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Preparation of zeolite NaA membranes on the inner side of tubular supports by means of a controlled seeding technique

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Abstract

Zeolite NaA membranes have been reproducibly prepared by seeded hydrothermal synthesis on the *internal* surface of porous α-alumina tubular supports. A cross-flow filtration technique has been developed to allow a controlled seeding of zeolite NaA crystals from a suspension according to transmembrane pressure, pH, seed suspension flow rate, crystal size and concentration. The optimal seeding weight gain was found to be around 0.40 mg cm^{-2} of membrane area. With this procedure, zeolite membranes with selectivities up to 600 at fluxes of 0.50 kg m^{-2} h^{-1} were obtained in the pervaporation of 92:8 wt.% ethanol/water mixtures at 323 K.

Keywords: Zeolite membrane; Pervaporation; Zeolite NaA; Alcohol dehydration; Centrifugal field synthesis

1. Introduction

Research on inorganic membranes has been steadily growing during the last decade because of the increasing demands from membrane materials, related to their thermal, mechanical and chemical stability, sterilization and biocompatibility [1]. Among inorganic membranes, zeolite membranes constitute a promising technology due to their potential applications in separation processes, and also as catalytic membranes, sensors, electrodes and optoelectronic devices [2]. These processes take advantage of the unique properties of zeolites when used in a film-type configuration.

Pervaporation has attracted widespread attention by industry as an energy-efficient technique for the separation of azeotropic and close-boiling liquid mixtures, and for the dehydration of organic solvents in many chemical and pharmaceutical processes [3,4]. Hydrophilic zeolite membranes have been found to be suitable for dehydrating water/organic mixtures by pervaporation, being zeolite A often the material of choice due to its high Al content and small pore size (4.1 Å). Zeolite A membranes with high selectivities (up to 10 000) and high fluxes for the separation of alcohol/water mixtures have been reported in the literature [5–9] and by now, zeolite NaA membranes are commercially available (Mitsui Engineering & Shipbuilding Co. Ltd. [10]).

Zeolite NaA membranes have been traditionally prepared by static discontinuous hydrothermal syntheses using either a milky-like gel or a clear solution onto the surface of a porous support with or without a previous seeding step [6,11–14]. The seeding of the support has been reported to improve the reproducibility in the synthesis of zeolite membranes [15] by decoupling the nucleation and crystal growth steps. Rubbing and dip coating constitute the most widely used seeding techniques, which are based, respectively, on a manual deposition of zeolite microcrystals onto the surface of the support, and on the formation of a layer of crystals from a suspension by controlling its pH and rate of dipping [16]. Other seeding techniques deal with the deposition of zeolite crystals by means of electrostatic forces, electrophoresis, pulsed laser ablation and sputtering [17–19]. More recently, it has been shown that an UV irradiation of titania supports can help the growth of zeolite NaA layers with a good pervaporation performance [20].

Given the seeding methods used, most of zeolite membranes prepared have been grown onto planar supports or onto the external surface of tubular supports, and only a few works attempted growth onto the internal surface of

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tubular supports (e.g. [21]). Growing zeolite films on the inner side of tubular supports is attractive from the point of view of industrial application, because the zeolite layer is better protected, and also because this configuration makes it easier to compensate the mismatch regarding the expansion coefficients of the zeolite materials and of the alumina support.

However, growing a layer in such a configuration represents a serious challenge for the present methods of preparation of zeolite membranes due to the low accessibility to the lumen of tubular supports, which complicates the use of the above-described seeding methods. In a previous work [21], a modified version of the rubbing method was used, in which the seeds were rubbed on the inside surface of tubular supports using a test-tube brush. Nevertheless, the main limitation of these techniques is that they are not reproducible, often yielding aggregates of crystals rather than a smooth coverage of seed particles. As an alternative for inner-side seeding, a cross-flow filtration technique adapted to seed individual zeolite NaA crystals could be an interesting option. This technique is based on a controlled cross-flow filtration of a dilute suspension of seeds of the desired material through a porous solid, and has been employed to prepare the so-called dynamic membranes [22]. Typical applications of this kind of membranes are in the field of reverse osmosis (RO) and ultrafiltration (UF). The most studied membranes are those based on ZrO_2 and ZrO_2/PAA (PAA = polyacrylic acid).

