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Long term pervaporation desalination of tubular MFI zeolite membranes

Martin Drobek [a], Christelle Yacou [b], Julius Motuzas [a], Anne Julbe [a], Liping Ding [b], João C. Diniz da Costa [b,*]

[a] *Institut Européen des Membranes (UMR 5635 CNRS), Université Montpellier 2, CC47, Place Eugène Bataillon, 34095 Montpellier Cedex 5, France*
[b] *The University of Queensland, FIMLab—Films and Inorganic Membrane Laboratory, School of Chemical Engineering, Brisbane, Qld 4072, Australia*

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ABSTRACT

Silicalite-1 (S-1) and ZSM-5 membranes prepared by secondary growth on tubular ceramic supports were tested using a pervaporation set up for the desalination of aqueous solutions containing NaCl in concentrations corresponding to brackish (0.3–1 wt%), sea (3.5 wt%) and brine (7.5–15 wt%) water. ZSM-5 membranes delivered higher water fluxes when compared with S-1 membranes due to enhanced hydrophilicity of the Al-rich zeolite structure leading to fluxes as high as 11.5 kg m^{-2} h^{-1} for 0.3 wt% NaCl feed solutions at 75 °C. At higher salt concentration the water flux decreased alongside with the salt rejection rate, however the hydrophilic ZMS-5 membrane became more susceptible to performance loss, particularly at high temperatures. Detailed stability experiments carried out for up to 560 h showed the dissolution of both S-1 and ZSM-5 top layers. This was attributed to the combined effects of ion exchange and water dissolution mechanisms. Interesting though, the MFI structure zeolite was still observed on the XRD patterns whilst EDX depth profile showed the presence of silica up to 30 μm depth into the support. These results suggest the formation/infiltration of a compact amorphous phase in the substrate, derived from the aggregation of the dissolved silicate species and possibly together with the arrangement of MFI nano-slabs during the desalination tests. Despite generating lower water fluxes, the S-1 membrane exhibited relatively high robustness under the long term testing conditions which included temperature cycling, delivering salt rejections from initial $>99\%$ to $<80\%$ at the end of the testing period (560 h).

1. Introduction

Zeolite membranes have attracted the concerted effort of the research community for gas [1,2] and liquid phase separations [3,4] and membrane reactor applications [5,6]. The main advantages of zeolite membranes are directly related to their high separation performance, in tandem with catalytic activity, good thermal and chemical stability, and low fouling tendencies [7,8]. These properties make them ideal to operate in processes which cannot be met by conventional polymeric membranes. In addition, the precise tuning of the pore sizes of zeolite membranes confers them great process capabilities for separation processes based on molecular size and shape [9].

In the case of liquid separation, zeolite membranes with relatively large pores have been considered as enabling technologies in reverse osmosis and nano- or ultrafiltration [10,11]. Recent studies have shown the zeolite membranes as unique materials in the field of desalination taking an advantage of their ability to remove ions from aqueous saline solutions, and leading to high ionic (i.e., salt) rejections [12]. The separation efficiency was found to increase with the ion valence suggesting that the separation mechanism is based on rejection of the hydrated ions by size exclusion and ions interactions, which in turn are influenced by the charged double layer formed in inter-crystalline gaps of zeolite membranes [10]. If the separation mechanism based on pore size exclusion cannot be achieved, a functionalization of the zeolite cage might be an option to enhance the membrane separation efficiency as observed in the case of Al-rich zeolite membranes [13], where the membranes properties like surface hydrophobicity and surface charge are significantly changed [14].

The number of zeolite membrane types reported in the literature for desalination is however quite limited. The major constraint of these membranes in desalination application is their pore size allowing the diffusion of the small water molecules (d_k=2.6 Å) and the larger molecules represented by salt ions e.g., Na^+ and Cl^-, whose hydrated sizes are 7.2 Å and 6.6 Å, respectively [10,15]. Ideally, if the zeolite pore size and intercrystalline interconnections are well below 6.6 Å, then zeolite membrane would selectively separate water from hydrate salt ions whilst delivering high ion or salt rejections. These criteria can be met theoretically by NaA and MFI zeolite membranes exhibiting ~4 Å [16] and ~5.5 Å pore sizes [17], respectively.

Table 1 lists the testing parameters and performance of zeolite membranes reported for desalination application. Membranes

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[*] Corresponding author. Tel.: +61 7 3365 6960; fax: +61 7 3365 4199.
E-mail address: j.dacosta@uq.edu.au (J.C. Diniz da Costa).

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Table 1
LTA and MFI zeolite membranes in desalination applications.

Membrane	LTA-NaA	MFI-S-1 (Si/Al $=\infty$)	MFI-ZSM-5 (Si/Al $=$ 50–65)	MFI-ZSM-5 (Si/Al $=$ 100)
Salt concentration (NaCl wt%)	3.1	0.5	0.5	3.8
Transmembrane pressure (MPa)	0.1*	2.07**	2.8**	0.1*
Support geometry	Tubular	Flat	Flat	Flat
Temperature(°C)	79	25	25	80
Flux (kg m^{-2} h^{-1})	4.392	0.121	1.129	0.7
Rejection (%)	99.9	75	93	99
Reference	[18]	[19]	[20]	[12]

* Membrane distillation.

