

Nano-Hybrid Thin-Film Composite Carbon Molecular Sieve Membranes

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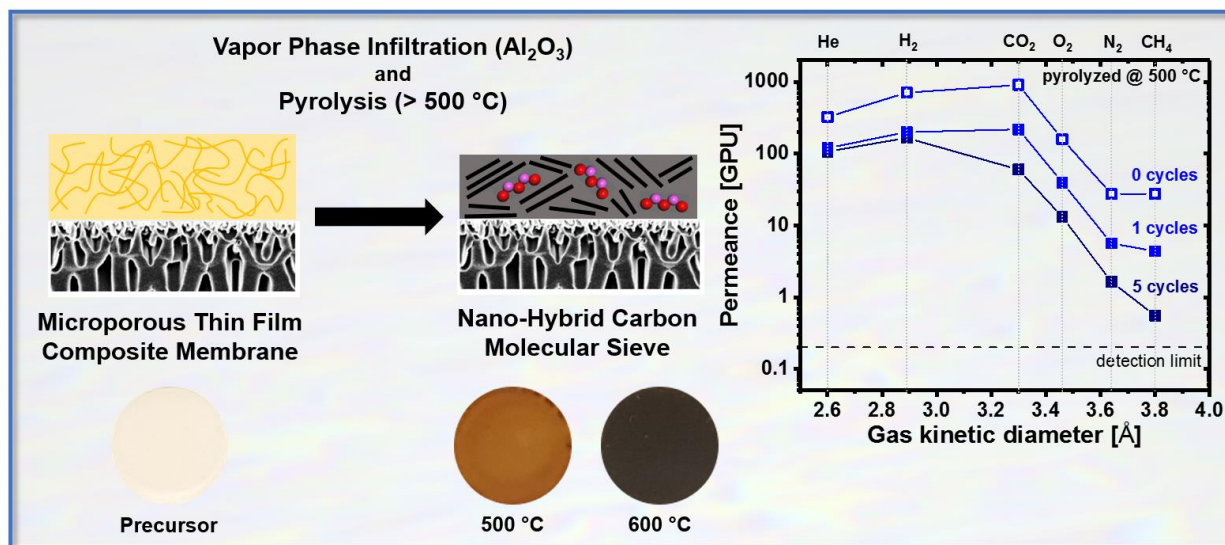
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Graphical Abstract



Keywords

carbon molecular sieves, thin-film composite membranes, gas separation, hybrid materials, nanocomposites, molecular sieving

Abstract

Industrial separations belong to some of the most energy-intensive technological processes because of the reliance on heat-consuming unit operations involving a phase change, such as distillation. Membrane technology promises large cuts to those energy needs; however, its progression is hindered as currently available membranes lack separation performance as well as chemical and mechanical stability. To address these challenges, carbon molecular sieves (CMS) have long been suggested as promising candidates providing excellent and robust molecular separation performance. In this work, we introduce nano-hybrid carbon molecular sieve membranes fabricated by pyrolyzing a polyimide of intrinsic microporosity (PIM-PI) precursor modified by vapor phase infiltration (VPI). In the VPI process a metal-organic precursor, trimethylaluminum (TMA), first diffuses into the high free volume matrix of the PIM-PI to form a complex with its functional groups. Afterwards, water vapor selectively and locally oxidizes the TMA to form nano-dispersed Al_2O_3 within the PIM-PI matrix. Subsequent inert-atmosphere pyrolysis leads to the formation of Al_2O_3 -doped, high quality, thin-film composite CMS membranes with excellent molecular separation properties for a number of technologically important gas pairs, *e.g.* $\text{CO}_2/\text{CH}_4 > 100$, $\text{O}_2/\text{N}_2 > 9$. The introduction of VPI-doped hybrid CMS membranes allows obtaining extraordinary gas separation performance typical to high temperature un-doped CMS at much lower pyrolysis temperatures. This presents significant advantages such as reduction of mechanical failure risk, wider spectrum of possible supports and reduced fabrication complexity.

Highlights

- Introduction of nano-hybrid thin-film composite carbon molecular sieve (CMS) membranes
- Combination of vapor phase infiltration (VPI) and pyrolysis leads to metal oxide doped CMS
- Nano-hybrid CMS membranes show excellent molecular sieving properties
- VPI allows reductions of pyrolysis temperatures by 200-300 °C
- The presented concept enables extremely wide fine-tuning possibilities

Introduction

The pressing need to improve industrial energy efficiency is one of the key elements to facilitate the urgent transition of our society towards a more sustainable economy. A very significant part of the total industrial energy consumption is related to separation processes that still largely rely on energy-intensive thermally driven unit operations, such as distillation, drying or evaporation. In this context, membrane technology offers extremely attractive opportunities to reduce those energy demands by up to 90% [1]. This, however, requires development of not only new membrane materials [2,3] but also design and fabrication of highly productive membrane structures. In particular, design of optimized thin-film composite membranes consisting of a thin, defect-free selective layer can provide high gas permeance (pressure-normalized gas flux) coupled with high gas-pair selectivity while a mechanically robust, low-cost porous support delivers durability and very low resistance to gas transport. These properties allow advanced membranes efficient realization of technologically important separation tasks such as natural gas production, air separation or carbon capture using only pressure difference with virtually no heat input.

