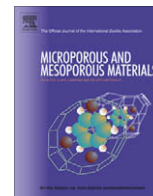




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Continuous synthesis of NaA zeolite membranes

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ABSTRACT

Zeolite NaA membranes were obtained by using a continuous recirculating flow, 0.25–5 ml min⁻¹ of synthesis solution along the inner side of asymmetric porous alumina tubular supports. The membranes of 5 μm in thickness showed a N₂ permeance of 5 × 10⁻⁷–1 × 10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹. The procedure developed in this work provides control of the synthesis and crystallization conditions at any position on the tubular support, thus implying scale-up.

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1. Introduction

Zeolites are crystalline aluminosilicates with uniform micrometer-sized pores [1]. Their unique frameworks and high specific surface areas make them, depending on composition and porous geometry, broadly applicable in petrochemical processes, in fine chemical and pharmaceutical production [2,3], in contamination abatement [4], in sensors [5,6], and in optoelectronic materials [7].

Among the zeolites, Linde Type A (LTA), has been the objective of many investigations/applications due to its long history. Zeolite A with sodium cations, denoted as NaA, has a formula of Na₁₂[(A-IO₂)₁₂(SiO₂)₁₂]⁻ · 27H₂O, and contains cages with orthogonal 3-D oriented apertures of approximately 0.4 nm. The pore dimension is changed to 0.45 or 0.30 nm, when the zeolite is ion exchanged with Ca²⁺ or K⁺, respectively [8].

Although zeolite A membranes have not been shown as very promising for gas separation based in molecular sieving effects, they are widely used for pervaporation purposes. The excellent water separation is based on the strong hydrophilic nature of the zeolite A membrane and not on molecular sieving. This zeolite A membrane has, therefore, a remarkable non-zeolite mass transport contribution which spoils shape selective gas phase separations and results in gas separations not far from the Knudsen factor. The gas permeation is controlled by intercrystalline transport through mesopores whereas liquid mixtures can be separated despite the presence of mes-

opores due to hydrophilic interactions [9]. Specifically, the preparation of zeolite membranes for dehydrating azeotropic mixtures by pervaporation has been the subject of many studies [10,11].

Worldwide the production of bio-ethanol could profit from low-energy membrane separation of water from the water–alcohol product. Especially for the ethanol/water and other water-containing azeotropes, this alternative process using a hydrophilic zeolite NaA is beneficial for systems with relative low volatility.

Mitsui-BNRI played a pioneering role in the cost reduction of the membrane separation by integrating distillation and membrane separation in the so-called “Membrane Separation and Distillation” (MDI process). By the MDI process dehydrated ethanol with less than 0.4 wt% residual water is produced from a liquid containing 8 wt% ethanol. The water flux measured in pervaporation operation for 90 wt% ethanol solution at 348 K is about 7 kg m⁻² h⁻¹. Ethanol hardly permeates through the membrane resulting in a separation factor α (water/ethanol) ≈ 10,000. The NaA membranes showed good stability with an operating lifetime of 3–5 years.

The use of inorganic membranes is an option because of their relatively low operational cost implications on the long term due to their chemical and thermal stability, although the inorganic membrane manufacture is more expensive than the production of the polymeric ones. Therefore, zeolite membrane production costs are a major factor to be considered for industrial applications. An estimated price limit of membranes for petrochemical applications is 200 € m⁻² [12], being estimated near € 1,000 m⁻² for zeolite membranes. Although the support is a major cost factor, reduction of the synthesis costs of the selective zeolite layer remains an important target. Concepts to reduce the price for the preparation of the zeolite layer comprise e.g. the template-free synthesis, an economic lower price support and a flow system synthesis [13].

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For developing industrial-sized modules, the preparation of membranes would ideally involve the use of a cheap tubular support and a continuous synthesis with recirculation to fully benefit and control the nutrient flow along the wall of the support tube during the synthesis, thus obtaining a high quality membrane.

Among the different synthesis strategies for zeolite membranes, zeolite NaA membranes have been conventionally prepared by hydrothermal synthesis onto a porous support in one or several batch cycles, either *in situ*, with a preliminary seeding procedure (i.e., secondary growth method) or by steam-assisted crystallization.

Advantages of seeding techniques are the decoupling of the nucleation step and the crystal growth [14]. A variety of seeding techniques exists which includes: rubbing zeolite crystals over the outer side of a tubular support [15], or on the inner side by brushing [16], laser ablation [17], cross flow filtration of a suspension of crystals [18], spin coating [19] and dip coating of a colloidal mixture of nanocrystals [20]. However, most of these techniques are not useful for all kinds of supports. In the case of tubular supports, e.g. the inner side of the support is not accessible for this technique. Preparing membranes on the inner side of tubular supports may be advantageous because the membrane layer is protected against physical damage during handling operations. It is also desirable in high-area applications such as capillary or multi-channel supports.

Another method to create a membrane is by means of chemical bonding between existing zeolite crystals and the support with covalent or ionic bonding. This procedure was employed by Van den Berg et al. [21] to synthesize membranes on pretreated titania supports with UV-photons, improving hydrophilic properties of the support, thus increasing the surface Ti-OH groups. Also Boudreau et al. [22] synthesized oriented zeolite NaA membranes by a surface modification of the support by ultrathin, self-assembled polymer films.