** Reverse osmosis.

were tested in either reverse osmosis (RO) with pressures in excess of 2 MPa or membrane distillation (MD) set up at 0.1 MPa. Results show that the MFI membranes prepared on flat supports with the optimized Si/Al ratio of 50 delivered the best water fluxes and maximum salt rejection. Duke et al. [12] demonstrated that ZSM-5 membranes with a higher Si/Al ratio and prepared by secondary growth gave similar high salt rejections. Generally speaking, the MFI (ZSM-5 and S-1) membranes delivered low water fluxes, associated with poor hydrophilicity as compared to LTA (NaA) membranes, in addition to small channel pore sizes which tend to increase the resistance to the permeation of water. Some level of intercrystalline gaps was also evident as salt rejections varied between 75 and 93% [19,20]. MFI membranes obtained by secondary growth clearly reduced the non-selective transport delivering higher salt rejections of 99%. Nevertheless, LTA zeolite ($\sim$ 4 Å) membranes yield water flux six-fold higher than ZSM-5 membranes operating in MD set up at similar conditions of salt concentration, pressure and temperature.

Secondary growth is a highly recognized method for preparing reproducible MFI membranes, although key steps such as seed formation, seed deposition and secondary growth conditions have to be carefully controlled in order to optimize both membrane quality and performance. Microwave-assisted heating (MW) is an attractive method for producing uniform nano-seeds yielding reproducible seed layers on macroporous supports [21]. The seed layer is non-infiltrated and sufficiently thin to avoid any remaining seed excess after the secondary growth step. The non-infiltration of the seed layer into the membrane support is advantageous as it reduces the overall membrane thickness and also the resistance of the preferentially permeated species at the interface of the zeolite film and substrate. Hence, high water flux can be expected as the flux in porous membranes is generally inversely proportional to the thickness of the rate limiting layer, in this case the zeolite film. In parallel, high salt rejection should be achieved with uniform zeolite membranes having a significantly low number of intercrystalline defects.

Uniform zeolite layer with defined composition and thickness can be grown in a reproducible way by either MW assisted or classical heating method. By employing these synthesis methods, it has been shown that MFI membranes can be also prepared on pre-assembled capillary supports with high surface to volume ratio ($>1000\ m^2\ m^{-3}$) [22], thus providing higher industrial potential when compared to low surface area flat membranes. Another important obstacle to industrial development of zeolite membranes is related to the long calcination step, due to the classically recommended extremely slow heating rates. This drawback can be easily overcome by ozonation [23]. It was also recently reported that a rapid thermal processing improves the quality and separation performance of thick columnar films of silicalite-1 by eliminating the defects, possibly by strengthening grain bonding at the grain boundaries [24].

In the present work, we report the performance for desalination of MFI membranes prepared by easily up-scalable secondary growth from MW-derived nano-seeds on mono-channel tubular ceramic supports and with a rapid heating rate for de-templating. Of particular interest, we compared the water fluxes, salt rejection and long-term stability of silicalite-1 and ZSM-5 zeolite membranes with Si/Al $=\infty$ and 100, respectively, in order to investigate the impact of surface hydrophobicity, surface charges and membrane steadiness on its performance in desalination process. All experiments were carried at a transmembrane pressure close to 1 atm, temperatures ranging from 21 °C to 75 °C, and for salt aqueous solutions containing NaCl concentrations corresponding to brackish (1 wt%), sea (3.5 wt%) and brine (7.5–15 wt%) waters.

2. Experimental

2.1. Membrane synthesis and characterization

MFI zeolite membranes were synthesized by secondary growth from a layer of silicalite-1 (S-1) nano-seeds deposited on Pall-Exekia asymmetric α-Al_2O_3 tubular supports (OD/ID$=$10/7 mm, length$=$50 mm, with 5 mm enamel on both ends) and with an internal 200 nm pore size layer. S-1 nanoseeds (50–60 nm size) were prepared by a two-step microwave-assisted synthesis as described elsewhere [25,26]. The molar composition of the sol used for seeds preparation was SiO_2: 0.4TPAOH: 19.5H_2O: 4C_2H_5OH and the reaction conditions were the followings: $T_1=80$ °C, $t_1=90$ min, $P_1=250$ W for the first step and $T_2=125$ °C, $t_2=60$ min, $P_2=400$ W for the second step. A suspension of seeds was used to cast a uniform S-1 seed layer inside the α-Al_2O_3 supports by dip-coating. The seeded supports were placed vertically in an autoclave containing a sol whose composition was adjusted for the membrane growth step: 3TPAOH: 25SiO_2: 100C_2H_5OH: 1500H_2O for S-1 membranes and 3TPAOH: 0.125Al_2O_3: 25SiO_2: 100C_2H_5OH: 1500H_2O for ZSM-5 (Si/Al$=$100) membranes. Membranes were grown at 160 °C for 9 h by conventional heating. After the synthesis the membranes were washed with distilled water, dried for 3 h at 155 °C and finally calcined in air, applying a heating rate of 17.7 °C min^{-1} up to 550 °C and a 4 h dwell time followed by cooling down to room temperature (20 °C min^{-1}). The morphology, thickness and homogeneity of both seed layers and membranes were studied by field emission scanning electron microscopy (FESEM, Hitachi S-4500). The chemical composition of both surface and cross section of the membranes was analyzed by energy-dispersive X-ray spectroscopy (EDX, Quanta 200 FEG Electron Microscopy). The membrane crystalline structure was examined by X-ray diffraction (XRD, PANanalytical X-Pert Pro).

2.2. Membrane testing

All the prepared membranes were initially tested by single gas permeation measurements to ensure their good quality in terms of affirming the absence of intercrystalline macro-defects (viscous flow contribution) and other irregularities in the zeolitic network. The permeation experiments were carried out in a stainless steel module with a dead-end set up equipped with silicon o-rings to fix the membrane. Single gas permeation was conducted (after outgassing the membranes) for N_2 ($d_k=0.364$ nm) and SF_6 ($d_k=0.55$ nm) at 21 °C, applying a transmembrane pressure $\Delta P=100$ kPa. Gas permeance was measured by a bubble flow meter connected to the atmosphere.

The desalination testing was carried out using a classical pervaporation set-up schematically depicted in Fig. 1. The desalination