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Effect of aluminium acetyl acetonate on the hydrogen and nitrogen permeation of carbon molecular sieves membranes

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Highlights
- Defect free CMSMs were developed from Novolac and various contents of Al(acac)3.
- Membrane thickness depends on the content of Al(acac)3 in the dipping solution.
- Elemental analysis shows that the O and H content in the CMSM increases with the Al content.
- Membranes were stable for H2 permeation for 720 h at 150 °C and 6 bar ΔP.

Abstract
With a growing interest in hydrogen as energy carrier, the efficient purification of hydrogen from gaseous mixtures is very important. This paper addresses the separation of hydrogen using Carbon Molecular Sieves Membranes (CMSM), which show an attractive combination of high permeability, selectivity and stability. Supported CMSM containing various amounts of aluminium have been prepared from novolac and aluminium acetyl acetonate (Al(acac)3) as carbon and alumina precursors. The thickness of the CMSM layers depend on the content of Al(acac)3 in the dipping solution, which also has influence in the pore size and pore size distribution of the membranes. The permeation properties of the membranes against the Al content in the membrane follows a volcano shape, where the membrane containing 4 wt (%) of Al(acac)3 has the best properties and was stable during 720 h for hydrogen at 150 °C and 6 bar pressure difference. All the CMSM have permeation properties well above the Robeson Upper limit.

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Introduction

Hydrogen is used as feedstock in different industrial applications, such as refineries, ammonia synthesis, and methanol production, and recently is used as energy carrier in the transport sector, for power generation and heating solutions. As consequence of the increase of CO₂ in the atmosphere, hydrogen is considered a sustainable energy carrier that can enable the much needed shift from fossil to renewable-based energy sources [1] and it is an important piece to reach net zero emissions by 2050. Besides its high energy density, the abundance of resources and zero carbon emission reaction to produce energy are considered the advantages of hydrogen compared to fossil-based fuels [2]. Hydrogen could be produced by water electrolysis, coal gasification and steam reforming mainly from natural gas [3–5], although the latter is still the dominant pathway [6]. Separation and purification of hydrogen in the production process or from industrial waste streams is considered one of the main challenges in the field. The state of art technologies for hydrogen purification includes pressure swing adsorption, cryogenic distillation, and membranes separation [7–11]. While membrane separation is a scalable and low energy demanding technology which can produce high purity hydrogen [12–14], the membranes need to exhibit high hydrogen permeation and selectivity, long-term stability under separation conditions and low cost in order to be competitive to the traditional purification technologies [15,16]. Among the membranes for H₂ separation, Pd based membranes exhibit the highest hydrogen permeances and selectivities due to their unique mechanism of hydrogen permeation. However, Pd is an expensive rare-earth element, and the stability decreases at low temperatures due to embrittlement which could destroy the membrane. As a result, permeation should be carried out at temperatures above 300 °C. In addition, Pd membranes could be poisoned by H₂S gas existing in the process streams as impurities. Microporous membranes (zeolite, silica, and carbon molecular sieve) are used to separate hydrogen based on size exclusion. However, defect free zeolite membranes are difficult to prepare, and silica membranes are not stable at high temperatures in presence of water [17]. In this context, carbon molecular sieve membranes (CMSM) are seen as one of the promising alternatives to purify hydrogen in an industrial scale [18–21]. They are produced from low-cost materials and can separate gases at room temperature. For mixtures where H₂ is present at low concentrations (<10%) and operating at high pressures, CMSM can surpass the permeation performance of Pd membranes [22]. CMSMs are product of the pyrolysis of a thermosetting polymer in an inert atmosphere. The resulted amorphous carbon structure contains micro and ultra-micro pores which are responsible for the separation of the gases by molecular sieving (size separation) and adsorption diffusion (through the interaction of the gas molecule with the pore walls [23]). Thus, the composition of the polymer precursors as well as the carbonization procedure largely influences the membrane properties and thereby its permeation performance. For example, previous research on CMSMs containing nanoparticles of boehmite (γ-AlO(OH)) using novolac (a phenol formaldehyde resin) as carbon precursor [24,25] demonstrates that the pore size and pore size distribution can be tuned by changing the temperature of carbonization of the membrane [24–30], and that the addition of boehmite increases the hydrophilicity of the membranes [31]. These features could be tuned towards the optimization of water permeation, for example as reported before [31]. Compared to previous works, here we demonstrate that very selective membranes can be produced by using aluminium acetylacetonate to increase the hydrophilicity of the membranes. In this work, the effect of the addition of various amounts of aluminium acetylacetonate (Al(acac)₃) in the preparation of CMSM from a novolac resin and their hydrogen permeation properties are reported.

