Supercritical Impregnation in Carboxylated Based MOFs

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Metal-Organic Frameworks (**MOFs**) are porous materials made of metal clusters connected by organic linkers, typically dicarboxylate ligands. These materials have been intensively studied in recent years due to the distinctive properties such as high surface area, surface functionalization and structural flexibility for some of them. The potential applications are broad in fields such as catalysis, separations or drug delivery.[1]

The supercritical CO_2 (sc-CO_2) has been recently used to activate MOFs, i.e. the removal of the excess of ligand and solvent from the pores, in substitution of procedures like calcination which can damage the crystallinity. Through this technology the highest surface area has been reported, around 7000 m^2/g.[2] Therefore supercritical fluids seem to be of potential interest in MOFs processing. In our case we have tested the impregnation with supercritical CO_2 in MOFs, in opposition to liquid impregnation which requires post processing steps, as separation and drying of the material.

In this work, sc-CO_2 have been used to impregnate caffeine in **MIL-53(Al),** which is composed by terephthalate linkers and Al^{3+}. The caffeine properties in supercritical fluids are widely reported because of the industrial use in coffee decaffeination and MIL-53(Al) is a flexible and very stable material of a MOF family with demonstrated use in controlled release.[3]

In Figure 1 the loading values of caffeine for different impregnation times with sc-CO_2 are shown. In liquid impregnation, a maximum loading of **14%** was reached for 24 h, lower than the **24%** achieved in sc-CO_2. It was more remarkable the difference in the other tested material, **Mg-MOF-74** for which the loading was of **27%** in sc-CO2 for 24 h, while the loading was **0%** in liquid impregnation for the same time.

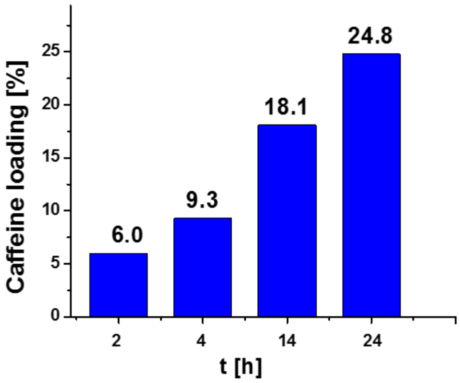

Figure 1. Loading values of caffeine in MIL-53(Al) for different impregnation contact times in sc-CO_2 at 40ºC and 100 bar.

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SUPERCRITICAL IMPREGNATION IN CARBOXYLATED-BASED MOFs

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1 INTRODUCTION

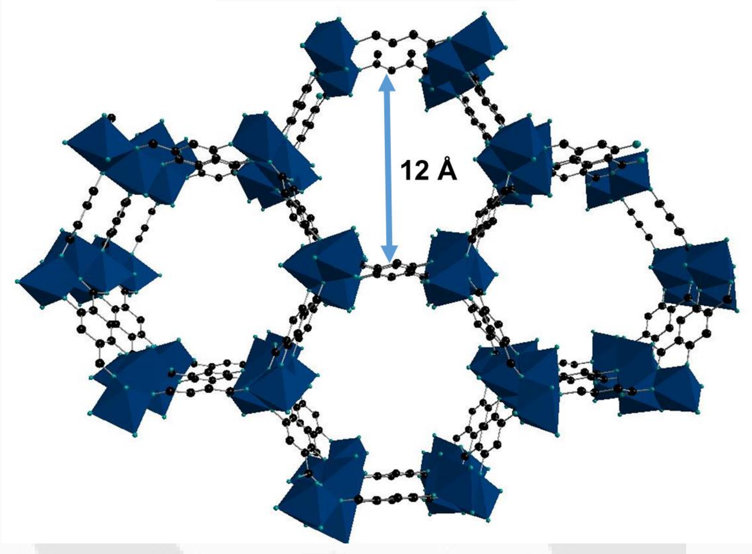
Metal-Organic Frameworks (MOFs) are actively studied due to their characteristics of permanent porosity, high specific surface area and large number of potential applications in fields such as catalysis, separations or drug delivery. The supercritical CO_2 (sc-CO_2) has been recently used to activate MOFs, i.e. the removal of the excess of ligand and solvent from the pores, in substitution of procedures like calcination which can damage the crystallinity. Through this technology the highest surface area has been reported. Therefore supercritical fluids seem to be of potential interest in MOFs processing.
In our case we have tested the impregnation with supercritical CO_2 in MOFs, in opposition to liquid impregnation which requires post processing steps, as separation and drying of the material. Additionally and taking into account the reduced pore size, the accessibility by conventional methods to the whole area is reduced. We tested the impregnation of caffeine in two carboxylated based MOF: **MIL-53(Al)** is a flexible material that adapts its porosity to the guest with a pore size of 8.5 Å in the *ht* form (after calcination) and 2.6x13.6 Å in the *lt* form (once it is hydrated) and **Mg-MOF-74** shows a rigid honeycomb structure of 12Å. Finally we compared the loading results with conventional liquid impregnation for the same contact time.