Currently available membrane materials, however, are often unable to combine all the necessary characteristics for fabrication of an effective and durable membrane structure. These requirements merely start with attractive intrinsic materials gas separation properties. Ease of thin film fabrication and scale-up, mechanical and chemical resistance, long-term stability, resistance to aging and plasticization (related with swelling induced by condensable gases, *e.g.* CO₂, hydrocarbons etc.) are also extremely important. In this view, carbon molecular sieves (CMS) [4–6] have long been considered as an attractive alternative to both pure polymeric and ceramic membranes. CMS membranes are fabricated by a high temperature (500 – 1000 °C) treatment of a polymer precursor under essentially inert atmosphere and separate gases predominantly based on the diffusivity differences related with the molecular sizes (hence “molecular sieving”). For example, larger gases, such as methane diffuse significantly slower than smaller gases, such as hydrogen or oxygen. As a result of the pyrolytic collapse, a turbostratic, amorphous, and highly microporous (pores < 20 Å) material is formed. The co-existence of ultramicropores (< 7 Å) together with larger micropores provides exceptionally attractive gas separation properties (usually far above the capabilities of polymeric membrane materials) with very good chemical and plasticization resistance. Simultaneously, the use of an organic polymer precursor contributes to good scalability of CMS membranes by allowing the exploitation of well-established solution coating techniques[7].

Recently, polymers of intrinsic microporosity (PIMs) [3,8,9] which possess high microporosity resulting from a highly frustrated chain packing in a solid state, have been utilized as CMS precursors. This has opened up particularly attractive avenues in energy intensive olefin/paraffin separations [10,11].

However, CMS membranes possess several shortcomings, which they partly share with other microporous amorphous materials when fabricated into thin films in the thickness range of a few microns or less. One of the most detrimental ones is physical aging where the excess fractional free volume or microporosity is progressively lost due to a naturally occurring densification of the structure. This process proceeds spontaneously, is accelerated in thin films, and leads to dramatic loss in gas permeability over timescales relevant in membrane processes (weeks to years) [12–15]. Despite its importance, physical aging in thin film CMS membranes has been very rarely reported in the literature [16]. Various efforts have been undertaken to inhibit physical aging, including the polymer design, mixing with fillers, post modification or blending [17–19]. While to some extent effective in thick isotropic films [18], the applicability and effectiveness of those approaches in thin films remain challenging. One of the hurdles more typical to thin film CMS membranes, is the need for cost-effective, mechanically stable supports that would allow tapping into the particularly attractive selectivities of high temperature carbons (pyrolyzed above 700 °C). This is usually achieved with relatively expensive porous ceramic supports. Alternatively, polymeric hollow fiber precursors have been utilized which, however, require additional procedures to avoid excessive support pore collapse [20].

Vapor Phase Infiltration (VPI) to create organic-inorganic hybrids has only recently been described to enhance the mechanical properties of spider silk [21]. However, the field is currently undergoing a very rapid development [22–25]. Numerous application areas are expected to benefit from a more widespread use of this relatively novel technique, such as improvement of mechanical properties of common polymers (polyolefins, polystyrene, polyamides, and block copolymers), sorbents, optics, lithography, or electronics etc. Recently, the application of atomic layer deposition (ALD), which is very similar to VPI, for the modification of membrane properties has been reviewed by Yang et al. [26]. Those approaches, however, mostly relied on surface (top interface or inner pore surface) modifications. In their recent work, McGuinness et al. have used VPI to improve stability of PIM-1 membranes for organic solvent applications [27] demonstrating that upon extensive doping and inorganic network formation demanding emerging applications could be addressed. In addition, only one more report exists on attempting to fabricate ceramic porous membranes with much larger pores (~10 nm) by using infiltrated block copolymers as templates [28]. To date, however, VPI has not been utilized in microporous membranes in conjunction with pyrolysis to produce metal oxide-doped CMS membranes.

In this work, we present a new method to fabricate nano-hybrid CMS thin-film composite membranes with microporosity fine-tuned on a molecular level by a dispersion of inorganic Al₂O₃ within the carbon matrix. The membranes were fabricated by vapor phase infiltration (VPI) of the thin-film PIM-PI precursor with a metal-organic, Al-containing compound (trimethylaluminum, TMA) followed by oxidation with water

vapor and, eventually, pyrolysis. The resulting nano-hybrid CMS membranes show excellent separation properties, typical to high-temperature carbons, yet achieved at moderate pyrolysis temperatures. This strategy could potentially simplify the choice of a suitable CMS membrane support for practical applications. Moreover, the physical aging characteristics of the obtained membranes are distinct from the typical fast loss of permeance with largely preserved selectivity typical to un-doped CMS thin films. The VPI-derived nano-hybrid CMS membranes, in contrast, seem to gain selectivity with aging up to 2 months after fabrication. Given a very large spectrum of available metal-organic VPI precursors, as well as broad possibilities to optimize the doping process we believe that the presented method shows a tremendous potential both for a precise fine-tuning of the CMS membrane properties and for scale-up.

