Defects-healing of SAPO-34 membrane by post-synthesis modification using organosilica for selective CO₂ separation

DOI:

[10.1016/j.memsci.2019.01.004](https://doi.org/10.1016/j.memsci.2019.01.004)

Document Version

Accepted author manuscript

[Link to publication record in Manchester Research Explorer](#)

Citation for published version (APA):

Mu, Y., Chen, H., Xiang, H., Lan, L., Fan, X., & Hardacre, C. (2019). Defects-healing of SAPO-34 membrane by post-synthesis modification using organosilica for selective CO₂ separation. *Journal of Membrane Science*, 575, 80-88. <https://doi.org/10.1016/j.memsci.2019.01.004>

Published in:

Journal of Membrane Science

Citing this paper

Please note that where the full-text provided on Manchester Research Explorer is the Author Accepted Manuscript or Proof version this may differ from the final Published version. If citing, it is advised that you check and use the publisher's definitive version.

General rights

Copyright and moral rights for the publications made accessible in the Research Explorer are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Takedown policy

If you believe that this document breaches copyright please refer to the University of Manchester's Takedown Procedures [<http://man.ac.uk/04Y6Bo>] or contact uml.scholarlycommunications@manchester.ac.uk providing relevant details, so we can investigate your claim.

Defects-healing of SAPO-34 membrane by post-synthesis modification using organosilica for selective CO₂ separation

Yibing Mu, Huanhao Chen, Huan Xiang, Lan Lan, Yan Shao, Xiaolei Fan, Christopher Hardacre

PII: S0376-7388(18)33210-1

DOI: <https://doi.org/10.1016/j.memsci.2019.01.004>

Reference: MEMSCI16774

To appear in: *Journal of Membrane Science*

Cite this article as: Yibing Mu, Huanhao Chen, Huan Xiang, Lan Lan, Yan Shao, Xiaolei Fan and Christopher Hardacre, Defects-healing of SAPO-34 membrane by post-synthesis modification using organosilica for selective CO₂ separation, *Journal of Membrane Science*, <https://doi.org/10.1016/j.memsci.2019.01.004>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting galley proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Defects-healing of SAPO-34 membrane by post-synthesis modification using organosilica for selective CO₂ separation

Yibing Mu¹, Huanhao Chen^{1*}, Huan Xiang¹, Lan Lan¹, Yan Shao^{1,2}, Xiaolei Fan^{1*}, Christopher Hardacre^{1*}

¹ School of Chemical Engineering and Analytical Science, The University of Manchester, M13 9PL, United Kingdom

² School of Chemical and Environmental Engineering, Wuyi University, Jiangmen 52920, China

huanhao.chen@manchester.ac.uk (HC)

xiaolei.fan@manchester.ac.uk (XF)

c.hardacre@manchester.ac.uk (CH)

*corresponding author:

Abstract:

It is challenging to avoid the formation of defects in zeolite membranes during their preparation. Herein, we present a facile vacuum-assisted deposition (VAD) method as a feasible solution to address this challenge. Defective SAPO-34 membranes supported on tubular porous alumina were healed using bis(triethoxysilyl)ethane (BTESE)-derived organosilica *via* VAD and these showed an improved performance in the selective CO₂ separation from an equimolar CO₂/CH₄ mixture. Specifically, by controlling the amount of organosilica deposited, the coating was able to heal the non-selective defects in SAPO-34 membranes without compromising the CO₂ permeance, but increased the CO₂/CH₄ selectivity notably (by a factor of *ca.* 2.5 at 25 °C and 200 kPa). An excessive coating of organosilica by VAD resulted in a thick layer on top of the SAPO-34 membrane which led to a significant decrease in the CO₂ permeance. Additionally, a modified membrane was also investigated for the CO₂/CH₄ gas feed with different CO₂ concentrations from 20-50 mol.% and this showed that a relatively concentrated CO₂ in the system could also be improved in terms of its separation performance.

Graphical Abstract

Keywords: SAPO-34 membrane; Vacuum-assisted deposition (VAD); Organosilica; Defects-healing; CO₂ separation

1. Introduction

Carbon dioxide (CO₂) emissions are the major contributor (~82%) to global warming and climate change as emphasised in the 21st Conference of the Parties (COP21, 2015 in Paris). CO₂ can be commonly found in many resources such as biogas, natural gas, flue gas and also a product of coal gasification [1]. Specifically, biogas is a mixture of CO₂ (25~60 vol%) and methane (CH₄, 40~75 vol%), including small amounts of other components such as water and H₂S [2, 3]. Biogas is produced by the anaerobic digestion of organic wastes such as sewage, manure, food wastes, landfill [4, 5]. The capture of CO₂ from biogas to generate an enriched biomethane that can be used as the transport fuel in the form of Liquid Natural Gas (LNG) or Compressed Natural Gas (CNG), is very important in the process of biogas upgrading [3, 5, 6].

Membrane-based CO₂ capture technology has shown potential for significant decreases in energy penalties and cost (e.g. in comparison to amine-based systems) due to its energy efficiency and ease of module construction [7, 8]. In this regard, zeolite membranes (e.g. SAPO-34 [9-15], DDR [16-18], AIPO-19 [19-22], and SSZ-13 [23-26]) have been widely studied for CO₂/CH₄ separation due to their adsorption properties, uniform molecular-sized pores, and outstanding thermal as well as chemical stabilities [14, 27, 28]. Among these zeolite membranes, small pore zeolites such as SAPO-

34 have attracted tremendous attention due to their size selective pore diameters. For example, SAPO-34 zeolite has a pore diameter of 0.38 nm which is similar in size to CH₄ (0.38 nm kinetic diameter), but larger than CO₂ (0.33 nm), allowing good CO₂ permeability over large hydrocarbons [14, 29]. In addition, SAPO-34 zeolite has strong adsorption affinity of CO₂ molecules compared with CH₄, resulting in a high CO₂/CH₄ selectivity [29]. Unfortunately, non-selective defects such as inter-crystal defects and cracks are always formed in these zeolite membranes during the hydrothermal synthesis and high-temperature calcination process [30]. The presence of boundary defects between zeolite crystals, which are much larger than the pore opening of SAPO-34 zeolite (i.e. 0.38 nm), has a significant negative impact on the separation selectivity [31]. Therefore, in order to improve the separation performance of zeolite membranes, it is crucial to develop strategies to eliminate these defects in the membrane [18, 23, 31-36].

