

b-Oriented MFI membranes prepared from porous silica coatings

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ABSTRACT

The preparation of *b*-oriented MFI films from porous silica layers was investigated and optimized. The alumina supported silica membranes were immersed in a concentrated TPAOH solution. Finally *b*-oriented and well-intergrown MFI crystal films were produced by carrying out an *in situ* hydrothermal synthesis using a synthesis solution 1 SiO₂:0.05 TPAOH:37.5–169 H₂O:0.15 NaOH. The main function of the silica is twofold, it serves as a nucleation layer for the silicalite-1 and provides a smooth surface for the oriented crystal growth into a continuous layer. Prolonged synthesis duration leads to the formation of a secondary layer with increasing *a*-orientation.

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1. Introduction

Many efforts have been focused on the preparation of zeolite films because of their envisaged application as membranes and membrane reactors [1,2], heat pumps [3], catalytic coating reactors [4], chemical sensors and components in microelectronic devices [5–7]. Most of the films available today contain randomly oriented crystals, though a more difficult task, a preferred orientation is often desirable [8–10].

Appropriate orientation of the sub-nanometer-sized channels in the zeolite crystals can positively affect the mass transport behavior within a zeolite film, and this is crucial for its applications. For instance, a dramatic performance improvement has been observed in the xylene isomer separation through *b*-oriented MFI crystal films versus *a*- and *c*-oriented crystal membranes [11]. Improved performance was also demonstrated for a mono-crystal layer of *b*-oriented pure silicalite-1 film on a stainless steel electrode [12].

Quite a few studies regarding fundamental understanding and basic systematic syntheses of continuous oriented crystal formation have been carried out for preparing ultimately MFI membranes. Several authors reported preparation of *b*-oriented MFI films on non-porous supports. Wang and Yan [13,14] carried out a study on the formation of continuous, thin, oriented MFI crystal

films on stainless steel and aluminum alloy substrates by direct *in situ* crystallization. Li et al. [15] investigated with TEM the formation mechanism of a mono-crystal thick *b*-oriented all-silica MFI film. They prepared even self-supporting film samples by dissolving the steel substrate with acid. Recently, an alternative method to prepare a *b*-oriented MFI film by steam-assisted crystallization has been reported [16]. Silicon wafers were coated with TPAOH and subsequently *in situ* crystallization was used. Besides serving as the support, the substrate itself was used as the source for silica building blocks; silicon wafers are usually covered with a thin layer of silica.

A seeded growth procedure has been reported that allows to fabricate a functional *b*-oriented membrane of MFI on α -alumina and stainless steel disk supports [11,17,18]. The supports were pre-coated with a mesoporous material acting as an intermediate layer to smoothen the surface. *b*-Oriented MFI seed monolayers were covalently attached to these mesoporous layers using 3-chloropropyltrimethoxysilane as the coupling agent. Finally *b*-oriented films were produced by carrying out secondary growth using a trimer of tetrapropylammonium iodide as a structure-directing agent. McLeary and Jansen [19] prepared supported silica-based microporous membranes. Mesoporous silica precursor layers seem to facilitate and promote the formation of a continuous layer of zeolite in the best way. A precursor phase of a 3-D mesoporous, sponge-type layer of activated TUD-1 (pore size \sim 2–3 nm), was prepared on a tubular alumina support. Subsequently this phase was impregnated with an aqueous solution of TPAOH. A hydrothermal synthesis on this template-loaded mesoporous coating was carried out with a standard MFI synthesis solution of TPA/silica.

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The objective was (i) a continuous layer formation as amorphous silicas do, (ii) sufficient supply of nutrient directly on the support and (iii) an extremely high nucleation rate based on the specific surface of the TUD-1 interfacial TPA.

Here, we report an alternative *b*-oriented zeolite MFI monolayer film preparation using a microporous amorphous silica membrane. The *b*-orientation is induced by a precursor phase comprising a TPAOH modified silica layer. The crystals grow at the interface of both nutrient phases. The membrane is cheap, allows scale-up and is easy in preparation. The preparation consists of the immersion of the silica membrane in an aqueous TPAOH solution followed by an *in situ* hydrothermal synthesis that provides an opportunity to prepare an oriented and well-intergrown zeolite crystal layer in a membrane configuration.

