



From disordered to ordered two-dimensional metal-organic frameworks on porous ceramic supports for membrane separation applications

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Carbon dioxide and hydrogen separation is a key step in several energy-related industrial applications, including natural gas purification (CH₄/CO₂) or clean-up of combustion exhaust gases (CO₂/N₂). Similarly, the selective removal of hydrogen from natural gas (H₂/CH₄; H₂/CO₂) injected for transportation is getting more and more attention. Gas separation membranes can play a key role here. Especially interesting are the membranes composed of two-dimensional Metal-organic frameworks showing remarkable CO₂ and H₂ separation performance owing to their fine-tuned pore chemistry defined by judicious selection of the organic linkers and metallic nodes [4]. The ideal 2D-based MOF membrane should be mechanically robust and as thin as possible in order to simultaneously withstand the harsh gas-separation conditions and continuous operation, as well as to enable the rapid transport of the gas molecules using preferential transport paths.

This is possible by tailoring the characteristics of both the porous support surface and the orientation of the 2D MOF materials. Only a few works in the literature address this challenge. Most of them focus on the preparation of 2D-based MOF membranes using bottom-up approaches on functionalized porous ceramic supports [2]. In some cases, a polymeric network is also used to heal the defects [3]. Such protocols lead to the formation of composite membrane materials with physisorbed or mechanically trapped polymer units in the support and between the MOF nanomaterials. Despite the successful engineering of these oriented 2D-based MOF membranes, most of the gas performances are evaluated using isobaric testing conditions which favors the slow diffusion of gases through the membranes and results in high selectivity not comparable with real-life cases where transmembrane pressures are used as the driving force [1].

In this work, a new generation of 2D-based MOFs was developed, in which the controlled growth and orientation of 2D MOFs at the pores and the surface of a porous ceramic support is driven by a grafted polymeric network (Fig.1). The preparation of these grafted and oriented 2D-based MOFs requires the controlled formation of covalent bonds between the MOF-nanomaterials and the functional groups of the polymeric network located at the support surface. Relevant methods have been explored to demonstrate the chemical anchoring of the 2D-based MOFs on/in alumina ceramic supports with units of polyimide network on their surface. In this presentation, the physicochemical characteristics and functional properties of the derived 2D-MOF membrane systems will be described and discussed.

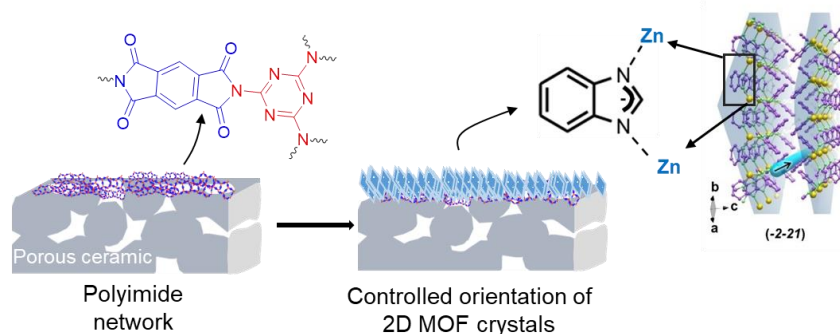


Fig 1. Schematic illustration of the controlled growth of 2D MOF crystal.

- [1] Kang D.Y., Lee J.S., "Challenges in Developing MOF-Based Membranes for Gas Separation," *Langmuir*, 39, 2871–2880, (2023).
- [2] Nian M., Ge K., Zhao J., Shen Y., Duan Y., Wu Y., *et al.*, "Orienting of metal-organic framework nanosheets into continuous membranes for fast hydrogen permeation," *J Memb Sci*, 672, 121447, (2023).
- [3] Shu L., Peng Y., Yao R., Song H., Zhu C., Yang W., "Flexible Soft-Solid Metal–Organic Framework Composite Membranes for H₂/CO₂ Separation," *Angewandte Chemie International Edition*, 61, (2022).
- [4] Zhang C., Wu B.-H., Ma M.-Q., Wang Z., Xu Z.-K., "Ultrathin metal/covalent–organic framework membranes towards ultimate separation," *Chem Soc Rev*, 48, 3811–3841, (2019).