MOF synthesis
- **Solvothermal**
- **Hydrothermal**
- Microwave assisted
- Ultrasounds assisted

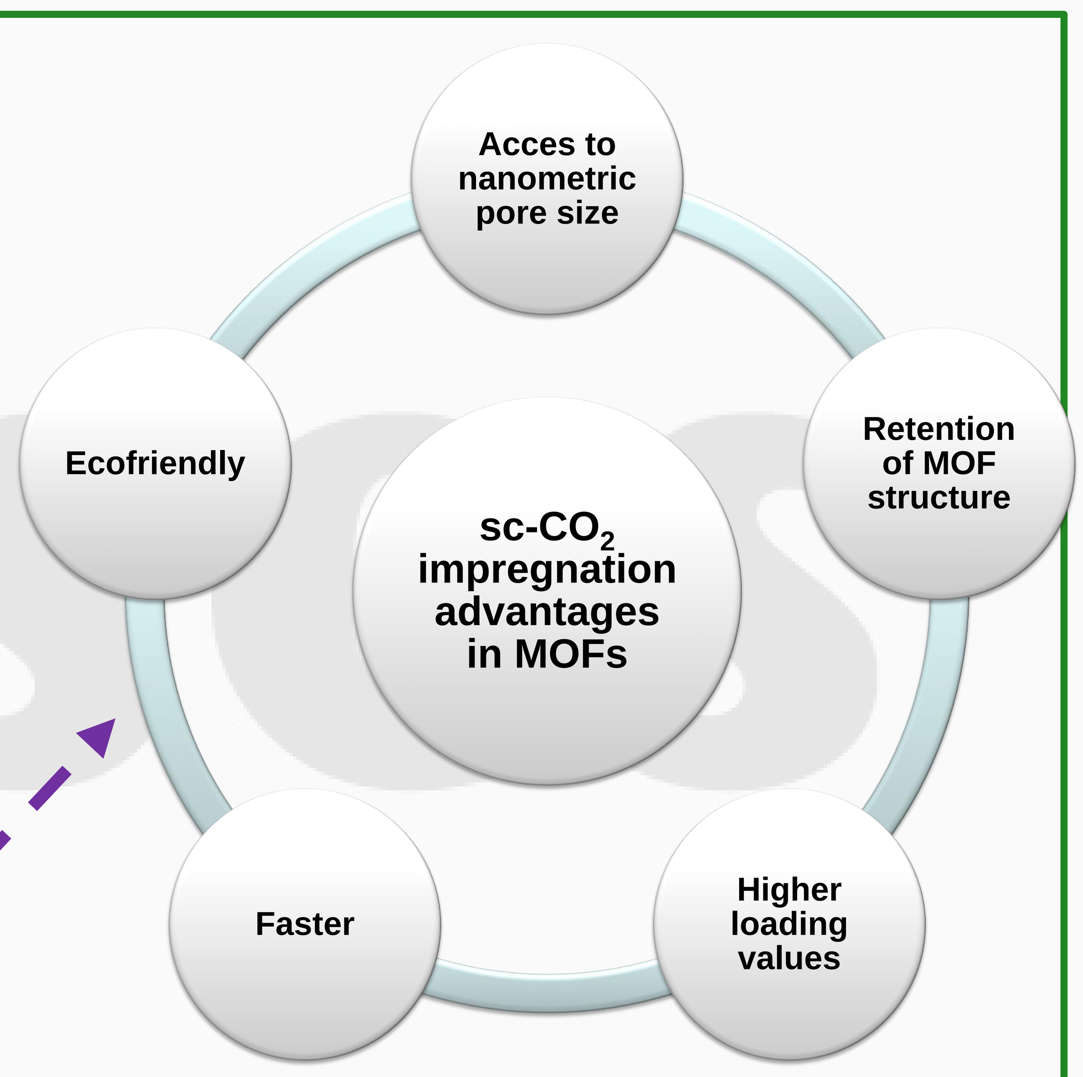
MOF activation
- Calcination → structure damage
- Solvent exchange → poorly efficient
- **Supercritical drying** → highest surfaces areas

Impregnation → **Use of sc-CO_2 as solvent for impregnation in potentially biocompatible MOFs**