Experimental part

Membrane fabrication

The CMS precursor, polyimide of intrinsic microporosity (PIM-PI) SBFDA-DMN, was synthesized by polymerization of a spirobifluorene-based dianhydride with 3,3'-dimethylnaphthidine, as described earlier [29]. The polymer possessed a molecular weight $M_n = 6.5 \times 10^4 \text{ g mol}^{-1}$ with a polydispersity index (PDI) of 1.92 and an internal surface area $S_{\text{BET}} = 686 \text{ m}^2 \text{ g}^{-1}$. The decomposition onset was determined by TGA at $\sim 520 \text{ }^\circ\text{C}$. The polymer combined a PIM character (high internal surface area and a rigid backbone) with a very high aromatic carbon content (84 wt.%) which was transformed into high quality carbon molecular sieve membranes following pyrolysis [30].

Thin-film composite membranes were fabricated by deposition of 50 μL of $\sim 1 \text{ wt.}\%$ SBFDA-DMN solution in chloroform on top of anodized aluminum substrates (Whatman AnodiscTM, Sigma Aldrich) with 20 nm surface pores. This resulted in a 1-1.5 micron layer thickness as measured with spectroscopic ellipsometry on five spots on the surface. The sufficiently small surface pores assured virtually no pore intrusion by the coating solution and resulted in a sharp, well-defined support/thin-film interface (**Figure S1**). For the XPS, SIMS, spectroscopic ellipsometry, AFM and optical imaging an additional set of samples were fabricated by spin-coating $\sim 3 \text{ wt.}\%$ polymer precursor solution on top of silicon wafers with 500 nm thermally grown silicon oxide. The resulting SBFDA-DMN films were about 300 nm thick. No additional treatment of either PIM-PI membranes or thin films was applied prior to VPI modification.

Membrane modification by Vapor Phase Infiltration (VPI)

A commercial atomic layer deposition system (Cambridge Nanotech, model Savannah S100) was used to perform the vapor phase infiltration (VPI) of the precursor polymer by using trimethylaluminum (TMA) as VPI precursor followed by subsequent oxidation with deionized water (vapor). The deposition was carried out at $200 \text{ }^\circ\text{C}$ with a constant N_2 flow of 15 sccm at 0.2 Torr pressure. The infiltration was accomplished

by isolating the ALD chamber from the pumping line and pulsing the precursor or water (15 ms pulse duration) followed by 10 s exposure before purging the chamber again. Exposure to TMA with a subsequent exposure to water vapor constituted one cycle. In this work, 1, 5 and 20 cycles were used to modify the polymer precursor. Control samples (0 cycles) underwent exactly the same heating protocol as VPI-modified samples without, however, exposure to either of the reactants.

Membrane characterization

Multiple characterization techniques were used to extensively characterize the fabricated hybrid samples. X-Ray photoelectron spectroscopy (XPS) analysis was performed on a Kratos Axis Ultra DLD instrument equipped with a monochromatic Al K_{α} X-ray source ($h\nu = 1486.6$ eV) operated at 120 W under UHV conditions ($\sim 10^{-9}$ mbar). The spectra were recorded in a hybrid mode using electrostatic and magnetic lenses and an aperture slot of 300 by 700 μm . The survey and high-resolution spectra were acquired at fixed analyzer pass energies of 160 eV and 20 eV, respectively. The samples were mounted in a floating mode to avoid differential charging. The spectra were acquired under charge neutralization conditions.

Atomic force microscopy (AFM) was performed using a TESPA probe in a tapping mode with the Dimension ICON instrument. Areas of 1 μm^2 were analyzed on all pristine, hybrid and pyrolyzed samples on Si wafer-deposited films. The optical microscope of the AFM device was used to take optical images of all samples under identical illumination conditions.

Dynamic secondary ion mass spectrometry (SIMS) was done using a Hiden instrument (Warrington, UK) operated under ultra-high vacuum conditions (typically 10^{-9} Torr). A continuous Ar^+ beam was employed at 4 keV to sputter the sample surface while the selected ions were sequentially collected using a MAXIM spectrometer equipped with a quadrupole analyzer. The raster of the sputtered area was approximately 750 x 750 μm . To avoid the edge effect during depth profiling data were recorded from a small area located in the middle of the eroded region. The acquisition area was adjusted using adequate electronic gating to about 75 x 75 μm . A conversion of the sputtering time to sputtering depth was carried out assuming a constant sputtering rate and accounting for the measurement of the crater depth with a stylus profiler from Veeco.

