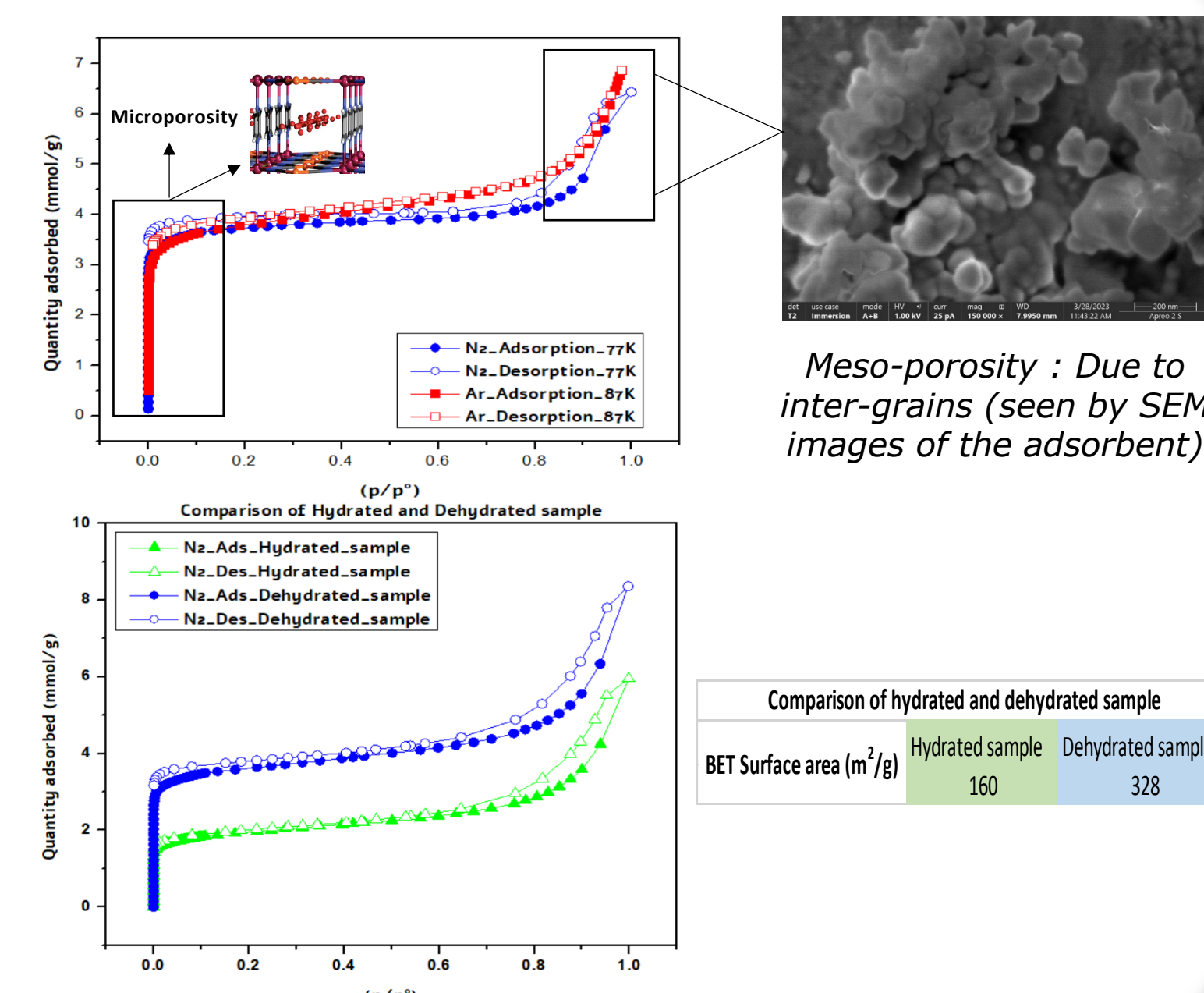


TGA/MS analysis to check the synthesis and the thermal stability of the synthesized sample