Mg-MOF-74

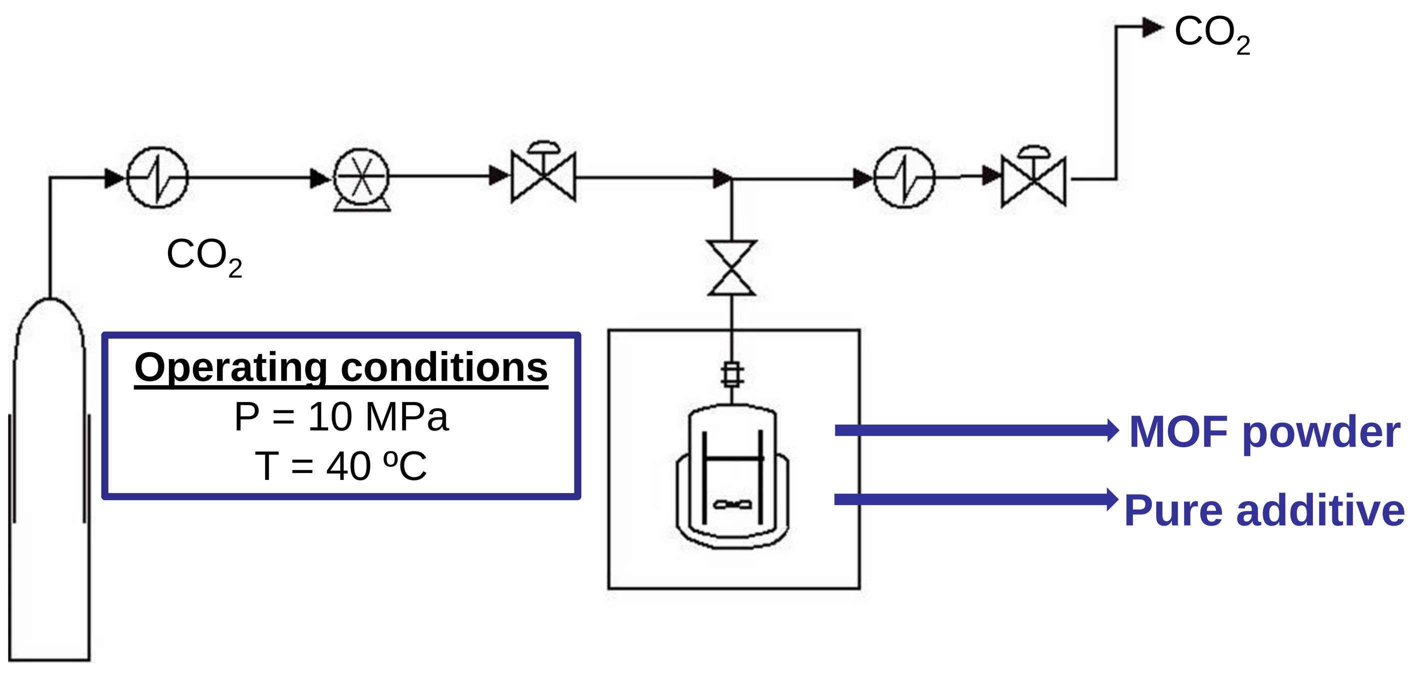


- ↑ High CO_2 storage capacity
- ↑ Relatively easy synthesis
- ↑ Potential biocompatibility
- ↓ Higly hydrated
- ↓ Porosity not accesible by normal liquid impregnation



2 EXPERIMENTAL SET-UP AND METHODS

The experimental set-up consists in a batch reactor which is designed to operate up to 15 MPa inside an oven. The MOF powder, MIL-53(Al) or Mg-MOF-74, and the additive, caffeine, are physically separated, and the additive is solubilized at the selected conditions in sc-CO2 meanwhile the MOF remains as powder.
Different contact times were tested and the results were compared with the loading performance in liquid phase (ethanol) for the same time at 25ºC.



Analysis and characterization

1) Characterization for raw and loaded materials:
- ✓Powder XRD (crystallinity before and after the process)
- ✓TGA (activation of MOFs)
- ✓SEM (morphology and particle size before and after the process)

2) Compositional analysis for the extracted additives:
- ✓ CG-MS (compositional analysis for liquid).

3 RESULTS AND DISCUSSION

- For the same contact time (24 h) by liquid and supercritical impregnation, the loading achieved with sc-CO_2 is higher for MIL-53(Al). It is remarkable that in case of Mg-MOF-74 it was only possible the loading with sc-CO_2 (no loaded caffeine was found by liquid impregnation) (Fig 1).