On the other hand, the growth of a layer on the inside surface of a porous tubular support also presents the additional challenge of maintaining an adequate supply of nutrients for crystal growth, something that in more easily achieved when the crystal layer grows on the outside. The rate of renovation of the gel inside the lumen of the support can be increased by rotating the autoclave or gel container to achieve mixture homogeneity [12]. It has also been reported that good quality zeolite layers can be obtained under a centrifugal field, which helps to set crystal nuclei of suitable size from the bulk of the solution on the support, thereby promoting intergrowth [23]. Both beneficial effects (gel renewal and setting of nuclei) have been combined in the device described in [21] for the synthesis of zeolite NaA membranes on the internal surface of tubular supports.

The present work is devoted to prepare zeolite NaA membranes onto the internal surface of α-alumina tubular supports by seeded hydrothermal synthesis. To this end, a cross-flow filtration technique has been developed as a means to obtain a controlled seeding of zeolite NaA crystals from a suspension.

2. Experimental

The zeolite NaA membranes were prepared by seeded hydrothermal synthesis onto the internal surface of α-alumina tubular supports (manufacturer: Inocermic, Hermsdorf, Germany) with pore diameters of 1.9 μm. These tubes (7 mm i.d. and 10 mm o.d.) were subjected to enameling at both ends, defining a permeation length of approximately 5 cm.

2.1. Cross-flow seeding: fundamentals and set-up

The main purpose of this kind of seeding is to seed individual zeolite NaA crystals in an ordered manner on the pores in the internal surface of tubular supports. The zeolite NaA crystals (2 and 7 μm) were supplied by IQE (Industrias Químicas del Ebro, Spain). Filtration flux across the supports becomes progressively reduced due to the formation of a layer of crystals on the surface of the support exposed to filtration, and the seeds initially concentrate around the pore mouths.

Because zeolite NaA and α-alumina have isoelectrical points (IEP) which are dependent on the presence of –OH surface groups [24], the pH could play an important role in the proposed seeding process. IEP values around 9.0 for α- and γ-alumina has been reported by several authors [24–26], but not many studies have been carried out concerning zeolite NaA. Therefore, some preliminary experiments were carried out to determine the IEP of zeolite NaA by the determination of the ζ-potential of zeolite NaA suspensions at a pH range 4–10 (below pH 4, zeolite NaA is not stable) in a Malvern Zeta Sizer equipment. The suspensions (500 mg L^{-1}) were stirred, immersed in an ultrasound bath for 1 h to avoid the formation of aggregates and then their pH was continuously monitored (Crison, micropH2002, Spain) and adjusted to the desired value. Care was taken to ensure that the pH was stabilized before the determination of the ζ-potential.

The experimental procedure used for seeding was as follows. A suspension of zeolite crystals was prepared, then stirred and kept in an ultrasound bath for 1 h to avoid the formation of aggregates. The pH of the suspension was adjusted to the desired value and continuously controlled during the seeding process. The suspension was fed to the lumen side of the tubular support at a given flow rate by means of a membrane pump. To this end, the tubular support was set inside a permeation module, where the desired value of transmembrane pressure, ΔP_m, could be fixed and continuously monitored. The pressure at the retentate side was adjusted by means of the regulation valve at the outlet of the module (see Fig. 1). The evolution of the seeding process was monitored from the evolution of the water permeability across the support.