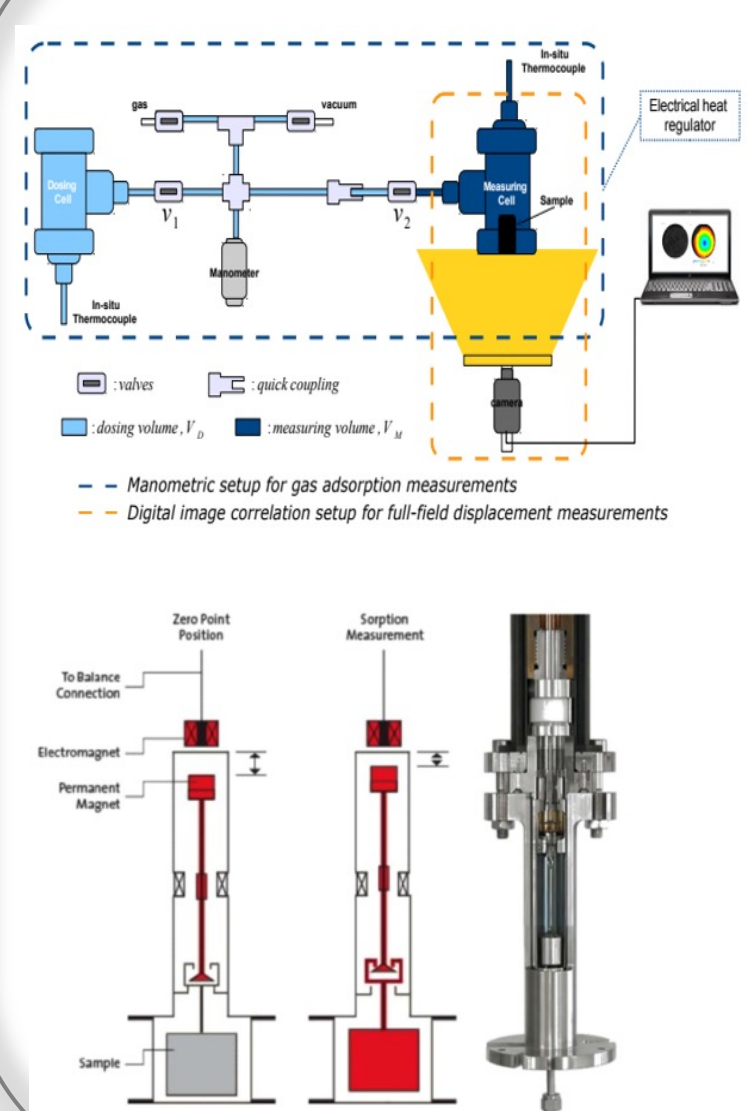
IR Spectroscopy to check the contaminants in the sample

