



## Nanocomposite MFI-alumina membranes via pore-plugging synthesis: Genesis of the zeolite material

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### ABSTRACT

This paper presents a study of MFI-type zeolite crystal growth during hydrothermal synthesis of nanocomposite MFI-alumina membranes by the pore-plugging method, using the standard protocol described in a previous study [S. Miachon, E. Landrивon, M. Aouine, Y. Sun, I. Kumakiri, Y. Li, O. Pachtová Prokopová, N. Guilhaume, A. Giroir-Fendler, H. Mozzanega, J.-A. Dalmon, Nanocomposite MFI-alumina membranes via pore-plugging synthesis: specific transport and separation properties, *J. Membr. Sci.* 281 (2006) 228]. To this aim, the materials have been characterized by SEM, EDX, pure H<sub>2</sub> gas permeance and n-butane/H<sub>2</sub> mixture separation at different stages of the synthesis. The effect of synthesis time in the range of 4–89 h and the effect of a 9-h interruption after a 8-h hydrothermal synthesis have been surveyed, as well as the mean pore size and the alumina phase of the support inner layer. Our results suggest that an interruption during the synthesis is necessary to allow the zeolite precursor to diffuse into the support pores. This diffusion leads to a further growth of zeolite crystals into the support matrix without formation of a continuous zeolite film on top of the support, as is usually reported in the literature. The zeolite crystals are fully embedded into the support top layer after at least 53-h synthesis time, leading to high quality membranes in only one synthesis run. The nanocomposite MFI-alumina architecture at the nanoscale has important consequences in improving the gas separation performance of this kind of materials when compared to more conventional film-like structures. A method based on gas transport measurements has been used to determine the effective thickness of the separating material.

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### 1. Introduction

Since the mid-1990s, much work has been done in the field of zeolite membranes for gas separation and pervaporation applications, as reported in several reviews [1–7]. Recently, A-type zeolite membranes have been implemented at the industrial scale for pervaporation dehydration applications [8]. The challenge is to prepare realistic membrane surface areas whose properties only depend on the intrinsic properties of zeolites. In fact, the membrane performance is determined by the quality and intergrowth of the zeolite material coating the porous support, whose thickness must be as low as possible to favour high permeances. Moreover, besides intercrystalline defects, the density and nature of grain boundaries may also affect the permeation and separation performance of the membranes [9–11].

MFI-type zeolite membranes have often been the target of the investigations for gas separation applications due to their small

pore sizes (~0.5 nm) and mild crystallization conditions [7]. Most often, the studies have focused on the synthesis of continuous and well-intergrown thin films on top of a porous support that ensures mechanical resistance. Zeolite films can be prepared by either *in situ* or seeded hydrothermal synthesis, or by dry-gel conversion methods [6]. Specific zeolite crystal orientation in the layers can be also achieved by fine-tuning the seed characteristics (size, shape, and concentration) prior to hydrothermal synthesis [12,13], which might influence the gas transport properties [14]. The main shortcoming of this configuration is the thermal expansion mismatch between the support and the zeolite layer, which can lead to crack formation during calcination and further cooling [4,7], or to intercrystalline opening when operated at elevated temperatures (>400 K), depending on the crystal size [15].

In previous studies [16–20], some of us have reported on the synthesis and improved gas permeation and separation performance of nanocomposite MFI-alumina membranes (prepared either as tubes or hollow fibres) to overcome these limitations. In this architecture, compared to a film, the active phase is embedded into the host ceramic alumina porous network via pore-plugging hydrothermal synthesis. Detailed transmission electron micrographs have

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revealed that zeolite crystals plug neighbouring support pores [16], which confers to the material higher resistance to long-range thermal stresses commonly observed in supported zeolite films [21–23]. Another consequence is that mass transfer within these membranes at high temperature is kept governed by zeolite pores instead of intercrystalline openings that may appear in film-like configurations.

Nanocomposite membranes have shown high potential in several separation applications (e.g., xylene isomer separation [24] and ammonia recovery [25]), and combined with a catalyst in membrane reactors (e.g., isobutane dehydrogenation [26] and xylene isomerization [24]). Besides, this nanocomposite configuration has also been applied to the synthesis of other membrane materials, such as Pd–ceramic [27] and MCM-41 ‘LUS’ [28] membranes, these latter showing high membrane quality together with high gas and water permeation performance and high structural stability.