2.2. Hydrothermal syntheses

The hydrothermal syntheses were carried out in a discontinuous system under a centrifugal field using a device similar to the one described in [21] (see Fig. 2). The support was attached to a rotor piece and rotated vertically around its longitudinal axis. The external surface of the

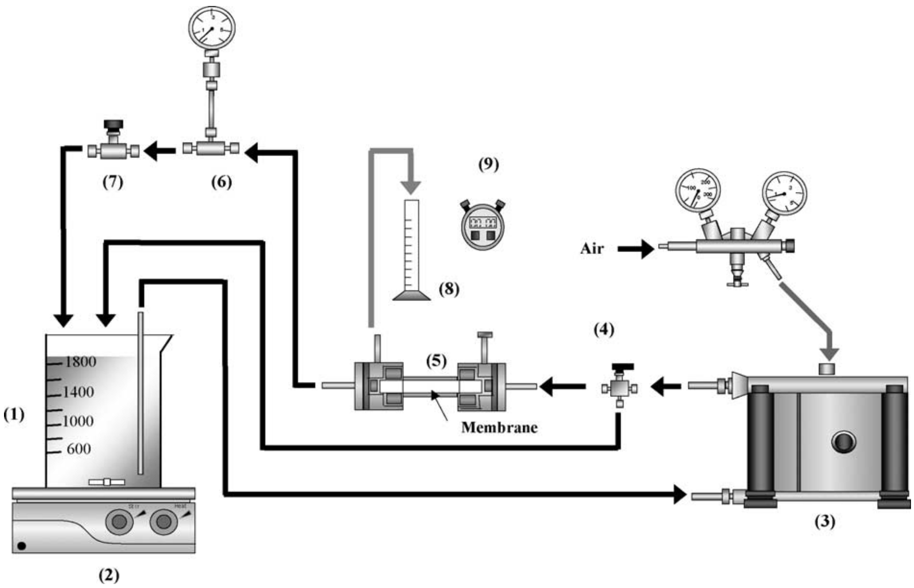

Fig. 1. Set-up used in the cross-flow seeding: (1) zeolite suspension; (2) stirrer; (3) membrane pump; (4) three-way valve; (5) membrane module; (6) manometer; (7) regulation valve; (8) test tube; (9) chronometer.

support was wrapped with Teflon tape to avoid any zeolitic deposition. The membrane was immersed in a synthesis glass vessel surrounded with boiling water to keep the temperature at 373 K inside the vessel. The upper section of the rotor had three rectangular holes of an area about 10 mm^2 each to achieve renovation of the gel. As a rotational speed of 100 rpm, centrifugal forces caused the exit of the gel through the rotor ports, creating an upwards movement inside the support.

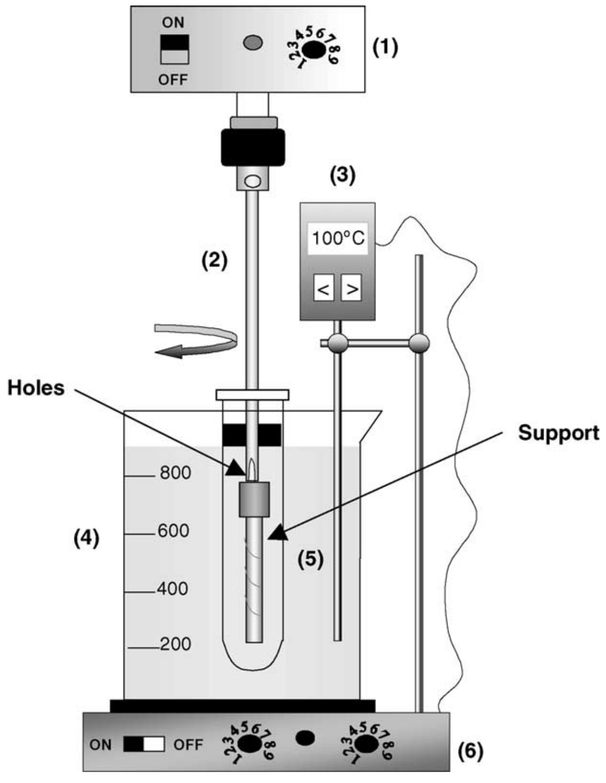

Fig. 2. Set-up used for membrane synthesis: (1) stirrer engine; (2) rotor; (3) thermostat; (4) boiling water bath; (5) glass vessel; (6) heater.

