

From amorphous to crystalline

Transformation of silica membranes into silicalite-1 (MFI) zeolite layers

Karakiliç, Pelin; Toyoda, Ryo; Kapteijn, Freek; Nijmeijer, Arian; Winnubst, Louis

DOI

[10.1016/j.micromeso.2018.09.020](https://doi.org/10.1016/j.micromeso.2018.09.020)

Publication date

2019

Document Version

Accepted author manuscript

Published in

Microporous and Mesoporous Materials

Citation (APA)

Karakiliç, P., Toyoda, R., Kapteijn, F., Nijmeijer, A., & Winnubst, L. (2019). From amorphous to crystalline: Transformation of silica membranes into silicalite-1 (MFI) zeolite layers. *Microporous and Mesoporous Materials*, 276, 52-61. <https://doi.org/10.1016/j.micromeso.2018.09.020>

Important note

To cite this publication, please use the final published version (if applicable).
Please check the document version above.

Copyright

Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

Takedown policy

Please contact us and provide details if you believe this document breaches copyrights.
We will remove access to the work immediately and investigate your claim.

From amorphous to crystalline: Transformation of silica membranes into silicalite-1 (MFI) zeolite layers

Pelin Karakiliç ^[a], Ryo Toyoda ^[a], Freek Kapteijn ^[b], Arian Nijmeijer ^[a], Louis Winnubst*, ^[a]

^[a] Inorganic Membranes, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

^[b] Catalysis Engineering, Chemical Engineering Department, Delft University of Technology, Van der Maasweg 9, Delft, Netherlands

Abstract

The transformation of microporous, amorphous silica membranes into b-oriented silicalite-1 (MFI) zeolite layers via *in-situ* crystallisation was investigated. The effect of synthesis parameters, such as the type and concentration of the silica precursor, crystallisation time and temperature, on the morphology of silicalite-1 (MFI) zeolite layers was studied. By optimizing these parameters, silicalite-1 zeolite layers were formed from the already-deposited silica layers, which promotes the crystallisation from the surface in the preferred b-orientation. The use of a monomeric silica precursor, which has slower hydrolysis kinetics than a colloidal one, resulted in the formation of zeolite crystals via heterogeneous nucleation on the surface and suppressed the formation of crystal nuclei in the liquid media via homogeneous nucleation, which then would further deposit onto the surface in a random orientation. Lastly, by optimizing the crystallisation time and temperature of the synthesis, thickness, coverage and orientation of silicalite-1 zeolite layers were controlled.

* Corresponding author. Tel.: +31 534982994. E-mail address: a.j.a.winnubst@utwente.nl (L. Winnubst).

Keywords: silicalite-1, MFI zeolite, silica transformation, sol-gel, in-situ crystallisation

1. Introduction

Zeolites are promising membrane materials for industrial separation applications thanks to their uniform pore size and chemical, thermal and mechanical stability under harsh conditions. In order to maximize the permeance by keeping high separation performance, the zeolite membrane layer should be well-defined in terms of thickness, homogeneity, orientation of the crystals and of a defect-free nature. A myriad of papers have been published about the synthesis and fabrication of zeolite materials, as they are widely used in catalysis [1–5], sensors [6–10], adsorbers [11–13], and in membranes [14–18]. There are 235 zeolite frameworks up to date reported by Structure Commission of the International Zeolite Association (SC-IZA). Among these are the following frameworks reported as zeolite structures used for membrane preparation: AEI [19], BEA [20], CHA [21,22], DDR [23,24], FAU [25,26], FER [27], LTA [28,29], LTL [30], MEL [31], MFI [32–34], MOR [35] and MWW [36]. MFI is the most studied structure due to having micropores which can accommodate and/or separate industrially high-valued molecules. Silicalite-1 is the all-silica zeolite having the MFI framework whereas ZSM-5 is the Al-containing analogue of it.

The channel system of the MFI framework is asymmetric and varies by the orientation of the crystal. The a-orientation (h00) has sinusoidal channels, which creates resistance against mass transfer, whereas the b-orientation (0k0) has straight channels, as shown in Figure 1. The diffusion along these straight channels are three times higher as compared to that along the sinusoidal channels, as reported by Caro et al. [37] and therefore, the b-oriented zeolite layer is preferred to maximise permeance.

The most common method to prepare zeolite membranes is growing zeolite crystals on a porous support. Ways of forming these layers are *in-situ* synthesis and secondary (seeded) growth methods. In the *in-situ* synthesis method, the porous support is placed in a zeolite precursor solution and the zeolite layer is formed via hydrothermal synthesis in an autoclave under autogenous pressure. Here, nucleation and growth of a crystal takes place simultaneously as being a one-step mechanism. On the contrary, the secondary growth method implies separate nucleation and growth steps. In the first step, the nucleation of the crystal occurs in an autoclave in the absence of the porous support, where these seed crystals are recovered from the solution and then deposited on the support. This seed attachment can be done by several methods such as electrophoretic deposition [38,39], dip-coating [40], rubbing [41], pulsed-laser ablation [42] and vacuum seeding [43]. Finally, the seeded support is grown into a continuous layer via a second hydrothermal treatment in the autoclave.

Wang and Yan [44] prepared continuous b-oriented zeolite MFI monolayer films with a thickness of less than 0.4 μm on metal substrates (stainless steel and an aluminium alloy) by *in-situ* crystallisation at 165°C using a solution with a molar ratio of 1 SiO_2 :0.32 TPAOH:165 H_2O where a silica precursor of (monomeric) tetraethyl orthosilicate (TEOS) or colloidal silica (LUDOX-30) was used. They reported that the continuity of the film with b-orientation was provided by using a silica source with a low degree of polymerisation such as TEOS, whereas a colloidal silica source, like LUDOX-30 resulted in the formation of randomly oriented large crystals.

Shan et al. [45] prepared silicalite-1 membranes on porous $\alpha\text{-Al}_2\text{O}_3$ hollow fibers by the secondary growth method. They used TEOS as a silica precursor and analysed the effect of the crystallisation time (2–12 h) and the concentration of structure directing agent tetrapropylammonium hydroxide (TPAOH) in the secondary growth solution having a molar ratio of 1 SiO_2 : 0.12–0.32 TPAOH: 165 H_2O . They reported that a low concentration of TPAOH resulted in a smoother surface. However extremely low

65 concentrations of the TPAOH template caused poor intergrowth of the crystals and formation of
66 intercrystalline pores because of preferential growth of the seed crystals along the c-axis. In addition,
67 the layer thickness and the zeolite crystal size were increasing after longer crystallisation time, providing
68 continuity of the membrane layer, whereas a short synthesis time resulted in empty spots and gaps.

69 Mintova and Valtchev [46] investigated the effect of different silica precursors, tetraethyl orthosilicate
70 (TEOS), colloidal silica (LUDOX LS-30) and fumed silica (Cab-O-Sil®), on the synthesis of nanosized
71 silicalite-1 zeolites using a molar composition of 25 SiO₂:9 TPAOH:0.13 Na₂O:420 H₂O:100 EtOH. They
72 reported that the size of the silicalite-1 nanocrystals was 15, 25 and 50 nm using TEOS, Cab-O-Sil and
73 LUDOX AS-30 precursors, respectively, as measured by in-situ dynamic light scattering (DLS) using the
74 backscattering technique. So clearly an influence of precursor used on silicalite-1 crystal size is observed.

75 Decoupling the nucleation and growth as is the case in the secondary growth method results in a better
76 control of zeolite growth compared with *in-situ* growth. Yet, the optimization of the thickness of the
77 zeolite layer as well as the possibility to obtain an oriented crystal structure by this method are issues
78 still to be tackled for the zeolite membrane fabrication. Hence, it is important to develop new
79 approaches for the fabrication of thin, preferentially-oriented and defect-free zeolite membranes.

