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

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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], AlPO-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 CH$_4$ (0.38 nm kinetic diameter), but larger than CO$_2$ (0.33 nm), allowing good CO$_2$ permeability over large hydrocarbons [14, 29]. In addition, SAPO-34 zeolite has strong adsorption affinity of CO$_2$ molecules compared with CH$_4$, resulting in a high CO$_2$/CH$_4$ 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]), Al$_2$O$_3$ [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. CO$_2$/CH$_4$ selectivity improved from 73 to 110), however, this treatment also lead to a decreased CO$_2$ 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 CO$_2$/N$_2$ separation selectivity increased by fifteen-fold, however, the CO$_2$ 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 CO$_2$/CH$_4$ selectivity by a factor of ca. nine and a decreased CO$_2$ 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 Al$_2$O$_3$ coating with controlled thickness on the defective membranes, the H$_2$/N$_2$ selectivity dramatically increased from 11 to 550 with a ca. 53% loss in H$_2$ 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 CO$_2$/N$_2$ and CO$_2$/CH$_4$ 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 CO$_2$ permselectivity have been recently developed via sol-gel and hot coating methods for gas separations (e.g. CO$_2$/CH$_4$, CO$_2$/N$_2$) [50-52]. The as-prepared BTESE-derived organosilica membrane showed good CO$_2$ permeance (ca. 7×10$^{-7}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$) and a CO$_2$/N$_2$ 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 CO$_2$/CH$_4$ 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 CO$_2$/CH$_4$ separation selectivity were carefully evaluated as a function of the pressure drop and CO$_2$ feed concentration.
2. Experimental section

2.1. Chemicals and materials

Aluminium isopropoxide (Al(i-C₃H₇O)₃, 98%), phosphoric acid (H₃PO₄, 85 wt.% aqueous solution), silica sol (Ludox AS-40, 40 wt% SiO₂), 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 α-Al₂O₃ tubes used as the membrane supports (α-Al₂O₃, 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 α-Al₂O₃ 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 α-Al₂O₃ 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 Al₂O₃: 1.0 P₂O₅: 0.6 SiO₂: 2.0 TEAOH: 60 H₂O [56]. The organic template TEAOH and Al(i-C₃H₇O)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, H₃PO₄ was added drop wise 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 Al₂O₃:1.0 P₂O₅:0.3 SiO₂:1.0 TEAOH:1.6 DPA:150 H₂O [56]. In a typical synthesis, Al(i-C₃H₇O)₃ and H₃PO₄ 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 \( \alpha\)-Al\(_2\)O\(_3\) 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 H\(_2\)O: 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 CuKα radiation (\(\lambda = 1.5406 \text{ Å}\)). 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. \(\text{CO}_2/\text{CH}_4\) separation measurements

A \(\text{CO}_2/\text{CH}_4\) 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.
\[ P_i = \frac{J_i}{\Delta P_i} \]  

(1)

where \( J_i \) is the permeation flux of component \( i \) through the membrane (mol m\(^{-2}\) s\(^{-1}\)), while \( \Delta P_i \) 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:

\[ \alpha_i = \frac{P_{CO_2}}{P_{CH_4}} \]  

(2)

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 \( \alpha \)-Al\(_2\)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 μm.

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. CO$_2$/CH$_4$ separation performances of SAPO-34 membranes at 25 °C as a function of the synthesis time and pressure drop (up to 500 kPa): (a) CO$_2$ (black solid symbols) and CH$_4$ (blue open symbols) permeance, (b) CO$_2$ (black solid symbols) and CH$_4$ flux (blue open symbols), and (C) CO$_2$/CH$_4$ separation selectivity (Feed composition: 50 mol.% CO$_2$/50 mol.% CH$_4$).

3.2. VAD-OS-SAPO-34 membranes: characterisation and performance in CO$_2$/CH$_4$ 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 $\alpha$-Al$_2$O$_3$ 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 μm) and the thickness of organosilica layer (maximum 1 μm), 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 -CH₂- 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.