Three precursor milky-like gels were used in this work to prepare zeolite NaA membranes, with different degrees of dilution. Their molar compositions were $1Al_2O_3$:$2SiO_2$:2.1-Na_2O:XH_2O, where X = 120, 270, 400 for gels 1, 2 and 3, respectively. The procedure to obtain the gels was based on the preparation of two separate solutions (A and B). Solution A was prepared by dissolving the appropriate amount of sodium aluminate powder supplied by Aldrich (Al_2O_3 = 53 wt.%, Na_2O = 43 wt.%, Fe_2O_3 = 4 wt.%) in a covered flask at 343 K and stirred until the aluminum was completely dissolved. The water in this flask represented half of the total water needed in the final composition of the gel. Solution B was prepared by dissolving a sodium silicate solution supplied by Aldrich (SiO_2 = 27 wt.%, NaOH = 14 wt.%) in the remaining water under stirring. Solution B was added in three consecutive steps to solution A under vigorous stirring and the temperature was kept at 343 K.

After the preparation of the gel, it was poured into the glass flask previously preheated at a temperature of 373 K. The duration of each synthesis step was 3 h with a rotation speed of 100 rpm. After each synthesis, the membrane was washed with boiling water for 1 h and kept at 343 K under vacuum overnight with a ramp of 1 K min^{-1} to avoid any thermal stress in the zeolitic layer.

2.3. Membrane characterization

In terms of permeation, the membranes were characterized by a N_2 permeation test, He/N_2 permeation selectivity measurements and pervaporation tests. For pervaporation, the membrane was placed in a module immersed in a temperature-controlled silicone oil bath. The temperature and pressure at the retentate side were continuously monitored and maintained at constant values. The 300 mL min^{-1} of an ethanol/water liquid mixture was fed to the retentate side of the membrane by means of a magnetically coupled centrifugal pump (Ismatec BVP-Z, Glattbrugg, Switzerland), and recirculated to the feed tank. Samples of the feed at the inlet and outlet of the membrane module could be taken by means of two needle valves. The pressure at the permeate was measured by a vacuum gauge (Schlee GmbH & Co. V-D3, Witten, Germany) and maintained below 2 mbar by the action of an oil vacuum pump (Telstar 2G-6, Sabadell, Spain). The permeated vapors were condensed and collected in a set of cold traps cooled with liquid nitrogen. Both the feed and the collected liquid were analyzed in a gas chromatograph (HP 6890 series with TCD detector, USA). The selectivity of the membrane was calculated as the ratio of the weight fractions of water and ethanol in the permeate side to that in the feed. The final values correspond to the mean of two consecutive steady-state measurements taken after 12 h of stabilization.

The phases present in the zeolite NaA membranes were characterized by X-ray diffraction (XRD) analysis, using Cu Kα radiation and a secondary graphite monochromator (Siemens D-500, Germany). The membranes were also examined by scanning electron microscopy (SEM), operating at 10 kV (Cambridge S120, USA).

3. Results and discussion

3.1. Seeding: effect of operating variables

A steady-state amount of zeolite crystals coating the support (i.e. seeding weight gain, SWG) can be attained by operating with a given suspension feed flow rate, zeolite concentration, transmembrane pressure and pH. The permeability of the support decreases to a stable value, as the pores of the support become progressively blocked by the seeded zeolite crystals (see Fig. 3). Fig. 3 also shows that all data can be roughly fit by the same curve and thus the seeding pattern of the supports does not seem to depend on the zeolite NaA crystal size or on the transmembrane pressure. This is a useful feature of the tangential filtration seeding procedure, as it shows that the process of covering the support surface with seeds is highly reproducible.

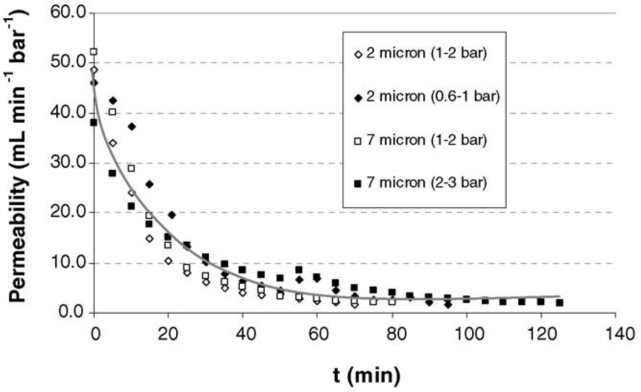

Fig. 3. Evolution of water permeability during the cross-flow seeding process with 2 and 7 μm zeolite NaA crystals at several transmembrane mean pressure ranges (pH 8, zeolite concentration = 20 mg L^{-1}, feed flow = 5.5 L min^{-1}).