80 Transformation of sol-gel derived amorphous microporous silica layers into zeolite membranes is a
81 recent and novel strategy used for the formation of a zeolite layer. The benefit of this method is that the
82 silica layer can act as a smooth nucleation layer to form all-silica zeolite membranes by *in-situ* zeolite
83 layer formation. As the zeolite crystals are formed from a silica precursor that is already deposited on
84 the surface (i.e. the amorphous silica layer), this method triggers the formation of b-oriented silicalite-1
85 zeolite crystals. Aguado et al. [47] proved the applicability of using an amorphous microporous silica
86 layer deposited on alumina discs by using colloidal silica as a precursor to prepare b-oriented MFI layers.
87 Moreover, Deng and Pera-Titus [48] used 200 nm thick mesoporous silica coated alumina discs and

prepared 500 nm thick b-oriented MFI films. Furthermore, Zhang et al. [49] showed that mesoporous silica coated alumina substrates improved the formation of b-oriented MFI zeolite layers whereas no silica layer coated alumina substrates yielded in random orientation of crystals with poor crystal intergrowth.

Here, in this work, we extend the investigation on transformation of microporous amorphous silica membranes into zeolite layers. By studying several process parameters such as the crystallisation time, crystallisation temperature, concentration and type of silica precursor used during the hydrothermal synthesis, a fundamental understanding was gained on the formation of zeolite layers by transforming an amorphous microporous silica membrane layers.

2. Experimental

The asymmetric silica membranes are prepared by sol-gel chemistry and the final structure is composed of the following three layers: 1) a macroporous, polished and disc-shaped α -Al₂O₃ substrate with 2mm thickness, 35% porosity and 80 nm pore size were obtained from Pervatech B.V. the Netherlands; 2) a mesoporous γ -Al₂O₃ layer with a pore size of 5nm and thickness of 3 μ m coated on the α -Al₂O₃ disc in order to create an intermediate layer working as a bridge to avoid penetration of the relatively small silica particles into the large pores of the α -Al₂O₃ layer; 3) an amorphous silica top layer with a uniform microstructure having a pore size of much less than 0.5 nm and thickness around 100 nm was coated via sol-gel techniques on the γ -Al₂O₃ intermediate layer [50,51]. The detailed preparation procedure of these silica multilayer membranes is described in [52].

The sides and bottom of these alumina-supported silica membranes were covered with Teflon tape to make sure that zeolite crystals were only formed via the amorphous silica layer. Then, the surface of the

110 membrane was soaked in a tetrapropylammonium hydroxide (TPAOH, 1.0 M in H₂O, Sigma Aldrich)
111 solution for 2 h prior to the hydrothermal synthesis in order to activate the silicon centres on the
112 amorphous silica network to react them with TPAOH for the further transformation into the zeolite
113 crystals during the hydrothermal treatment. In this way all nutrients required for the zeolite synthesis,
114 being the structure directing agent and the silica source, are available on the membrane surface.

115 For this *in-situ* zeolite synthesis method two different silica precursors were used: LUDOX® AS-40
116 colloidal silica (40 wt.% suspension in H₂O, Sigma Aldrich) and tetraethyl orthosilicate (TEOS, ≥ 99.0%
117 (GC), Sigma Aldrich) as a monomeric silica. The LUDOX® AS-40 colloidal silica precursor solution was
118 prepared by mixing 7.76 g LUDOX AS-40 with 3.15 g of TPAOH, 0.32 g of sodium hydroxide (NaOH, ACS
119 reagent ≥98% pellets, Sigma Aldrich) and 27.65 g Milli-Q water. In this way a molar ratio was obtained of
120 1 Si: 0.05 TPAOH: 0.15 NaOH: 37.5 H₂O. The TEOS precursor solution was prepared by mixing 10.8 g of
121 TEOS with 3.15 g of TPAOH, 0.32 g of NaOH and 37.5 g Milli-Q water, resulting in a molar ratio of 1 Si:
122 0.05 TPAOH: 0.15 NaOH: 37.5 H₂O. So, both precursor solutions have identical concentrations.

123 In both cases the solution was aged for 1.5 h under vigorous stirring. After that, the solutions were
124 diluted with Milli-Q water to obtain the final molar ratios of 1 Si: 0.05 TPAOH: 0.15 NaOH: 94 H₂O and 1
125 Si: 0.05 TPAOH: 0.15 NaOH: 130 H₂O, and continued to stir for an additional 30 min. The TPAOH-
126 activated silica membranes were placed horizontally on the bottom of the 125 mL Teflon-lined stainless
127 steel autoclave (Parr Instrument Company) and 70 mL of the solution was added. After sealing, the
128 autoclave was placed into a furnace (FED 56, BINDER) for the hydrothermal synthesis under autogenous
129 pressure. After cooling the autoclave, the membranes were recovered and washed thoroughly with
130 Milli-Q water and dried at 80°C for 12h in BINDER FED 56 drying oven.

131 The surface morphology and thickness (by means of cross sections) of the zeolite layers were
132 determined by JEOL JSM 6010LA scanning electron microscope (SEM) at an accelerating voltage of 5 kV.

The SEM was equipped with an energy dispersive X-ray spectrometer (EDX) to have a semi-quantitative elemental analysis of the samples. The surface and cross section of the membrane layers were coated with 5 nm thick Cr which was deposited by sputter coating prior to the analysis.

The XRD patterns are collected by a Bruker D2 Phaser X-ray diffraction with Cu-K α radiation ($\lambda = 1.5418$ nm) in the 2θ range 5 – 45°, using steps of 0.02°. The peaks were normalized with respect to the highest intensity peak in the 2θ spectrum from 5 to 45°. Then, the crystal structure and orientation of the zeolite layer was analysed by comparing the measured XRD patterns with the reference pattern obtained from the website of the International Zeolite Association [53].

3. Results and discussion

3.1. Zeolite layers using colloidal and monomeric silica precursors at different crystallisation time

In a first series of experiments, the zeolite layers were fabricated by using two different silica precursors: Colloidal silica (LUDOX® AS-40) and monomeric silica (TEOS). The *in-situ* synthesis took place at 170°C using a molar composition of 1 Si: 0.05 TPAOH: 0.15 NaOH: 94 H₂O for a varying synthesis times as given in Table 1.

The effect of the crystallisation time on the thickness and crystal orientation of the zeolite layer is clearly shown; an increase in crystallisation time results in an increase in layer thickness. In addition to the formation of the crystals on the surface via heterogeneous nucleation, at longer crystallisation time also seed crystals are formed in the solution by homogeneous nucleation and deposited on the surface. Therefore, at longer crystallisation time, due to the random deposition of the crystals formed via

homogeneous nucleation in the solution, the zeolite layer was found to be randomly oriented (as determined by XRD).

In addition to the crystallisation time, also the effect of precursor type was studied: colloidal or monomeric. For 4 hours of synthesis, even though the thickness of the colloidal silica and monomeric silica derived zeolite layers are similar (20nm for S4 and 18µm for S7), the crystal orientation was found to be random when using a colloidal silica precursor. On the other hand, the use of monomeric silica results in b-oriented structure with only minor amounts of a-oriented crystals after 4 hours of hydrothermal treatment at 170 °C. This influence of the type of precursor used on crystallographic orientation can be seen from the XRD patterns as given in Figure 2. By using the monomeric silica, b-oriented silicalite-1 layer was formed which has all the reference peaks of (0k0). On the contrary, colloidal silica derived silicalite-1 layer has many other peaks showing the random orientation of the crystals.

Wang and Yan [44] argued that the low degree of condensation in the TEOS precursor favours the formation of oriented layers whereas a colloidal silica precursor results in randomly oriented zeolite layers. This difference can be explained by the fact that crystallisation using a monomeric silica, like TEOS, is three times slower compared to colloidal silica, like LUDOX AS-40 [54]. Therefore, compared to colloidal silica, the formation of nuclei (by homogeneous nucleation) in the liquid phase is suppressed when using a monomeric silica. When colloidal silica is used, deposition of the homogeneously nucleated crystals on the membrane surface results in the formation of an irregular arrangement of zeolite crystals and a relative thick layer on the surface (see Figure 3b). So, by using monomeric silica mainly heterogeneous nucleation occurs from the already deposited amorphous silica layer. This promotes formation from the surface of a zeolite layer along the b-orientation. This is also visible on the surface images of TEOS and LUDOX derived zeolite layers as given in Figure 3.

The results, as summarized in Table 1, showed that the layer thickness can be reduced by reducing the synthesis time and that TEOS silica precursor promotes the formation of a b-oriented layer. Therefore, in the next sections only TEOS as precursor is discussed in the search for the most optimal experimental conditions to obtain a thin and b-oriented silicalite-1 layer homogeneously covered on a porous support.