Gas Porosimetry : Nitrogen & Argon Adsorption



HIGH PRESSURE CO₂ and CH₄ ISOTHERMS : Measurements and Modelling

Apparatus



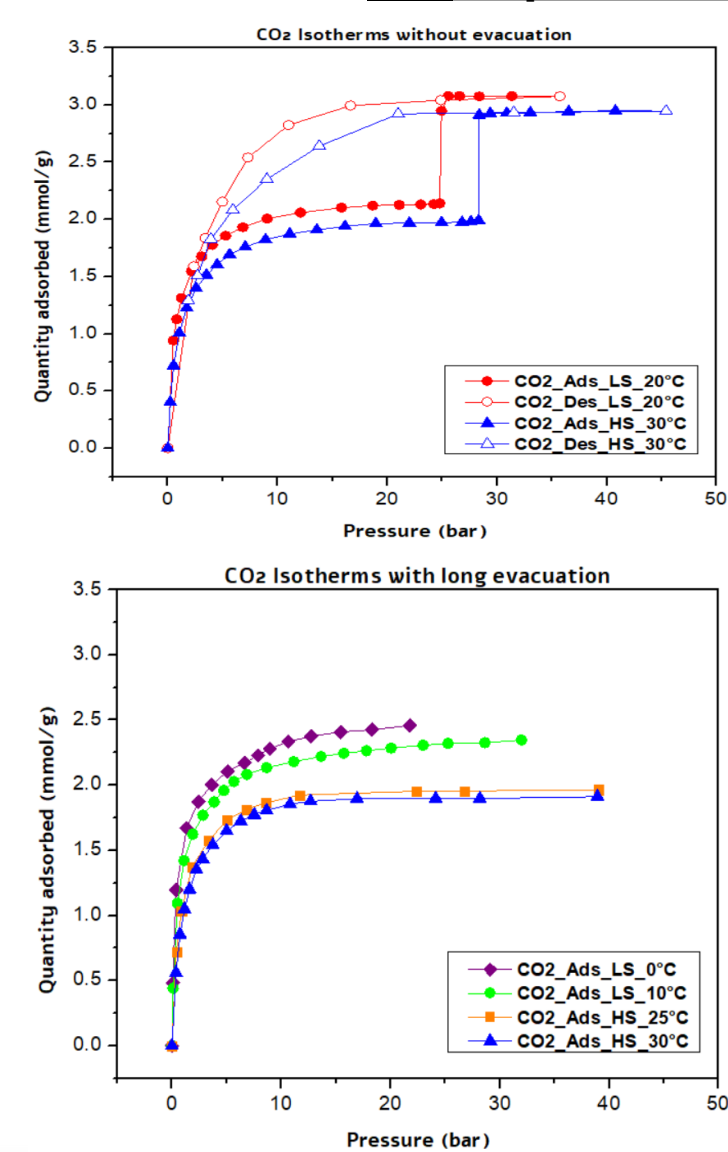
High pressure isotherms (0-60 bar)

Homemade Manometric setup coupled with DIC [3]

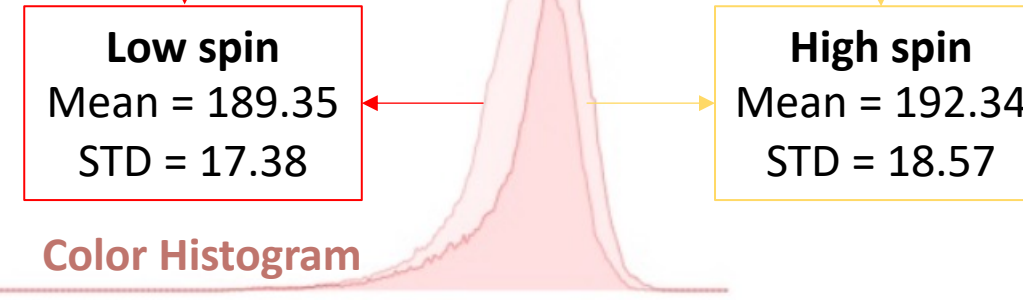
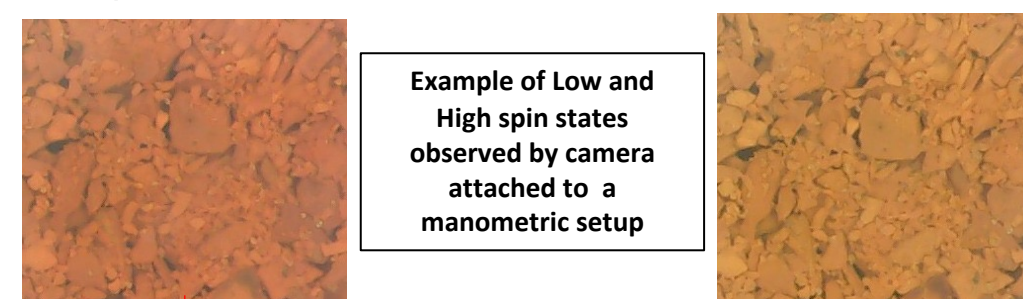
High pressure isotherms (0-150 bar)