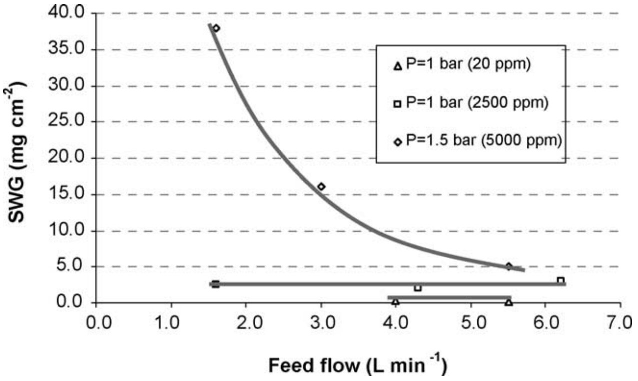

Fig. 4. Evolution of steady-state seeding weight gain (SWG) with the feed flow in the cross-flow filtration seeding process for different transmembrane pressures (1 and 5 bar) and suspension zeolite concentrations (20, 2500, 5000 mg L^{-1}). Average particle size 2 μm; pH 8.

As can be seen in Fig. 4, no effect of the feed flow rate in the SWG was found at the rates studied for concentrations lower than 2500 mg L^{-1}, except for the most concentrated solutions (>5000 mg L^{-1}), where a decrease of SWG with flow rate was observed. In any case, as could be expected, SWG values increased with the concentration of the suspension.

Regarding the effect of the pH on the SWG (see Fig. 5), a maximum in the SWG was observed around pH 8. This is consistent with the IEP measurements carried out with zeolite NaA. The evolution of the ζ-potential of zeolite NaA with pH (see Fig. 6) reflects an IEP around 8, somewhat higher than the value of 7.2 reported by Huang and Rhoads

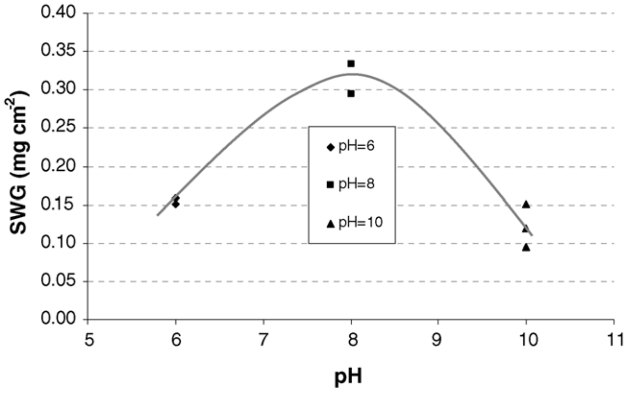

Fig. 5. SWG as a function of pH in the cross-flow filtration seeding process for α-alumina with 1 bar transmembrane mean pressure difference. Average particle size 2 μm. Other conditions as in Fig. 3.

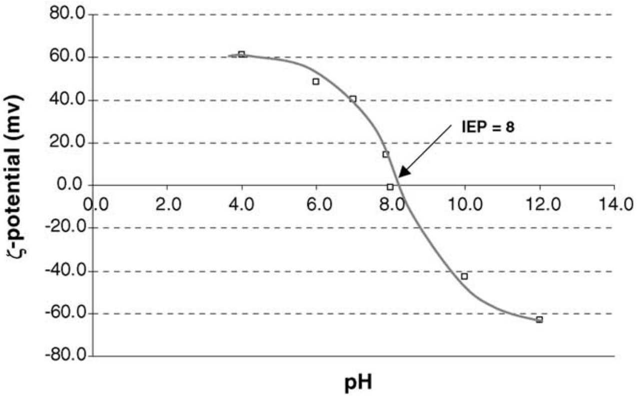

Fig. 6. ζ-Potential of zeolite NaA as a function of pH (average particle size 2 μm). The values indicated correspond to the mean of three consecutive replicates.