3.2. Influence of Si:H₂O ratio and crystallisation temperature

TEOS as precursor and 4 h of synthesis time were used while studying the effect of the Si concentration in the precursor on silicalite-1 layer formation. Two zeolite layers were prepared using precursor solutions with Si:H₂O ratios of 1:94 and 1:130 respectively. The cross-sectional SEM images of these layers are given in Figure 4.

The α -alumina support and γ -alumina layer remained intact and are visible in the SEM images. The transformed zeolite layer with lower silica concentration (Si:H₂O of 1:130) showed a thinner layer (8 μ m, Figure 4b) if compared to the one with the higher silica concentration (Si:H₂O of 1:94, 18 μ m, Figure 4a). Also, the XRD patterns were studied and given in Figure 5.

XRD results of both zeolite layers were found to have almost similar peaks, as can be seen in Figure 5. Most of the peaks correspond to the b-orientation (0k0). In addition a small (501) signal was found, while the zeolite layer, made from a precursor with a lower silica concentration (Si:H₂O of 1:130), also showed a peak belonging to (101). Both (501) and (101) signals confirm the presence of a small amount of randomly oriented crystals formed using higher silica concentration.

Based on these results of having thinner layer and less randomly oriented crystals, further studies were done with the lower Si:H₂O ratio of 1:130. In order to investigate at which point the crystallisation starts and the surface is completely covered with b-oriented zeolite crystals, the crystallisation time (at 170 °C) was further decreased from 4h to 3.5, 3 and 2h respectively, while keeping TEOS as a silica precursor

and the molar ratio of 1 Si:0.05 TPAOH:0.15 NaOH:130 H₂O. The results of these experiments are summarized in Figure 6. As can be seen from these SEM images a synthesis time shorter than 4 h only results in the formation of a few crystals and not in the formation of a complete zeolite layer on the γ -alumina layer of the support.

The XRD patterns of these layers, formed after different crystallisation times, were given in Figure 7.

After 2 and 3 h of synthesis the XRD peaks with the highest intensity originate from the Al₂O₃ substrate (Figure 7a and 7b). This is due to the incomplete zeolite layer formation. The peaks belonging to the (0k0) b-oriented silicalite-1 structure become more visible when the synthesis time was increased. Only in the layer formed for 4 h of synthesis, all b-orientation peaks were visible in addition to some weak peaks such as (501) due to randomly placement of some crystals as also found in Figure 6d. After 3.5 h of synthesis time the surface was not completely covered with a zeolite layer (Figure 6c) So, it was concluded that the 4 h of synthesis is required to form complete and b-oriented zeolite layer while keeping TEOS precursor and the Si:H₂O ratio of 1:130.

3.3. Influence of crystallisation temperature

Finally the crystallisation temperature was varied in order to find the optimal synthesis conditions. The molar composition was kept on 1 Si: 0.05 TPAOH: 0.15 NaOH: 130 H₂O, while TEOS was used as silica precursor and 4 h crystallization time where the crystallisation temperature was varied from 130 to 190°C. The results of the different surface morphologies as function of crystallisation temperature are summarized in Figure 8.

It can be clearly seen that 130°C was far too low for transforming the amorphous silica layer into silicalite-1 crystals and covering the surface completely (Figure 8a). When temperature was increased to 140°C, the layer was covered with crystals. Further increase in temperature to 150°C and 160°C gave b-

oriented monolayer coverage of the crystals on the surface with some visible gaps in between the crystals. At 170°C, the complete coverage of b-oriented zeolite was visible on the membrane surface together with some loosely bound secondary crystals on the surface as seen in Figure 8e. These latter crystals were presumably formed by homogeneous nucleation of zeolite crystals from the solutions and subsequently deposited on the surface. When the crystallisation temperature increased even further to 180 and 190°C, the crystals grew too rapidly and deposited randomly on the surface as also observed in other work [44,55].

The XRD pattern of the layers formed at different crystallisation temperatures are provided in Figure 9.

The intensity of the (0k0) peaks (ascribed to b-orientation) from the layers at lower temperatures (130°C and 140°C) were too low and insignificant as compared to the peaks coming from the alumina support due to uncomplete coverage of the zeolite layer, which was also clearly seen in Figure 8. The peaks, corresponding to the b-orientation, were all visible in the samples synthesized at 150°C, 160°C and 170°C. The layers prepared at 180 and 190°C consist of randomly oriented crystals as observed by XRD by having many peaks other than those belonging to b-orientation. This more random orientation of the crystals is also clearly shown in the SEM images in Figure 8f and g if compared with e.g. Figure 8e. Also, the lower signal from the substrate as compared to the zeolite layer peaks is clearly observed in these two layers which is due to very thick layer formation consisting of large crystals. Furthermore, at these high temperatures the crystals were randomly oriented due to the rapid growth and random deposition of the crystals.

All these results indicate the following optimal synthesis parameters when using the novel synthesis method of the transformation an amorphous and microporous silica layer to a b-oriented silicalite-1 layer: Using TEOS silica precursor in the in-situ synthesis solution with a molar composition of 1 Si:0.05 TPAOH:0.15 NaOH:130 H₂O and perform the crystallization reaction in an autoclave for 4 hours at

temperatures varying from 150 to 170°C to fabricate a thin and b-oriented silicalite-1 zeolite layer with complete surface coverage.

3.4. Elemental analysis on the *in-situ* transformed silicalite-1 layers

In order to confirm the all-silica nature of the silicalite-1 layer without any incorporation of aluminium that would possibly leach from the alumina substrate, SEM/EDX analyses were done on a cross section, which image is given in Figure 10. This is a SEM picture of a sample, made by one of the optimal synthesis conditions; i.e. TEOS precursor, 4h of crystallisation at 150 °C. From this figure it can also be seen that the γ -alumina layer preserves its initial thickness of 3 μm after the hydrothermal synthesis, while the zeolite crystals are nicely oriented in the b-direction perpendicular to the surface (compare with Figure 1). The letters in the image represent the spots where the elemental analyses were performed and the results on Al, Si and O elemental composition are tabulated in Table 2. The zeolite layer (points A and B in Figure 10) was found to be Al-free, proving that it is an all-silica silicalite-1 (MFI) layer. In addition, the Al:O atomic ratios of around 1:1.5 of the γ -Al₂O₃ (point C) and α -Al₂O₃ (point D) layers indicate no elemental change on the substrate.

4. Conclusions

In this work an optimal route is developed for the synthesis of a b-oriented silicalite-1 layer by starting from an amorphous, microporous, silica layer as applied on an α -alumina supported γ -alumina membrane. The synthesis parameters studied were the type and concentration of silica precursor, the hydrothermal crystallization time and temperature. By optimizing all these parameters, a thin layer and complete coverage of a b-oriented silicalite-1 layer was obtained and a better understanding was achieved on how a pre-deposited silica layer transformed under specific synthesis parameters. These optimal conditions are the use of a monomeric (TEOS) silica precursor instead of colloidal silica (LUDOX®

AS-40) and a molar composition of 1 Si:0.05 TPAOH:0.15 NaOH:130 H₂O, while performing the crystallization reaction in an autoclave for 4 hours at temperatures varying from 150 to 170 °C. EDX analysis showed that no aluminium leaching from the α/γ -alumina support to the zeolite layer was found during the *in-situ* transformation, indicating that all-silica zeolite layers are formed.

Further research could be dedicated to applying post-treatment methods for healing any defects or pinholes between these zeolite crystals in order to take advantage of these preferably-oriented layers for use as a membrane material for gas and liquid separation, having high fluxes provided by its b-oriented channels.

Acknowledgment

This research is supported by Netherlands Technology Foundation (STW-13941). The authors acknowledge Cindy Huiskes and Mieke Luiten-Olieman from University of Twente, and Xuerui Wang from Delft University of Technology for their helpful discussions in this work and Frank Morssinkhof from University of Twente for technical support. The authors declare no conflict of interest.

References

- [1] X. Lu, Y. Peng, Z. Wang, Y. Yan, Rapid fabrication of highly b-oriented zeolite MFI thin films using ammonium salts as crystallization-mediating agents, *Chem. Commun.* 51 (2015) 11076–11079. doi:10.1039/C5CC02980E.
- [2] M.S. Holm, E. Taarning, K. Egeblad, C.H. Christensen, Catalysis with hierarchical zeolites, *Catal. Today*. 168 (2011) 3–16. doi:10.1016/j.cattod.2011.01.007.

