Synthesis of capillary titanosilicalite TS-1 ceramic membranes by MW-assisted hydrothermal heating for pervaporation application

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ABSTRACT

Titanium silicalite-1 (TS-1) membranes were obtained on α-Al_2O_3 capillaries by secondary growth of silicalite-1 seeds under microwave irradiation. TS-1 membranes were grown at 180–190 °C either on the outer side or on both sides of the capillaries, from sols with a molar ratio Si/Ti = 16–75. All the derived membranes were gas-tight before template calcination (no macro-defects) although the highest Si/Ti ratios lead to higher membrane quality with $N_2/SF_6 > 100$ for single gases and separation factors up to 65 for $EtOH/H_2O$ mixture separation by pervaporation (EtOH flux up to 2.2 kg/h m^2 at 65 °C). The reproducibility of membrane performance, with good balance between flux and selectivity, is highly attractive for further industrial applications of these TS-1 membranes which are currently developed on multi-capillary modules.

1. Introduction

Zeolite membranes have been considered for a number of applications in gas separation, pervaporation and catalysis because of their adsorption and molecular sieving properties, coupled with their higher thermal, chemical and structural stability compared with polymeric membranes [1–4]. Pervaporation (PV) is a quite effective method for dehydration of organic substances, especially for separation of azeotropic mixtures. Pervaporation is a highly efficient separation processes, involving simple operation, low-energy consumption [5], no sweep fluid [6] and having low-environmental impact [7]. Processing parameters such as operating pressure, temperature and hydrodynamic conditions strongly impact the efficiency of the PV process, although membrane structure and properties are far-reaching issues. The PV process is economically more attractive when the preferentially permeable component is present at low concentration in the feed, as far as much lower evaporation heat consumption is required for the small fraction component. Therefore, this separation technique could be very effective to concentrate ethanol in fermentation broths with high (around 95 wt.%) water concentration.

Zeolite membranes are attractive for separating mixtures of components with differences in molecular sizes or in adsorption properties, but which are hardly or costly separated using conventional separation methods or polymeric membranes [3]. Hence,

zeolite membranes have been widely used for pervaporation at both laboratory [3] and industrial [8,9] scales for the dehydration of solvents. Although hydrophilic membrane structures, such as LTA and FAU, are the most largely developed for the dehydration of organics by PV, promising performance were recently published for the extraction of organics from aqueous mixtures with hydrophobic MFI type membranes [10,11]. The most studied MFI hydrophobic membrane is silicalite-1 (S-1), which is composed of pure silica, but the titanium-substituted silicalite-1 (TS-1) has been reported to perform even better than pure S-1 for the separation of $EtOH/H_2O$ mixtures by pervaporation [11].

TS-1 zeolite is an excellent selective oxidation catalyst with hydrogen peroxide as the oxidant, for e.g. the selective oxidation of olefins to epoxies, alcohols to aldehydes or ketones, the hydroxylation of aromatic compounds, and the ammoximation of cyclohexanone [12]. Normally, TS-1 is crystallized by hydrothermal process that often lasts between 3 and 10 days [13]. The required long crystallization time often leads to large TS-1 zeolite crystals and formation of extra-framework titanium in form of anatase, decreasing the hydrophobicity of the zeolite. Also, in the case of membranes, the insertion of support species (e.g. Al by leaching of alumina supports) within the TS-1 structure during the long synthesis process could strongly impact the PV performance. Indeed if Al Lewis sites are formed in the TS-1 membranes (Ti-ZSM-5), the membrane becomes more hydrophilic and preferably adsorb/permeate water.

In order to prepare Ti-rich TS-1 membranes, free of both Al and extra-framework species, Motuzas et al. [14] employed a MW-assisted secondary growth hydrothermal method, using tubular

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α-Al_2O_3 supports. Microwave (MW) heating is a fast, simple, uniform and energy efficient method, which can reduce significantly the synthesis time of zeolite membranes [16] and then decrease the chance of support etching. Uniform sol heating and good control of the chemical integrity of the support helps providing reproducible and good quality MFI zeolite membranes from MW derived S-1 nanoseeds [15,16]. When growing TS-1 membranes by MW-assisted heating a competition is expected between: (i) MFI network distortion due to Ti incorporation in the growing zeolite and (ii) selective MW absorption by Ti species which are potentially overheating centers due to their high coordination ability (higher than Si) which attracts H_2O molecules and charged species [15].