[24]. At pH values far from 8, both the zeolite NaA crystals and the support (IEP ~ 9) would sustain charges of the same sign (positive at $pH < 8$ and negative at $pH > 9$). The resulting electrostatic repulsive forces could partially compensate the hydrodynamic effect of filtration in the deposition of crystals onto the surface. However, as the pH approaches the IEP of zeolite NaA, attractive Van der Waals forces would be predominant and higher amounts of crystals would be deposited onto the surface of the support and the trend of Fig. 6 would be obtained.

3.2. Preparation of zeolite NaA membranes

The synthesis conditions for the membranes prepared in this work together with their pervaporation performance are summarized in Table 1. The effect of rotation of a seeded support at 100 rpm with gel 1 on the N_2 permeance during the synthesis steps is clearly shown in Fig. 7. A sharp decrease of N_2 permeance is observed in the first synthesis when the membrane is prepared under a centrifugal field (ZA5), while for the membrane prepared with a static support (ZA12) the permeance decreased slowly with successive syntheses. This is consistent with the hypothesis put forward in [22] that the formation of the membrane is accelerated when the synthesis is carried out under a centrifugal field.

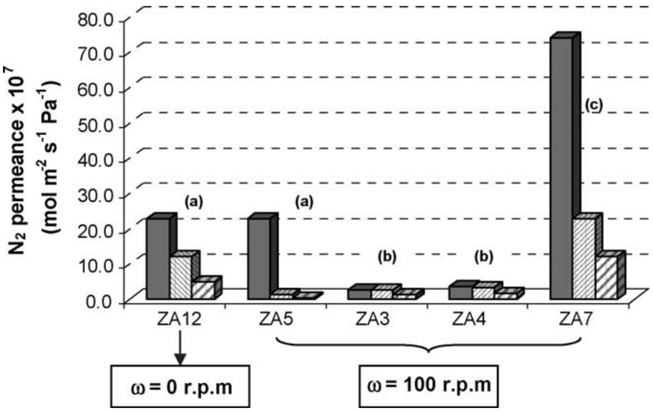

Fig. 7. Effect of the presence of a centrifugal field and effect of the concentration of the gel on the N_2 permeance: (a) syntheses carried out with gel 2; SWG ≈ 0.15 mg cm^{-2}; (b) syntheses carried out with gel 2; SWG ≈ 0.40 mg cm^{-2}; (c) syntheses carried out with gel 3; SWG ≈ 0.15 mg cm^{-2}.

The weight gain of each synthesis increases by increasing the concentration of the synthesis gel, because of a faster supply of nutrients to the growing crystal layer. In the syntheses carried out with a concentrated gel, the first synthesis step typically gives rise to a drop of two orders of magnitude with respect to the N_2 permeance of the fresh support. However, for gel 3, even though the N_2 permeance progressively decreases with the number of syntheses, the N_2 permeances are kept at higher values. These results agree with the He/N_2 selectivities (not shown), which are close to the Knudsen ideal selectivity value (2.64) for membranes prepared with gels 1 and 2, while lower values are obtained with gel 3, suggesting the presence of a higher concentration of defects.

The SWG seems to play an important role in the properties of the membranes prepared. As could be expected, as the SWG increases, the weight gain of the membranes for each synthesis step does also so. Thus, for an

Table 1
Seeding and synthesis tested conditions and pervaporation performance for the membranes prepared