- 286 [3] J. Weitkamp, Zeolites and catalysis, *Solid State Ionics*. 131 (2000) 175–188. doi:10.1016/S0167-
287 2738(00)00632-9.
- 288 [4] D. Fu, J.E. Schmidt, Z. Ristanović, A.D. Chowdhury, F. Meirer, B.M. Weckhuysen, Highly oriented
289 growth of catalytically active zeolite ZSM-5 films with a broad range of Si/Al ratios, *Angew.
290 Chemie - Int. Ed.* 56 (2017) 11217–11221. doi:10.1002/anie.201704846.
- 291 [5] I. Yarulina, A. Dikhtiarenko, F. Kapteijn, J. Gascon, Consequences of secondary zeolite growth on
292 catalytic performance in DMTO studied over DDR and CHA [†], *Catal. Sci. Technol.* 7 (2017) 300–
293 309. doi:10.1039/C6CY02307J.
- 294 [6] W.L. Rauch, M. Liu, Development of a selective gas sensor utilizing a perm-selective zeolite
295 membrane, *J. Mater. Sci.* 38 (2003) 4307–4317. doi:10.1023/A:1026331015093.
- 296 [7] P. Yang, X. Ye, C. Lau, Z. Li, X. Liu, J. Lu, Design of efficient zeolite sensor materials for n-hexane,
297 *Anal. Chem.* 79 (2007) 1425–1432. doi:10.1021/ac061811+.
- 298 [8] A. Satsuma, D. Yang, K. Shimizu, Effect of acidity and pore diameter of zeolites on detection of
299 base molecules by zeolite thick film sensor, *Microporous Mesoporous Mater.* 141 (2011) 20–25.
300 doi:10.1016/j.micromeso.2009.12.002.
- 301 [9] X. Xu, J. Wang, Y. Long, Zeolite-based materials for gas sensors, *Sensors*. 6 (2006) 1751–1764.
302 doi:10.3390/s6121751.
- 303 [10] S. Mintova, S. Mo, T. Bein, Humidity sensing with ultrathin LTA-type molecular sieve films grown
304 on piezoelectric devices, *Chem. Mater.* 13 (2001) 901–905. doi:10.1021/cm000671w.
- 305 [11] R. V. Siriwardane, M.S. Shen, E.P. Fisher, J. Losch, Adsorption of CO₂ on zeolites at moderate
306 temperatures, *Energy and Fuels*. 19 (2005) 1153–1159. doi:10.1021/ef040059h.

- 307 [12] S.M. Kuznicki, V.A. Bell, S. Nair, H.W. Hillhouse, R.M. Jacubinas, C.M. Braunbarth, et al., A
308 titanosilicate molecular sieve with adjustable pores for size-selective adsorption of molecules,
309 Nature. 412 (2001) 720–724. doi:10.1038/35089052.
- 310 [13] S. Velu, X. Ma, C. Song, Selective adsorption for removing sulfur from jet fuel over zeolite-based
311 adsorbents, Ind. Eng. Chem. Res. 42 (2003) 5293–5304. doi:10.1021/ie020995p.
- 312 [14] J.L. Hang Chau, C. Tellez, K.L. Yeung, K. Ho, The role of surface chemistry in zeolite membrane
313 formation, J. Memb. Sci. 164 (2000) 257–275. doi:10.1016/S0376-7388(99)00214-8.
- 314 [15] N. Kosinov, C. Auffret, C. Gücüyener, B.M. Szyja, J. Gascon, F. Kapteijn, et al., High flux high-silica
315 SSZ-13 membrane for CO₂ separation, J. Mater. Chem. A. 2 (2014) 13083–13092.
316 doi:10.1039/C4TA02744B.
- 317 [16] L. Sandström, E. Sjöberg, J. Hedlund, Very high flux MFI membrane for CO₂ separation, J. Memb.
318 Sci. 380 (2011) 232–240. doi:10.1016/j.memsci.2011.07.011.
- 319 [17] J. Jiang, L. Wang, L. Peng, C. Cai, C. Zhang, X. Wang, et al., Preparation and characterization of
320 high performance CHA zeolite membranes from clear solution, J. Memb. Sci. 527 (2017) 51–59.
321 doi:10.1016/j.memsci.2017.01.005.
- 322 [18] Y. Hasegawa, T. Ikeda, T. Nagase, Y. Kiyozumi, T. Hanaoka, F. Mizukami, Preparation and
323 characterization of silicalite-1 membranes prepared by secondary growth of seeds with different
324 crystal sizes, J. Memb. Sci. 280 (2006) 397–405. doi:10.1016/j.memsci.2006.01.044.
- 325 [19] T. Wu, B. Wang, Z. Lu, R. Zhou, X. Chen, Alumina-supported AIPO-18 membranes for CO₂/CH₄
326 separation, J. Memb. Sci. 471 (2014) 338–346. doi:10.1016/j.memsci.2014.08.035.
- 327 [20] T.C.T. Pham, H.S. Kim, K.B. Yoon, Growth of uniformly oriented silica MFI and BEA zeolite films on

328 substrates, *Science*. 334 (2011) 1533–1538. doi:10.1126/science.1212472.

329 [21] H. Kalipcilar, S.K. Gade, R.D. Noble, J.L. Falconer, Synthesis and separation properties of B-ZSM-5
330 zeolite membranes on monolith supports, *J. Memb. Sci.* 210 (2002) 113–127. doi:10.1016/S0376-
331 7388(02)00380-0.

332 [22] K. Kida, Y. Maeta, K. Yogo, Preparation and gas permeation properties on pure silica CHA-type
333 zeolite membranes, *J. Memb. Sci.* 522 (2017) 363–370. doi:10.1016/j.memsci.2016.09.002.

334 [23] S. Yang, Z. Cao, A. Arvanitis, X. Sun, Z. Xu, J. Dong, DDR-type zeolite membrane synthesis,
335 modification and gas permeation studies, *J. Memb. Sci.* 505 (2016) 194–204.
336 doi:10.1016/j.memsci.2016.01.043.

337 [24] C. Gücüyener, J. van den Bergh, A.M. Joaristi, P.C.M.M. Magusin, E.J.M. Hensen, J. Gascon, et al.,
338 Facile synthesis of the DD3R zeolite: performance in the adsorptive separation of buta-1,3-diene
339 and but-2-ene isomers, *J. Mater. Chem.* 21 (2011) 18386–18397. doi:10.1039/c1jm13671b.

340 [25] L. Sandström, J. Lindmark, J. Hedlund, Separation of methanol and ethanol from synthesis gas
341 using MFI membranes, *J. Memb. Sci.* 360 (2010) 265–275. doi:10.1016/j.memsci.2010.05.022.

342 [26] T.F. Mastropietro, E. Drioli, S. Candamano, T. Poerio, Crystallization and assembling of FAU
343 nanozeolites on porous ceramic supports for zeolite membrane synthesis, *Microporous*
344 *Mesoporous Mater.* 228 (2016) 141–146. doi:10.1016/j.micromeso.2016.03.037.

345 [27] N. Nishiyama, T. Matsufuji, K. Ueyama, M. Matsukata, FER membrane synthesized by a vapor-
346 phase transport method: its structure and separation characteristics, *Microporous Mater.* 12
347 (1997) 293–303. doi:10.1016/S0927-6513(97)00076-X.

348 [28] A. Huang, F. Liang, F. Steinbach, J. Caro, Preparation and separation properties of LTA

349 membranes by using 3-aminopropyltriethoxysilane as covalent linker, *J. Memb. Sci.* 350 (2010) 5–
350 9. doi:10.1016/j.memsci.2009.12.029.

351 [29] I. Tiscornia, S. Valencia, A. Corma, C. Téllez, J. Coronas, J. Santamaría, Preparation of ITQ-29 (Al-
352 free zeolite A) membranes, *Microporous Mesoporous Mater.* 110 (2008) 303–309.
353 doi:10.1016/j.micromeso.2007.06.019.

354 [30] F. Ghoroghchian, H. Aghabozorg, F. Farhadi, H. Kazemian, Controlled synthesis of a thin LTL
355 zeolitic membrane using nano-sized seeds: Characterization and permeation performance, *Chem.*
356 *Eng. Technol.* 33 (2010) 2066–2072. doi:10.1002/ceat.200900543.

