



## Polymer communication

## New organophilic mixed matrix membranes derived from a polymer of intrinsic microporosity and silicalite-1

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## ABSTRACT

The preparation and characterization of novel PIM-1/silicalite-1 (MFI) mixed matrix membranes (MMMs) are reported. Silicalite-1 crystals of size 350 nm were synthesized and functionalized with 2-phenylethyl groups to favour a higher hydrophobicity in the PIM-1 matrix. MMMs with different functionalized crystal loadings (from 8.4 to 35.5 v%) were prepared, characterized and tested in the separation of ethanol from aqueous mixtures with different concentration (5 and 9 wt%) via pervaporation. Pure gas transport properties were also measured for the MMM with the highest filler loading. The enhancement in both ethanol/water separation factor (5.7 vs. 4.3) and CO<sub>2</sub>/N<sub>2</sub> selectivity (30 vs. 24) compared to neat PIM-1 indicates a positive effect of the silicalite-1 on the molecular separations investigated.

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## 1. Introduction

Membranes based on PIM-1, a polymer of intrinsic microporosity, have attracted great attention for gas separation due to the combination of outstanding permeability with moderate selectivity, which define the 2008 Robeson upper bound trade-off for the O<sub>2</sub>/N<sub>2</sub> and the CO<sub>2</sub>/CH<sub>4</sub> gas pairs [1]. PIM-1 membranes have also been investigated for the separation by pervaporation of phenol/water [2] and aliphatic alcohol/water mixtures [3]. Budd et al. and McKeown et al. were the first to report this new class of rigid ladder-type polybenzodioxane containing highly contorted chains [4–6].

Possible routes to novel PIM membranes include changes to the polymer structure by varying the monomer used for the polymerization [7,8], by copolymerization with additional monomers [9,10] or by post modification [11,12]. Previous work by Mason et al. [13] adopted the latter strategy: a new polymer of intrinsic microporosity incorporating thioamide functionality was reported, with increased ideal selectivity at the expense of a reduced permeability.

Another route can be followed: the addition of inorganic fillers, i.e. the preparation of mixed matrix membranes (MMMs) based on

a PIM as the polymeric matrix. There are limited references in this area, with a patent concerning the use of impermeable ALPO-14 (AFN) and permeable ALPO-18 (AEI) crystals [14] and one paper by Ahn et al. [15] dealing with the dispersion of silica nano-particles in PIM-1 matrix and its effect on the gas transport properties. In this last example, the non-porous inorganic filler loosened the inherent polymer chain packing causing a loss of selectivity.

The pervaporation (PV) process has attracted great interest in industry due to its great capabilities, for example as an easy and economical method of recovering organic solvents, removing alcohol from aqueous solutions, or recovering aroma compounds from fruit juices [16–20]. In particular, research on new high-productivity hydrophobic membrane materials selective to ethanol in the pervaporation of ethanol/water mixtures is highly active, as the growing number of papers on this subject indicates [21–26]. Polymers with high gas permeability are objects of interest as prospective pervaporation materials. Poly(dimethylsiloxane) (PDMS) [24,27], polyether block amides (Pebax) [23,26], poly(1-trimethylsilylpropyne) (PTMSP) [21,22,28] and amorphous Teflon AF [29] are examples of such polymers. Mixed matrix membranes (MMMs) based on the aforementioned polymers and hydrophobic inorganic fillers have been found to favour the selective transport of ethanol in mixtures with water. As reported in literature ([21,23,25,30–32]), the most selective porous fillers are zeolites with MFI topology, high silica ZSM-5 or silicalite-1, due to their

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hydrophobic character. In particular, Vankelecom et al. [32] studied the influence of different zeolites on the PV of water/alcohol mixtures: zeolite Y (FAU), ZSM-5 (MFI) and silicalite-1 (MFI). In all cases the zeolites reduced the swelling of the PDMS. The hydrophilic zeolite Y increased water fluxes; ZSM-5 reduced both water and alcohol fluxes, probably due to lower diffusion rates of ethanol and water in its pores; hydrophobic silicalite-1 filled membranes yielded the best selectivity for ethanol. For what concerns purely zeolitic membranes, silicalite-1 is the material with highest ethanol selectivity, characterized by ethanol/water separation factors up to 106 [33]. Molecular dynamics indicates that the selective adsorption of ethanol in the hydrophobic silicalite-1 pores is the determining factor to achieve such a high selectivity [34].

In most cases, soft polymeric materials (PDMS and Pebax) have been selected to host unfunctionalized hydrophobic MFI fillers: the difficulties to obtain defect free MMMs by using rigid glassy polymers and the strategies adopted during the fabrication to favour the adhesion between the polymer and the fillers, loaded usually with low percentages in weight, are widely reported in literature [35–39].

High free volume polymers such as polyacetylenes and polymers of intrinsic microporosity (PIMs) display very high diffusion coefficients, and so are expected to give high flux and eventually high selectivity pervaporation membranes.

