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A novel seeding procedure for preparing tubular NaY zeolite membranes

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ABSTRACT

A good seeding is a mandatory step to have defect-free zeolitic membranes prepared by means of a secondary growth method. The transport properties of the zeolitic membranes depend strongly on the seeding procedure of zeolite crystals during which the whole support surface has to be covered uniformly and sufficiently. A new seeding procedure, involving cross-flow filtration of a water suspension combined with rotation and tilting of the membrane support, was developed and utilized for the first time.

Porous α-alumina tubes were seeded using a water suspension of 0.2 wt.% in zeolite crystals, at a pH of ca. 9.2 and room temperature. Cumulative stage-cut of the seeding phase was used as design parameter in order to tailor the permeation properties (e.g., permeance) of the resulting NaY zeolite membranes. The secondary growth was accomplished by a hydrothermal treatment.

SEM, EDX and XRD analyses show dense intergrown FAU layers with Si/Al ratios of 1.8–2.0 typical of the NaY zeolite.

The measured permeance was 5–10% of that showed by the bare support. Another evidence of the membrane quality can be found considering their application in CO selective oxidation reaction [P. Bernardo, C. Algieri, G. Barbieri, E. Drioli, Catal. Today 118(1–2) (2006) 90]: a complete conversion of carbon monoxide which falls down 1000 times from 10,000 to ca. 10 ppm indicates very few defects in the zeolite layer.

1. Introduction

Zeolite membranes have attracted much interest for applications in many industrial processes owing to their crystalline structure and to their pore diameters close to molecular size of different species. These features allow the continuous separation of mixtures on the basis of differences in the molecular size and shape (e.g., isomers [1], azeotropic mixtures [2]) and also on the basis of different adsorption properties [3]. Owing to their thermal and chemical resistance, zeolite membranes are also interesting for the use in membrane reactors. Recently, FAU membranes loaded with catalytically active metal have been used in flow-through membrane reactors for CO selective oxidation contained in H_2-rich streams [4,5].

The FAU type zeolite has cavities with a diameter of 1.3 nm interconnected by pores of 0.74 nm; depending on the Si/Al ratio, it can be distinguished into X-type (Si/Al = 1.0–1.5) and Y-type (Si/Al > 1.5). FAU membranes were studied for the separation of CO_2/N_2 (separation factors of 20–100) [6], benzene/cyclohexane (separation factor of 160) [7], propylene/propane (separation factor of 6.2), ethylene/methane (separation factor of 8.4) [7] mixtures.

Zeolite membrane application at industrial level is strongly limited by costs (particularly support cost [8]) and reproducibility problems in the preparation step [9]. Today, industrial applications are only relative to LTA zeolite membranes for organic solvent dehydration by means of pervaporation and vapour permeation processes [8]. However, because of the high Al content the membranes with LTA topology are stable in a limited range of pH (6.5–7.5). For this reason, a lot of research groups are studying the application of FAU membranes, more chemically stable than LTA membranes, in pervaporation.

Self standing zeolite layers larger than a few square centimetres are difficult to form, and the resulting structures are fragile [10]. Therefore, zeolite membranes are typically deposited on mechanically resistant support. The most used support material is alumina. This is probably mainly due to the availability of high quality micro-, nano- and ultra-filtration ceramic membranes with smooth top surfaces. A smooth top surface is an important requirement for the preparation of thin continuous zeolite layers. Stainless steel supports are also used but generally have rougher surfaces and larger pore sizes (>100 nm) [11]. Another disadvantage of stainless steel is the higher thermal expansion coefficient with respect to alumina. Therefore, stainless-steel-supported zeolite membranes are more susceptible to cracks induced thermally and to adhesion problems. However, the cost of these support types makes the membranes expensive. Therefore, it is important to study the

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possibility to use cheaper supports. Mullite is another good candidate for its low cost and easy processability giving a support with a regular structure. It is obtained by sintering of kaolin clays. The synthesis of supported defect-free zeolite membranes is a challenge although different methods were developed to improve the quality of the membranes. The most promising preparation method for zeolite membranes is the secondary growth [12], mainly aimed to cover the surface of the support with a layer of zeolite seeds. Subsequently, a hydrothermal treatment is carried out on the seeded support to favour the crystal growth. Therefore, decoupling zeolite nucleation from crystal growth, the optimization of the conditions of each step independently is allowed. This methodology enhances the crystallization kinetics, avoiding the nucleation step. Important implications are: shorter synthesis times needed for a continuous zeolite layer to grow on the support, more easily achieved preferential orientation, and thinner zeolite layers [9]. Thus, this method has potential advantages in terms of reproducibility and control of membrane structure if compared with the *in situ* synthesis method [13].