2. Experimental

Silica membranes of 100 nm of thickness were prepared by a dipcoating procedure on α -alumina disk supports with a γ -alumina top layer containing pores smaller than 2 nm [20].

The silica membrane was immersed in 2 g of a 1 M solution of TPAOH for 2 h. The solution used for the synthesis of silicalite-1 film had a molar composition of 1 SiO₂:0.05 TPAOH:37.5 H₂O:0.15 NaOH, and was adapted from Jia et al. [21]. The solution was made by adding colloidal silica (Ludox AS-40, Aldrich) to a solution of sodium hydroxide (NaOH, BDH), tetrapropylammonium hydroxide (TPAOH, 1 M, Aldrich) and water. After aging for about 1 h under stirring at room temperature, the solution was transferred to a 45 ml Teflon-lined Parr autoclave. The silica coated alumina disk material was horizontally placed on the bottom of the autoclave, unless otherwise specified. The autoclave was then placed in an oven for the one-stage hydrothermal *in situ* synthesis at 443 K for 17 h. The samples were recovered and thoroughly washed with deionized water. Although the samples may contain aluminum leached from the support during the hydrothermal synthesis, the MFI structure is denoted here as silicalite-1.

The surface and cross-section morphology of the as-synthesized membranes was examined by scanning electron microscopy (SEM) using a Philips XL20 microscope.

The crystalline materials were analyzed by X-ray diffraction (XRD) using a Bruker-AXS D5005 with CuK α ₁ radiation.

3. Results and discussion

Table 1 lists immersion and synthesis conditions applied to the alumina supported silica membranes, as well as the orientation of the crystals, the film continuity and thickness. From the immersion

conditions and different synthesis solutions, an optimal condition for the preparation of *b*-oriented silicalite films was concluded from the following systematic analysis. The silica membrane was immersed in a 1 M solution of TPAOH and subsequently used in synthesis at 443 K for 17 h, sample S01, resulting in a non-continuous *a*-, *b*-oriented layer with relatively large crystals, Fig. 1a. This suggests that the silica was not only supplied by the solution but also by the substrate that could easily be converted to zeolite. This hypothesis is supported by the synthesis on a native alumina support, where random orientation was obtained in spite of the use of the same immersion and synthesis conditions.

Regarding the amount of TPAOH used for the immersion of silica membranes, two smaller amounts of TPAOH solutions were used. Sample S03 was immersed in 0.32 g of 1 M TPAOH solution ($\sim 0.5 \text{ g cm}^{-2}$) and S04 covered with 0.08 g solution ($\sim 0.12 \text{ g cm}^{-2}$). Both were applied in the silicalite-1 synthesis. SEM micrographs, Fig. 1b and c, respectively, show that when the amount of TPAOH used decreased, the crystals increase in number and decrease in size while the aspect ratio is almost 1. Simultaneously an increase in *a*, *b*-oriented intergrowth is observed. However, in contrast to S01, the crystals are not oriented relative to the support surface. Apparently there was not enough TPAOH adsorbed on silica, which seems to be mandatory in order to grow crystals parallel to the support, and resulting in the *b*-direction perpendicular to the membrane surface.

Chaikittisilp et al. [16] reported a coating of silicon wafers with approximate 0.008 g cm^{-2} of 1 M TPAOH solution. In both cases the amount of TPAOH coated is about hundred times higher than the required amount for crystallizing MFI zeolite. It seems evident that to cover the silica membrane used in our study, a larger amount of TPAOH is necessary than in the case of a non-porous silicon wafer. McLeary and Jansen [19] claimed that a mesoporous silica precursor layer seems to facilitate and promote the formation of a continuous layer of zeolite in the best way. The reason is the high specific surface area of this material providing a large interface between the silica and the TPA⁺ solution and therefore a high nucleation rate resulting in complete coverage. The current work confirms this model even for a microporous silica layer if it is sufficiently thin. The conclusion is that an optimal amount of TPA is needed for the coating synthesis.

Fig. 2 shows SEM micrographs of a silicalite-1 film formed at 443 K with a reaction time of 24 h. A continuous layer is formed, but the *b*-orientation is not well developed, which is probably caused by the increase in synthesis time, promoting a random orientation of the crystals constituting the film.