Membrane	SWG (mg cm^{-2})	Synthesis gel[a]	Support rotational speed (rpm)	Number of synthesis steps	Pervaporation results	
					Selectivity, W/E (–)	Flux (kg m^{-2} h^{-1})
ZA1	0.40	1	100	4	502	0.62
ZA2	0.20	1	100	4	237	0.43
ZA3	0.40	2	100	3	294	0.32
ZA4	0.41	2	100	3	437	0.51
ZA5	0.15	2	100	3	154	0.62
ZA6	1.75	2	100	4	73	0.52
ZA7	0.15	3	100	3	14	>1
ZA9	0.05	1	100	4	56	0.57
ZA10	1.60	1	100	3	2	0.70
ZA12	0.15	2	0	3	3	>1
ZA17	0.00	2	100	3	5	>1

[a] Gel 1: $1Al_2O_3:2SiO_2:2.1Na_2O:120H_2O$; gel 2: $1Al_2O_3:2SiO_2:2.1Na_2O:270H_2O$; gel 3: $1Al_2O_3:2SiO_2:2.1Na_2O:400H_2O$.

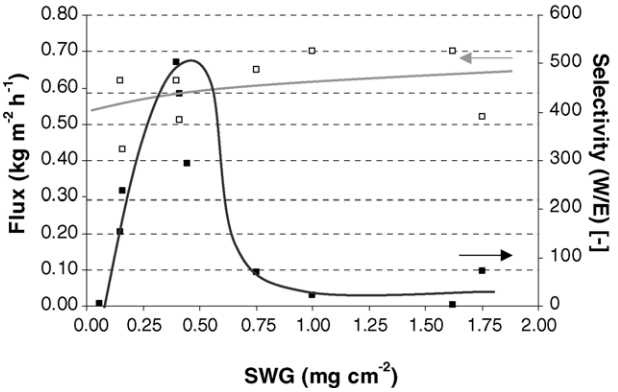

Fig. 8. Water/ethanol (W/E) selectivity (full symbols) and flux (empty symbols) as a function of SWG (wt.% of ethanol in the feed = 92, temperature = 50 °C, total feed pressure = 2 bar, permeate pressure = 2 m-bar vacuum).

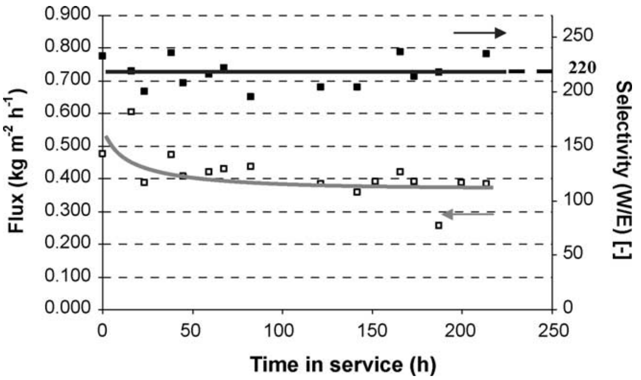

Fig. 9. Water/EtOH (W/E) selectivity (empty symbols) and flux (empty symbols) as a function of time for membrane ZA2. Other conditions as in Fig. 8.

unseeded membrane, the weight gain after two syntheses steps with gel 1 was approximately 1.9 mg cm^{-2} (ZA17). This value increased to almost 3.3 mg cm^{-2} (ZA5) for a SWG value of 0.15, and 17.3 mg cm^{-2} (ZA1) when the SWG value was 0.40 mg cm^{-2}. The SWG was also a key variable regarding the selectivity observed during the pervaporation of ethanol/water mixtures (see Fig. 8). A maximum in the selectivity of the zeolite membranes has been found at SWG values around 0.40 mg cm^{-2} after 2–3 synthesis steps. For lower and higher SWG values, the membranes provide a poor ethanol/water selectivity, which is in agreement with the results already presented for N_2 permeances and He/N_2 selectivities. The highest water/ethanol selectivity obtained in this work was around 600, with a flux up to 0.50 kg m^{-2} h^{-1} at the conditions tested. On the other hand, the total flux tends to slightly increase with the SWG probably due to a higher contribution of the defects to the overall flux.

The stability of one of the membranes prepared by the seeding technique described (ZA2) was tested in the pervaporation of a 92:8 water/ethanol mixture (see Fig. 9). The membrane preserved its separation effectiveness during 230 h, with a water/ethanol selectivity around 220 and a flux around 0.40 kg m^{-2} h^{-1}.