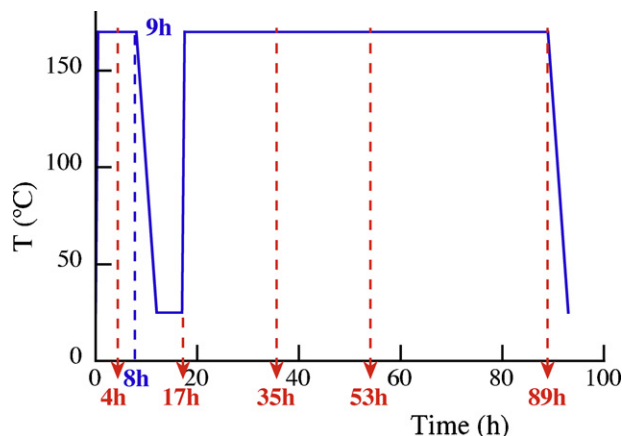
In a previous study [16], the composition of the precursor solution and the support pore size were shown to play a crucial role on the final membrane quality. An optimum on membrane quality is obtained using a TPAOH/Si molar ratio of 0.45, corresponding to  $[\text{TPAOH}] = 0.9 \text{ mol/l}$ . This concentration, when compared to others, involves a lower proportion of  $Q^3$ , and a higher proportion of  $Q^2$  oligomers,<sup>1</sup> long enough to favour zeolite crystallization, but at the same time short enough to diffuse into the support pores. This has been inferred from  $^{29}\text{Si}$  NMR analysis. Light absorption analysis of the precursor also showed a strong influence of the precursor concentration on precursor size. Moreover, the introduction of a heating interruption during hydrothermal synthesis leads to higher membrane separation performance. However, no detailed study has been published to date reporting on the effect of this interruption on the MFI zeolite crystal growth mechanism. This paper is therefore devoted to gain insight into this aspect, as a follow-up to two previous articles devoted to this type of membranes [15,16]. In this third contribution, our research strategy has focused on the analysis of the effect of the two main variables addressed in Ref. [16]: (1) the synthesis time in the range of 4–89 h, including a 9-h interruption after 8 h, and (2) the pore size and alumina phase of the support top layer.

Moreover, on conventional film-like structured materials, the membrane thickness is usually deduced from film thickness as measured from SEM imaging [1,7]. In nanocomposite materials, however, microscopy techniques cannot be applied, since no film is formed. Accordingly, a specific method based on mass transport measurements is proposed here to determine the effective thickness. This is the thickness of closed material corresponding to the real mass transfer resistance during operation, and responsible for the selectivity.

## 2. Experimental

### 2.1. Membrane supports

The membranes were prepared on porous asymmetric 15-cm long tubular supports with 7 mm i.d. and 10 mm o.d. provided by Pall Exekia (Membralox T1-70). The quality of the supports was deduced from the values of the first bubble point pressure, higher than 80 kPa in all cases. Two of these supports consisted of three  $\alpha$ -alumina layers with mean pore size and thickness decreasing from the outer to the inner side of the tube, with the following pore-size sequences (as given by the tube provider): 12–0.8–0.2  $\mu\text{m}$  and



**Fig. 1.** Standard temperature program during synthesis, including a 9-h interruption after 8-h synthesis. Material samples were analysed after the times indicated by the dotted line arrows on bottom (4–89 h).

12–0.8–0.1  $\mu\text{m}$  (top-layer thickness: 10  $\mu\text{m}$  in both cases). The first 12- $\mu\text{m}$  layer had a porosity of 33%, whereas that of the other two was 30%. Moreover, a third support, also supplied by Pall Exekia, was also used, which consisted of a three-layered  $\alpha$ -alumina tube (0.2- $\mu\text{m}$  mean pore size of the last layer) with a fourth 5-nm  $\gamma$ -alumina top layer deposited on the inner surface of the tube.

In all cases, both ends of the supports were enamelled (1 cm at each side) for sealing purposes, defining a permeation length of 15 cm and an active surface of 28.6 cm<sup>2</sup>.

### 2.2. Hydrothermal synthesis

The nanocomposite MFI-alumina membranes were prepared by *in situ* hydrothermal synthesis using the pore-plugging method as described in previous studies [16,17]. Shortly, a clear solution containing a molar composition of 1.0  $\text{SiO}_2$ : 0.45 TPAOH: 27.8  $\text{H}_2\text{O}$  was matured for 72 h. The support tube was soaked in the solution placed in a Teflon-lined autoclave. The closed autoclave was then placed vertically in an oven preheated at 170 °C. The standard temperature program is depicted in Fig. 1. It included a 9-h interruption after 8-h synthesis, its total duration being 89 h. In order to follow the growth of the nanocomposite material, some syntheses were stopped after different times (see Fig. 1) and the corresponding materials were then characterised by gas transport and other techniques. In each case, some support slices were added to the autoclave on top of the tube during the synthesis for further electron microscopy analysis.

After the synthesis, the autoclave was cooled down to room temperature, the synthesized membranes were removed, washed with deionised water until pH neutrality, and dried overnight at room temperature and subsequently at 120 °C for 12 h. A membrane integrity test ( $\text{N}_2$  permeation under 400 mbar differential pressure) was performed at this stage to assess for the presence of large defects or cracks. The dried membranes were then calcined at 500 °C for 8 h under air stream for template removal.

The tube weight was measured before synthesis, after the drying step and after calcination, the samples being kept under dry atmosphere in all the measurements.

### 2.3. Membrane characterization

#### 2.3.1. Electron microscopy characterization

Scanning electron microscopy (SEM) images on membrane tube slices were obtained using a Philips-XL-30 microscope at 20 kV equipped with EDS analysis (EDAX-phoenix).

<sup>1</sup>  $Q^n$  is a notation referring to the number  $n$  of siloxane bridges around a Si atom (the other being –OH groups). Larger  $n$  values are usually associated with larger oligomer particles.

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