In focusing on total oriented coverage of the substrate, experiments with a more diluted synthesis solution were carried out. A

Table 1
Immersion and synthesis conditions of the silicalite membranes

Sample ^a	Specific conditions	Synthesis time (h)	Crystals on substrate		
			Orientation	Coverage	Thickness (μm)
S01		17	<i>b</i> -Oriented	Incomplete	8
S02	No TPAOH in synthesis mixture	17	Random	Incomplete	9
S03	Immersion in 0.32 g of TPAOH	17	<i>a</i> , <i>b</i> -Oriented	Complete	8
S04	Immersion in 0.08 g of TPAOH	17	<i>a</i> , <i>b</i> -Oriented	Complete	8
S05		24	Random	Complete	15
S06		5	<i>a</i> -Oriented	Complete	3
S07	Vacuum after immersion	17	Random	Complete	250
S08		17 (rotation)	Random	Incomplete	5
S09	Dilution 1:3. Vertical position	17	<i>b</i> -Oriented	Incomplete	9
S10	Dilution 1:3. Horizontal position	17	<i>b</i> -Oriented	Complete	10
S11	Dilution 1:3. Vertical position	48	<i>a</i> , <i>b</i> -Oriented	Complete	8
S12	Dilution 1:3. Horizontal position	48	<i>a</i> , <i>b</i> -Oriented	Complete	30

^a All samples immersed for 2 h in 2 g of TPAOH solution (1 M). Synthesis at 443 K for 17 h. Synthesis solution molar composition: 1 SiO₂:0.05 TPAOH:37.5 H₂O:0.15 NaOH, unless otherwise specified.

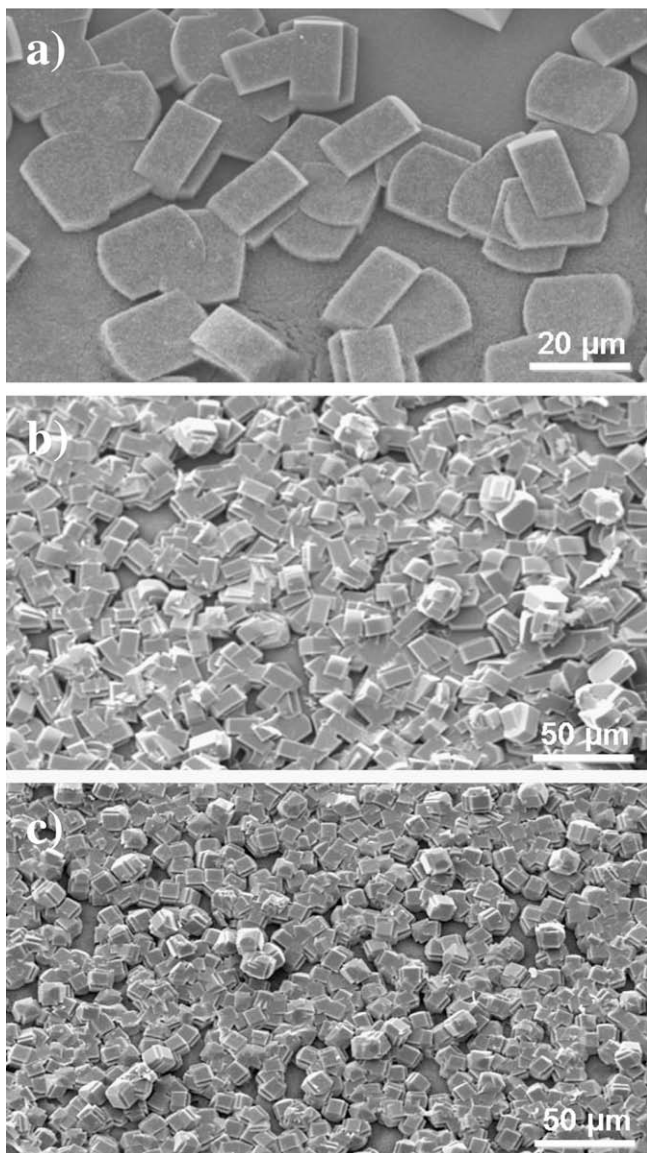


Fig. 1. SEM micrographs of silicalite films immersed in different amounts of 1 M TPAOH solution (synthesis at 443 K for 17 h). (a) S01 immersed in 2 g of TPAOH solution ($\sim 3 \text{ g cm}^{-2}$); (b) S03 immersed in 0.32 g of TPAOH solution ($\sim 0.5 \text{ g cm}^{-2}$); (c) S04 immersed in 0.08 g of TPAOH solution ($\sim 0.12 \text{ g cm}^{-2}$).