Magnetic Suspension Balance (MSB)

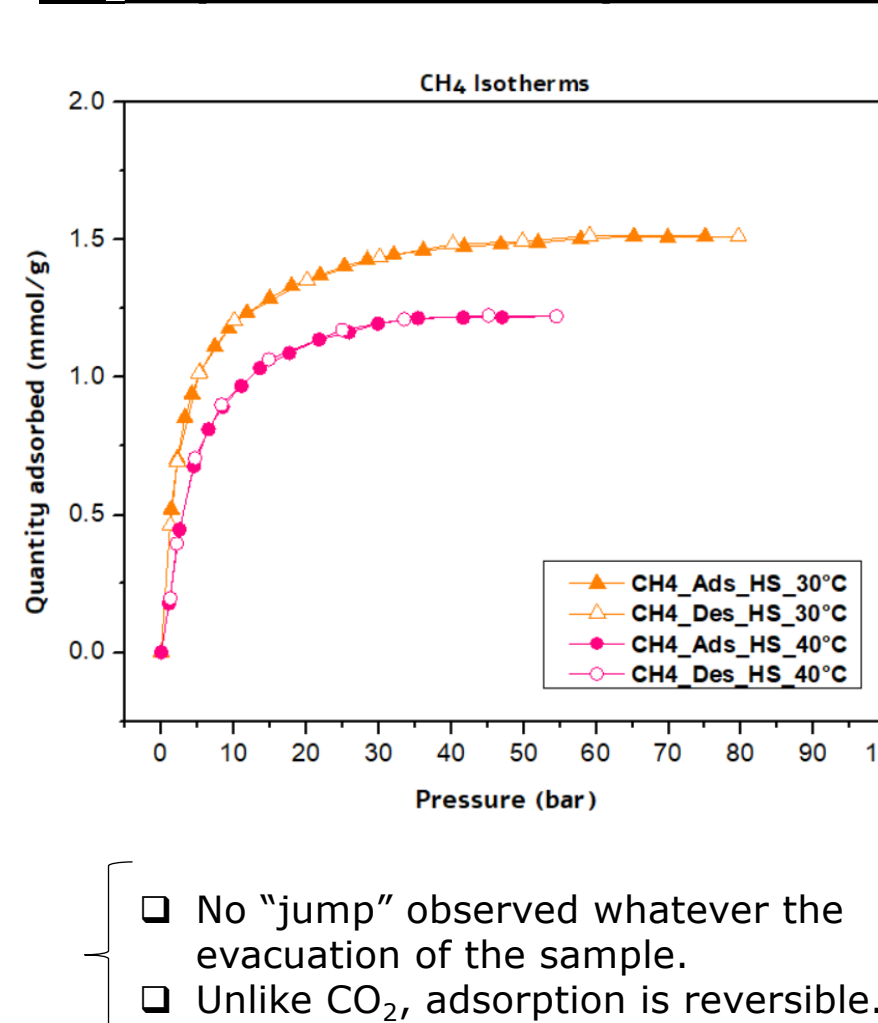
CO₂ experimental adsorption isotherms



- 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.