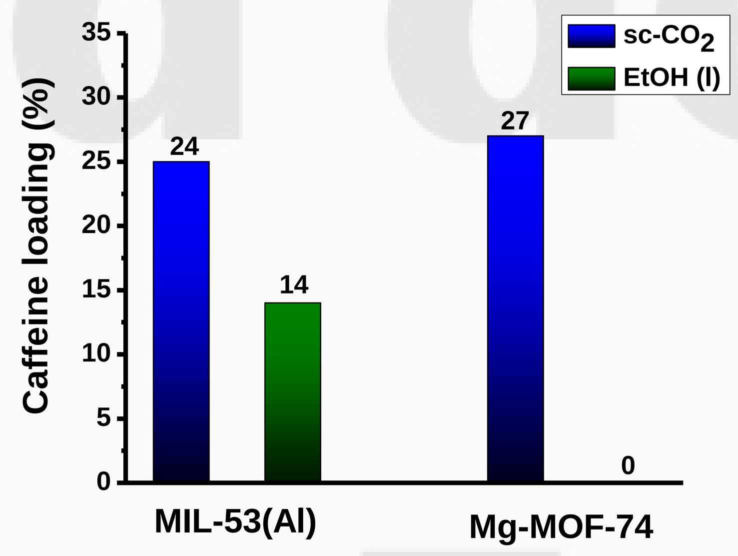


Figure 1.

- The TGA graph (see Fig 2) shows the difference between the two samples in which the degradation step for caffeine appears only by sc-CO_2 impregnation for Mg-MOF-74

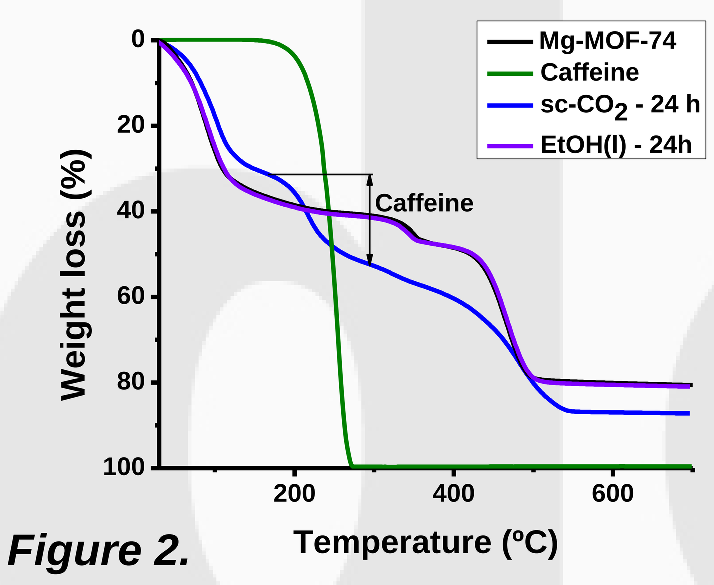


Figure 2.

- The relatively mild conditions of sc-CO_2 impregnation allows to preserve MOF structure. In both methodologies for the tested conditions, the Mg-MOF-74 structure was preserved. In the case of MIL-53(Al), the pore size is adapted to the additive inside therefore XRD changes were observed but no crystalized caffeine was found (see Fig 3).

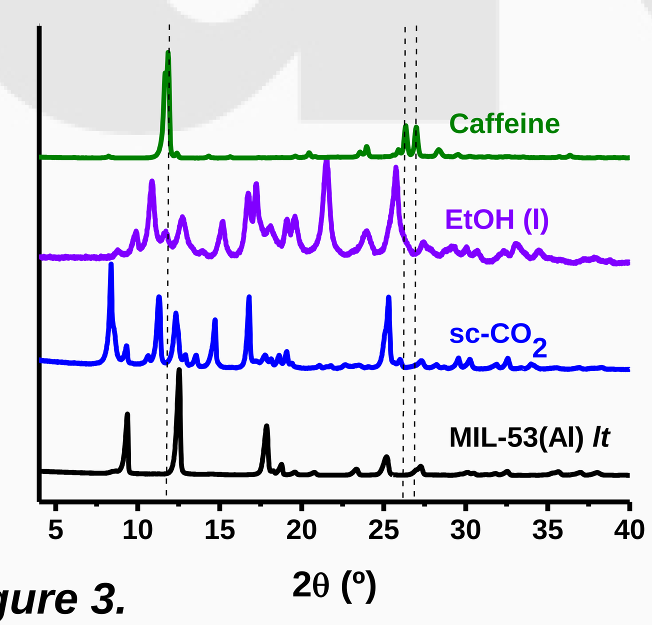


Figure 3.

4 CONCLUSIONS

- High caffeine loading (> 20%) have been achieved in both carboxylated based MOFs, MIL-53(Al) and Mg-MOF-74, by sc-CO_2 impregnation.
- It has been shown that supercritical CO_2 impregnation is a more effective for impregnation in MOFs than conventional liquid impregnation for drug delivery.

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