Many studies have been undertaken to heal such boundary defects using post-treatment methods such as catalytic cracking deposition (CCD) [37-39], chemical vapor deposition (CVD) [40], molecular layer deposition (MLD) [36], chemical liquid deposition (CLD) [32] and silica coating [41-43]. In these approaches, various fillers have been selectively deposited in the defective pores/voids/cracks in zeolite membranes, such as silica precursors (e.g. tetramethyl orthosilicate [44], tetraethyl orthosilicate [44-47], and methyldiethoxysilane [38, 48]), organic molecules (e.g. α -cyclodextrin and β -cyclodextrin [34]), Al₂O₃ [36], and dye molecules (e.g. fluorescein sodium salt [23]). Methyldiethoxysilane has also been applied to modify the zeolite membranes (MFI and SAPO-34) *via* CCD in order to increase the separation performance. The zeolite membrane, after CCD modification, showed an increased gas separation selectivity (e.g. CO₂/CH₄ selectivity improved from 73 to 110), however, this treatment also lead to a decreased CO₂ permeance by *ca.* 23% [39]. Zhang et al. developed a counter-diffusion CLD method for patching defects in the silicate-1 membrane selectively via the hydrolysis of silicone [32]. After modification, the CO₂/N₂ separation selectivity increased by fifteen-fold, however, the CO₂ permeance decreased by *ca.* 30%. Yu et al. grafted a siloxane polymer coating with imidazole group on the surface of defective SSZ-13 membranes by CLD [31]. The modified membranes showed increased CO₂/CH₄ selectivity by a factor of *ca.* nine and a decreased CO₂ permeance of only *ca.* 21%. An MLD technique was also developed for the surface modification of SAPO-34 membranes [36]. Through the deposition of microporous Al₂O₃ coating with controlled thickness on the defective membranes, the H₂/N₂ selectivity dramatically increased from 11 to 550 with a *ca.* 53% loss in H₂ permeance. Recently, Hong et al. applied a dye-based (dye molecular size of *ca.* 1 nm) post-synthesis treatment to heal micro-defects in SSZ-13 membranes, resulting in the improvement of gases separation performances

(e.g. for CO₂/N₂ and CO₂/CH₄ separation) [23]. As demonstrated by the previous studies, the selective healing of the defective pores in zeolite membranes via various techniques is highly desirable in order to achieve improved gas separation selectivity. Nevertheless, the key to applying such techniques is to select the appropriate filler which has molecular or particle size much larger than the pore size of zeolites so that they can only selectively penetrate into the inter-crystalline defects and cracks rather than zeolite pores. Most importantly, the ideal filler should have a nanoporous structure which can provide fast gas diffusion and moderate gas separation selectivity, in order to not compromise the gas permeance.

Herein, a technique to improve the separation performance of SAPO-34 membrane *via* the facile vacuum-assisted deposition (VAD) of bis(triethoxysilyl)ethane (BTESE)-derived organosilica was examined. To the best of our knowledge, this is the first report on the application of porous organosilica in defect-patching of a zeolite membrane. Specifically, the BTESE-derived organosilica networks have a tuneable nanoporous structure [49], which may facilitate much faster gas diffusion than other conventional fillers (e.g. coke) for patching the zeolite membranes. The hybrid organosilica membranes with high CO₂ permselectivity have been recently developed *via* sol-gel and hot coating methods for gas separations (e.g. CO₂/CH₄, CO₂/N₂) [50-52]. The as-prepared BTESE-derived organosilica membrane showed good CO₂ permeance (*ca.* 7×10^{-7} mol m⁻² s⁻¹ Pa⁻¹) and a CO₂/N₂ separation selectivity of *ca.* 36 [53]. Recently, Kong et al. [49] developed a novel strategy to prepare thin metal-organic framework (MOF)-incorporated organosilica membranes which can display much higher selectivity and permeance for CO₂/CH₄ separation in comparison with the typical organic polymer matrix membrane because of the much faster gas diffusion properties of nanoporous organosilica than polymer. In addition, the organosilica networks present several advantages such as excellent hydrothermal stability and mechanical strength, high affinity towards ceramic materials (e.g. zeolite), and also easy fabrication [54, 55]. Therefore, the organosilica has the potential to be an effective filler with which to heal the defects in zeolite membranes and thus improve their gas separation performance significantly.

The present paper details the fabrication of SAPO-34 membranes supported on the outside surface of alumina tubes with controlled thickness using conventional hydrothermal synthesis method. In addition, BTESE-derived organosilica has been examined as a surface modifier of the as-synthesised SAPO-34 membranes in order to patch the defects. Specifically, the separation performances of modified SAPO-34 membranes regarding gas permeance and CO₂/CH₄ separation selectivity were carefully evaluated as a function of the pressure drop and CO₂ feed concentration.

2. Experimental section

2.1. Chemicals and materials

Aluminium isopropoxide ($\text{Al}(\text{i-C}_3\text{H}_7\text{O})_3$, 98%), phosphoric acid (H_3PO_4 , 85 wt.% aqueous solution), silica sol (Ludox AS-40, 40 wt% SiO_2), tetraethylammonium hydroxide (TEAOH, 35 wt% aqueous solution), diphenylamine (DPA, 99%), hydroxypropyl cellulose (99%), ethanol (100%) and hydrochloric acid (HCl, 37%) were purchased from Merck. 1,2-bis(triethoxysilyl)ethane (BTESE, 95%) was purchased from Alfa Aesar. All chemicals were used as received without further treatment. All porous $\alpha\text{-Al}_2\text{O}_3$ tubes used as the membrane supports ($\alpha\text{-Al}_2\text{O}_3$, *ca.* 500 nm pore size for the outer surface layer, 12 mm outside diameter, 8 mm inside diameter) were purchased from Jiexi Lishun Technology Co., Guangdong, China. All $\alpha\text{-Al}_2\text{O}_3$ tubes were pre-treated using sandpaper to make the surface rough for seeding.

2.2. Preparation of SAPO-34 membranes

SAPO-34 membranes were prepared on the outer surface of $\alpha\text{-Al}_2\text{O}_3$ tubes by secondary hydrothermal growth, as reported previously [56]. Specifically, the SAPO-34 seeds were prepared using a gel with a molar ratio of 1.0 Al_2O_3 : 1.0 P_2O_5 : 0.6 SiO_2 : 2.0 TEAOH: 60 H_2O [56]. The organic template TEAOH and $\text{Al}(\text{i-C}_3\text{H}_7\text{O})_3$ were mixed in deionised (DI) water, and then vigorously stirred at *ca.* 1000 rpm for 12 h, followed by the addition of Ludox AS-40 colloidal silica. The resulting solution was continuously stirred for another 2 h to form a homogeneous sol. Thereafter, H_3PO_4 was added dropwise into the resulting sol, followed by a further 12 h stirring at *ca.* 600 rpm. The final solution was transferred into a Teflon-lined stainless steel autoclave and heated in a convection oven at 200 °C for 24 h. After the synthesis, the solution was centrifuged at 8000 rpm for 10 min and thoroughly washed with DI water to obtain the SAPO-34 seeds. Centrifugation and washing were repeated at least three times to remove the residual acid and organic template on the surface of the SAPO-34 seeds. Then the resulting powder product was dried in a convection oven at 100 °C overnight, followed by calcination in stagnant air at 550 °C for 6 h with a temperature ramp of 0.7 °C min⁻¹ to remove the organic template.