solution–deionized water ratio of 1:3 was used. Table 2 summarizes some selected synthesis conditions and molar compositions of synthesis solutions reported in the literature. With the dilution of the synthesis solution, the amount of water is comparable to

what is found in the literature in similar cases. SEM photographs of samples S09–S12 are shown in Fig. 3. For a synthesis time of 17 h, the *b*-orientation is observed, although a continuous layer is only obtained when the substrate is placed horizontally during the synthesis. In fact, a mono-crystalline layer is obtained in both cases, without formation of a second layer with random orientation. When the synthesis time is increased to 48 h, *a*, *b*-oriented films are obtained. This increase in the amount of *a*-oriented crystals is more marked when the substrate is placed horizontally. So, a diluted mixture and short synthesis time indeed resulted under precise conditions in a continuous *b*-oriented layer, which is formed both through conversion of the silica membrane precursor layer and supply from the solution. At longer synthesis times the silica from solution starts to grow a second layer which is not oriented (see below).

From Table 1, it is clear that three distinct orientations (i.e., *b*-oriented, *a*, *b*-oriented and random-oriented) of a thin continuous MFI film on silica membranes can be obtained using direct *in situ* crystallization. To confirm the orientation, the films were examined by XRD (Fig. 4). For the *b*-oriented film (Fig. 4c), only (0*k*0) reflections are observed, confirming that the *b*-axis of the MFI crystals is perpendicular to the substrate surface. Similarly, only (*h*00) and (0*k*0) reflections are observed for an *a*, *b*-oriented film (Fig. 4a and b). There is a clear decrease of the intensity of the reflections related to *a*-orientation from sample S04 to sample S10, where a constant decrease of the intensity of the (400), (600) and (800) reflections can be observed.

Although extensive efforts have been made towards the control strategy of orientation, the true film formation mechanism remains elusive. Two models have been proposed.

According to the heterogeneous nucleation model, a silica gel layer is formed on the surface of a silicon wafer substrate by agglomeration of primary gel particles present in solution. Nucleation occurs only at the gel/solution interface where both the structure-directing agent (TPA) and the silica source are present in abundance. Crystal growth proceeds into the gel phase until the crystals bind with the substrate and finally align with their (010) faces parallel to the substrate. This model can account well for the fact that *b*-oriented crystals are formed on both horizontally and vertically placed substrates, but it is difficult to use this model to explain why *a*-oriented crystals sometimes appear in the film. This model also does not explain the formation of secondary layers under certain conditions [22]. It has been demonstrated that larger MFI crystals generally result from the growth of different subunits with channel directions perpendicular to that expected from the overall crystal geometry [23,24]. These subunits may grow out further, leading to different orientations and may explain the formation of the *a*-orientation upon prolonged film growth. It may be an intrinsic property of the crystal growth under the applied synthesis conditions. It implies that the synthesis time should be optimized in order to avoid the formation of a secondary layer.

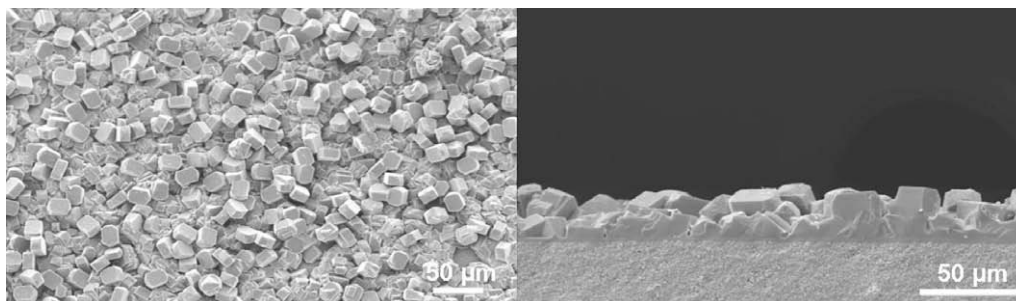


Fig. 2. SEM micrographs of sample S05 synthesized at 443 K for 24 h. Left: top view. Right: cross sectional view.

