

Nanocomposite MFI-alumina membranes via pore-plugging synthesis Preparation and morphological characterisation

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Abstract

A specific synthesis protocol, based on zeolite crystallisation within the pores of a host support, the pore-plugging method, has been designed and optimised. A composite membrane has been obtained and its quality evaluated using the separation of adsorbing and non-adsorbing gas mixture.

A series of parameters were studied, including the pore size of the support, the composition of the precursor solution and the hydrothermal synthesis temperature program. Accordingly, the membrane quality showed large variations.

The material structure was characterised using scanning and transmission electron microscopies. These observations showed a composite organization at the support pore scale, with an architecture very different from conventional supported zeolite films.

The final optimisation of the synthesis conditions concluded to a precursor solution containing 2 mol/l of silica, 0.9 mol/l of TPAOH, and the use of an interrupted hydrothermal temperature program, among other parameters. Thanks to this optimisation process, an average increase of one order of magnitude in the separative performance was obtained.

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1. Introduction

Inorganic porous membranes, beside their current commercial applications in liquid separation, have been recently implemented at the industrial scale for pervaporation processes [1] and are widely studied at the lab level, for gas separation. The future of gas separation inorganic porous membranes will be based on their selectivity, permeability and stability characteristics. Moreover, the development of such commercial applications will depend on the availability of high quality, defect-free membranes, preferentially synthesized through simple protocols leading to cost-effective processes [2].

Due to their defined crystal structure, microporous architecture, thermal and chemical stability, zeolite materials are well adapted to make molecular sieving membranes. Moreover, they

offer a range of pore size and tuned adsorption properties that can be selected or adapted (ionic substitution and exchange) according to the targeted separation.

The very first paper using the word zeolitic membranes can be traced back to 1939 [3]. The number of papers increased rapidly after 1990, and more than 3000 research papers and patents have been published, including several reviews [4–15]. This continuous research activity shows that the preparation of high quality zeolite membrane is a difficult task. The challenge is to prepare realistic membrane areas whose properties depend only on the intrinsic capabilities of the zeolite. In fact, the membrane performance is determined by the quality of the zeolite coating on the support, whose thickness must be as low as possible to favour high permeances. Moreover, beside defects, the number and nature of crystal boundaries may also influence permeation and separation properties [10,16,17].

The small pores of MFI zeolite membranes, about 0.5 nm, make them suitable for gas molecules separation. Therefore, this type of material has been widely studied, and showed most of the promising results that have been published in gas separation [18].

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Most of the membranes are based on a porous support that ensures mechanical resistance and allows a thin zeolite separative top-layer formation. Several strategies have been developed to achieve the preparation of such zeolite layers [10]. Among them, three are frequently used:

- The first one is a one-step process during which both nucleation and growth of the zeolite material take place in presence of the support. In this method, also called “In-situ crystallization” [19], the bare porous support is put in contact with the zeolite precursors and submitted to hydrothermal synthesis conditions. This simple strategy presents however some drawbacks. As a matter of fact, the zeolite layer should be formed from nuclei that appear during the hydrothermal treatment. Their number and distribution homogeneity on the support depend on different parameters, such as the local support surface properties, that are difficult to control. Moreover, the nuclei formation competes with the crystal growth process, which may limit the nuclei density due to mass-transfer limitations towards the support. Therefore, the formation of a thick zeolite supported film layer may be necessary to obtain a continuous layer made of intergrown zeolite crystals.
- A second method aims to favour nucleation processes by using a dry-gel conversion in the so-called “Vapor phase transport” method [20,21]. It is a two-step method. An amorphous gel containing silica, aluminium is first coated on the support. The crystallization occurs in a second step, the water for the hydrothermal synthesis coming as saturated vapor from the bottom of the autoclave. The template may be present either in the water or in the gel. This approach allows a strict control of the zeolite amount deposited. Also, the location and concentration of seeds is favoured. A drawback is the possibility of cracks formation in the amorphous gel layer.
- The third method, known as “Secondary Growth Synthesis” includes an initial seeding step, during which small zeolite seed crystals are deposited on top of the support. These seeds are then grown under hydrothermal zeolite synthesis conditions in order to form a continuous zeolite layer on the substrate surface. This two-step method favours the density of initial nuclei and has been widely used [22]. The choice of the seed allows determining the nature of the membrane zeolite. Seed characteristics (size, shape, concentration) can also affect the zeolite crystal orientation in the layer [23,24] which may influence the transport properties [25].

The first, single-step, strategy appears simpler but the two other methods favour the important initial stages of the membrane structuring. However, the main goal of all three is to generate a thin, defect-free zeolite layer on top of the porous support.

Some years ago [26–28], we reported on another strategy for the preparation of zeolite membranes. The idea was to grow zeolite crystals within the pores of a ceramic alumina substrate, until complete blocking of the pore by the zeolite material (Fig. 1). The result was a continuous composite zeolite–alumina membrane, obtained via the pore-plugging method. This nanocomposite membrane led to high separation factors, the separative

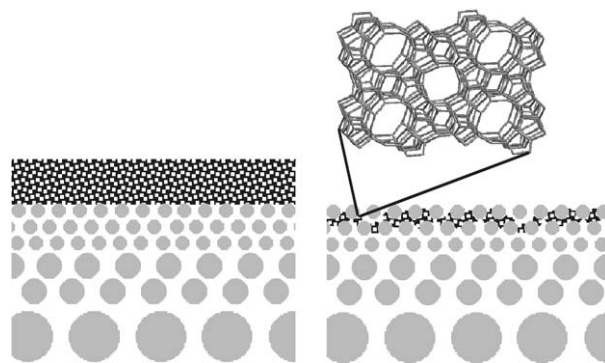


Fig. 1. Schematic comparison between film (left) and nanocomposite (right) membrane structures.

layer being located inside the pores of the host ceramic support [26].

When compared to conventional zeolite toplayers grown on porous supports, the nanocomposite structure shows some potential advantages:

- In such nanocomposites, there are only discrete, small zeolite crystals, with a size in the same order as the pore diameter. Due to the intricacy of both components, when the material is submitted to large temperature changes, the thermal expansion mismatch between support and zeolite will have little effects. On the contrary, in the supported zeolite layer system, long-range stresses can build up and lead to crack formation. Such a benefit may also play a positive role during the template thermal removal, a step often considered as critical for defect-free zeolite membrane synthesis [10].
- The pore-plugging preparation route appears less challenging than the conventional methods, especially when large membrane areas are concerned. An initial imperfection will not originate a large defect, at least one not larger than the pore of the host material. This may help the scaling-up of the preparation procedure at the commercial level, with less-demanding conditions (no clean room needed).
- The separative layer is inside the porosity of the ceramic support. It is protected against abrasion and shocks. This should facilitate membrane handling and module assembling, for example when handling a catalyst in contact with the membrane for catalytic membrane reactor applications [29].

As far as we know, nanocomposite zeolite membranes have not been widely studied and only few papers describe such materials [26]. Some authors have observed such structures in parallel with conventional zeolite film growth [16]. Besides, the concept of pore plugging has been used for other membrane materials, such as Pd–ceramic composite membrane [30–32].

In this paper we mainly report on membrane synthesis and material characterization. The preparation method has been optimised using as an evaluation criterion a gas separation experiment of a mixture of adsorbing and non-adsorbing species.

Since the start of research on zeolite membrane synthesis, few authors have stressed the difficulty linked to reproducibility. This paper tries to face this problem, by dealing with many prac-

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