The membrane gel of the secondary hydrothermal growth had a molar ratio of 1.0 Al_2O_3 :1.0 P_2O_5 :0.3 SiO_2 :1.0 TEAOH:1.6 DPA:150 H_2O [56]. In a typical synthesis, $\text{Al}(\text{i-C}_3\text{H}_7\text{O})_3$ and H_3PO_4 were firstly mixed with DI water, followed by vigorous stirring at *ca.* 1000 rpm for 4 h. Thereafter, Ludox AS-40 colloidal silica was added. After 1 h stirring, TEAOH was introduced, followed by the continuous stirring for 1 h. After adding DPA, the final solution was stirred and aged for a further 48

h before membrane fabrication. The outer surface of α -Al₂O₃ tubular supports was seeded by dip-coating. Specifically, the support was immersed into the seed solution (i.e. SAPO-34 seed aqueous solution containing 0.05 wt% hydroxypropyl cellulose) followed by a 90 s dwell time to allow the sufficient interaction between the support and the seed solution for complete wetting. This procedure was repeated three times in order to form a uniform seeds layer on the support. The seeded supports were then dried at 80 °C overnight, followed by 4 h calcination at 400 °C in order to enhance the binding between seeds layer and the support surface. Both ends of the seeded supports were sealed using Teflon tape in order to prevent the formation of membranes on their inner surfaces. After that, the seeded supports were immersed in the synthesis gel, then the autoclave was sealed and kept in a convection oven at 210 °C for different synthesis times (8, 12, and 22 h). After the hydrothermal synthesis, membranes were thoroughly washed with DI water and dried at 100 °C overnight. To remove the organic template, SAPO-34 membranes were calcined at 400 °C for 10 h with heating and cooling ramps of 0.7 °C min⁻¹. All membranes were stored in a convection oven with 220 °C before testing.

2.3 Defects-healing of SAPO-34 membranes

In order to improve the separation performance, the as-prepared SAPO-34 membranes prepared with a synthesis time of 8 h were selected for the post-modification using BTESE-derived organosilica. The technique includes (i) the vacuum-assisted deposition (VAD) of organosilica polymer sol and (ii) calcination, as illuminated in Fig. 1. Specifically, BTESE-derived organosilica polymer sol was prepared with a molar ratio of 1.0 BTESE: 46 ethanol: 60 H₂O: 0.1 HCl [52]. Ethanol and HCl (as the catalyst) were mixed with DI water and stirred for 10 min before adding BTESE. Then, the mixture was vigorously stirred for 5 h at room temperature to obtain the organosilica polymer sol. Subsequently, the as-synthesised SAPO-34 membranes were immersed into organosilica polymer sol for 5 mins under vacuum condition (at a pressure difference of 35 kPa) in order to selectively repair the boundary defects in SAPO-34 membrane. VAD was repeated different cycles (i.e. 1, 3, and 6 cycles) in order to determine the optimized deposition cycles. Finally, the VAD organosilica modified SAPO-34 membranes (denoted as VAD-OS-*x*-SAPO-34, where *x* is the number of VAD treatment) were calcined in the tubular furnace at 300 °C for 30 min under a nitrogen flow (50 ml min⁻¹). VAD-OS-SAPO-34 membranes were pretreated in a convection oven at 220 °C before testing.

Fig. 1. Schematic diagram of post-synthesis modification of SAPO-34 membranes *via* VAD using BTESE-derived organosilica to prepare VAD-OS-SAPO-34 membrane.

2.4. Characterisation

X-ray diffraction (XRD) analysis of SAPO-34 seeds and membranes was performed using a Philips X'Pert X-ray diffractometer operating at 40 kV and 30 mA with $\text{CuK}_{\alpha 1}$ radiation ($\lambda = 1.5406 \text{ \AA}$). Scanning electron microscopy (SEM) images of surface and cross sections of SAPO-34 membranes were obtained using FEI Quanta 200 ESEM with a high voltage mode of 20 kV. Energy dispersive X-ray (EDX) spectroscopy for element mapping was carried out using an Oxford Ultim[®] Max system to investigate the effectiveness of defect-healing of SAPO-34 membranes by VAD. All samples were coated with platinum (Pt) before SEM analysis.

2.5. CO_2/CH_4 separation measurements

A CO_2/CH_4 binary gas mixture (50 mol. %/50 mol. %) was separated at 25 °C in a continuous-flow system (as shown in Fig. 2, without a sweep gas) with a total feed pressures ranging from 3 to 6 bar (g). The permeate side pressure was kept at 1 bar. To prepare the laboratory gas separation unit, a zeolite membrane supported tube was mounted in a tubular stainless steel (SS) module, and each end was sealed by one silicone O-ring and one SS ring in turn (shown in Fig. S1). Flow rates (and the molar ratio of the binary mixture) were controlled by mass flow controllers (Bronkhorst[®], F-201CV-500-RAD-11-V). The pressure in the membrane module was maintained by a Swagelok back-pressure regulator (KBP1G0A4C5A20000). The flux of the permeate and retentate side was measured using bubble flow-meters with different measuring ranges. Gas compositions of the permeate and retentate side were measured by a gas chromatograph (GC, PerkinElmer, Clarus[®] 590) equipped with an Elite-Carbon molecular sieve packed column (N9303926), methanizer, thermal conductivity detector (TCD) and flame ionization detector (FID). Samples from the permeate and retentate side were collected *via* an automated six-way valve containing a sample loop. The gas permeance of the component i (P_i , $\text{mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$) is defined as in Eq. 1.

$$P_i = \frac{J_i}{\Delta P_i} \quad (1)$$

where J_i is the permeation flux of component i through the membrane ($\text{mol m}^{-2} \text{s}^{-1}$), while ΔP_i is the transmembrane pressure drop of component i (Pa), which is the logarithmic mean pressure drop (Eq. S1).

In this study, the separation selectivity (dimensionless) for CO_2 over CH_4 can be calculated using Eq. 2, defined as:

$$\alpha_i = \frac{P_{\text{CO}_2}}{P_{\text{CH}_4}} \quad (2)$$

Fig. 2. Laboratory-scale experimental rig for gas separation using membranes.

3. Results and discussion

3.1. As prepared SAPO-34 membranes: characterisation and performance in CO_2/CH_4 separation

Fig. S2a presents the XRD pattern of the as-synthesised SAPO-34 seeds, showing characteristic diffraction peaks related to the chabazite (CHA) topology of SAPO-34 zeolites [27]. SEM (Fig. S3b) shows the morphology of SAPO-34 seed crystals, i.e. nanosheets with lengths of *ca.* 700 nm. After seeding *via* dip-coating, as shown in Fig. S3, a uniform SAPO-34 seeds layer was successfully coated on the outside surface of the $\alpha\text{-Al}_2\text{O}_3$ tube.

Generally, the thickness of zeolite membranes plays a role in the trade-off between gas permeability and selectivity. Whilst a thin membrane can increase the gas permeability this often leads to a reduction in the selectivity since the formation of defects and cracks is very likely during the synthesis of thin zeolite membranes on the surface of a support, especially cylindrical ones [43, 57, 58]. The synthesis time is a key factor for SAPO-34 crystallisation, and hence the membrane thickness. Therefore, in the present study, the thickness of the SAPO-34 membrane was varied by the synthesis time between 8 and 22 h at 210 °C. XRD analysis (Fig. S4) shows that SAPO-34 zeolite phase was formed on the tube surface after different synthesis times under study. The surface and cross-sectional SEM micrographs of the as-synthesised membranes are shown in Fig. S5, demonstrating the effect of synthesis time on the crystal size, morphology and thickness of SAPO-34 membranes on the outer surface of the α -Al₂O₃ tube. In general, by extending the synthesis time, SAPO-34 membranes with the large crystal size, dense and thick layer were produced. For example, by increasing the synthesis time from 8 to 22 h, the thicknesses membrane increased from 6 to 12 μ m.

