



Microwave-assisted hydrothermal rapid synthesis of capillary MFI-type zeolite–ceramic membranes for pervaporation application

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ABSTRACT

The supported zeolite membranes prepared in this work have been synthesised under microwave heating in order to reduce synthesis time, to prevent support dissolution, and to reproducibly obtain a thin defect-free zeolite layer. The MFI-type zeolite membranes were synthesised on ceramic capillaries, with a high membrane surface area-to-volume ratio ($>1000 \text{ m}^2 \text{ m}^{-3}$), which is by far higher than that of classical tubular supports ($\ll 500 \text{ m}^2 \text{ m}^{-3}$). The selective layer was deposited inside, outside or on both sides of the capillaries. These hydrophobic membranes were characterized and tested in pervaporation for the separation of an EtOH/H₂O: 5/95 wt.% mixture. The best results obtained at a pervaporation temperature of 45 °C, in terms of flux (1.5 kg/h m^2) and selectivity ($\alpha_{\text{EtOH/H}_2\text{O}} = 54$), were achieved with the double-sided membranes.

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1. Introduction

Over the last decade increasing attention has been paid to the development of zeolite membranes, due to the application of such membranes in a wide range of industrially interesting applications including gas separation, pervaporation, membrane reactors and catalysis [1–4].

In the scope of alternative energy saving and high efficiency separation processes, pervaporation is a promising candidate because the low energy consumption could lead to 40–60% energy reductions [5], simple operation and low environmental impact [6]. In addition, no entrainer is required, thus there is no contamination of the original mixtures, which is of utmost importance in the pharmaceutical or fine-chemical production [7].

Different types of membranes are being used for pervaporation: polymeric, ceramic, and composite membranes. Ceramic membranes show better resistance toward harsh chemicals, pressure and thermal conditions. Particularly, zeolite membranes have the unique properties of zeolites in terms of chemical composition, crystallinity and molecular pore size in a film-like

configuration. In contrast, zeolite membranes production costs are significantly higher than those for polymeric ones [3,7]. Zeolite membranes are an attractive alternative for separating mixtures whose components have adsorption or size differences, but are difficult to separate using polymeric membranes and other conventional separation methods [3]. Hence, zeolite membranes have been widely used for pervaporation at both laboratory [3] and industrial [8,9] scales for the dehydration of solvents.

In the case of a non-aqueous pervaporating component, such as in the extraction of low content alcohols from water, the preferred adsorption of alcohol molecules onto the surface of hydrophobic silicalite-1 zeolite provides the primary separation selectivity. Nomura et al. [10] examined the transport phenomena of ethanol through intracrystalline and intercrystalline pathways of silicalite-1 membranes separately, and an intercrystalline–intracrystalline model was proposed. According to this model, ethanol was permselectively extracted from ethanol/water mixtures through intracrystalline pathways. However, it is well known that non-zeolite pores, intercrystalline defects, are hydrophilic and should reduce the EtOH/H₂O selectivity of a hydrophobic zeolite membrane [3,11]. Therefore, aiming at the pervaporation application of silicalite-1 membranes, it is expected that the selectivity will be improved by increasing the hydrophobicity of the membrane.

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Besides, by decreasing the membrane thickness, the flux could be also increased.

To achieve high fluxes and selectivities in the ethanol/water separation, it is important to optimize all the transport steps that occur during pervaporation: (i) adsorption, in this sense it is important to maximize the hydrophobicity of the zeolite layer, (ii) transport resistance in the zeolite layer, by minimizing the thickness, and (iii) transport through the porous support, by decreasing its thickness and synthesising the zeolite layer on both sides of the support.

The ideal zeolite membrane consists of a continuous microporous layer grown on a porous support substrate. The layer thickness must be thin and defect-free enough to balance a high flux and a high selectivity. Up to now, alumina and stainless steel have been frequently used as support materials. Alumina support tends to dissolve into the synthesis solution during the hydrothermal treatment which would result in less hydrophobic ZSM-5 membranes, but not in the desired silicalite-1 membranes, even though both zeolites have the same MFI-type structure. In 1994, Sano et al. [12] first reported that silicalite-1 membranes synthesised on stainless steel disks performed better than those prepared on alumina disks. However, for MFI-type membranes synthesised on stainless steel supports, cracks are formed easily during calcination because stainless steel has higher thermal expansion coefficient than Al_2O_3 and SiO_2 .

Microwave (MW) heating is a fast, simple, and energy efficient method, which reduces significantly the synthesis time of zeolites and decreases the chance of support etching. A conventional hydrothermal treatment, in an alkaline media, in a convection oven for MFI zeolite membranes lasts from 8 h up to 3 days, depending on synthesis gel composition and temperature, which can cause chemical attack of the alumina support and aluminium incorporation into the zeolite layer. Consequently, it is feasible for a better control of the zeolite composition to maintain the chemical integrity of the support and to provide cheap and good quality zeolite membranes by the rapid MW-assisted synthesis [13–15].