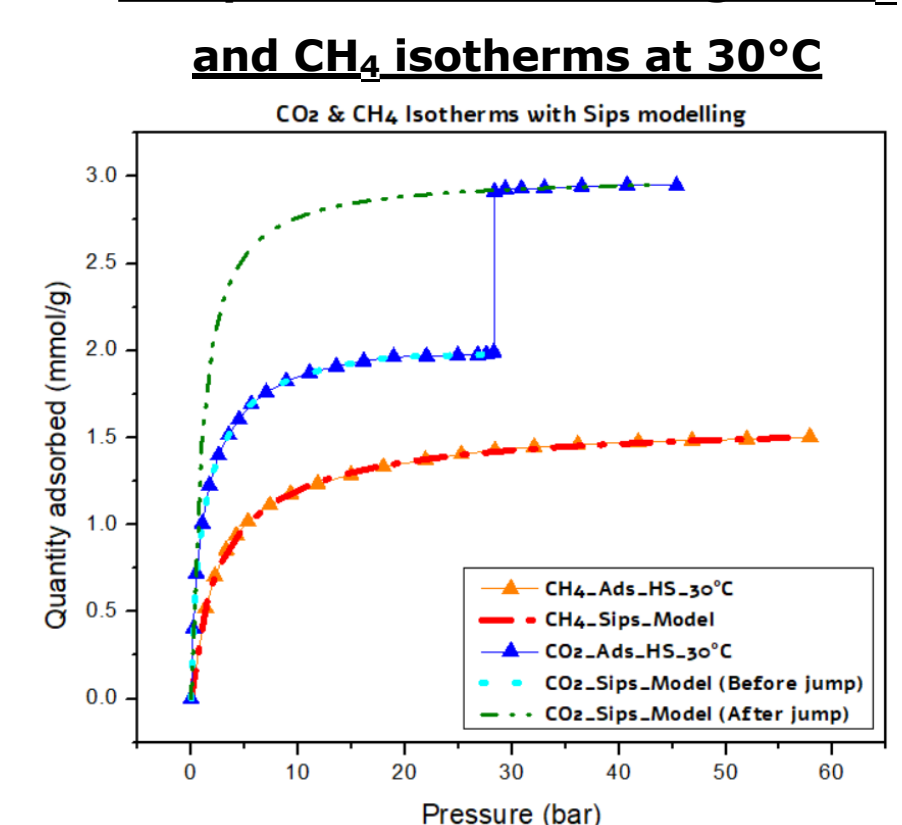


CH₄ experimental adsorption isotherms



- 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

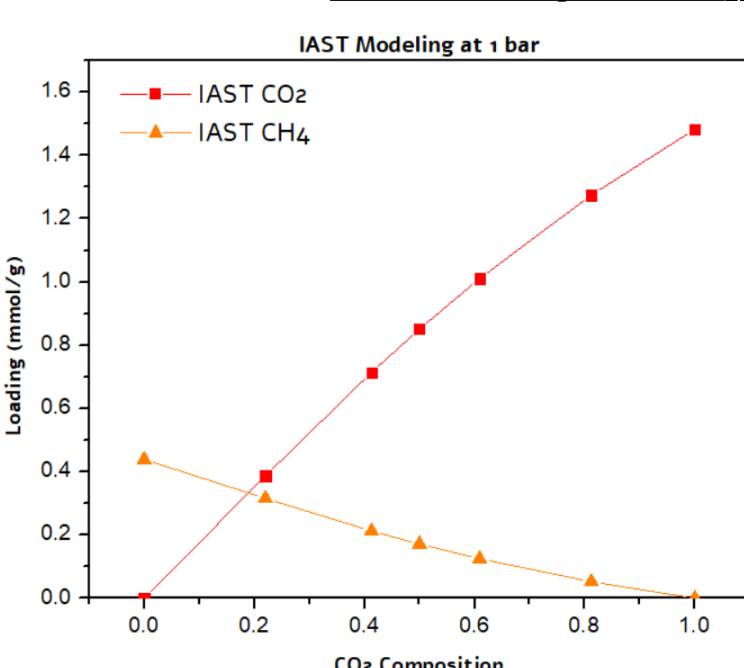


Sips Modeling Parameters	CO ₂ & CH ₄ Isotherms with Sips modelling		
	CH ₄ at 30°C	CO ₂ at 30°C (Before Jump)	CO ₂ at 30°C (After Jump)
q _m (mmol/g)	1.61	2.13	3.00
b (bar) ⁻¹	0.33	0.84	0.98
n	1.12	1.17	0.93