The effect of hydrothermal synthesis time on the CO₂ permeation flux and CO₂/CH₄ selectivity was investigated. Fig. 3 shows the separation performance of SAPO-34 membranes as a function of the synthesis time using an equimolar CO₂/CH₄ gas mixture. It can be seen in Figs. 3a and 3b that the permeance and flux of CO₂ decreased significantly as the hydrothermal synthesis time increased from 8 to 22 h, whilst that of the CH₄ only decreased slightly. As a result, the CO₂/CH₄ selectivity increased greatly. The CO₂ permeance for membrane synthesized at 8 h was *ca.* 2.5×10^{-7} mol m⁻² s⁻¹ Pa⁻¹ (pressure drop = 200 kPa), which is *ca.* 2.5 times higher than the membrane synthesised over 22 h. However, the resulting CO₂/CH₄ selectivity was about 60, which is 40 % lower than that of the membrane synthesised over 22 h. These results are reasonable because a thinner zeolite membrane was produced after 8 h synthesis (as evidenced by SEM images of according cross-sections in Fig. S4), resulting in a reduced resistance of gas permeation and diffusion. In addition, after calcination, inter-crystal defects and cracks (as shown in Fig. S4) were formed a thin zeolite membrane (8 h synthesis). Therefore, the existence of such non-selective defects in the membrane inevitably increased both the CO₂ and CH₄ permeation flux, as well as limiting the CO₂/CH₄ selectivity. Considering the trade-off between the CO₂ permeance and CO₂/CH₄ selectivity, a thin SAPO-34 membrane (prepared by 8 h synthesis) has the potential to be optimized by healing its non-selective defects. In order to support this hypothesis, the SAPO-34 membrane prepared at 210 °C for 8 h was modified by VAD using organosilica (i.e. VAD-OS-SAPO-34 membranes) and evaluated in CO₂/CH₄ separation.

Fig. 3. CO₂/CH₄ separation performances of SAPO-34 membranes at 25 °C as a function of the synthesis time and pressure drop (up to 500 kPa): (a) CO₂ (black solid symbols) and CH₄ (blue open symbols) permeance, (b) CO₂ (black solid symbols) and CH₄ flux (blue open symbols), and (c) CO₂/CH₄ separation selectivity (Feed composition: 50 mol.% CO₂/50 mol.% CH₄).

3.2. VAD-OS-SAPO-34 membranes: characterisation and performance in CO₂/CH₄ separation

Using the SAPO-34 membrane prepared over 8 h as the benchmark, a comparative characterisation of the modified membranes was performed using SEM, EDX and XRD. The surface morphology of the as-prepared SAPO-34 membrane (after 8 h at 210 °C) by SEM (Fig. 4a) shows the presence of membrane defects. After VAD treatments, the formation of organosilica layer in/on the zeolite membrane is evident, as shown in Figs. 4b–4d. After the 1st deposition (i.e. VAD-OS-1-SAPO-34), the zeolite phase was covered by organosilica, however, the defects were still clearly shown (Fig. 4b). By repeating the VAD three cycles (denoted VAD-OS-3-SAPO-34), the organosilica started to fill these defects, but the morphology of SAPO-34 zeolite crystal could still be observed, as seen in Fig. 4c, suggesting that defect-healing had occurred without compromising the gas permeance significantly. After six VAD treatments (i.e. VAD-OS-6-SAPO-34), most SAPO-34 crystals (Fig. 4d) were fully covered by organosilica, which could lead to a significant decrease in the gas permeability as the thick organosilica layer would block the accessibility to the porous SAPO-34 zeolite and thus increase the gas diffusion resistance. SEM analysis of the cross-section of VAD-OS-SAPO-34 membranes (Fig. 5) showed that an additional organosilica layer with the thickness of *ca.* 1 μm was formed on the surface of zeolite membrane after six VAD treatments, indicating additional gas diffusion resistance. In these SEM images, the porous sections indicate to the macro-porous α -Al₂O₃ support (*ca.* 500 nm), and the dense sections are the zeolite membrane and/or organosilica layers with different VAD treatments. In contrast, as shown in Figs. 5a and 5b, the thicknesses of organosilica layers are insignificant in comparison to that of zeolite membranes. By combining the surface and cross-sectional morphologies of VAD-OS-SAPO-34 membranes, the SAPO-34 zeolite

membranes after three treatments could have the optimal defects-healing effect, i.e. organosilica only penetrate into the defects of cracks and voids in zeolite membranes without fully covering zeolite crystals.

Fig. 4. SEM micrographs of surface morphologies of (a) as-prepared SAPO-34, (b) VAD-OS-1-SAPO-34, (c) VAD-OS-3-SAPO-34, and (d) VAD-OS-6-SAPO-34 membranes.

Fig. 5. Cross-sectional SEM images of (a) VAD-OS-1-SAPO-34, (b) VAD-OS-3-SAPO-34 and (c) VAD-OS-6-SAPO-34 membranes.

Fig. 6 shows XRD patterns of SAPO-34 and VAD-OS-SAPO-34 membranes. XRD patterns of VAD-OS-SAPO-34 are very similar to that of SAPO-34 membrane, showing the characteristic diffraction peaks of SAPO-34 (the weak intensity of these peaks is due to the relatively strong intensity of alumina support). Considering the penetration depth of the X-ray ($>5\ \mu\text{m}$) and the thickness of organosilica layer (maximum $1\ \mu\text{m}$), the XRD results are explainable. EDX analysis of materials confirms the successful deposition of organosilica on SAPO-34 membranes, as shown in Fig. 7 and Table 1. The point elemental analysis shows that the concentration of Si and C increased by increasing the number of VAD treatments (due to the Si-O-Si structure of organosilica after the hydrolysis and condensation of BTESE monomers [52, 59] and the presence of $-\text{CH}_2-$ in the organosilica network [52]). For example, the Si concentration in the VAD-OS-SAPO-34 membrane increased by about 8-fold after six synthesis cycles in comparison with that of SAPO-34 membrane (the composition of membrane elements was obtained by averaging the results from three measuring points on samples, Figs. S6–S7). As shown in Table 1, the Al concentration in the membrane decreased due to the organosilica deposition, resulting in an increase in the Si/Al ratio in VAD-OS-SAPO-34 membranes, i.e. *ca.* 0.16 for SAPO-34 membrane *vs.* 0.78 for VAD-OS-3-SAPO-34 membrane.

Fig. 6. XRDs pattern of the as-prepared SAPO-34 and VAD-OS-SAPO-34 membranes.