Spectroscopic ellipsometry (SE) was used to determine the thickness of the precursor membranes deposited on the alumina substrates, as well as the thickness and optical properties of the Si wafer deposited samples. This approach has been previously demonstrated for studies on similar composite membrane systems [30–32]. SE was conducted using M-2000 DI instrument from J. A. Woollam Co. equipped with focusing optics (300 μm short axis) in a wavelength range 192 – 1700 nm at five angles of incidence (55, 60, 65, 70 and 75°). The analysis was performed as previously reported [30] and involved utilization of either the Cauchy model in a range of 500 – 1700 nm (with included Urbach tail to handle the light absorption) or B-Spline

model [33] in a full spectral range. Effective medium approximation theory [34] (EMA) was used to extract the volume fractions of Al_2O_3 within the polymer film by assuming molecular level inclusion of the inorganic domains into the organic polymer thereby satisfying the EMA requirements. The pristine polymer dielectric function was first fitted using the B-Spline to serve as the first component in the EMA mixture. The optical properties of the second component, Al_2O_3 , were taken from a literature database [35]. A 15-layer graded optical dispersion was used to approximate the distribution of the Al_2O_3 within the interface of the hybrid films.

Gas permeances, expressed in ‘gas permeation units’, with $1 \text{ GPU} = 1 \times 10^{-6} \text{ cm}^3(\text{STP}) \text{ cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$ or $3.35 \times 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, were measured at $21 \pm 1 \text{ }^\circ\text{C}$ by the constant pressure/variable volume method (utilizing bubble flow meter) using the previously reported protocol [30]. In brief, following VPI and pyrolysis the membranes were placed in stainless steel high pressure 47 mm diameter permeation cells (Milipore) with appropriate ring-shaped masks and rubber o-rings. Active membrane area was 0.65 cm^2 . Maximum pressure for each single gas test was 8 bar with the exception of CO_2 for which 4 bar was used to limit plasticization effects. After stabilization of gas flow (which occurred within 2 hours) the cells were thoroughly purged before proceeding to the next gas. Ideal gas selectivities ($\alpha_{i/j}$) were calculated by dividing permeances of i and j gases, respectively. Prior to gas separation performance testing all membrane samples were coated by a protective thin layer of polydimethylsiloxane, PDMS (500 – 1000 nm). The PDMS coating is commonly employed both in academic research as well as in industry to help eliminate the detrimental influence of occasional pinhole membrane defects. The presence of a highly permeable PDMS layer had a negligible effect on the intrinsic CMS thin film performance as thoroughly evaluated earlier [30].

Results and discussion

Figure 1a shows the scheme of the VPI process applied directly to the thin (CMS) PIM-PI precursor film followed by inert atmosphere pyrolysis to form the carbon molecular sieve and final protective thin film PDMS deposition. The VPI process itself can be repeated multiple times thereby allowing for precise tuning of the resulting aluminum oxide volume fraction (as determined by spectroscopic ellipsometry and XPS, Supporting Information). Trimethylaluminum (TMA), present in the vapor phase as a dimer, is suggested to form a reversible complex with the functional groups of the polymer matrix [36] (imide groups in the case of our PIM-PI), **Figure 1b**. Subsequent oxidation with water vapor results in aluminum oxide formation loosely bound with the polymer matrix, however no exact mechanism for this process is known [23,27]. Simultaneously, the high microporosity of the PIM-PI facilitates efficient diffusion of TMA deep into the selective polymer layer. These large penetration depths for short exposure times are uncommon in conventional low-free-volume polymers (*e.g.* polyolefins or polyamides) where, in contrast, a thin dense layer of Al_2O_3 tends to form at the top interface (at least at comparatively high deposition temperatures to

assure fast oxidation kinetics) [37]. Larger penetration depths (several microns) in those conventional polymers would require significant increase in the exposure time or changes of process conditions, in particular temperature [38]. The significant penetration depth is confirmed by the secondary ion mass spectrometry data, **Figure 2a**, where in the case of infiltrated samples the Al-ion signal persists up to depths of about 150-200 nm. Additionally, the Al-ion signal shows almost no variation upon subsequent high temperature (500 and 600 °C) pyrolysis. The easy tunability of the Al₂O₃ volume fraction is demonstrated in additional SIMS diagrams (**Figure S2**) where its intensity increases with increasing number of VPI cycles. Optical images of the pristine polymer samples, as well as the pyrolyzed and non-pyrolyzed hybrids showed no changes to the top film surface (**Figure S3**). AFM confirmed a very low surface roughness (RMS <0.5 nm) with a slight increase for the hybrid sample pyrolyzed at 500 °C (**Figure S4**).