Most of the zeolite membranes reported in literature have either a flat plate or tubular geometry, although monolithic supports have also been used [10]. The flat plate geometry is advantageous for the homogeneity in seeding and synthesis on the small disks used for academic studies, but it has a low surface area to volume ratio (S/V). The S/V ratio of tubular membranes is larger and easier to scale-up, consequently, commercially available zeolite membranes for pervaporation have a tubular geometry [8,9].

In order to achieve high ethanol fluxes and selectivities in the ethanol/water separation, it is important to optimize all the transport steps occurring during the pervaporation process: (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 its thickness, and (iii) transport through the porous support, by decreasing its thickness and, eventually, by synthesizing the zeolite layer on both sides of the support for limiting concentration–polarization phenomena [17]. In this work a series of TS-1 zeolite membranes have been prepared under MW irradiation from a series of sols with different Si/Ti molar ratios on ceramic capillary supports with a high membrane surface area-to-volume ratio (>1000 $m^2\,m^{-3}$), which is twice higher than that of classical tubular supports ($\ll$500 $m^2\,m^{-3}$) [17]. The selective layer was deposited either outside or on both sides of the capillaries. Membrane series have been characterized by both XRD and SEM methods, their quality was evaluated by single gas permeance with both N_2 and SF_6, and their performance has been compared for the separation of $EtOH/H_2O$ mixture by pervaporation.

2. Experimental

2.1. Membrane synthesis by secondary growth

The ceramic α-Al_2O_3 capillary supports (Hyflux CEPAration Technologies, The Netherlands) have a symmetric pore structure that corresponds to a pore diameter of 200 nm. The capillary has an inner–outer diameter of 2.0–3.0 mm 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 is equipped with both pressure and temperature sensors, which make feasible to follow the evolution of temperature and pressure during each experiment. The experimental conditions such as synthesis temperature and duration were fixed on the basis of previous results [14,18,19].

TS-1 membranes were obtained by seeded secondary growth. The S-1 seeds were prepared by a two-step MW-assisted hydrothermal synthesis according to the procedure reported by Motuzas et al. [20]. The molar composition of the starting seed synthesis solution was $SiO_2:0.4TPAOH:19.5H_2O:4C_2H_5OH$. 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.%).

The deposition of the silicalite-1 seed layer was made either outside or on both sides of the α-Al_2O_3 capillaries by dip-coating with the above mentioned seeds suspension. In case the zeolite layer was synthesized 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 secondary growth sol was prepared by mixing TEOS, TBOT, ultra-pure water and TPAOH; it was aged before synthesis in air under stirring for 3 h at room temperature. The molar composition of the sol was $25SiO_2:xTiO_2:3TPAOH:1500H_2O:100C_2H_5OH$ [14], the Ti content in the sol ($\times$) was varied in the range of 0.33–1.31. The secondary growth temperature was set from 180 to 190 °C, with synthesis duration in the range of 2–2.5 h.

For comparison purposes in PV performance, silicalite-1 (S-1) membranes were also synthesized. The S-1 membranes were obtained according to procedure described by Motuzas et al. [15], here briefly described. The S-1 seed layer was deposited following the same procedure aforementioned and the molar composition of the secondary growth sol was $25SiO_2:3TPAOH:1500H_2O:100C_2H_5OH$. The sol was aged for 3 h at room temperature and the secondary growth step was performed at 160 °C for 2 h.

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 °C/min.

The membranes were named according to the following nomenclature "number 1–number 2–number 3–text", where number 1 corresponds to the Si/Ti molar ratio in the mother sol, number 2 is the synthesis temperature (180 or 190 °C), number 3 is the synthesis time and the text corresponds to the type of synthesis (inside, outside or double-sided).

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 the membranes (surfaces and fractured cross-sections) were studied by Field Emission Scanning Electron Microscopy (FESEM, Hitachi S-4500 and S-4800). The zeolite phase purity and crystal orientation were checked by X-ray diffraction (Rygaku/Max System RU 300).

The integrity of the TS-1 layers was checked by measuring single gas permeance of N_2 and SF_6. The kinetic diameter of N_2 (0.364 nm) is smaller than the pore size of TS-1, while SF_6 has a kinetic diameter of 0.55 nm, i.e. almost very similar to the size of TS-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. [21] 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 discriminate between membranes with few defects and ones with many defects. In the present work, the N_2/SF_6 ideal selectivity was used as a first indication of membrane quality.

Template molecules were used during zeolite crystallization. They are located both in the zeolite pores and in the small non-zeolite pores in the intercrystalline boundaries. To check the presence of large defects in the grown membranes, N_2 permeance was measured before calcinations: defect-free membranes were impermeable to N_2.

2.3. Pervaporation (PV)

The experimental set-up for the pervaporation system was previously described [22]. The membrane module was immersed in