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**Synergy gas separation effects when using fillers of different natures (MOFs and zeolites) in the same mixed matrix membrane**

B. Zornoza<sup>\*1</sup>, B. Seoane<sup>1</sup>, J.M. Zamara<sup>2</sup>, C. Téllez<sup>1</sup>, J. Coronas<sup>1</sup>  
<sup>1</sup>University of Zaragoza, Spain, <sup>2</sup>INCAPE, Argentina

The incorporation of inorganic or hybrid fillers, such zeolites or metal-organic frameworks (MOFs), into polymeric membrane materials in the form of mixed-matrix membranes (MMMs) has become an increasingly important field of research over the last few years. These MMMs have the advantage of combining the benefits of both phases: the superior gas transport properties of molecular sieves with the desirable mechanical properties, low price and good processability of polymers<sup>[1]</sup>.

Zeolites are one of the most versatile nanoporous fillers when considering aspects such as chemical composition, particle size, shape, and textural properties. However, from the point of view of compatibility between the polymer phase and the filler, MOFs have an evident advantage over zeolites. Besides sharing the crystallinity and textural properties common to zeolites, by choosing the appropriate organic linker in MOFs it is possible to determine the size, shape and chemical functionality of their cavities<sup>[2]</sup>.

In this work, we suggest the preparation of MMMs by combinations of two different kinds of porous fillers: zeolite silicalite-1 (S1C) and MOF (HKUST-1 or ZIF-8) within the polysulfone (PSF) polymer matrix. By using fillers of a different nature in the same MMM, synergy effects may appear leading to membranes with better permeation properties than those of MMMs with only one filler type.

MMMs using filler mixtures containing ZIF-8 and silicalite-1 and HKUST-1 and silicalite-1, with total loadings up to 16 wt. % have been prepared. Figures 1a and b correspond to SEM and TEM cross sections of ZIF-8/S1C-PSF and HKUST-1/S1C-PSF MMMs where a homogeneous dispersion and intimate filler-polymer interaction can be observed. Other characterization techniques of the fillers (Ar and CO<sub>2</sub> adsorption-desorption isotherms, not shown) and MMMs (X-ray diffraction, thermogravimetric analysis, differential scanning calorimetry, contact angle and attenuated total reflection–Fourier infrared spectroscopy, not shown) were performed showing a good contact between the continuous and disperse phases with a subtle synergy effect between both fillers.

The MMMs were applied to the separation of CO<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/CH<sub>4</sub>, O<sub>2</sub>/N<sub>2</sub>, and H<sub>2</sub>/CH<sub>4</sub> mixtures finding important selectivity improvements in separation performance with the HKUST-1-silicalite-1 system for CO<sub>2</sub>-containing mixtures (Figure 1c) (CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> selectivities of 22.4 and 38.0 with CO<sub>2</sub> permeabilities of 8.9 and 8.4 Barrer, respectively). On the other hand, ZIF-8-containing MMMs gave rise to the best performance when mixtures are separated based on diffusion differences between permeating molecules (see Figure 1d for H<sub>2</sub>/CH<sub>4</sub> and O<sub>2</sub>/N<sub>2</sub> mixtures).

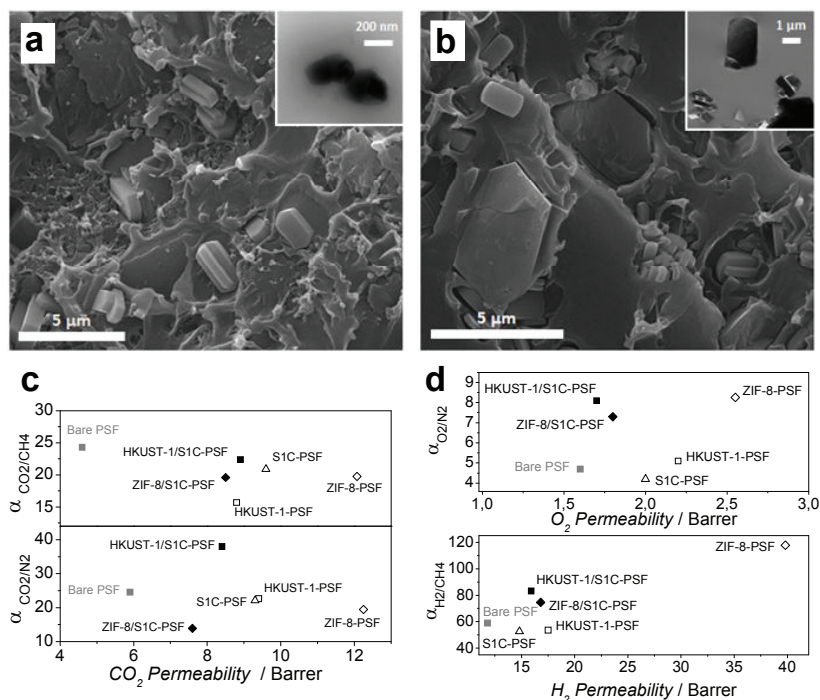


Figure 1. Cross section SEM images of MMMs: (a) 8 wt. % ZIF-8 + 8 wt. % S1C-PSF (with TEM inset showing ZIF-8 particle) and (b) 8 wt. % HKUST-1 + 8 wt. % S1C-PSF (with TEM inset showing silicalite-1 particle). Gas separation permeabilities and selectivities for: (c) CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> mixtures, (d) O<sub>2</sub>/N<sub>2</sub> and H<sub>2</sub>/CH<sub>4</sub> mixtures.

Using filler particles of different natures in the same MMM may produce synergy effects leading to membranes with better permeation properties than those corresponding to MMMs with only one filler type. The different surface chemistry of both types of fillers may help the dispersion and disaggregation inside the polymer matrix<sup>[3]</sup>. The results achieved herein clearly point towards a new research scenario in which not only MOF-zeolite but also MOF-MOF, zeolite-zeolite and other combinations, could be examined in the search for improvements in gas separation using MMMs.

## References

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