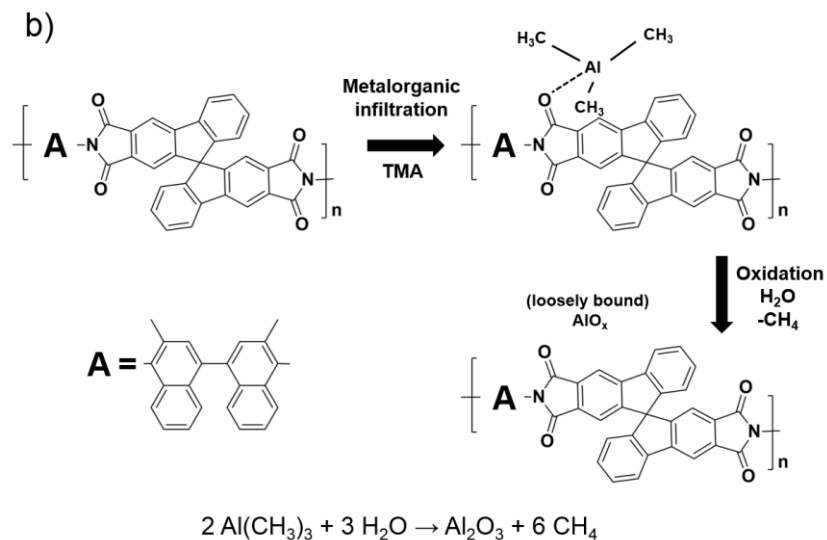
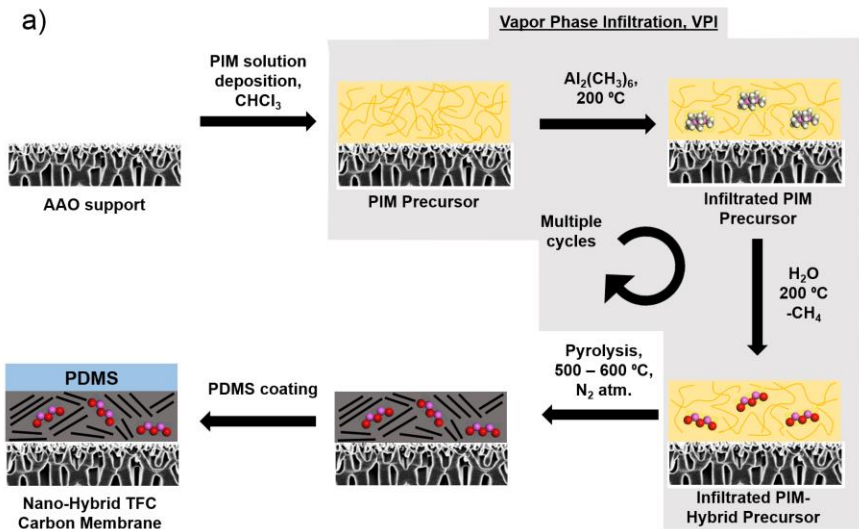


Figure 1. a) Scheme of the thin-film composite carbon membrane fabrication process based on a PIM-polymide with incorporated vapor phase infiltration step, which can be repeated multiple times prior to pyrolysis, and application of the protective PDMS coating; b) proposed chemical scheme showing the creation of the organic-inorganic complex around the imide functional group of the pristine polymer followed by an oxidation reaction leading to a nano-dispersed Al_2O_3 within the PIM matrix.

XPS data, presented in **Figure 2b** and **Table S1**, strongly suggests that Al is efficiently incorporated at a molar fraction of about 7.7% after just 5 VPI cycles and remains in the structure following the pyrolysis. The peak shape analysis for Al 2p peaks, **Figure 2b**, indicates that Al exists within the structure predominantly as aluminum oxide (a shift from 72.6 eV for oxidation state of 0 to around 74.6 eV in Al_2O_3) and thus presumably remains rather loosely (physically) bound to the polymer chains. This observation is in agreement with extensive previous studies and seems to be a general feature of the VPI process in most typical cases *e.g.* deposition of Al_2O_3 , ZnO or TiO_2 [23]. With respect to O 1s peak, the control samples (0 cycles) show a rather symmetrical peak shape centered at around 532.3 eV, which can be ascribed to the carbonyl groups of the pristine polymer. For the Al incorporated samples (both before and after pyrolysis), the O 1s peak is broadened due to an additional contribution shifted toward lower binding energy, which can be assigned to formation of Al oxide bonds. Clearly, Al_2O_3 remains within the structure following pyrolysis.