357 [31] N. Kosinov, E.J.M. Hensen, Synthesis and separation properties of an α -alumina-supported high-
358 silica MEL membrane, *J. Memb. Sci.* 447 (2013) 12–18. doi:10.1016/j.memsci.2013.07.028.

359 [32] Z.A.E.P. Vroon, K. Keizer, A.J. Burggraaf, H. Verweij, Preparation and characterization of thin
360 zeolite MFI membranes on porous supports, *J. Memb. Sci.* 144 (1998) 65–76. doi:10.1016/S0376-
361 7388(98)00035-0.

362 [33] M. Zhou, D. Korelskiy, P. Ye, M. Grahn, J. Hedlund, A uniformly oriented MFI membrane for
363 improved CO₂ separation, *Angew. Chemie - Int. Ed.* 53 (2014) 3492–3495.
364 doi:10.1002/anie.201311324.

365 [34] M.Y. Jeon, D. Kim, P. Kumar, P.S. Lee, N. Rangnekar, P. Bai, et al., Ultra-selective high-flux
366 membranes from directly synthesized zeolite nanosheets, *Nature.* 543 (2017) 690–694.
367 doi:10.1038/nature21421.

368 [35] A. Tavoraro, A. Julbe, C. Guizard, A. Basile, L. Cot, E. Drioli, Synthesis and characterization of a
369 mordenite membrane on an α -Al₂O₃ tubular support, *J. Mater. Chem.* 10 (2000) 1131–1137.

doi:10.1039/b000047g.

[36] K. Makita, Y. Hirota, Y. Egashira, K. Yoshida, Y. Sasaki, N. Nishiyama, Synthesis of MCM-22 zeolite membranes and vapor permeation of water/acetic acid mixtures, *J. Memb. Sci.* 372 (2011) 269–276. doi:10.1016/j.memsci.2011.02.007.

[37] J. Caro, M. Noack, J. Richter-Mendau, F. Marlow, D. Petersohn, M. Griepentrog, et al., Selective sorption uptake kinetics of n-hexane on ZSM-5. A new method for measuring anisotropic diffusivities, *J. Phys. Chem.* 97 (1993) 13685–13690. doi:10.1021/j100153a043.

[38] M. Abdollahi, S.N. Ashrafizadeh, A. Malekpour, Preparation of zeolite ZSM-5 membrane by electrophoretic deposition method, *Microporous Mesoporous Mater.* 106 (2007) 192–200. doi:10.1016/j.micromeso.2007.02.051.

[39] T. Seike, M. Matsuda, M. Miyake, Preparation of FAU type zeolite membranes by electrophoretic deposition and their separation properties, *J. Mater. Chem.* 12 (2002) 366–368. doi:10.1039/b106774p.

[40] X. Wang, Z. Yang, C. Yu, L. Yin, C. Zhang, X. Gu, Preparation of T-type zeolite membranes using a dip-coating seeding suspension containing colloidal SiO₂, *Microporous Mesoporous Mater.* 197 (2014) 17–25. doi:10.1016/j.micromeso.2014.05.046.

[41] T.C.T. Pham, T.H. Nguyen, K.B. Yoon, Gel-free secondary growth of uniformly oriented silica MFI zeolite films and application for xylene separation, *Angew. Chemie - Int. Ed.* 52 (2013) 8693–8698. doi:10.1002/anie.201301766.

[42] D. Coutinho, K.J. Balkus, Preparation and characterization of zeolite X membranes via pulsed-laser deposition, *Microporous Mesoporous Mater.* 52 (2002) 79–91. doi:10.1016/S1387-

391 1811(02)00273-1.

392 [43] A. Huang, Y.S. Lin, W. Yang, Synthesis and properties of A-type zeolite membranes by secondary
393 growth method with vacuum seeding, *J. Memb. Sci.* 245 (2004) 41–51.
394 doi:10.1016/j.memsci.2004.08.001.

395 [44] Z. Wang, Y. Yan, Oriented zeolite MFI monolayer films on metal substrates by in situ
396 crystallization, *Microporous Mesoporous Mater.* 48 (2001) 229–238. doi:10.1016/S1387-
397 1811(01)00357-2.

398 [45] L. Shan, J. Shao, Z. Wang, Y. Yan, Preparation of zeolite MFI membranes on alumina hollow fibers
399 with high flux for pervaporation, *J. Memb. Sci.* 378 (2011) 319–329.
400 doi:10.1016/j.memsci.2011.05.011.

401 [46] S. Mintova, V. Valtchev, Effect of the silica source on the formation of nanosized silicalite-1: an in
402 situ dynamic light scattering study, *Microporous Mesoporous Mater.* 55 (2002) 171–179.
403 doi:10.1016/S1387-1811(02)00401-8.

404 [47] S. Aguado, E.E. McLeary, A. Nijmeijer, M. Luiten, J.C. Jansen, F. Kapteijn, b-Oriented MFI
405 membranes prepared from porous silica coatings, *Microporous Mesoporous Mater.* 120 (2009)
406 165–169. doi:10.1016/j.micromeso.2008.08.059.

407 [48] Z. Deng, M. Pera-Titus, In situ crystallization of b-oriented MFI films on plane and curved
408 substrates coated with a mesoporous silica layer, *Mater. Res. Bull.* 48 (2013) 1874–1880.
409 doi:10.1016/j.materresbull.2013.01.020.

410 [49] F. Zhang, M. Fuji, M. Takahashi, In situ growth of continuous b-oriented MFI zeolite membranes
411 on porous α -alumina substrates precoated with a mesoporous silica sublayer, *Chem. Mater.* 17

(2005) 1167–1173. doi:10.1021/cm048644j.

[50] R.M. de Vos, H. Verweij, High-selectivity, high-flux silica membranes for gas separation, *Science*. 279 (1998) 1710–1711.

[51] M. ten Hove, M.W.J. Luiten-Olieman, C. Huiskes, A. Nijmeijer, L. Winnubst, Hydrothermal stability of silica, hybrid silica and Zr-doped hybrid silica membranes, *Sep. Purif. Technol.* 189 (2017) 48–53. doi:10.1016/j.seppur.2017.07.045.

[52] P. Karakiliç, C. Huiskes, M.W.J. Luiten-Olieman, A. Nijmeijer, L. Winnubst, Sol-gel processed magnesium-doped silica membranes with improved H₂/CO₂ separation, *J. Memb. Sci.* 543 (2017) 195–201. doi:10.1016/j.memsci.2017.08.055.

[53] Database of Zeolite Structures, (n.d.). <http://www.iza-structure.org/databases/> (accessed April 27, 2018).

[54] M.D. Oleksiak, J.A. Soltis, M.T. Conato, R.L. Penn, J.D. Rimer, Nucleation of FAU and LTA zeolites from heterogeneous aluminosilicate precursors, *Chem. Mater.* 28 (2016) 4906–4916. doi:10.1021/acs.chemmater.6b01000.

[55] A.E. Persson, B.J. Schoeman, J. Sterte, J.-E. Otterstedt, The synthesis of discrete colloidal particles of TPA-silicalite-1, *Zeolites*. 14 (1994) 557–567. doi:10.1016/0144-2449(94)90191-0.