Fig. 7. EDX analysis of (a) the as-prepared SAPO-34, (b) VAD-OS-1-SAPO-34, (c) VAD-OS-3-SAPO-34 and (d) VAD-OS-6-SAPO-34 membranes.

Table 1 Elemental analysis of the as-prepared SAPO-34 and VAD-OS-SAPO-34 membranes.

Elements	Elemental content (wt.%)			
	SAPO-34	VAD-OS-1-SAPO-34	VAD-OS-3-SAPO-34	VAD-OS-6-SAPO-34
Si	3.3±0.4	5.6±0.9	12.5±1.8	24.5±3.9
C	7.1±0.2	16.4±1.0	17.0±0.6	19.2±1.0
Al	20.9±2.6	17.4±0.7	16.1±0.3	13.5±3.0
O	53.4±3.2	46.9±2.6	40.0±1.5	31.4±2.3
P	15.3±2.3	13.7±1.3	14.4±0.5	11.4±1.6
Si/Al ratio	0.16	0.32	0.78	1.81

Previous research has shown that calcination (to remove organic templates) was prone to create inter-crystal defects/cracks in the resulting membrane due to the opposite thermal/mechanical behaviours of zeolite (contraction) and substrate (expansion) [57, 60], especially a zeolite layer on a tubular substrate, i.e. a material with curvature [57]. Particularly, therefore, the SAPO-34 zeolite membranes supported on the outer surface of tubular alumina substrate were subjected to a radial force due to the heat-derived expansion of the substrate and the contraction of SAPO-34 zeolite layer, leading to the formation of inter-crystal defects and even cracks, as illustrated in the Fig. 8a. Accordingly, the post-synthesis VAD treatment using BTESE-derived organosilica could potentially patch these defects and cracks in SAPO-34 membranes (Fig. 8b), thus improving the separation performance (regarding CO₂/CH₄ selectivity and CO₂ permeance) of the modified membranes, i.e. VAD-OS-SAPO-34 membranes.

Fig. 8. Schematic illustration of the healing of inter-crystal defects in SAPO-34 zeolite membranes on the outer surface of tubular alumina support.

Fig. 9 shows the comparison of separation performances of the SAPO-34 membrane prepared at 210 °C over 8 h (denoted SAPO-34 membrane) and VAD-SO-SAPO-34 membranes for separating CO_2 from an equimolar CO_2/CH_4 mixture. Compared with the SAPO-34 membrane, the VAD-SO-1-SAPO-34 and VAD-SO-3-SAPO-34 membranes showed similar performances with respect to the CO_2 permeance and permeation flux as shown in Fig. 9a and 9b, respectively. However, the CH_4 permeance and permeation flux in the two membranes were reduced, indicating that the post-treatment using organosilica diminished the presence of non-selective defects (which allows the permeation CH_4 through the membrane) to a certain extent (in a good agreement with the SEM analysis, Fig. 3). Comparably, the CO_2 permeance and permeation flux of VAD-SO-6-SAPO-34 dropped significantly (At 200 kPa, permeation dropped by 36% by comparing VAD-SO-6-SAPO-34 membrane to SAPO-34 membrane) due to the excessive deposition of BTESE-derived organosilica on SAPO-34 membrane. CO_2/CH_4 selectivity of the membrane benefited from the VAD treatment (Fig. 9c) by increasing the number of VAD treatment, VAD-SO-SAPO-34 membranes presented greatly increased CO_2/CH_4 selectivity compared with SAPO-34 membrane, e.g. by a factor of 2-3 at a pressure of 200 kPa. It should be noted that the selectivity of VAD-SO-6-SAPO-34 membrane was close to 100 at a pressure of 500 kPa, indicating that the SAPO-34 membrane was completely covered by the organosilica coating. This indicates that the VAD modifications of the membrane is a trade-off between the CO_2 permeance (flux) and CO_2/CH_4 selectivity which is controlled by the thickness of the coating, as expected, and controlled by the number of synthesis cycles. Based on the presented results, the VAD-SO-3-SAPO-34 membrane demonstrated the optimum performance by maintaining the CO_2 permeance (flux), as well as improving the CO_2/CH_4 selectivity, especially at pressures of <300 kPa.

The developed VAD-SO-3-SAPO-34 membrane was compared with other small-pore CHA/AEI zeolite membranes (e.g. SAPO-34, SSZ-13, AIPO-18) with respect to their ability to separate the equimolar CO₂/CH₄ mixture [23, 31, 34]. Table 2 shows that the VAD-SO-3-SAPO-34 membrane demonstrated good CO₂ permeance (which was comparable to that of the original SAPO-34 membrane), while enhancing the CO₂/CH₄ separation selectivity by *ca.* 159%. In contrast, the CO₂ permeance of other zeolite membranes was compromised significantly (i.e. decreased from *ca.* 20% to 52% as shown in Table 2) after relevant modifications using other fillers.

Fig. 9. CO₂/CH₄ separation performances of SAPO-34 and VAD-SO-SAPO-34 membranes at 25 °C as a function of the number of VAD treatment and pressure drop (up to 500 kPa): (a) CO₂ (black solid symbols) and CH₄ permeance (blue open symbols), (b) CO₂ (black solid symbols) and CH₄ flux (blue open symbols) and (c) CO₂/CH₄ separation selectivity (Feed composition: 50 mol. % CO₂/50 mol. % CH₄).

Table 2 Comparison of CO₂/CH₄ separation performance for small-pore zeolites membranes and their modified analogues (by post-synthesis treatments).

Zeolites	Treatment	T [°C]	ΔP^a [bar]	Sweep gas	GP ^b × 10 ⁻⁷ [mol m ⁻² s ⁻¹ Pa ⁻¹]	% O-GP- D ^c	GS ^d	% GS- I ^e	Refs
SAPO-34	Untreated	25	2.2	No	4.7	-	110	-	[34]
	1.8% β -cyclodextrin	25	2.2	No	3.2	31.9	272	147	
SSZ-13	Untreated	25	2.0	He	2.2	-	14	-	[31]
	Siloxane polymer	25	2.0	He	1.6	27	119	750	
AIPO-18	Untreated	25	2.0	He	1.6	-	16	-	[31]

Siloxane polymer		25	2.0	He	0.8	52	60	275	
SSZ-13	Untreated	30	2.0	He	1.0	-	50	-	[23]
	Dye molecules	30	2.0	He	0.8	20	100	100	
SAPO-34	Untreated	25	2.0	No	2.5	-	61	-	This work
	Organosilica	25	2.0	No	2.4	4	158	159	

^a ΔP is the pressure difference between retentate side and permeate side; ^b GP is the CO₂ permeance of membrane; ^c % O-GP-D is the percentage change in CO₂ permeance after modification; ^d GS is the selectivity to CO₂ in CO₂/CH₄ separation; ^e % GS-I is the percentage change in CO₂ selectivity in CO₂/CH₄ separation after modification.