Seeding is a very critical step since it influences the membrane quality. Many seeding procedures were considered to cover the support surface with seed crystals and the main are listed in Table 1.

The seeding procedures reported in Table 1 improve the quality of the membranes with respect to the *in situ* synthesis method but they also present some limitations.

Rubbing is a simple procedure in which small brushes are used to implant the seeds on the outer or inner surface of tubular supports. This method difficultly produces a continuous and regular seed layer. It is more appropriate for preparing membranes having the selective layer on the outer support surface and therefore not so much suited for practical applications. Hasegawa et al. [16] prepared FAU membranes by using this procedure and obtained an ideal H_2/N_2 separation factor of 4.3 at 100 °C.

Dip-coating is one of the seeding procedures mostly used. In this procedure, the capillary force aids the crystal seeds deposition. However, it is necessary to repeat it more times to have a uniform zeolite layer owing to the negative effect of the gravitational force [22]. Gu et al. [23] synthesized FAU membranes by dip-coating and obtained a CO_2/N_2 separation factor in the range 0.82–20 at 50 °C.

Spin-coating is another seeding procedure more appropriate for flat supports [19]. The use of a cationic polymer (negative charged surfaces are modified by the adsorption of a cationic polymer) introduces another step before seeding, complicating the application for large-scale membrane synthesis. MFI membranes produced by this method [20] showed a separation factor of 1.5 for a *n*-butane/*i*-butane mixture. FAU zeolite membranes showed an ideal H_2/N_2 separation factor in the range 3–4 [21].

More controllable seeding procedures described in literature involve the filtration (Table 2) of a water suspension of zeolite crystals through a porous support.

In the filtration procedure, the zeolite crystals move towards the support surface under the action of a pressure difference applied. Filtration is a dynamic process which initially happens through the larger pores. However, during the time the smaller pores become the larger and are also involved in this mechanism. Therefore, it potentially allows a complete coverage of the support surface. This dynamic coverage modality is absent in the seeding procedures reported in Table 1. The two modes of filtration are schematised in Fig. 1. The dead-end filtration (Fig. 1a) causes an excessive crystals accumulation, while, the cross-flow mode (Fig. 1b) allows a more uniform and compact zeolite layer because of the suspension is pumped tangentially along the surface of the support. In cross-flow filtration separation systems, a high velocity is typically adopted to increase the sweeping action across the membrane. This is not desired for seeding purpose which requires low linear velocity to enable an uniform support coverage, avoiding shearing forces on the deposited layer.

Coverage uniformity problems can happen when tubular supports are used horizontally and without any rotation. In this case, zeolite seeds will be deposited preferentially in the bottom of the support for the effect of the gravitational force. Besides, when the support is vertically placed the thickness of seed layer in the lower part of the support will be greater, again for the gravitational force effect. In the present work, a new seeding procedure for tubular membranes was designed [27]. It is a simple procedure without using organic polymeric cations or pre-treated zeolite crystals. The proposed method combines:

Table 1
Seeding procedures reported in different papers and patents.

Seeding procedure	References
Rubbing	[14–16]
Dip-coating	[12,17,18]
Spin-coating	[19]
Cationic polymer use	[20,21]

Table 2
Seeding procedures by filtration reported in different papers and patents.

Seeding procedures	References
Cross-flow filtration	[24,25]
Dead-end filtration (vacuum seeding)	[22,26]

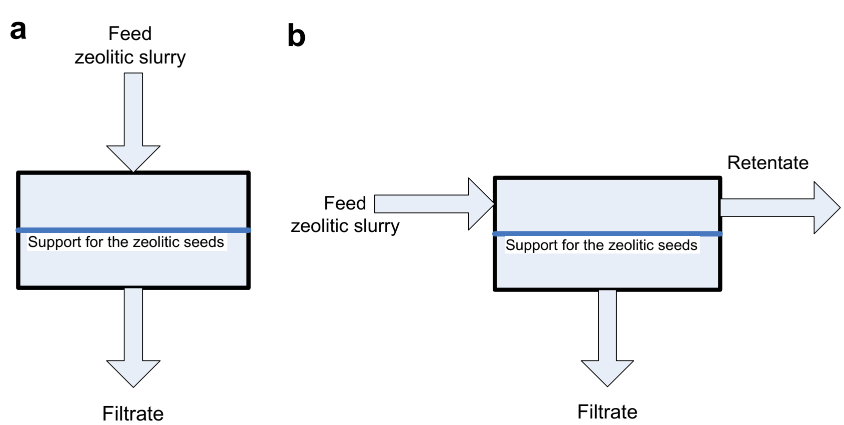

Fig. 1. (a) dead-end and (b) cross-flow filtration.