430 Tables and Figures

431 *Table 1: Thickness and crystal orientation of zeolite layers, made by the in-situ synthesis mechanism, using different silica*
 432 *precursors and crystallization time. In all cases the crystallization temperature was 170°C and the molar composition was 1 Si:*
 433 *0.05 TPAOH: 0.15 NaOH: 94 H₂O*

Sample No	Precursor	Crystallisation time [h]	Thickness [μm]	Orientation
S1	Colloidal (LUDOX)	17	200	random
S2	Colloidal (LUDOX)	14	147	random
S3	Colloidal (LUDOX)	10	56	random
S4	Colloidal (LUDOX)	4	20	random
S5	Monomeric (TEOS)	10	80	random
S6	Monomeric (TEOS)	7	65	random
S7	Monomeric (TEOS)	4	18	b-oriented*

434 *: minor amounts of a-oriented crystals

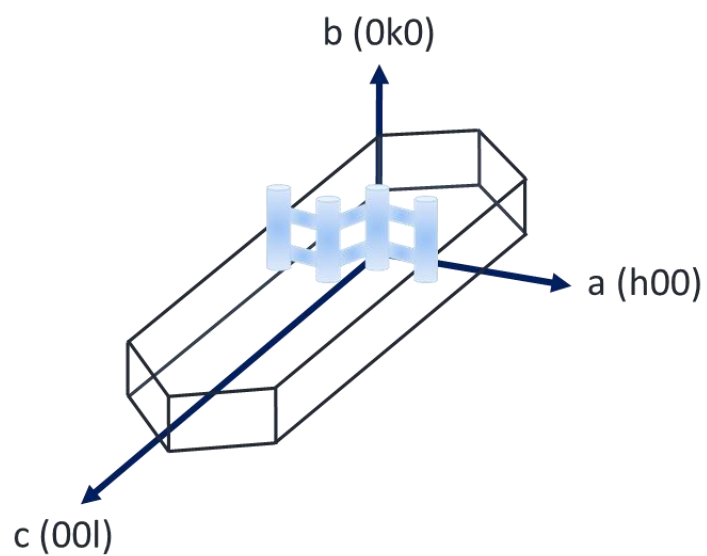
435

436 *Table 2: Elemental EDX analysis results from SEM image in Figure 10*

Position	Si [atom%]	Al [atom%]	O [atom%]
A	32	0	68
B	31	0	69
C	0	29	71
D	0	39	61

437

438



439

440 *Figure 1: The channel system along the a - and b -direction of MFI zeolite crystals*

441

442

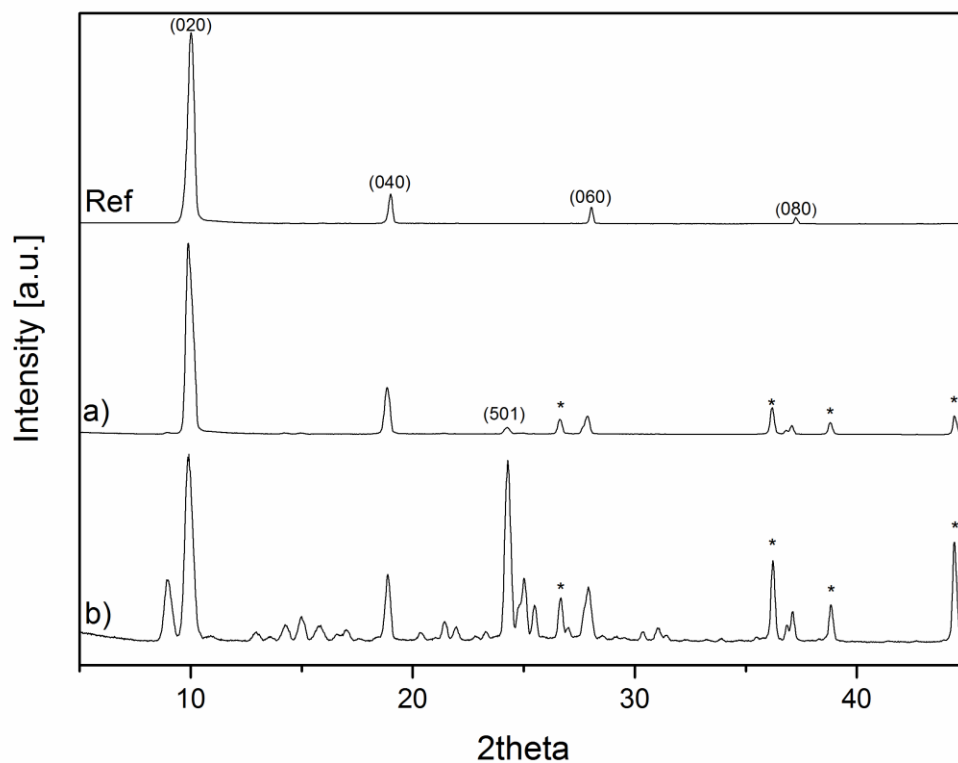


Figure 2: XRD patterns of layers formed using a) monomeric b) colloidal silica precursor with the same molar ratio in the in-situ synthesis solution of 1 Si: 0.05 TPAOH: 0.15 NaOH: 94 H₂O at 170°C and for 4h of synthesis. Ref stands for b-oriented (0k0) crystal peaks of MFI structure obtained from [53] and asterisk (*) represents the peaks originating from the alumina substrate.

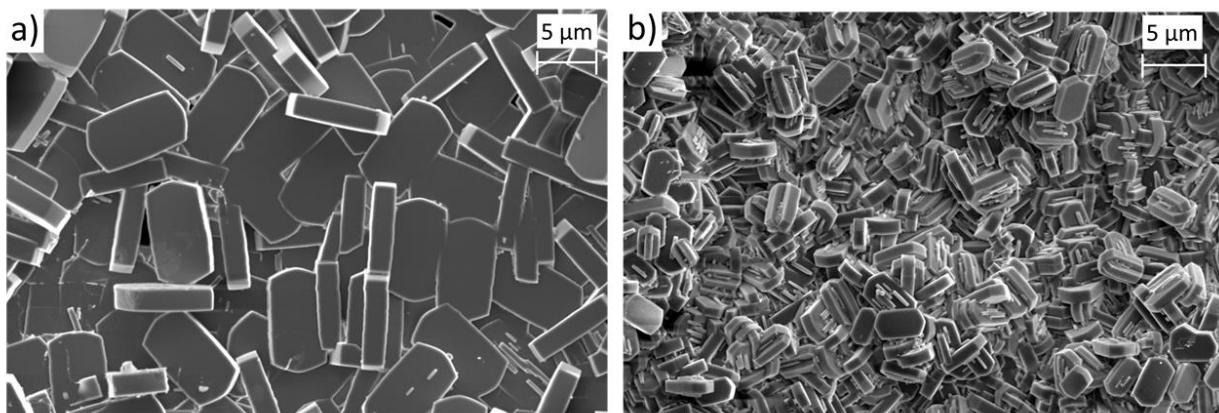


Figure 3: The surface images of zeolite layers using a) monomeric and b) colloidal silica precursor with the same molar ratio in the in-situ synthesis solution of 1 Si: 0.05 TPAOH: 0.15 NaOH: 94 H₂O and for 4h of synthesis at 170°C.

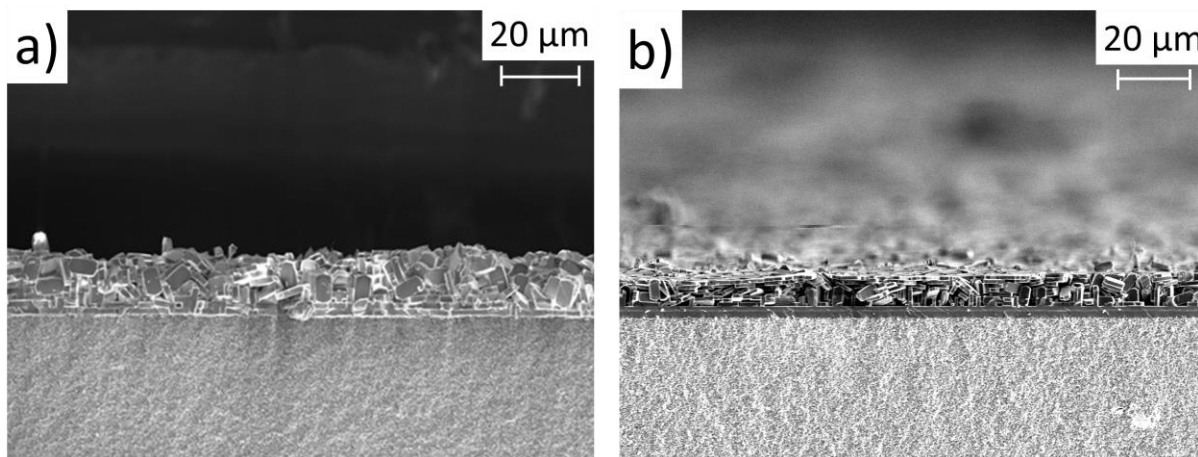


Figure 4: Cross-sectional SEM images of TEOS-derived silicalite-1 zeolite membrane with different dilution of the precursor solution, a) and b) represent the Si:H₂O ratio of 1:94 and 1:130 respectively, using TEOS silica precursor, at 170°C and for 4h of synthesis.