In general, membranes reported in literature have either a flat plate or tubular geometry, although monolithic supports have also been used [11]. The flat plate geometry is advantageous for the homogeneity in seeding and synthesis on the small disks used for academic studies, but on the contrary it has a low surface area-to-volume ratio. The surface to volume ratio of tubular membranes is larger and easier to scale-up, consequently, commercially available zeolite membranes for pervaporation have a tubular geometry [8,9].

The supported zeolite layers prepared in this work have been synthesised under microwave irradiation, for reducing synthesis time, preventing the dissolution of the alumina support, and creating a thin defect-free zeolite layer [13]. The MFI-type zeolite layers were synthesised on ceramic capillaries, with a high membrane surface area-to-volume ratio ($>1000\text{ m}^2\text{ m}^{-3}$), which is by far higher than that of classical tubular supports ($\ll 500\text{ m}^2\text{ m}^{-3}$) [16]. The selective layer was deposited, inside, outside or on both sides of the capillary.

2. Experimental

2.1. Membrane synthesis by secondary growth

The ceramic $\alpha\text{-Al}_2\text{O}_3$ capillary supports (Hyflux CEPARation Technologies, The Netherlands) have a symmetric pore structure that corresponds to a pore diameter of either 200 or 800 nm. The 200 and 800 nm pore size capillary have an inner–outer diameter of 2.0–3.0 and 3.0–4.0 mm, respectively, and a total

length of 50 mm, in order to properly fit in the microwave autoclave.

The microwave (MW) oven used in this study was a computer controlled Milestone ETHOS 1600, with a fixed frequency of 2.45 GHz (length of a single full wave is 12.2 cm). One of the MW Teflon lined autoclaves are equipped with both pressure and temperature sensors, which make feasible to follow the evolution of temperature and pressure during each experiment. The power applied is also recorded. The experimental conditions such as synthesis temperature and duration were fixed on the basis of previous results [13].

The MFI-type zeolite membranes were obtained by seeded secondary growth. The seeds were prepared by a two-step MW-assisted hydrothermal synthesis according to the procedure reported by Motuzas et al. [17]. The molar composition of the starting seed synthesis solution was $\text{SiO}_2:0.4\text{TPAOH}:19.5\text{H}_2\text{O}:4\text{C}_2\text{H}_5\text{OH}$. The synthesis parameters were as follows: first step at 80°C for 90 min; second step at 120°C for 60 min. The final seed suspension, with a uniform size in the range 50–60 nm, was obtained by dispersing the seeds in distilled water (0.65 wt.% in water).

The deposition of the silicalite-1 seed layer was made on both sides of the $\alpha\text{-Al}_2\text{O}_3$ capillaries by dip coating with the above mentioned seeds suspension. The outside layer of the support was wrapped with Teflon tape if the seed layer was only deposited in the lumen of the tube. In case the zeolite layer was synthesised only on the outer surface of the capillary support, its ends were plugged with two Teflon caps, preventing any zeolite growth inside the capillary.

The molar composition of the secondary growth sol was $25\text{ SiO}_2:3\text{ TPAOH}:1500\text{ H}_2\text{O}:100\text{ C}_2\text{H}_5\text{OH}$ [13], and it were aged before synthesis in air under stirring for 3 h at room temperature. According to Motuzas et al. [13], 2 h synthesis is not sufficient to grow a MFI-type layer at 120°C , being required a minimum temperature of 130°C , whereas synthesis conditions of 2 h and 160°C make feasible to obtain a high quality membrane with an ideal n/i butane selectivity of 52 at near room temperature. In the present work the synthesis duration was 120 min and the temperatures selected were 155 and 160°C . After synthesis, the autoclave was cooled down and the membranes were thoroughly washed with distilled water and calcined in air for 4 h at 550°C , with a heating rate of $0.2^\circ\text{C}/\text{min}$.

For comparison purposes, an outside type membrane was also synthesised by classical heating (CL) in a convection stove at 180°C during 5 h, the seeding procedure was the one described above and the synthesis gel composition was the previously referred as secondary growth sol.

2.2. Membrane characterization

The amount of zeolite which was grown on the capillaries was quantified by the weight gain (mg of zeolite/g of support). The thickness and morphology (crystal size and shape) of both the seed layers and membranes (surfaces and fractured cross-sections) were studied by field emission scanning electron microscopy (FESEM, Hitachi S-4500 and S-4800).

The integrity of the S-1 (silicalite-1) layers was checked by measuring the single-gas permeation of N_2 and SF_6 . The kinetic diameter of N_2 (0.364 nm) is smaller than the pore size of S-1, while SF_6 has a kinetic diameter of 0.55 nm which is almost the same as the size of the silicalite-1 pores. Although N_2/SF_6 ideal selectivity (defined as the ratio of single-gas permeances) is a method commonly used in literature, it can be highlighted that according to Lee et al. [18] the N_2/SF_6 couple is not adequate to assess membrane quality. This is mainly because permeation measurements in the presence of molecules that swell the crystals, such as SF_6 , cannot

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