By considering the possible range of CO₂ concentration in biogases, VAD-SO-3-SAPO-34 membrane was further investigated to show the effect of CO₂ feed concentration on its separation performance at 25 °C and 300 kPa (Fig. 10). By increasing the feed CO₂ concentration from 20 to 50 mol.% (Fig. 10a), the CO₂ permeance dropped by *ca.* 45.5%, which could be attributed to the saturation of CO₂ at a low partial pressure drop of CO₂, which is similar to previously reported phenomenon [61, 62]. However, a relatively high CO₂ feed concentration has positive impacts on the CO₂ flux and selectivity of VAD-SO-3-SAPO-34 membrane. CO₂ flux and selectivity increased by 35% and 58%, respectively, with increasing CO₂ molar concentration in the feed from 20 to 50 mol.%, as shown in Figs. 10a and 10b. Such enhancements can be explained by the competitive permeation of two gas molecules which is a function of the relative population of one molecule over another. However, the opposite is true for the separation performance related to CH₄ in the system, which was suppressed by the increased CO₂ feed concentration. Therefore, a feed with relatively concentrated CO₂ benefits the competitive permeation through VAD-SO-3-SAPO-34, and hence the separation efficiency of CO₂. For the system under study, CO₂ concentration at the permeate side can reach up to about 97% when the CO₂ concentration in the feed is 50 mol.%, showing a very low loss of CH₄. Concerning the full upgrading of biogas, in order to remove CO₂ from biogas and subsequently convert it via a methanation system (to produce CH₄), it is desirable to obtain ultra-high CO₂ concentration at the permeate side (as the feed for the methanation unit) to drive CO₂ conversion and CH₄ selectivity. Regarding the CH₄ concentration at the retentate-side, one can easily circulate the retentate stream into the feed of the membrane module in order to increase CH₄ purity.

Fig. 10. CO₂/CH₄ separation performance of VAD-SO-3-SAPO-34 membrane as a function of CO₂ concentration in the feed (25 °C and 300 kPa pressure drop): (a) CO₂ and CH₄ permeances (black solid symbols) and CO₂/CH₄ separation selectivity (blue open symbols), (b) CO₂ and CH₄ flux, and (c) CO₂ concentration at permeate side.

4. Conclusions

In this study, a facile vacuum-assisted deposition (VAD) method was applied effectively to heal the non-selective defects of SAPO-34 membranes using BTESE-derived organosilica in order to improve the CO₂ capture performances at low pressure (i.e. pressure drop of 200~500 kPa) and room temperature. The nanoporous BTESE-derived can selectively patch the defects, thus improving the separation performance of the modified SAPO-34 membranes greatly. Compared with the original SAPO-34 membrane, in an equimolar CO₂/CH₄ mixture at pressure drop of 200 kPa and 25 °C, the membrane modified with three depositions of organosilica (i.e. VAD-SO-3-SAPO-34 membrane) showed comparable CO₂ permeance at ca. 2.5×10^{-7} mol m⁻² s⁻¹ Pa⁻¹, but with an increased CO₂/CH₄ selectivity by a factor of ca. 2.5 (CO₂/CH₄ selectivity of 160). The mechanism of healing non-selective defects in SAPO-34 membranes supported on tubular porous alumina tubes was proposed and discussed. By using the developed methods, excessive deposition of organosilica (up to six cycles) could form a thick layer (about 1 μm) on top of a zeolite membrane. Since the nanoporous BTESE-derived organosilica only has the relatively low CO₂ permeance and CO₂/CH₄ selectivity, the organosilica layer affected adversely on the CO₂ permeation flux and selectivity of the composite membrane. Overall, the developed post-treatment VAD method using organosilica could be a promising and generic approach to heal the non-selective defects in other membranes such as SSZ-13 and ZIF-8 in order to improve the CO₂ capture performances, without compromising the permeance, from biogas or flue gas.

Acknowledgements

HC thanks the financial support from the European Commission Marie Skłodowska-Curie Individual Fellowship (H2020-MSCA-IF-NTPleasure-748196). HX thanks The University of Manchester President's Doctoral Scholar (PDS) Award and the China Scholarship Council (CSC, file no. 201606150068) for supporting her PhD research. LL thanks the CSC (file no.201706950035)-University of Manchester joint studentship for supporting her PhD research. YS thanks the CSC for her academic visiting fellowship at the University of Manchester (file no. 201708440477), and the Foundation of Department of Education of Guangdong Province (No. 2016KTSCX144, 2017KZDXM085) for supplying the porous α -Al₂O₃ tubes.

References

- [1] Y. Zhang, J. Sunarso, S. Liu, R. Wang, Current status and development of membranes for CO₂/CH₄ separation: A review, *International Journal of Greenhouse Gas Control* 12 (2013) 84-107.
- [2] E. Ryckebosch, M. Drouillon, H. Vervaeren, Techniques for transformation of biogas to biomethane, *Biomass and Bioenergy* 35 (2011) 1633-1645.
- [3] Y. Jiang, J. Ling, P. Xiao, Y. He, Q. Zhao, Z. Chu, Y. Liu, Z. Li, P.A. Webley, Simultaneous biogas purification and CO₂ capture by vacuum swing adsorption using zeolite NaUSY, *Chemical Engineering Journal* 334 (2018) 2593-2602.
- [4] F. Monlau, C. Sambusiti, E. Ficara, A. Aboulkas, A. Barakat, H. Carrère, New opportunities for agricultural digestate valorization: current situation and perspectives, *Energy & Environmental Science* 8 (2015) 2600-2621.
- [5] N. Scarlat, J.-F. Dallemand, F. Fahl, Biogas: Developments and perspectives in Europe, *Renewable Energy* 129 (2018) 457-472.
- [6] K. Starr, X. Gabarrell, G. Villalba, L. Talens, L. Lombardi, Life cycle assessment of biogas upgrading technologies, *Waste Management* 32 (2012) 991-999.
- [7] D. Nikolaeva, I. Azcune, M. Tanczyk, K. Warmuzinski, M. Jaschik, M. Sandru, P.I. Dahl, A. Genua, S. Loïs, E. Sheridan, A. Fuoco, I.F.J. Vankelecom, The performance of affordable and stable cellulose-based poly-ionic membranes in CO₂/N₂ and CO₂/CH₄ gas separation, *Journal of Membrane Science* 564 (2018) 552-561.
- [8] A. Guo, Y. Ban, K. Yang, W. Yang, Metal-organic framework-based mixed matrix membranes: Synergetic effect of adsorption and diffusion for CO₂/CH₄ separation, *Journal of Membrane Science* 562 (2018) 76-84.
- [9] L. Bai, N. Chang, M. Li, Y. Wang, G. Nan, Y. Zhang, D. Hu, G. Zeng, W. Wei, Ultrafast synthesis of thin SAPO-34 zeolite membrane by oil-bath heating, *Microporous and Mesoporous Materials* 241 (2017) 392-399.
- [10] M.A. Carreon, S. Li, J.L. Falconer, R.D. Noble, Alumina-Supported SAPO-34 Membranes for CO₂/CH₄ Separation, *Journal of the American Chemical Society* 130 (2008) 5412-5413.
- [11] T.L. Chew, A.L. Ahmad, S. Bhatia, Rapid synthesis of thin SAPO-34 membranes using microwave heating, *Journal of Porous Materials* 18 (2011) 355-360.
- [12] H.H. Funke, B. Tokay, R. Zhou, E.W. Ping, Y. Zhang, J.L. Falconer, R.D. Noble, Spatially resolved gas permeation through SAPO-34 membranes, *Journal of Membrane Science* 409-410 (2012) 212-221.
- [13] S. Li, J.L. Falconer, R.D. Noble, Improved SAPO-34 Membranes for CO₂/CH₄ Separations, *Advanced Materials* 18 (2006) 2601-2603.
- [14] S. Li, J.L. Falconer, R.D. Noble, SAPO-34 membranes for CO₂/CH₄ separations: Effect of Si/Al ratio, *Microporous and Mesoporous Materials* 110 (2008) 310-317.