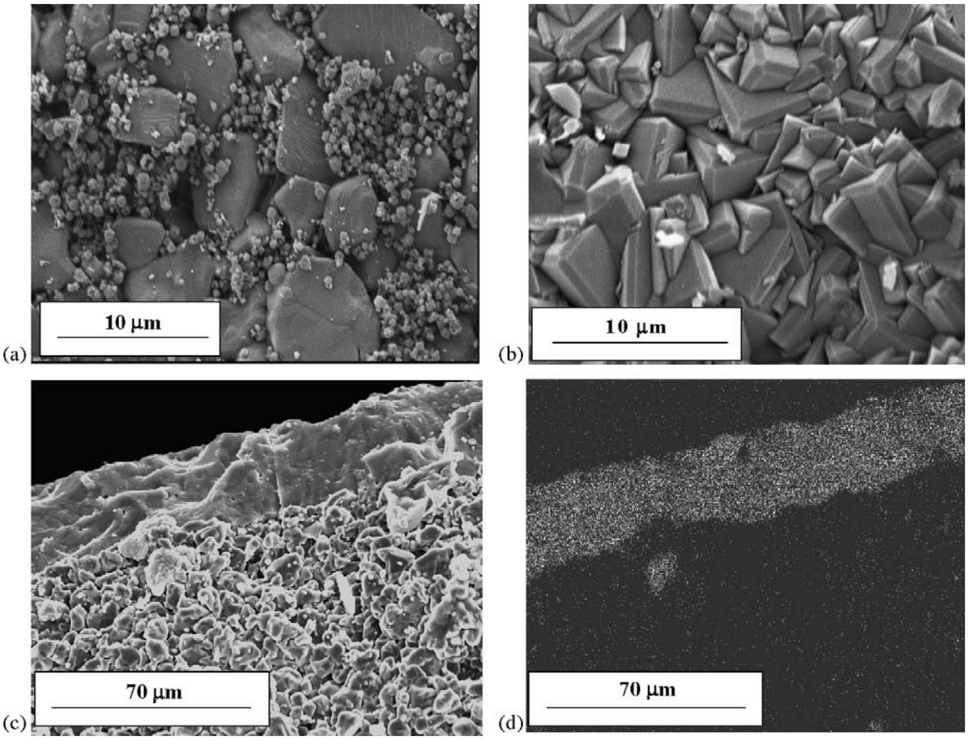

Fig. 10. SEM microphotographs of membrane ZA2: (a) top view of a seeded support; (b) top view after synthesis; (c) cross-section; (d) Si mapping of the cross-section.

3.2.1. Characterization by XRD and SEM analyses

The XRD patterns of the membranes prepared (not shown) indicated that pure zeolite NaA was the only zeolitic phase on the inner surface of the membrane. Some SEM pictures are shown in Fig. 10. Fig. 10a shows the top view photograph of a seeded support at pH 8. It can be observed that most of the crystals agglomerate in particular zones of the support, which might correspond to the macropores of the solid. Furthermore, the inspection of the top view micrograph of membrane ZA2 in Fig. 10b reveals the presence of cubic crystals typical of zeolite A randomly oriented in a continuous well-intergrown top layer of thickness around 30 μm (Fig. 10c and d).

4. Conclusions

Zeolite NaA membranes have been successfully prepared by means of a secondary growth method onto the internal surface of porous α-alumina tubular supports. To this end, a new version of a cross-flow filtration seeding process was specifically developed to obtain a controlled deposition of zeolite NaA crystals on tubular supports. The key variables are pH and transmembrane pressure drop during the seeding. Furthermore, it has been shown that the presence of a centrifugal field promotes the growth of zeolite layers in the subsequent synthesis steps. The optimal weight during the seeding was around 0.40 mg cm^{-2}, leading to well-intergrown zeolite NaA membranes with a good pervaporation performance, especially after 2–3 synthesis steps. A membrane (ZA2) showed a stable performance in stability experiments lasting 230 h.

Acknowledgements

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