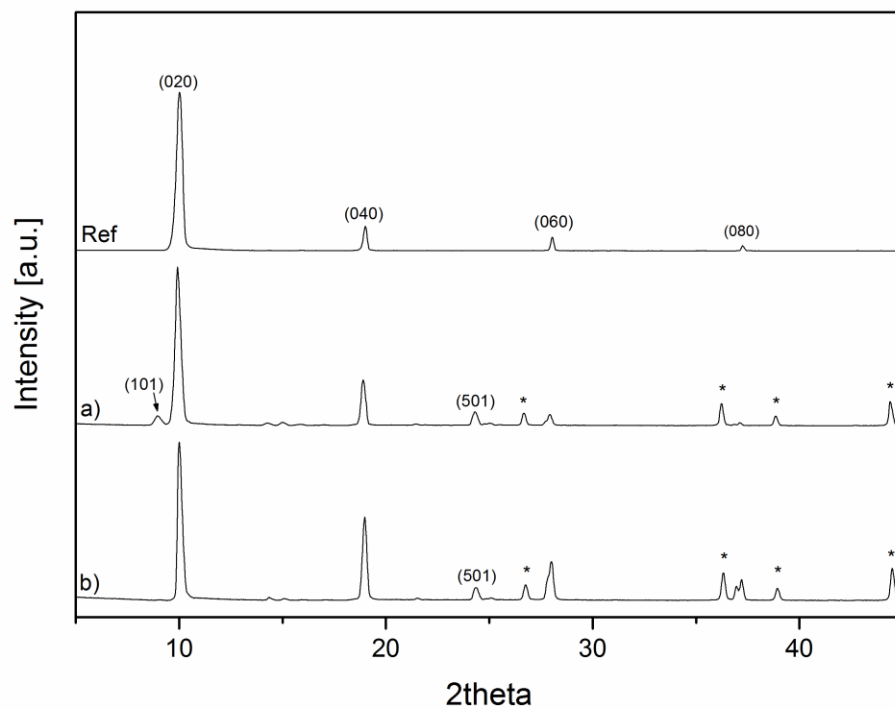


Figure 5: XRD patterns of layers formed using Si:H₂O ratio of a) 1:94 b) 1:130 using TEOS silica precursor, at 170°C and for 4h of synthesis. Ref stands for b-oriented (0k0) crystal peaks of MFI structure obtained from [53] and asterisk (*) represents the peaks originating from the alumina substrate.

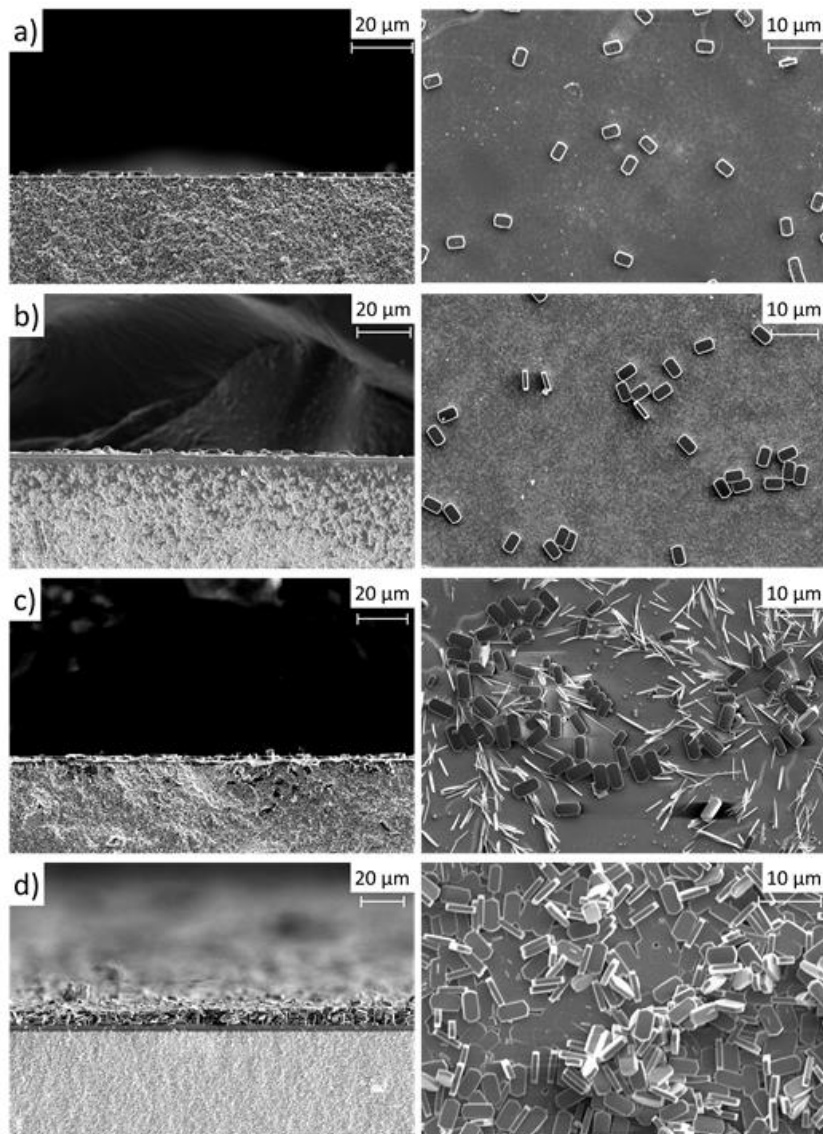


Figure 6: The cross-sectional (left) and surface images (right) of TEOS derived silicalite-1 layers formed after a) 2h, b) 3h, c) 3.5h and d) 4h of synthesis at 170°C

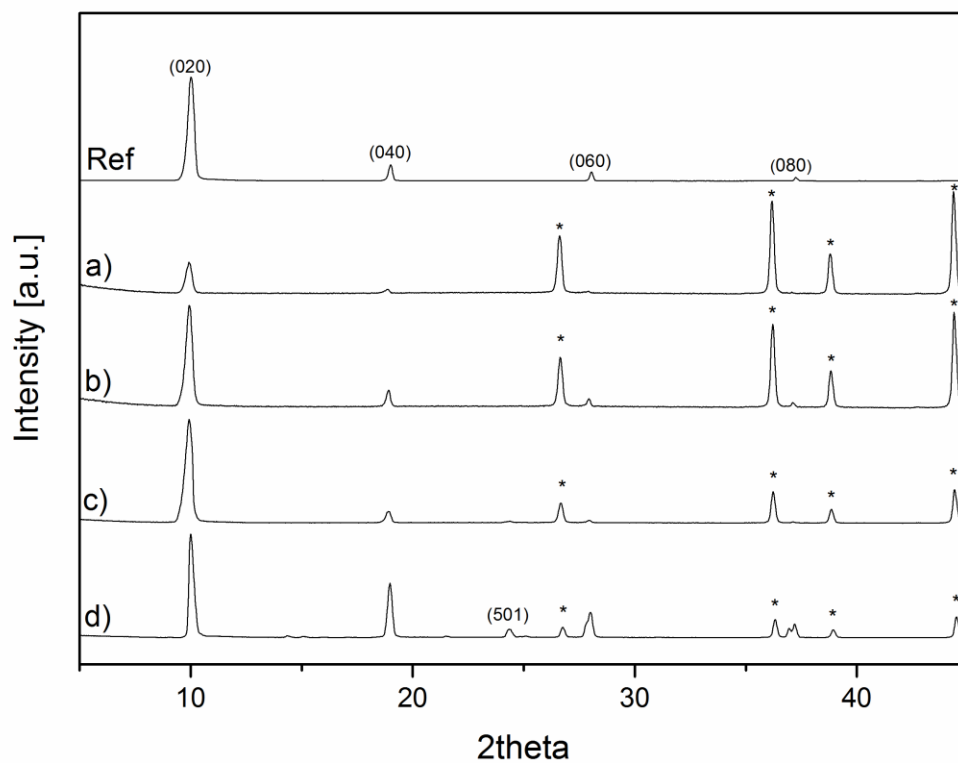


Figure 7: The XRD pattern of the layers produced for a) 2h, b) 3h, c) 3.5h and d) 4h of crystallization time. Ref stands for b-oriented (0k0) crystal peaks of MFI structure obtained from [53] and asterisk (*) represents the XRD signals of the alumina substrate.