In 2010 high free volume poly[1-(trimethylsilyl)-1-propyne] (PTMSP) loaded with impermeable fillers (fumed silica) has been proposed as a new membrane material for pervaporative separation of ethanol/water mixtures [21]. The symmetric dense sample showed an increase of the flux of 70% and an improvement of the ethanol/water separation factor of 5.5% compared to the pure reference sample (similar thickness and  $M_w$ ) of PTMSP. The fumed silica nanoparticles affect only the polymer packing, inducing changes in the free volume of the polymer.

In the present work, for the first time in the literature, silicalite-1 (MFI) crystals were dispersed into PIM-1 polymer and novel defect-free MMMs were obtained. The silicalite-1 crystals (size of 0.35  $\mu\text{m}$ ) have been functionalized with aromatic moieties to improve their hydrophobic character and, at the same time, their compatibility with the aromatic chains of PIM-1. MMMs with different silicalite-1 loadings have been prepared and their integrity verified with gas permeation experiments, before being tested in the pervaporation of ethanol/water mixtures. The effects of the feed composition, of the temperature and of the filler loading on the ethanol/water separation have been investigated.

## 2. Experimental

### 2.1. Materials

PIM-1 was synthesized according to the procedure reported in Ref. [2]. Ethanol (Carlo Erba, reagent grade), was used without further purification. For the preparation of MMMs, reagent grade chloroform was distilled from calcium chloride onto 4 Å molecular sieve.

### 2.2. Silicalite-1 synthesis and functionalization

Silicalite-1 crystals of size 350 nm were synthesized and functionalized on the outer surface with  $-(\text{CH}_2)_2\text{Ph}$  groups according to a procedure reported elsewhere [40].

### 2.3. Filler characterization

The BET (Brunauer–Emmet–Teller) surface area of non-functionalized and functionalized crystals was measured with a Micromeritics TRISTAR 3020 II apparatus. The samples were degassed by heating at 140 °C.

Contact angle measurements were performed with a CAM 200 contact angle meter (KSV Instruments LTD, Helsinki, Finland). The powder was packed to approximate a flat surface. The sessile drop was formed by depositing water from the above using an automatic microsyringe on the surface. The instrument is able to record images at 2 ms intervals and contains an on-screen trigger. This exclusive feature makes it possible to follow the evolution of the contact angle of the liquid with the solid surface at high speed, and to quantify the wetting behaviour. If the real contact angle is greater than 90° penetration should not occur and reproducible contact angles may be measured.

XPS study was performed to characterize the outer surfaces of the native and functionalized crystals (maximum measurement depth of 100 Å) with an XPS spectrometer PHI 5600 ci, equipped with a double anode X-ray source (Mg/Al) and a monochromatic Al X-ray source.

### 2.4. Membrane preparation

A PIM-1 solution in dry chloroform (3 wt%) was stirred vigorously overnight. A suspension of silicalite-1 (0.79 wt%) in anhydrous chloroform was stirred and sonicated. The PIM-1 solution was added to the suspension and the final mixture was sonicated for at least 1 h. For membranes PIM–MFI1 and PIM–MFI2, the solution was filtered through glass wool into the suspension.

The final suspension was poured into a glass support (PIM–MFI3) or a teflon mould (PIM–MFI1 and PIM–MFI2) kept on a level surface. The support was covered to slow down the evaporation of solvent (30 °C). The resulting membranes were dried under ambient conditions and then under vacuum at 40 °C to remove the remaining solvent. Table 1 summarizes the composition and thicknesses of the membranes prepared.

The volume fractions of silicalite-1 (MFI) have been worked out with the hypothesis of additivity of volumes, i.e. by assuming that the filler does not influence the density of the polymeric matrix, and refer to dry, non-swollen membranes. The density values used in the calculations are 1.76 g/cm<sup>3</sup> for silicalite-1 [41] and the average between 1.061 and 1.092 g/cm<sup>3</sup> for PIM-1 [42]. A membrane of neat PIM-1 (thickness 94.4  $\mu\text{m}$ ) was used as a reference.

### 2.5. Membrane morphology

The morphology of the membranes was observed by scanning electron microscopy (SEM) (ESEM FEG QUANTA 200, FEI Philips, Peabody, MA, USA) at 0.2/30 kV. Sample specimens were freeze-fractured in liquid nitrogen to guarantee a sharp brittle fracture.

The thickness of each membrane was directly read from the SEM image of the cross section and was also determined by a multiple-point measurement, using a digital micrometer (Carl Mahr, Germany).

### 2.6. Gas permeability measurements

The pure gas steady state permeability of the membranes was measured in a home-built fixed pressure/variable volume instrument described elsewhere [43]. The temperature and the

**Table 1**  
Composition and thickness of the MMMs prepared.

Membrane code	MFI:PIM-1 weight ratio	Silicalite-1 content (v%)	Membrane thickness ( $\mu\text{m}$ )
PIM–MFI1	15:100	8.4	63
PIM–MFI2	39:100	19.3	72
PIM–MFI3	90:100	35.5	110

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