HIERARCHICALLY POROUS 3D SHAPING OF METAL-ORGANIC FRAMEWORK

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Metal-Organic Frameworks (MOFs) have attracted a lot of attention over the past two decades mainly because their unique set of properties, notably their high porosity and surface area, are useful for gas storage and separation, but these materials are also well suited to the decontamination of liquid effluents. They are synthesized as crystalline solid powders but, for a broad applicability, producing MOFs as handleable materials is crucial. Furthermore, the main challenge for their use in fix bed processes consists in creating and controlling a meso- and macroporous network in the body of the material while ensuring the MOF's micropores remain accessible.[1] Different routes have been proposed to shape MOFs in this way, namely various mechanical processes (granulation, pressing, extrusion or spray drying), finely controlled metal-organic gel formation, thin film deposition, and sacrificial templating.

Our strategy was shaping MOF monolith by using Pickering emulsions.[2] The emulsions are stabilized by MOFs solid particles with a high internal phase emulsions (HIPE) (Figure 1). Then, by growing a solid skeleton in the continuous phase to support the global structure and eliminating the internal phase, a macro porous material can be obtained with the pore size defined by the size of the initial droplets of the emulsion.

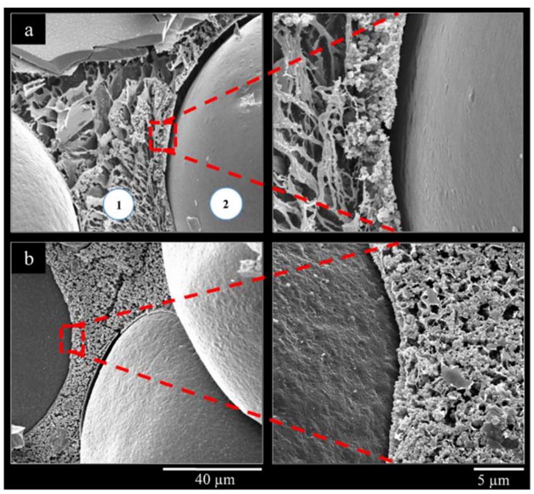

Figure 1. Cryo scanning electron micrographs of emulsions with a paraffin volume ratio of 0.8 v/v and MOFs concentrations of (a) 1 wt.% and (b) 3.5 wt.%. (1) Continuous aqueous phase concentrated in MOFs and (2) oil droplet.

Controlling the properties of the emulsion was crucial both to optimizing the microstructural design of the MOF-functionalized materials and to ensuring that the fluid is workable into an appropriate structure (e.g. by extrusion or additive manufacturing) without any degradation of the internal microstructure and to obtain a rigid monolith (Figure 2).[3]

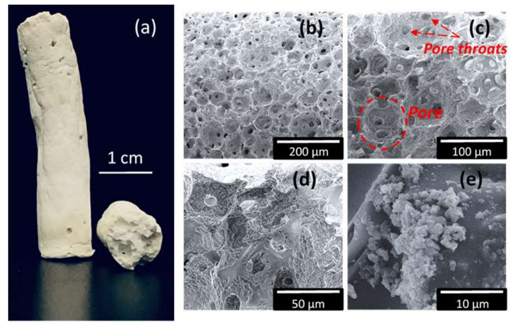

Figure 2. (a) Photograph of the M100/10/0.5 monolith, seen from the front and from below; (b-e) SEM images of the M100/10/0.5 monolith at different magnifications

We are also developing method to shape porous MOFs materials by using 3D-printers.[4] Different strategies are ongoing but our first effort has been focused on direct-ink writing (DIW). In this technique, the extruder of the printer will be replaced to support a syringe connected to a peristaltic pump to deposit directly a paste (ink) containing the MOF on the hot bed of the printer conducting to the solidification of the ink. Additive formulation are often composed of solvent/thermosetting polymers/adhesive polymers. Such formulation is close to those that we have used to form monoliths by Pickering emulsion and need a research effort to optimize and characterize the viscosity and other rheological properties of the ink to optimize the deposition.

Although relatively few studies have been published to date, the field is expanding fast in terms of the technics proposed and the understanding of the stability of MOFs and their performances as hierarchically porous materials rather than powders.

[1] Lorignon F., Gossard A., Carboni M. - **Hierarchically porous monolithic MOFs: An ongoing challenge for industrial-scale effluent treatment** - *Chemical Engineering Journal* (2020) 393, 124765.

[2] Lorignon F., Gossard A., Carboni M., Meyer D. **- From wastes to interconnected porous monolith: Upcycling of Al-based metal organic framework via pickering emulsion template** - *Materials Letters* (2021) 296.

[3] Lorignon F., Gossard A., Carboni M., Meyer D. - **Microstructural and rheological investigation of upcycled metal-organic frameworks stabilized Pickering emulsions** - *Journal of Colloid and Interface Science* (2021) 586, 305-314.

[4] Pianca D., Carboni M., Meyer D. - **3D-Printing of porous materials: Application to Metal-Organic Frameworks** - *Materials Letters-X* (2022) 13, 1001