

## KN4 Nanocomposite membranes with PIM-1 matrix

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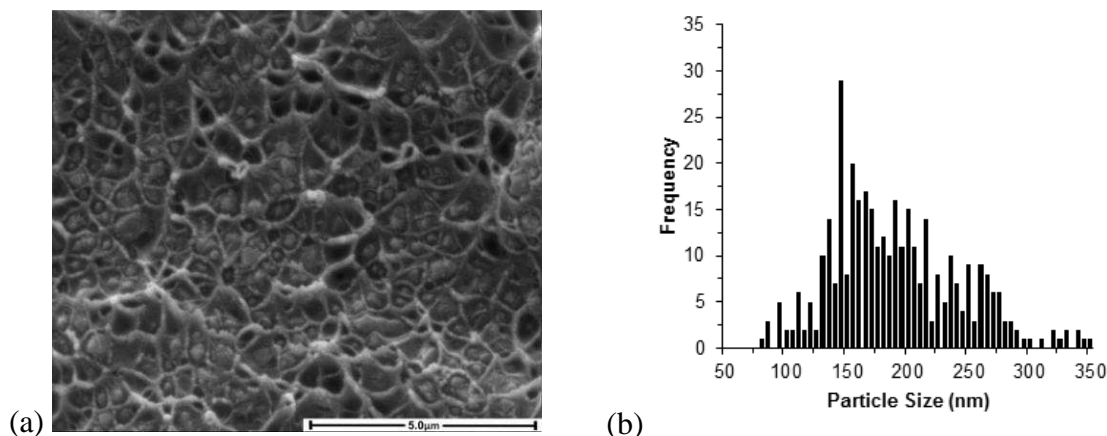
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Most commercial membranes for molecular separations are polymeric and, despite extensive research over the past decades, are based on a mere handful of polymers. However, if membrane technology is to penetrate new and demanding application areas, such as carbon dioxide capture from flue gases, better and more robust membrane materials are needed. For high-volume applications, high permeability is necessary in order to minimize membrane area. It is well known that high permeability is generally associated with poor selectivity, as illustrated by double logarithmic “Robeson” plots of selectivity against permeability [1]. The challenge is to push the bounds of membrane performance to higher permeability, whilst also achieving long-term stability under demanding conditions of use. A step-change in performance is most likely to come through a synergistic combination of materials. Thus, “mixed matrix” or “nanocomposite” membranes have been the focus of much recent research. In the context of the “DoubleNanoMem” project, a wide variety of nanofillers have been utilised with a single polymer, PIM-1 [2], enabling the effects of different kinds of filler to be investigated. A range of porous crystalline materials have been incorporated into PIM-1, including inorganic molecular sieves and metal-organic frameworks, as listed in Table 1.

**Table 1.** Type, source, BET surface area and approximate particle size for porous crystalline fillers used in mixed matrix membranes with PIM-1.

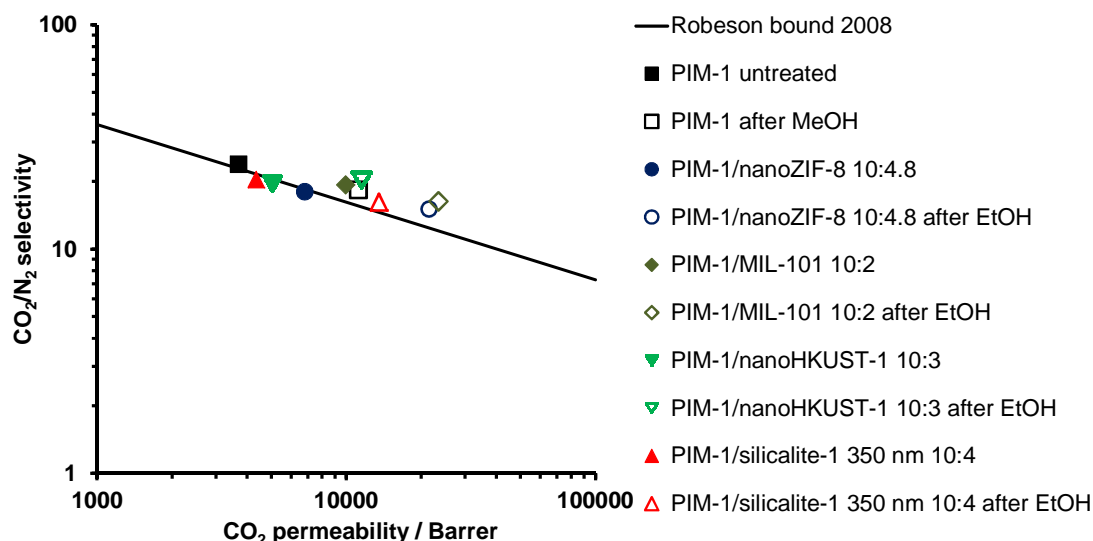
Filler	Source	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Particle size (nm)
Silicalite-1 (MFI)	University of Calabria	390	350
Phenethyl silicalite-1	University of Calabria	330	350
Phenethyl silicalite-1	University of Calabria	360	180
SAPO-34 aspect ratio 10	University of Calabria	625	1000
SAPO-34 aspect ratio 2.2	University of Calabria	510	1000
Zeolite 13X	University of Edinburgh	390	
ZIF-8	University of Manchester	1700	2000-10000
nanoZIF-8	University of Manchester	1200	20-80
HKUST-1	University of Manchester	1400	2000-10000
nanoHKUST-1	University of Manchester	1400	40-80
MIL-101	University of Manchester	2640	75-200
nanoMIL-101	University of Bath	2845	50
Mg-MOF-74	University of Manchester	700	
Mg-CPO-27 mod.	University of St. Andrews	295	

The fillers and nanocomposite membranes have been characterized by scanning electron microscopy (SEM). Figure 1 shows an example of a SEM image for a PIM-1/MIL-101 membrane, and the particle size distribution of MIL-101 determined from the SEM image.



**Figure 1.** (a) Scanning electron micrograph of cross-section of a PIM-1/MIL-101 nanocomposite membrane with weight ratio PIM-1:MIL-101 = 10:2. (b) Particle size distribution of MIL-101 in the membrane.

Permeation properties have been investigated for nanocomposite membranes both as prepared and after alcohol treatment. Representative selectivity/permeability data for the CO<sub>2</sub>/N<sub>2</sub> pair are shown in Fig. 2. For various fillers, significant enhancements in permeability, compared to pure PIM-1, are achieved for both as prepared and ethanol-treated membranes, with selectivities that are close to, or exceed, Robeson's 2008 upper bound.



**Figure 2.** Dependence of CO<sub>2</sub>/N<sub>2</sub> selectivity on CO<sub>2</sub> permeability for PIM-1 [2] and representative examples of nanocomposite membranes with PIM-1 matrix, both as prepared (solid symbols) and after ethanol-treatment (open symbols). The solid line is Robeson's 2008 upper bound [1].

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### References

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