- [15] S.R. Venna, M.A. Carreon, Amino-functionalized SAPO-34 membranes for CO₂/CH₄ and CO₂/N₂ separation, *Langmuir* 27 (2011) 2888-2894.
- [16] H. Hasegawa, K. Nishida, S. Oguro, Y. Fujimura, K. Yajima, M. Niino, M. Isomura, T. Tomita, Gas Separation Process for CO₂ Removal from Natural Gas with DDR-type Zeolite Membrane, *Energy Procedia* 114 (2017) 32-36.
- [17] L. Wang, C. Zhang, X. Gao, L. Peng, J. Jiang, X. Gu, Preparation of defect-free DDR zeolite membranes by eliminating template with ozone at low temperature, *Journal of Membrane Science* 539 (2017) 152-160.
- [18] S. Yang, Z. Cao, A. Arvanitis, X. Sun, Z. Xu, J. Dong, DDR-type zeolite membrane synthesis, modification and gas permeation studies, *Journal of Membrane Science* 505 (2016) 194-204.
- [19] M.L. Carreon, S. Li, M.A. Carreon, AlPO-18 membranes for CO₂/CH₄ separation, *Chemical Communications* 48 (2012) 2310-2312.
- [20] T. Wu, J. Lucero, Z. Zong, S.K. Elsaïdi, P.K. Thallapally, M.A. Carreon, Microporous Crystalline Membranes for Kr/Xe Separation: Comparison Between AlPO-18, SAPO-34, and ZIF-8, *ACS Applied Nano Materials* 1 (2018) 463-470.
- [21] T. Wu, B. Wang, Z. Lu, R. Zhou, X. Chen, Alumina-supported AlPO-18 membranes for CO₂/CH₄ separation, *Journal of Membrane Science* 471 (2014) 338-346.
- [22] Z. Zong, S.K. Elsaïdi, P.K. Thallapally, M.A. Carreon, Highly Permeable AlPO-18 Membranes for N₂/CH₄ Separation, *Industrial & Engineering Chemistry Research* 56 (2017) 4113-4118.
- [23] S. Hong, D. Kim, Y. Jeong, E. Kim, J.C. Jung, N. Choi, J. Nam, A.C.K. Yip, J. Choi, Healing of Microdefects in SSZ-13 Membranes via Filling with Dye Molecules and Its Effect on Dry and Wet CO₂ Separations, *Chemistry of Materials* 30 (2018) 3346-3358.
- [24] B. Liu, R. Zhou, N. Bu, Q. Wang, S. Zhong, B. Wang, K. Hidetoshi, Room-temperature ionic liquids modified zeolite SSZ-13 membranes for CO₂/CH₄ separation, *Journal of Membrane Science* 524 (2017) 12-19.
- [25] H. Kalipcilar, T.C. Bowen, R.D. Noble, J.L. Falconer, Synthesis and Separation Performance of SSZ-13 Zeolite Membranes on Tubular Supports, *Chemistry of Materials* 14 (2002) 3458-3464.
- [26] Y. Zheng, N. Hu, H. Wang, N. Bu, F. Zhang, R. Zhou, Preparation of steam-stable high-silica CHA (SSZ-13) membranes for CO₂/CH₄ and C₂H₄/C₂H₆ separation, *Journal of Membrane Science* 475 (2015) 303-310.
- [27] S. Li, Z. Zong, S.J. Zhou, Y. Huang, Z. Song, X. Feng, R. Zhou, H.S. Meyer, M. Yu, M.A. Carreon, SAPO-34 Membranes for N₂/CH₄ separation: Preparation, characterization, separation performance and economic evaluation, *Journal of Membrane Science* 487 (2015) 141-151.
- [28] M.P. Bernal, J. Coronas, M. Menéndez, J. Santamaría, Separation of CO₂/N₂ mixtures using MFI-type zeolite membranes, *AIChE Journal* 50 (2004) 127-135.
- [29] J.C. Poshusta, V.A. Tuan, E.A. Pape, R.D. Noble, J.L. Falconer, Separation of light gas mixtures using SAPO-34 membranes, *AIChE Journal* 46 (2000) 779-789.
- [30] J. Caro, D. Albrecht, M. Noack, Why is it so extremely difficult to prepare shape-selective Al-rich zeolite membranes like LTA and FAU for gas separation?, *Separation and Purification Technology* 66 (2009) 143-147.
- [31] R. Zhou, H. Wang, B. Wang, X. Chen, S. Li, M. Yu, Defect-Patching of Zeolite Membranes by Surface Modification Using Siloxane Polymers for CO₂ Separation, *Industrial & Engineering Chemistry Research* 54 (2015) 7516-7523.
- [32] B. Zhang, C. Wang, L. Lang, R. Cui, X. Liu, Selective Defect-Patching of Zeolite Membranes Using Chemical Liquid Deposition at Organic/Aqueous Interfaces, *Advanced Functional Materials* 18 (2008) 3434-3443.
- [33] Z. Chen, D. Yin, Y. Li, J. Yang, J. Lu, Y. Zhang, J. Wang, Functional defect-patching of a zeolite membrane for the dehydration of acetic acid by pervaporation, *Journal of Membrane Science* 369 (2011) 506-513.
- [34] Y. Zhang, A.M. Avila, B. Tokay, H.H. Funke, J.L. Falconer, R.D. Noble, Blocking defects in SAPO-34 membranes with cyclodextrin, *Journal of Membrane Science* 358 (2010) 7-12.
- [35] M.X. Xu, Y. He, Y.P. Wang, X.M. Cui, Preparation of a non-hydrothermal NaA zeolite membrane and defect elimination by vacuum-inhalation repair method, *Chemical Engineering Science* 158 (2017) 117-123.
- [36] M. Yu, H.H. Funke, R.D. Noble, J.L. Falconer, H₂ Separation Using Defect-Free, Inorganic Composite Membranes, *Journal of the American Chemical Society* 133 (2011) 1748-1750.
- [37] Z. Tang, J. Dong, T.M. Nenoff, Internal Surface Modification of MFI-Type Zeolite Membranes for High Selectivity and High Flux for Hydrogen, *Langmuir* 25 (2009) 4848-4852.