Table 2
Comparison of applied conditions for the preparation of *b*-oriented silicalite-1 films

References	Synthesis procedure	Source		Molar composition						Temperature (K)	Synthesis time (h)
		SiO ₂	TPA	SiO ₂	TPA	H ₂ O	NaOH	KOH	EtOH		
This work	<i>In situ</i>	Ludox AS-40	TPAOH	1	0.05	37.5	0.15	–	–	443	17
[14]	<i>In situ</i>	TEOS	TPAOH	1	0.32	165	–	–	–	438	2–3
[11]	Secondary growth	TEOS	Trimer TPAOH	1	0.12	237	–	4	0.2	448	24
[19]	<i>In situ</i>	Aerosil 200	TPAOH	1	0.32	165	–	–	–	448	4
[18]	Secondary growth	TEOS	Trimer TPAI	1	0.13	238	–	–	0.2–0.58	448	24

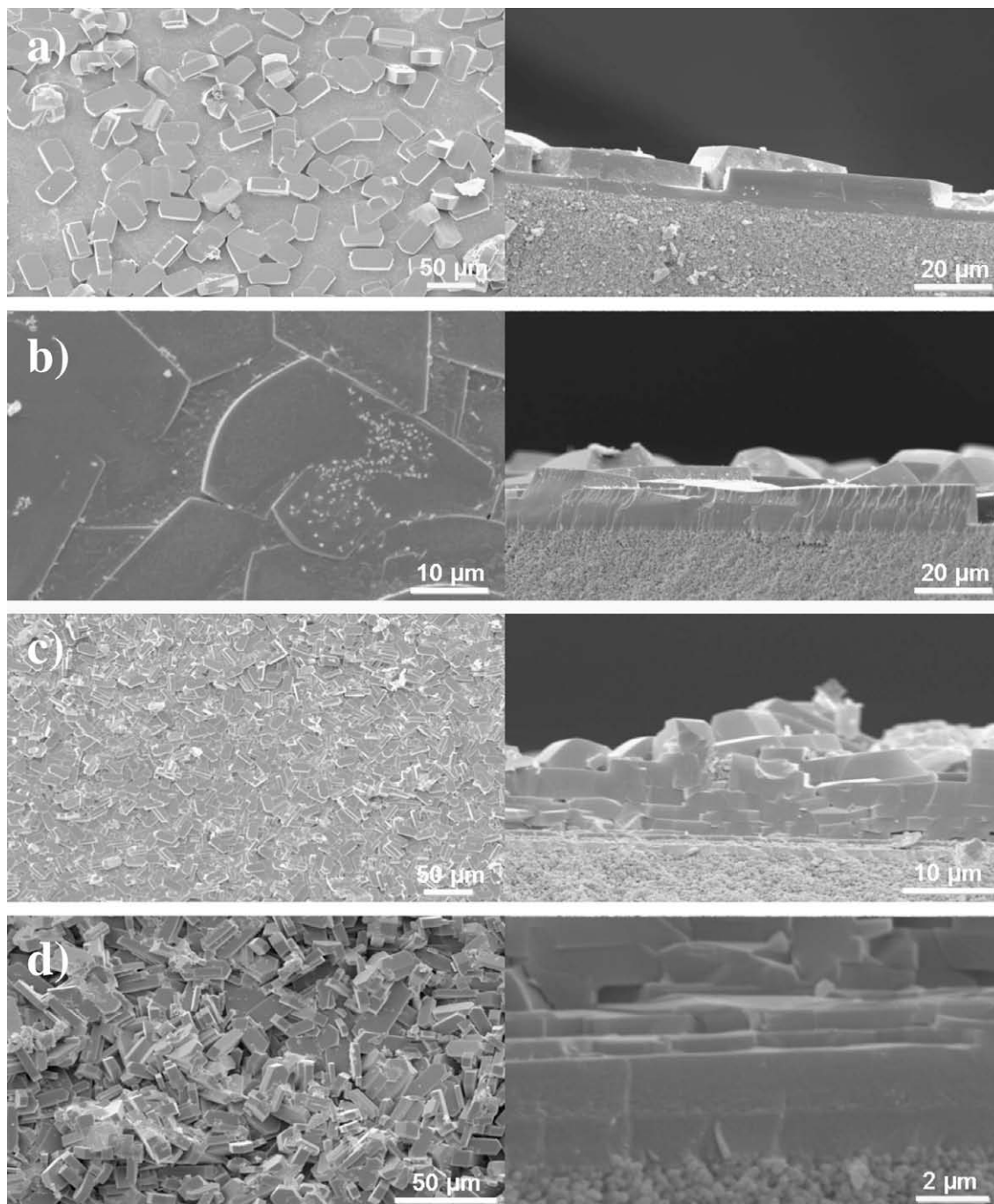


Fig. 3. SEM micrographs of samples S09–S12 synthesized at 443 K for 17 and 48 h, using a diluted synthesis mixture (1:3) on horizontally and vertically oriented substrates. *Left:* top view. *Right:* cross sectional view. (a) S09 placed vertically for 17 h; (b) S10 placed horizontally for 17 h; (c) S11 placed vertically for 48 h; (d) S12 placed horizontally for 48 h.

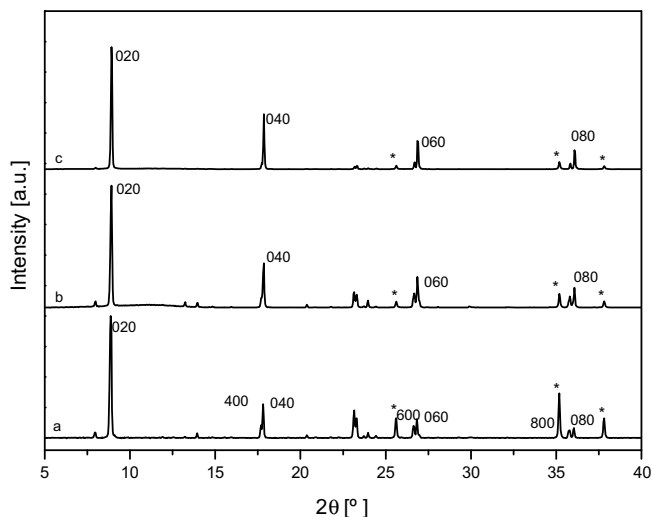


Fig. 4. XRD patterns of silicalite-1 films (a) S04; (b) S11; (c) S10. Reflections marked by (*) correspond to the alumina support.

With the homogeneous nucleation model, nucleation occurs homogeneously in the bulk solution and the nuclei grow into small disk-shape crystals with (010) as the largest flat surfaces. Since under the particular pH the interaction between the crystals and the surface is favorable, it is energetically preferred for these crystals to settle onto the substrate with *b*-oriented positions [13].

Evaluating the results the major role of the TPAOH modified silica top layer is twofold. It provides a smooth surface for membrane formation and serves as a heterogeneous nucleation layer for silicalite-1 formation, taking advantage of the locally high concentration of the template and silica source and resulting in an intergrowth of the silicalite-1 crystals in the plane of the support. The layer itself is too thin to act as a sufficient silica source and additional silica has to be supplied from the synthesis solution.

4. Conclusions

Microporous silica layers can be employed for the formation of oriented MFI films on porous supports. Preimpregnation with a TPAOH solution is essential. The silica layer provides a smooth sup-

port surface, and acts as a heterogeneous nucleation centre for the silicalite-1 crystals by providing locally high nutrient concentrations of template and silica, resulting in a continuous layer. Silica must be provided by the synthesis solution since the silica layer of the support is very thin.

The synthesis conditions for the *b*-orientation of MFI are comparable to those found in the literature, but it is essential to avoid the growth of a secondary layer from the solution at the particular conditions by adjusting the synthesis time.

This procedure provides an opportunity for the preparation of oriented and well-intergrown zeolite crystals in a membrane configuration. The membrane is cheap, allows scale-up and is easily prepared.

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