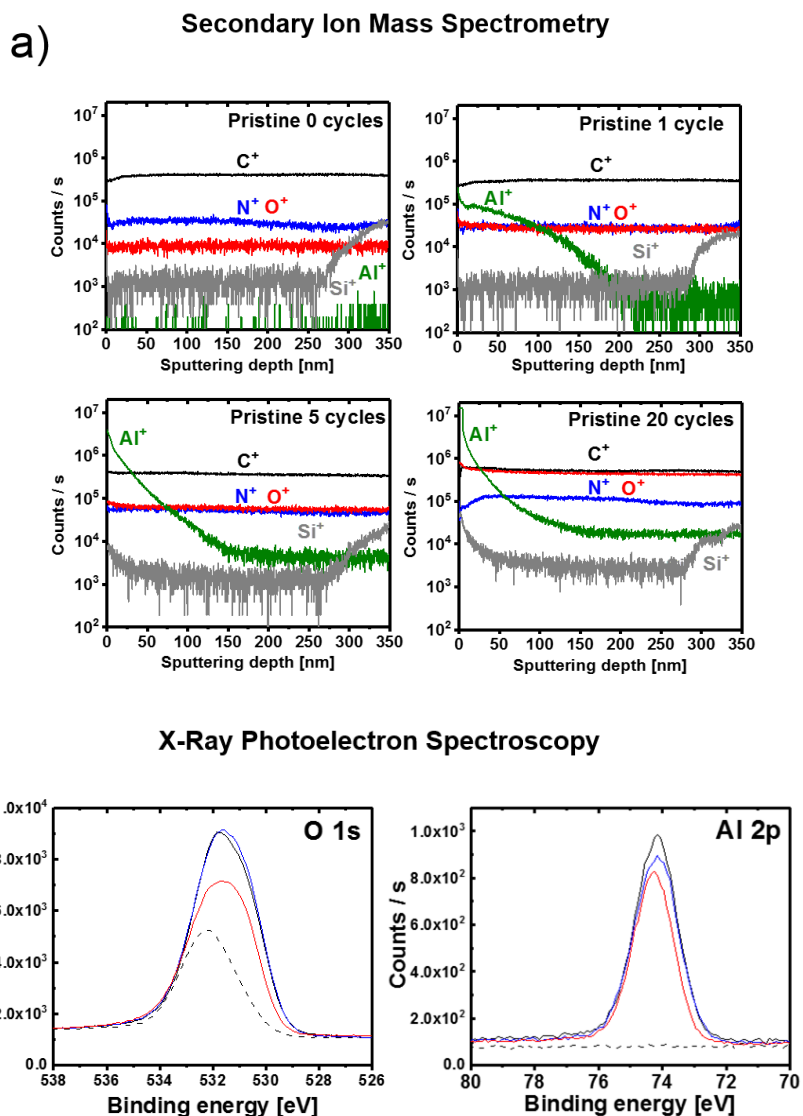


Figure 2. a) Secondary ion mass spectrometry (SIMS) data showing a graded infiltration of Al from the surface up to about 150-200 nm depth into the ~250-300 nm PIM precursor film; the Al ion deposition is preserved upon high temperature treatment (pyrolysis); additional SIMS data are shown in the Supporting Information. b) X-Ray photoelectron spectroscopy data for O 1s and Al 2p peaks, indicating that Al_2O_3 is chemically intact and loosely (physically) bound within the PIM precursor as well as after the pyrolysis.

Following VPI and pyrolysis, the alumina-supported nano-hybrid CMS membranes were tested with respect to their ideal gas separation performance. In **Figure 3**, data for freshly made samples (aged for 1 day) are presented. Remarkably, the VPI resulted in strong enhancement of the molecular sieving character of the pyrolyzed membranes, **Figure 3**. The unmodified CMS membranes (denoted as “0 cycles”) showed some solubility contribution of the more condensable CO_2 (as expected from the solution-diffusion mechanism [39]) and, therefore, permeated faster than the significantly smaller He and H_2 . After just one VPI cycle the character started to change and by five VPI cycles the membranes displayed very strong

molecular sieving with the permeances closely following the molecular size of the gas molecules. Simultaneously, permeances of all gases reduced significantly. In particular, for the five VPI cycles sample pyrolyzed at 600 °C a very strong sieving effect was revealed by a drastically reduced (to below detection limit) permeance of methane, the largest gas in our test series. The changes in the gas separation performance of the hybrid CMS membranes indirectly indicate that introduction of molecularly dispersed Al₂O₃ appeared to tighten the ultramicropores and reduce the overall porosity. These effects are similar to those that occur in bulk CMS membranes upon increase of pyrolysis temperatures [40]. However, a direct characterization of porosity and pore size distribution in ~1 micron films remains extremely challenging because of a lack of suitable experimental techniques.

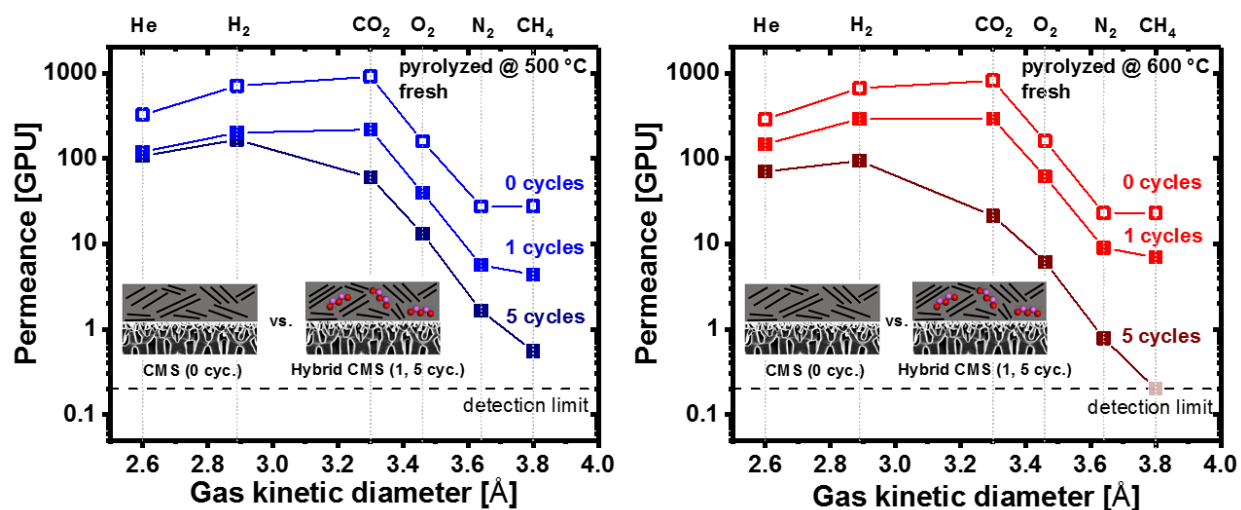


Figure 3. Membrane permeances as a function of the kinetic gas diameters showing an increasing molecular sieving ability with increasing number of vapor infiltration cycles for samples pyrolyzed at 500 and 600 °C.