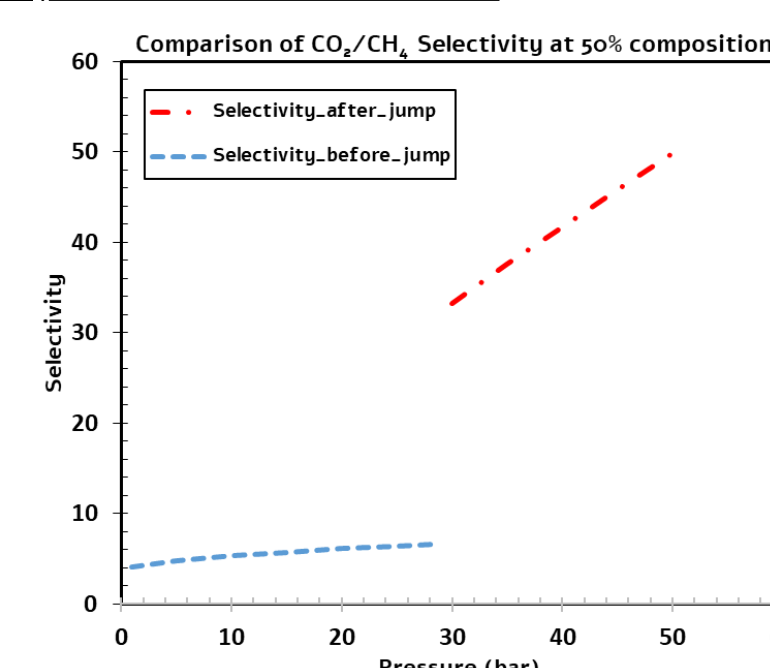
IAST MODELLING FOR CO₂/CH₄ SEPARATION

CONCLUSIONS

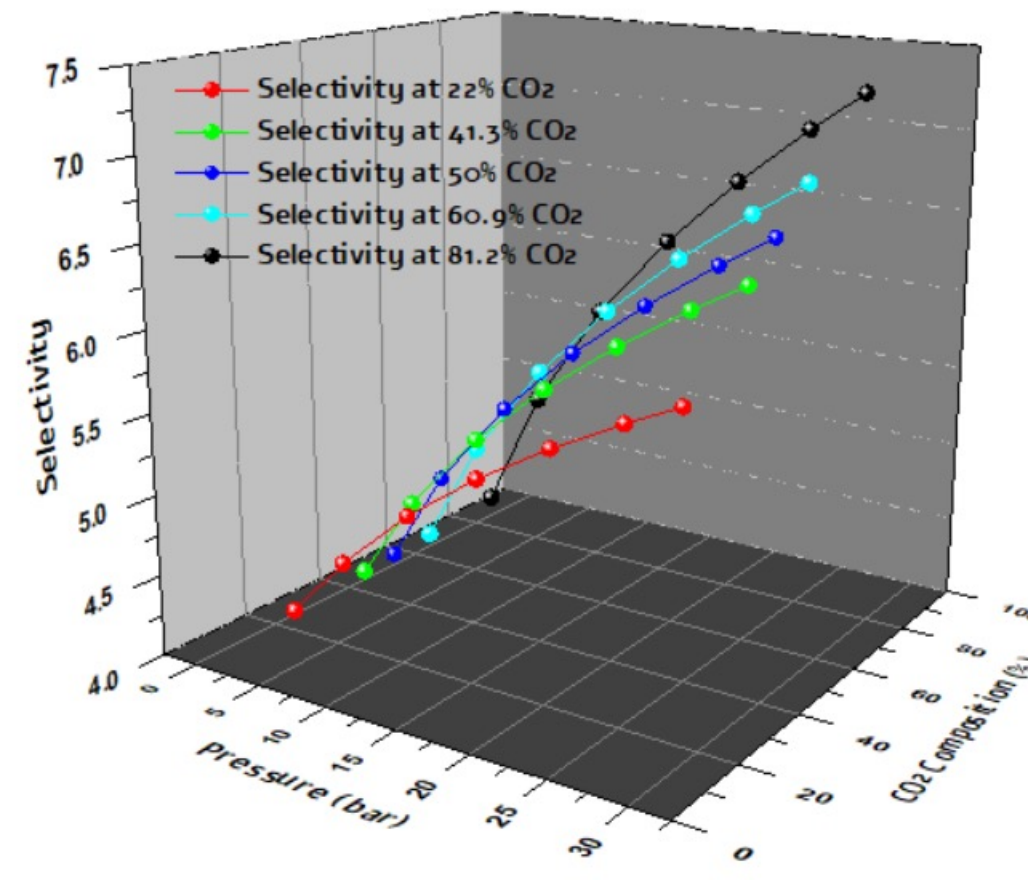
Selectivity of CO₂/CH₄ at 1 bar and 30°C



