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Metal organic framework based mixed matrix membranes: An increasingly important field of research with a large application potential

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ABSTRACT

The combination of metal organic frameworks (MOFs) and polymers in the form of mixed matrix membranes (MMMs) has become an increasingly important field of research over the last few years. The first examples of membranes outperforming state of the art polymers have already been presented, emphasizing the high application potential of these composites. In this paper, the recent progress on the topic is thoroughly reviewed and the main advantages and limitations of the use of MOFs as MMMs fillers are evaluated.

1. Introduction

As energy costs rise, membrane technology is likely to play an increasingly important role in reducing the environmental impact and operational costs of industrial processes. Furthermore, gas separation membrane units are smaller than other types of plants, like amine stripping, and therefore have relatively small footprints [1]. With this decreasing in the ratio between equipment size and production capacity, membrane technologies address the requirements of process intensification [2]. Conventional technologies, such as distillation and absorption based processes, require a phase change in the mixture that is to be separated. This phase change adds a significant energy penalty. Membrane gas separation, on the other hand, does not require a phase change [3].

Separation through membranes is usually based on the size and shape of the molecules to be separated and on their interaction with the membrane material [4]. Despite the superior performance of membranes only based on crystalline materials with well defined pore systems like zeolites [4,5] or metal organic frameworks (MOFs) [6], low flux polymeric membranes rule the commercial scene thanks to their easy processing and mechanical strength [7]. Furthermore, synthetic reproducibility and therefore scale up of pure zeolite- or MOF-based membranes is still a major bottleneck [8], as recently discussed by Caro [9].

However, the existing polymeric membrane materials are not optimal: improvement in permeability is always at the expense of selectivity, and vice versa (see Fig. 1) [10]. Meantime, plasticization hampers the application of polymeric membranes at high pressures since high concentration of adsorbates might swell and dilate the polymer, increasing the mobility of the polymer chains. The overall result is a reduction in the membrane selectivity far below the pure-gas values [7].

During the last few decades, several solutions have been proposed to boost the performance of polymeric membranes. Various polymers have been modified with inorganic fillers such as zeolites, mesoporous silicas, activated carbons, carbon nanotubes and even non-porous solids to produce mixed matrix membranes (MMMs) [11–15]. A MMM is an intimate and homogeneous dispersion of filler particles in a polymeric matrix. Both polymer and filler properties affect MMM morphology and separation performance [16,17]. Regarding the filler, its chemical structure, surface chemistry, particle size distribution and aspect ratio are the most important variables. Indeed, poor filler-polymer compatibilities and filler segregation or blocking of its porosity by the polymer are the main reasons why traditional MMM fillers like zeolites, silicas or activated carbons have not made the final steps towards industrial implementation. Due to these limitations, in general only low filler loadings can be achieved without compromising the separation performance unless laborious filler post-treatments are applied [18,19]. As to the polymer, mostly low flux glassy polymers result in MMMs with enhanced separation performance, while MMMs of highly permeable, poorly selective rubbery polymers have hardly been successful when using inorganic fillers [16,17].

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Recent advances have shifted towards the addition of new fillers, namely carbon nanotubes, layered silicates (sometimes after delamination) and MOFs as potential fillers in the polymer matrix [20]. MOFs are among the most sophisticated nanostructured materials. Next to a high surface area and pore volume, their chemical environment can be fine-tuned by selecting the appropriate building blocks [21] and/or by post-synthetic modification [22]. More importantly, the porosity of MOFs is, in general, much higher than that of their inorganic counterpart, zeolites, justifying the designation 'framework' and challenging the scientific community to make an effective use of such an empty space. In addition to the facile functionalization, many MOFs are known to undergo structural changes upon adsorption of different molecules ('breathing') [23,24], facilitating the design of, for instance, dynamic composites.

Given the vast possibilities that MOFs offer in terms of design together with their intrinsic hybrid nature, it was only a matter of time until the first MOF based MMMs were reported. The incorporation of MOFs into a polymer matrix for gas separation was first explored by Yehia et al. [25]. Since then, this field of research has experienced a rapid growth and the first examples of outstanding MMMs have been reported in the literature. With this manuscript, we critically review the progress made on MOF-based MMMs since the seminal work of Yehia et al. with the aim of exploring the main limitations and opportunities that MOFs offer as MMM fillers.