Table 1 displays the performance data for the freshly prepared (1 day aged) nano-hybrid CMS membranes prepared in this work, nano-hybrids aged for 60 days (500 and 600 °C 1 VPI cycle each), as well as data for undoped analogical samples pyrolyzed between 500 and 800 °C from our previous study [30]. We note here, that Raman spectra of the undoped samples pyrolyzed at 500 and 600 °C, **Figure S9**, indicate that at 500 °C the CMS structure does not yet fully form (this is the transition carbon region with partly degraded polymer precursor) while at 600 °C the D and G peaks typical to the amorphous turbostratic carbon structure do appear. All VPI-modified membranes showed excellent separation performance combining high gas-pair selectivities with high permeances. Increasing the number of VPI cycles strongly correlated with enhancement in gas-pair selectivity, for instance membranes pyrolyzed at 600 °C exhibited CO₂/CH₄ selectivity of 35.3, 41.9 and 106 by applying 0, 1 and 5 VPI cycles, respectively. The VPI process followed by pyrolysis at 500-600 °C enables shifting the molecular sieving properties of the hybrids close to that of

undoped CMS membranes prepared at 200-300 °C higher pyrolysis temperatures. This remarkable finding suggests that the introduction of the molecularly dispersed Al₂O₃ is able to tighten the microporosity essentially mimicking the very strong sieving capabilities of extremely dense, high-temperature CMS membranes *without* the need for extremely high treatment temperatures. This feature may present very significant practical advantages by extending the spectrum of available less heat resistant porous supports for preparation of CMS membranes. In addition, the risk of mechanical damage because of the thermal stress, like pore collapse in all-polymer fibers or cracking, could be greatly reduced. Lastly, avoiding very high pyrolysis temperatures may have obvious practical implications in terms of membrane fabrication complexity and cost.

Table 1. Permeances and Ideal Selectivities of Freshly Fabricated (1 day aged) Nano-Hybrid and Control (Un-doped) Carbon Molecular Sieve Membranes.

Membrane	Permeance [GPU]						Ideal Selectivity, α [-]		
	He	H ₂	N ₂	O ₂	CH ₄	CO ₂	O ₂ /N ₂	CO ₂ /CH ₄	H ₂ /N ₂
Pristine 0 cycles	420	1127	120	396	168	1948	3.3	11.6	9.4
Pristine 5 cycles	378	882	104	303	133	1461	2.9	11.0	8.5
500 °C 0 cycles	324	707	27.4	159	27.6	907	5.7	30.3	25.8
600 °C 0 cycle	288	665	22.9	161	23.1	813	7.0	35.3	28.9
700 °C 0 cycle	70	196	6.4	38.7	4.3	228	6.1	53.0	30.8
800 °C 0 cycle	96.2	178	1.1	12.9	0.47	58.3	11.5	124	159
500 °C 1 cycle	146	271	13.0	65.8	15.0	356	5.1	23.8	20.9
600 °C 1 cycle	150	290	9.0	61.4	6.9	291	6.8	41.9	32.2
500 °C 5 cycles	107	165	1.6	13.1	0.56	59.9	8.0	108	101
600 °C 5 cycles	70.2	93.5	0.8	6.2	0.2	21.2	7.9	106	120

Table 2. Permeances and Ideal Selectivities of Aged Nano-Hybrid and Control (Un-doped) Carbon Molecular Sieve Membranes.

Membrane	Permeance [GPU]						Ideal Selectivity [-]		
	He	H ₂	N ₂	O ₂	CH ₄	CO ₂	O ₂ /N ₂	CO ₂ /CH ₄	H ₂ /N ₂
500 °C 0 cycle* (30 days aged)	94.0	193.3	12.1	51.1	9.2	278.0	4.2	30.2	16.0
600 °C 0 cycle* (30 days aged)	119.0	254.3	12.6	79.1	10.9	402.7	6.3	36.9	20.1
500 °C 1 cycle (30 days aged)	57.4	95.0	2.1	12.6	1.1	76.5	6.0	69.5	45.2
600 °C 1 cycle (30 days aged)	33.5	83.9	0.95	7.4	0.46	36.2	7.8	78.7	88.3
500 °C 1 cycle (60 days aged)	39.7	66.8	0.95	6.9	0.62	38.1	7.2	62.6	69.9
600 °C 1 cycle (60 days aged)	31.4	51.7	0.43	4.0	(-)	16.8	9.1	>85	118.3

(-) below detection limits; * - data from our earlier study [30]