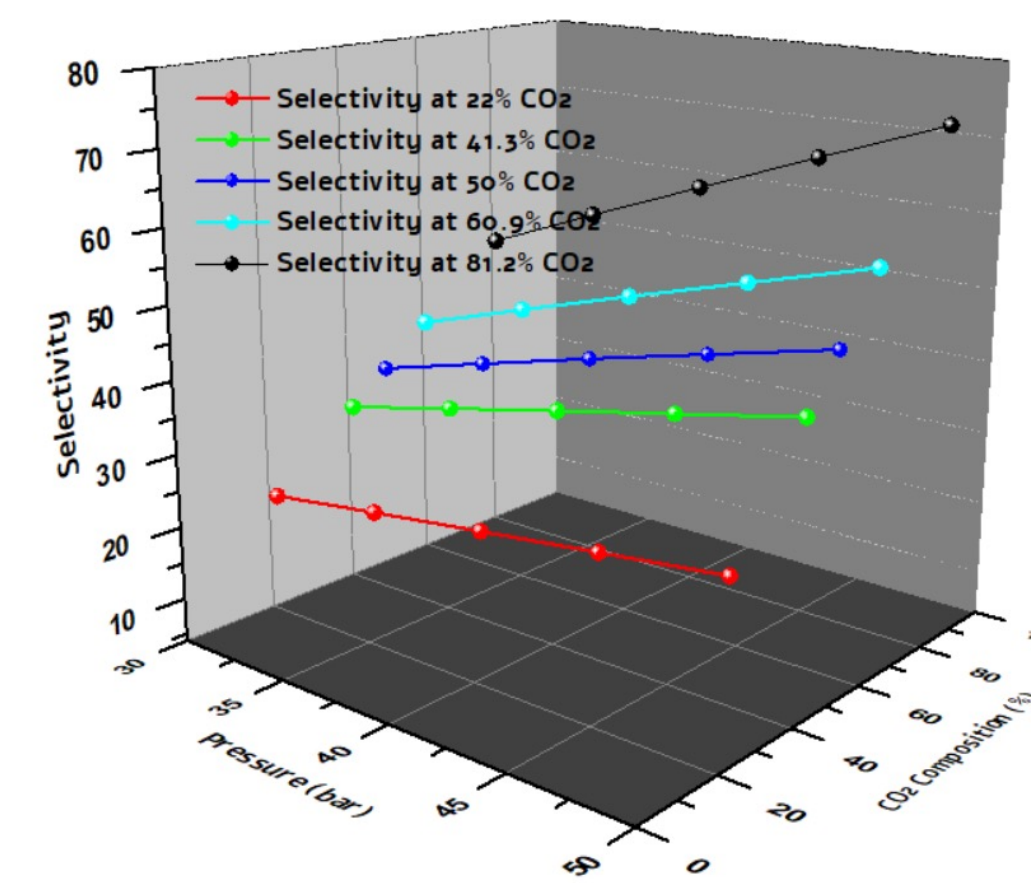
Comparison of CO₂/CH₄ Selectivity at 50% composition



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



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



- 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 material 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.

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