Regarding work related to obtain a zeolite NaA membrane by a non-batch synthesis, only a few studies have been reported in the literature. Some authors reported the preparation of outer side [15] or inner side [18] zeolite NaA membranes using a semi-continuous synthesis system that allows pulse-renewal of the synthesis solution in an autoclave at periodic intervals by the action of a set of electro-pneumatic valves.

Richter et al. [23] reported the synthesis of ZSM-5 membranes on the inner side of alumina tubes and capillaries. Culfaz et al. [24] prepared MFI-type zeolite membranes on alumina tubular supports in one to three cycles with a circulation of the synthesis gel applying a peristaltic pump at a flow rate of 6–48 ml min⁻¹.

The use of a flow system for zeolite NaA membrane synthesis has only been reported by a few authors. Yamazaki and Tsutsumi [25] synthesized membranes on flat supports at 353–403 K for 24–48 h at a flow rate of 50 ml min⁻¹. Kita [26] obtained a zeolite A membrane without seeding and by microwave synthesis with a selectivity water/ethanol of 4100 and a flux of water of 1.2 kg m⁻² h⁻¹. More recently, the hydrothermal synthesis of tubular inner-side zeolite NaA membranes in a continuous flow system is performed through gravity [27].

In this work we propose the preparation of NaA zeolite membranes, on tubular supports by *in situ* hydrothermal continuous synthesis in a flow system. This procedure avoids depletion of nutrients in the liquid phase, allows a better control of the composition of the reacting mixture and improves the feasibility of the scale-up the synthesis process.

2. Experimental

α -Alumina tubular supports, with an I.D./O.D. of 7/10 mm, and a length of 80 mm having a top layer on the inner surface containing

pores of 200 nm, were purchased from Inoceramic GmbH. The effective length was 60 mm because a glazing of 10 mm was applied at both ends. After coating on each support end with the home made glazing (IN 1001 Clear, Envision Glaze, Duncan) the supports were heated at 1000 °C for 15 min at a heating rate of 1–3 °C min⁻¹. The tube was covered on the outer side with teflon tape in order to avoid during synthesis any mass transfer of nutrients from inside to outside the tube with consequently crystallization phenomena on the outer surface of the tube.

The clear solution used for the synthesis of NaA zeolite membrane had a molar composition of 12 Al₂O₃:53 SiO₂:503 Na₂O:10,000 H₂O, adapted from the work of Zhu et al. [28]. Two reactant solutions were prepared by dissolving sodium metasilicate pentahydrate (97%, Sigma) and anhydrous sodium aluminate (Riedel-de Haen) in freshly made sodium hydroxide solutions. The total amount of sodium was distributed in a ratio of 1:1.38 between the corresponding silicate and aluminate solutions while the water was divided evenly. The silicate and aluminate solutions were aged for approximately 1 h at room temperature; then the aluminate solution was added to the silicate solution under continuous stirring. The synthesis solution was further aged for 1 h at room temperature.

The experimental set-up employed for the flow system synthesis of NaA zeolite membranes, is shown in Fig. 1. The tubular support was placed inside a home-made autoclave having an inlet and an outlet to allow the synthesis solution to flow through the tubular support. The autoclave is placed vertically in the oven. Simultaneously with this set-up constant conditions are provided in the autoclave between the inner and outer surface of the tubular support. Fresh clear solution was supplied from a vessel (2 l), by a HPLC pump with a flow rate between 0.25 and 5.00 ml min⁻¹. At the end of the synthesis, the as-synthesized membranes were decoupled from the module and the tape was removed. The membrane was washed with deionized water for 1 h and dried in an oven at 353 K overnight. The hold-up of the experimental set-up is 10 ml, only a 0.5% of the total volume. So, there is a negligible amount decrease of the nutrients in the solution during the experiment, due to the low hold-up volume and because a small amount of solution is necessary to create the zeolite layer. Besides, working at this range of flow rate, a laminar flow is ensured inside the tubular support. Reynolds numbers of 1–55 are achieved for flow rates of 0.10–5.00 ml min⁻¹, respectively. A homogeneous deposition at any site of the inner wall of the support is expected this way.

Single gas permeation experiments were carried out to examine the quality of the membranes and the possible existence of defects. The membrane was placed in a permeation module with the inner side of the tube facing the feed. Single gas permeation of nitrogen was measured using a soap-film bubble flow meter at room temperature under a pressure difference of 0.3–1 bar. The surface and cross-section morphology of the as-synthesized membranes was examined by scanning electron microscopy (SEM) using a Philips XL20 microscope.

The pervaporation experiments of water/isopropanol (35/65 wt.%) mixtures were carried out in a laboratory scale set-up at 363 K. The membrane was placed in a membrane module and put in the oven of the pervaporation set-up. The liquid feed was stored in a vessel (5 l) at atmospheric pressure. The feed stream was pumped to the module at a constant flow rate of 6 ml/min using a HPLC pump and the retentate stream was recycled back to the feed vessel. In order to reduce the temperature gradient between the oven and the feed vessel and to avoid the liquid feed from boiling, the feed vessel was heated independently. The feed pressure was regulated using a backpressure controller and maintained at 4 bars to ensure a liquid phase feed at higher temperatures.

The permeate side of the pervaporation unit was evacuated by a two-stage vacuum pump, keeping the pressure at the permeate

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