<table>
<thead>
<tr>
<th>Elements</th>
<th>SAPO-34</th>
<th>VAD-OS-1-SAPO-34</th>
<th>VAD-OS-3-SAPO-34</th>
<th>VAD-OS-6-SAPO-34</th>
</tr>
</thead>
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<tr>
<td>Si</td>
<td>3.3±0.4</td>
<td>5.6±0.9</td>
<td>12.5±1.8</td>
<td>24.5±3.9</td>
</tr>
<tr>
<td>C</td>
<td>7.1±0.2</td>
<td>16.4±1.0</td>
<td>17.0±0.6</td>
<td>19.2±1.0</td>
</tr>
<tr>
<td>Al</td>
<td>20.9±2.6</td>
<td>17.4±0.7</td>
<td>16.1±0.3</td>
<td>13.5±3.0</td>
</tr>
<tr>
<td>O</td>
<td>53.4±3.2</td>
<td>46.9±2.6</td>
<td>40.0±1.5</td>
<td>31.4±2.3</td>
</tr>
<tr>
<td>P</td>
<td>15.3±2.3</td>
<td>13.7±1.3</td>
<td>14.4±0.5</td>
<td>11.4±1.6</td>
</tr>
<tr>
<td>Si/Al ratio</td>
<td>0.16</td>
<td>0.32</td>
<td>0.78</td>
<td>1.81</td>
</tr>
</tbody>
</table>

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 CO₂ from an equimolar CO₂/CH₄ 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 CO₂ permeance and permeation flux as shown in Fig. 9a and 9b, respectively. However, the CH₄ 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 CH₄ through the membrane) to a certain extent (in a good agreement with the SEM analysis, Fig. 3). Comparably, the CO₂ 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. CO₂/CH₄ 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 CO₂/CH₄ 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 CO₂ permeance (flux) and CO₂/CH₄ 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 CO₂ permeance (flux), as well as improving the CO₂/CH₄ 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, AlPO-18) with respect to their ability to separate the equimolar CO$_2$/CH$_4$ mixture [23, 31, 34]. Table 2 shows that the VAD-SO-3-SAPO-34 membrane demonstrated good CO$_2$ permeance (which was comparable to that of the original SAPO-34 membrane), while enhancing the CO$_2$/CH$_4$ separation selectivity by ca. 159%. In contrast, the CO$_2$ 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](image)

**Fig. 9.** CO$_2$/CH$_4$ 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) CO$_2$ (black solid symbols) and CH$_4$ permeance (blue open symbols), (b) CO$_2$ (black solid symbols) and CH$_4$ flux (blue open symbols) and (c) CO$_2$/CH$_4$ separation selectivity (Feed composition: 50 mol. % CO$_2$/50 mol. % CH$_4$).

**Table 2** Comparison of CO$_2$/CH$_4$ separation performance for small-pore zeolites membranes and their modified analogues (by post-synthesis treatments).

<table>
<thead>
<tr>
<th>Zeolites</th>
<th>Treatment</th>
<th>$T$ [°C]</th>
<th>$\Delta P^a$ [bar]</th>
<th>Sweep gas</th>
<th>GP$^b \times 10^{-7}$ [mol m$^2$ s$^{-1}$ Pa$^{-1}$]</th>
<th>% O-GP-D$^c$</th>
<th>GS$^d$</th>
<th>% GS-I$^e$</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAPO-34</td>
<td>Untreated</td>
<td>25</td>
<td>2.2</td>
<td>No</td>
<td>4.7</td>
<td>-</td>
<td>110</td>
<td>-</td>
<td>[34]</td>
</tr>
<tr>
<td></td>
<td>1.8% β-cyclodextrin</td>
<td>25</td>
<td>2.2</td>
<td>No</td>
<td>3.2</td>
<td>31.9</td>
<td>272</td>
<td>147</td>
<td></td>
</tr>
<tr>
<td>SSZ-13</td>
<td>Untreated</td>
<td>25</td>
<td>2.0</td>
<td>He</td>
<td>2.2</td>
<td>-</td>
<td>14</td>
<td>-</td>
<td>[31]</td>
</tr>
<tr>
<td></td>
<td>Siloxane polymer</td>
<td>25</td>
<td>2.0</td>
<td>He</td>
<td>1.6</td>
<td>27</td>
<td>119</td>
<td>750</td>
<td></td>
</tr>
<tr>
<td>AlPO-18</td>
<td>Untreated</td>
<td>25</td>
<td>2.0</td>
<td>He</td>
<td>1.6</td>
<td>-</td>
<td>16</td>
<td>-</td>
<td>[31]</td>
</tr>
</tbody>
</table>
By considering the possible range of CO₂ concentration in biogases, VAD-SO₃-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-SO₃-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-SO₃-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.
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References


Highlights:

- A vacuum-assisted deposition (VAD) method using organosilica to heal defects in SAPO-34 membranes
- An organosilica modified membrane shows insignificant changes in CO$_2$ permeance in CO$_2$/CH$_4$ separation
- CO$_2$ selectivity of the membrane was increased by a factor of ca. 2.5 after VAD using organosilica