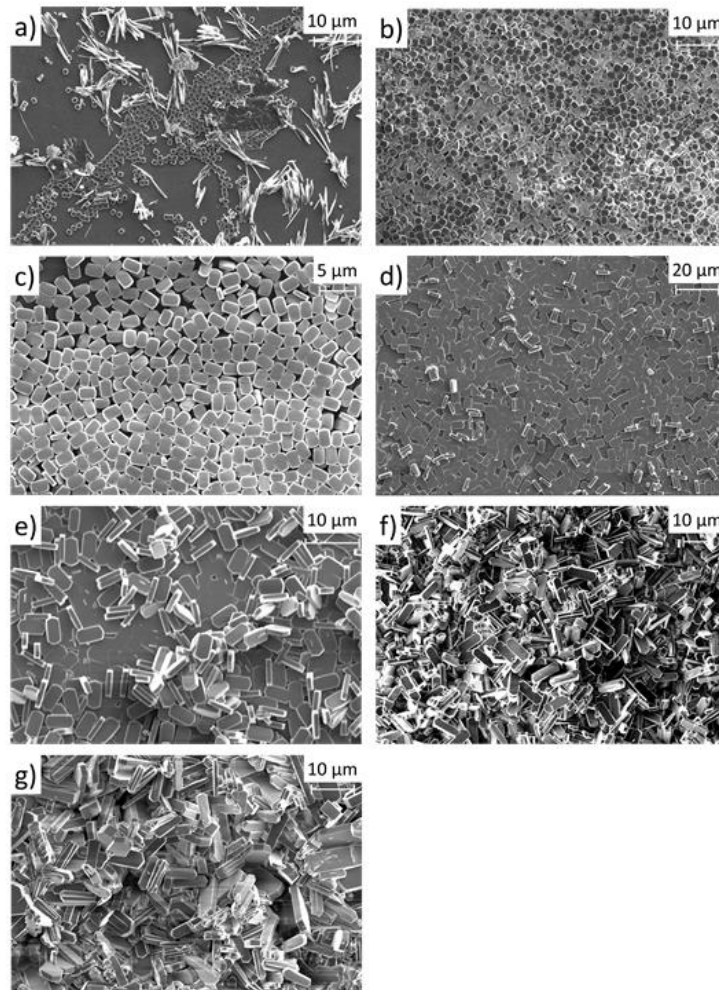


Figure 8: The effect of synthesis temperature on the size of crystals and surface coverage of the zeolite layer where letters represent the synthesis temperature: a) 130°C, b) 140°C, c) 150°C, d) 160°C, e) 170°C, f) 180°C and g) 190°C

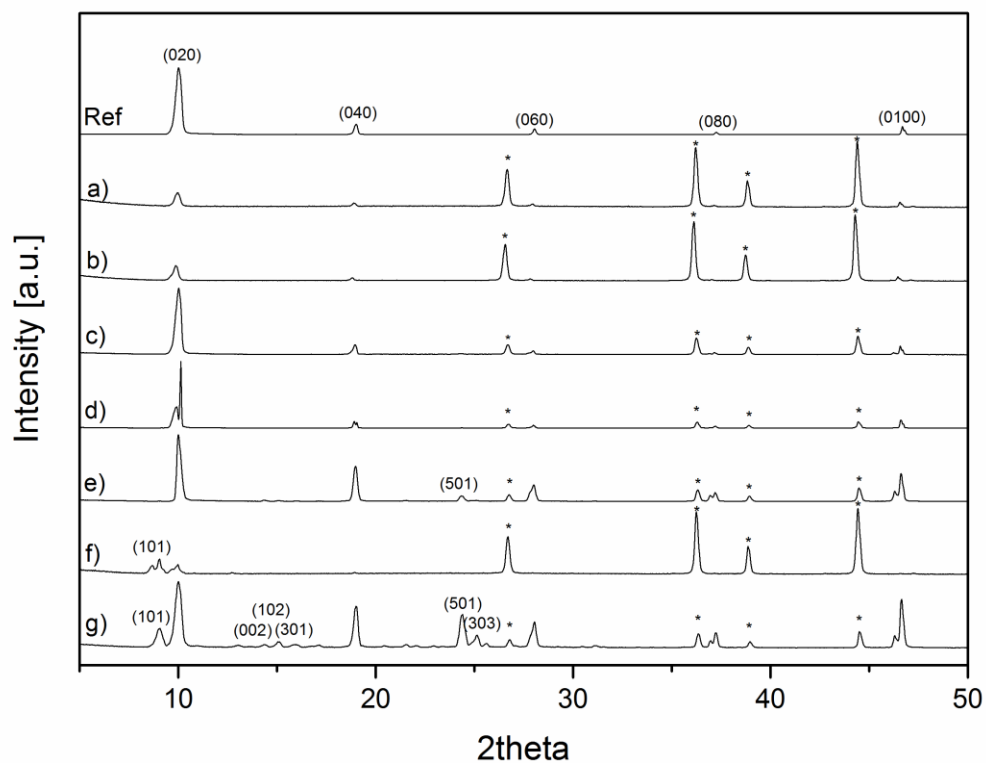
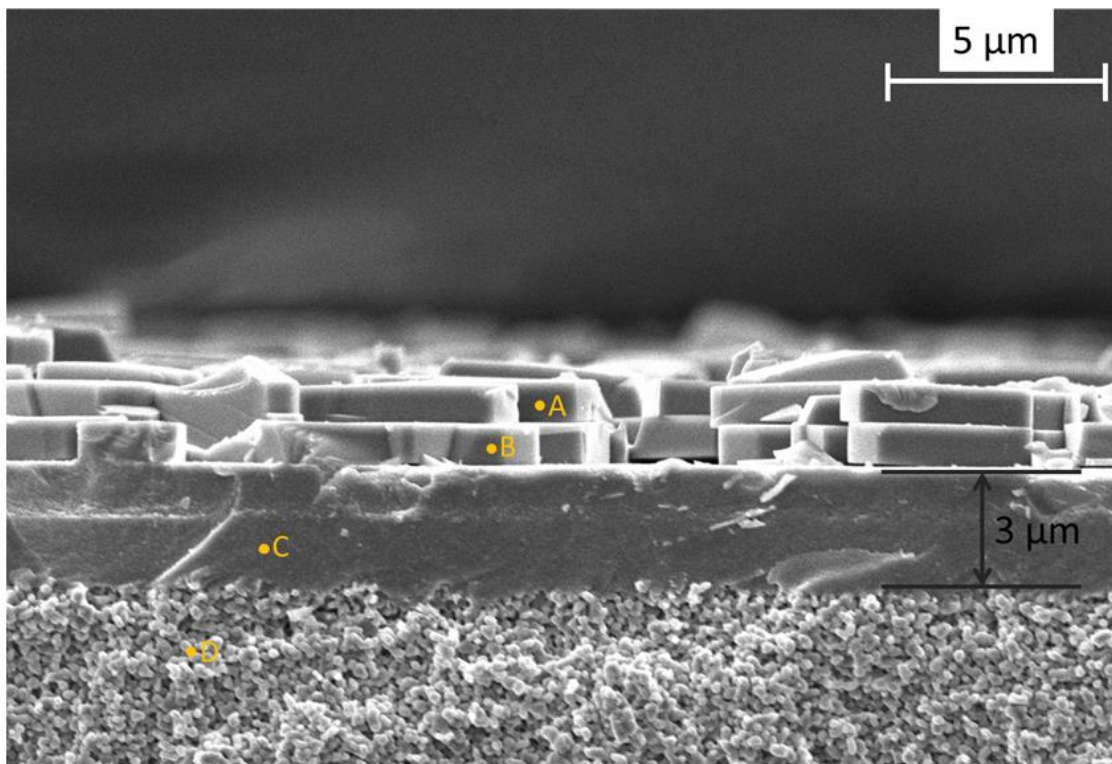


Figure 9: The powder pattern of the layers formed at a) 130°C, b) 140°C, c) 150°C, d) 160°C, e) 170°C, f) 180°C and g) 190°C. Ref stands for b-oriented (0k0) crystal peaks of MFI structure obtained from [53] and asterisk (*) represents the peaks coming from the alumina substrate.

488 *Figure 10: SEM image of the in-situ synthesized silicalite-1 layers using TEOS precursor, 4h of crystallisation and 150°C of*
489 *synthesis temperature. The letters A, B, C and D correspond to the regions analysed by EDX, to determine the elemental*
490 *composition*



491