- [38] Z. Hong, Z. Wu, Y. Zhang, X. Gu, Catalytic Cracking Deposition of Methyl-diethoxysilane for Modification of Zeolitic Pores in MFI/ α - Al_2O_3 Zeolite Membrane with H^+ Ion Exchange Pretreatment, *Industrial & Engineering Chemistry Research* 52 (2013) 13113-13119.
- [39] M. Hong, J.L. Falconer, R.D. Noble, Modification of Zeolite Membranes for H_2 Separation by Catalytic Cracking of Methyl-diethoxysilane, *Industrial & Engineering Chemistry Research* 44 (2005) 4035-4041.
- [40] M. Kanezashi, J. O'Brien-Abraham, Y.S. Lin, K. Suzuki, Gas permeation through DDR-type zeolite membranes at high temperatures, *AIChE Journal* 54 (2008) 1478-1486.
- [41] S. Karimi, D. Korelskiy, L. Yu, J. Mouzon, A. Ali Khodadadi, Y. Mortazavi, M. Esmaili, J. Hedlund, A simple method for blocking defects in zeolite membranes, *Journal of Membrane Science* 489 (2015) 270-274.
- [42] D.W. Shin, S.H. Hyun, C.H. Cho, M.H. Han, Synthesis and CO_2/N_2 gas permeation characteristics of ZSM-5 zeolite membranes, *Microporous and Mesoporous Materials* 85 (2005) 313-323.
- [43] G. Xomeritakis, Z. Lai, M. Tsapatsis, Separation of Xylene Isomer Vapors with Oriented MFI Membranes Made by Seeded Growth, *Industrial & Engineering Chemistry Research* 40 (2001) 544-552.
- [44] M. Nomura, T. Yamaguchi, S.-i. Nakao, Silicalite Membranes Modified by Counterdiffusion CVD Technique, *Industrial & Engineering Chemistry Research* 36 (1997) 4217-4223.
- [45] E. Kim, T. Lee, H. Kim, W.-J. Jung, D.-Y. Han, H. Baik, N. Choi, J. Choi, Chemical Vapor Deposition on Chabazite (CHA) Zeolite Membranes for Effective Post-Combustion CO_2 Capture, *Environmental Science & Technology* 48 (2014) 14828-14836.
- [46] M. Kanezashi, Y.S. Lin, Gas Permeation and Diffusion Characteristics of MFI-Type Zeolite Membranes at High Temperatures, *The Journal of Physical Chemistry C* 113 (2009) 3767-3774.
- [47] H. Wang, Y.S. Lin, Synthesis and modification of ZSM-5/silicalite bilayer membrane with improved hydrogen separation performance, *Journal of Membrane Science* 396 (2012) 128-137.
- [48] X. Zhu, H. Wang, Y.S. Lin, Effect of the Membrane Quality on Gas Permeation and Chemical Vapor Deposition Modification of MFI-Type Zeolite Membranes, *Industrial & Engineering Chemistry Research* 49 (2010) 10026-10033.
- [49] C. Kong, H. Du, L. Chen, B. Chen, Nanoscale MOF/organosilica membranes on tubular ceramic substrates for highly selective gas separation, *Energy & Environmental Science* 10 (2017) 1812-1819.
- [50] I. Agirre, P.L. Arias, H.L. Castricum, M. Creatore, E. Johan, G.G. Paradis, P.H. Ngamou, H.M. van Veen, J.F. Vente, Hybrid organosilica membranes and processes: Status and outlook, *Separation and purification technology* 121 (2014) 2-12.
- [51] H.L. Castricum, G.G. Paradis, M.C. Mittelmeijer-Hazeleger, W. Bras, G. Eeckhaut, J.F. Vente, G. Rothenberg, J.E. ten Elshof, Tuning the nanopore structure and separation behavior of hybrid organosilica membranes, *Microporous and Mesoporous Materials* 185 (2014) 224-234.
- [52] X. Yang, H. Du, Y. Lin, L. Song, Y. Zhang, X. Gao, C. Kong, L. Chen, Hybrid organosilica membrane with high CO_2 permselectivity fabricated by a two-step hot coating method, *Journal of Membrane Science* 506 (2016) 31-37.
- [53] X. Ren, K. Nishimoto, M. Kanezashi, H. Nagasawa, T. Yoshioka, T. Tsuru, CO_2 Permeation through Hybrid Organosilica Membranes in the Presence of Water Vapor, *Industrial & Engineering Chemistry Research* 53 (2014) 6113-6120.
- [54] M. Kanezashi, K. Yada, T. Yoshioka, T. Tsuru, Design of Silica Networks for Development of Highly Permeable Hydrogen Separation Membranes with Hydrothermal Stability, *Journal of the American Chemical Society* 131 (2009) 414-415.
- [55] H.F. Qureshi, A. Nijmeijer, L. Winnubst, Influence of sol-gel process parameters on the micro-structure and performance of hybrid silica membranes, *Journal of Membrane Science* 446 (2013) 19-25.
- [56] Y. Huang, L. Wang, Z. Song, S. Li, M. Yu, Growth of High-Quality, Thickness-Reduced Zeolite Membranes towards N_2/CH_4 Separation Using High-Aspect-Ratio Seeds, *Angew Chem Int Ed Engl* 54 (2015) 10843-10847.
- [57] C.-H. Chen, L. Meng, K.-L. Tung, Y.S. Lin, Effect of substrate curvature on microstructure and gas permeability of hollow fiber MFI zeolite membranes, *AIChE Journal* 64 (2018) 3419-3428.
- [58] Y.H. Kwon, B. Min, S. Yang, D.-Y. Koh, R.R. Bhavé, S. Nair, Ion-Exchanged SAPO-34 Membranes for Krypton–Xenon Separation: Control of Permeation Properties and Fabrication of Hollow Fiber Membranes, *ACS Applied Materials & Interfaces* 10 (2018) 6361-6368.
- [59] B. Karmakar, G. De, D. Ganguli, Dense silica microspheres from organic and inorganic acid hydrolysis of TEOS, *Journal of Non-Crystalline Solids* 272 (2000) 119-126.

- [60] J. Dong, Y.S. Lin, M.Z.C. Hu, R.A. Peascoe, E.A. Payzant, Template-removal-associated microstructural development of porous-ceramic-supported MFI zeolite membranes, *Microporous and Mesoporous Materials* 34 (2000) 241-253.
- [61] N. Chang, H.B. Tang, L. Bai, Y.F. Zhang, G.F. Zeng, Optimized rapid thermal processing for the template removal of SAPO-34 zeolite membranes, *Journal of Membrane Science*, 552 (2018) 13-21.
- [62] S.G. Li, J.G. Martinek, J.L. Falconer, R.D. Noble, High-Pressure CO₂/CH₄ Separation Using SAPO-34 Membranes, *Ind. Eng. Chem. Res.*, 44 (2005) 3220-3228.

Highlights:

- A vacuum-assisted deposition (VAD) method using organosilica to heal defects in SAPO-34 membranes
- An organosilica modified membrane shows insignificant changes in CO₂ permeance in CO₂/CH₄ separation
- CO₂ selectivity of the membrane was increased by a factor of ca. 2.5 after VAD using organosilica