The physical aging process was tracked up to 60 days for the nano-hybrid CMS membranes prepared using 1 VPI cycle and pyrolyzed at 500 and 600 °C. As mentioned earlier, physical aging presents a considerable challenge especially in thin-film composite membranes where the natural densification of the amorphous glassy structures leads to dramatic loss of permeability [41,42]. Yet, physical aging behavior has very rarely been reported especially in studies dealing with thin-skinned CMS membranes [16]. In our previous work [30], we have established that indeed thin-film CMS membranes tend to rapidly densify with time and that reduction of film thickness had a dramatic effect on the permeability but exerted a rather insignificant influence on the selectivity, **Table 2**. This was explained by a predominant collapse of the larger micropores in the range roughly 7 – 20 Å that were principally responsible for the drop in permeability. For ~ 1 micron thick unmodified CMS membranes 30 days of aging under ambient conditions resulted in a 3-5 fold reduction of permeability (particularly for higher pyrolysis temperatures >700 °C) with almost no change in selectivity [30]. In this regard, the physical aging behavior of the VPI-derived nano-hybrid CMS membranes appears significantly different. In the case of three of the most technologically important gas pairs, CO₂/CH₄, O₂/N₂ and H₂/N₂, physical aging led to very large increases in selectivity concurrently with unavoidable reductions of permeances. For example, for the control (un-doped) samples pyrolyzed at 600 °C, 30 days of aging resulted in only small or detrimental changes of O₂/N₂, CO₂/CH₄ and H₂/N₂ selectivities from 7.0 to 6.3, 35.3 to 36.9, and 28.9 to 20.1, respectively. On the other hand, hybrid CMS membranes recorded very significant selectivity increases of 6.8 to 7.8, 41.9 to 78.7, and 32.2 to 88.3, respectively, for the same aging period. The already high selectivities continued to increase beyond 30 days of aging, Table 2, accompanied with a commensurate drop in gas permeances.

Finally, we note that the VPI process itself builds on the extensive experience of the vapor deposition community (in particular, atomic layer deposition ALD) and presents a very wide tunability with: (i) multitude of organo-metallic precursors available (trimethylaluminum, diethyl zinc, titanium tetrachloride etc.), (ii) multiple deposition sequences (continuous, semi-static, pulsed depositions) or (iii) protocols (contacting time of the organo-metallic precursor with the polymer matrix, reaction temperature). In addition, infiltration depths and profiles could be further tuned by pre-treatment of PIM-PI precursors with organic solvents which is known to lead to even more open structures that could, in turn, facilitate metalorganic precursor diffusion. This leads to very attractive optimization possibilities to further fine-tune the separation properties as well as the long-term performance of hybrid, organic-inorganic thin-film composite membranes. These possibilities are not necessarily limited to approaches relying on a subsequent pyrolysis and fabrication of CMS-type membranes. Furthermore, because of its limited invasiveness we further envision a possibility to modify the as-fabricated composite membranes (either flat-sheet or hollow fibers) by exposing them to the organo-metallic precursor and an oxidant after the principal membrane formation step. This would present an attractive membrane modification strategy with a minimal impact on the entire process of membrane fabrication. VPI-derived introduction of specific catalytic functionalities provided by some heavy metal atoms (like Pd) might represent another possibility for novel hybrid membrane properties.

Conclusions

In this work, we introduced nano-hybrid thin-film composite carbon molecular sieve (CMS) membranes by combining vapor phase infiltration (VPI) with high temperature pyrolytic collapse of an intrinsically microporous organic polymer matrix. While Al_2O_3 was used in this study, VPI allows for a molecular level dispersion of a wide range of metal oxides and a high tunability of the process by building on the extensive experience of the vapor deposition community. The synthesized nano-hybrid CMS membranes showed excellent gas separation performance and position themselves near or above state-of-the-art polymeric membranes. VPI enables obtaining very high gas-pair selectivities (e.g. $\text{CO}_2/\text{CH}_4 > 100$) typical to high-temperature pyrolyzed CMS membranes at, however, temperatures lower by 200 – 300 °C. This may have significant practical applications for the scale up by enabling a much wider spectrum of available CMS supports and alleviating some of the challenges related with very high pyrolysis temperatures such as poor mechanical membrane stability and fabrication complexity.

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Supporting Information

Supporting information contains additional data on X-Ray photoelectron spectroscopy, scanning electron microscopy, optical imaging, atomic force microscopy, secondary ion mass spectrometry and spectroscopic ellipsometry analyses.

Data Availability

The raw and processed data required to reproduce these findings are available to download from https://www.dropbox.com/s/9rcump755cgvuan/VPI%20ano13%20SBFDA-DMN_NEW1.opj?dl=0

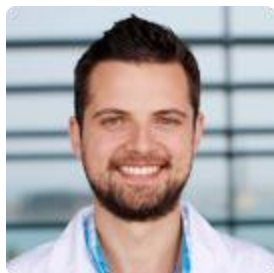
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Vitae



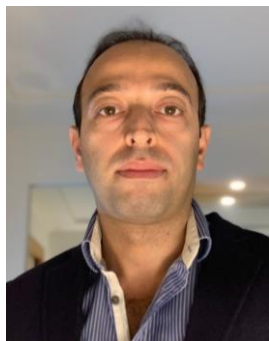
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