2. Preparation, testing and modelling of MOF mixed matrix membranes

2.1. Preparation and testing

In principle, the lab-scale fabrication procedure of MOF-based MMMs is similar to the one applied for the synthesis of other MMMs. In the general procedure for the preparation of MMMs the first step is the dispersion of the filler in the solvent in an ultrasonic bath. Polymer is then added, usually maintaining a ratio 90/10 wt.% solvent/filler-polymer mixture. The whole mixture is stirred overnight. Before the casting, different intervals of sonication and stirring take place to ensure a well dispersion. Subsequently, the membranes are cast on a flat surface, either Petri-type dishes or Doctor Blade system, and then left overnight for evaporation of solvent at room temperature. Once dried, the films are placed in a vacuum oven for 24 h at a specific temperature (depending on the polymer glass transition temperature) high enough to remove the remaining solvent. Fig. 2 presents the general procedure for the MMM preparation.

Permeability and separation factor are the two key parameters generally used to characterize polymeric membranes. Permeability $\boldsymbol{P}_A$, a normalized productivity of a specific gas component by the membrane, is defined (Eq. (1)) [26] as the gas diffusive *Flux* of the gas *A* through the membrane (flow per unit area *A*) normalized by the partial pressure difference of that component across the membrane per unit thickness of the membrane $\frac{\Delta P_A}{l}$,

$$\begin{aligned} \mathbf{P}_A &= \frac{Flux_A \cdot \ell}{\Delta p_A} \\ Flux_A &= \frac{Flow_A}{A} \end{aligned} \quad (1)$$

Permeability values are typically reported in Barrer units (1 Barrer = 1×10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} cm Hg^{-1} = 3.348×10^{-16} mol m m^{-2} Pa^{-1} s^{-1}).

The separation factor reflects the capability of a polymer membrane to separate one gas from another. If the permeabilities of two individual components are known, the ideal selectivity, S_{AB} (Eq. (2)), is given by the ratio of the two pure gas permeabilities:

$$S_{AB} = \frac{\boldsymbol{P}_A}{\boldsymbol{P}_B} \quad (2)$$

For permeation of actual A/B mixtures, the mixed gas selectivity, also called separation factor (α_{AB}), is calculated from composition analysis as the ratio of the mole fractions of the components in the permeate stream, *y*, and the feed stream, *x* (Eq. (3)). In the case where the gases do not interact strongly with each other or with the membrane material, the ideal selectivity is equal to the actual separation factor, but frequently this is not the case

$$\alpha_{AB} = \frac{(y_A/y_B)}{(x_A/x_B)} \quad (3)$$

For every MOF-polymer couple, the MOF loading should be maximized. Fig. 3 illustrates the usual effect of MMM MOF filler loading over selectivity and permeability. Loadings lower than a certain value do not alter in a significant way the transport properties of the

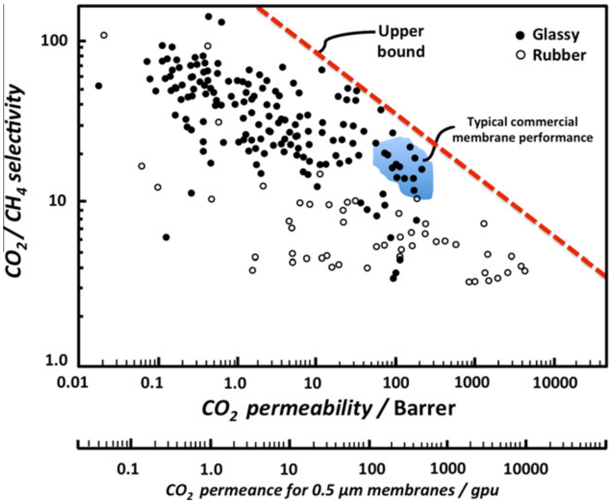

Fig. 1. *Robeson* plot for the separation of CO_2 from CH_4 [123]. This represents the selectivity obtained from the ratio of pure-gas permeabilities plotted against carbon dioxide permeability for different polymeric membranes. A permeance of 1 GPU corresponds to a membrane exhibiting an intrinsic permeability of 1 Barrer and having a selective layer thickness of 1 µm.

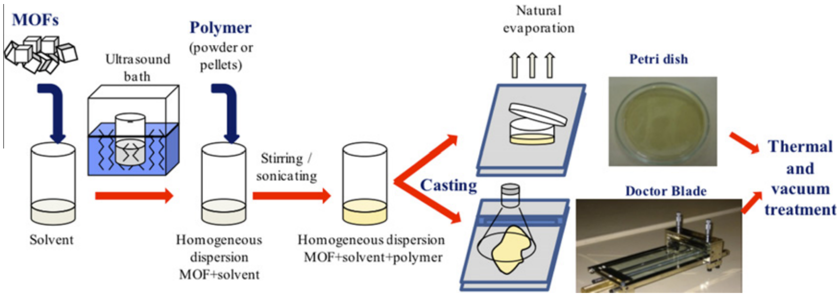

Fig. 2. General scheme for the fabrication of MOF–MMMs.