Materials and methods

Formaldehyde (37% VWR chemicals), N-methyl-2-pyrrolidone (NMP, 99.5%), aluminium acetylacetonate (>98%) and phenol (>99%) from Sigma-Aldrich and oxalic Acid (98%) from Acros organics were used without further purification. Asymmetric tubular porous alumina with outer diameter (OD) of 10 mm and inner diameter (ID) of 7 mm with an external layer of alumina having 100 nm pore size, and length of 50 cm supplied by Inopore Gmbh. were used as support after cutting to 15 cm in length. The porous supports were connected to the dense alumina tube on one side, on the other side the supports were closed via glass sealing which required the heating of the supports to 900 °C with a heating ramp of 1.5 °C/min, dwelling time of 10 minutes and cooling rate of 3 °C/min.

Preparation of the supported CMSM

Novolac precursor synthesis

The synthesis is based on the method reported previously [24,25]. 65 g of phenol was placed inside a three neck round bottom flask equipped with a reflux condenser and heated to 50 °C for 60 min, then 1 g oxalic acid was added while mixing at 500 rpm with magnetic stirrer for 30 min; the temperature was increased to 85 °C and 46 g of formaldehyde was added dropwise in a period of 60 min. After 10 h of reaction, the solution was centrifuged three times at 4400 rpm and 10 °C to separate water and unreacted reactants. In the final step, the precursor was dried under vacuum at 50 °C and 4 mbar for 24 h. The resulted novolac powder was used as carbon precursor in the synthesis of CMSMs.

Dipping solution preparation

20 g of the prepared novolac was mixed with 78 g of NMP in a high shear force mixer (Thinky ARE-310) at 2000 rpm for 30 min; then, the equipment was left to rest for 10 min to prevent the overheating of the solution; this cycle was repeated 3 times. Next, 1.6 g of formaldehyde was introduced to the solution and mixed at 2000 rpm for 30 min. Then, 0.4 g of oxalic acid was added and mixed at 2000 rpm for another 30 min. This mixture was used to prepare dipping solutions with various contents of Al(acac)₃.
Dip coating, drying and carbonization
The prepared porous alumina supports, were dipped at room temperature for 30 s with a dipping solution listed in Table 1 using a custom-made dip-coating machine and withdrawal at speed of 5 mm/s. This dipping cycle was repeated five times with an interval of 20 s between cycles. Next, the membranes were immediately moved to a rotary dryer oven where the coated supports were dried under Argon atmosphere at 140 °C for 6 h. Then, the tubes were carbonized in a tubular oven (Nabertherm R 170/1000/12) using a heating ramp of 1 °C/min until 500 °C where the temperature was kept for 3 h in a flowing argon atmosphere (100 l/h). After the carbonization, the CMSMs were stored in a humidification chamber with a 100% Relative Humidity (RH) to stabilize the hydrophilic sites in the CMSMs [32] for one month. Non-supported membranes were prepared by pouring the dipping solution in a Teflon dish and then heating in an oven at 80 °C for 24 h; the film formed was carbonized using the same conditions of the supported membranes.

Membrane characterization
Physicochemical characterization
The thickness of the membranes was measured using a Scanning Electron Microscopy (SEM) Quanta 200 FEG-3D equipped with EDX (Phenom, ProX) applying a potential of 10 kV. Before analysis, the samples were sputtered (Quorum, Q150RS) with Au for 30 s and 40 mA current. The thickness reported is the average of at least 4 measurements of different sections of the membrane. Viscosity of the dipping solution was measured with a Brookfield, Ametek DV2T viscosimeter at 20 °C. X-ray diffraction (XRD) analysis was performed on the support free carbon films with variation of Al(acac)3 loading in them in the 2θ range of 10–120°. Ni β-filtered Cu-Kα radiation at 40 kV, 30 mA and a scan step of 0.05°/min was used with a MiniFlex 600 machine from Rigaku. The JCPDS database was used to analyse to identify the existing peaks in the spectrum.

The composition of the membranes was carried out using the non-supported membranes. CHO was determined using a 40 kV, 30 mA and a scan step of 0.05°/min was used with a MiniFlex 600 machine from Rigaku. The JCPDS database was used to analyse to identify the existing peaks in the spectrum.

The composition of the membranes was carried out using the non-supported membranes. CHO was determined using a Thermo Scientific, Flash smart-CHNS/O analyser. The Al content was obtained by calcination of the film at 600 °C for 3 h under air in the box oven (Nabertherm N 500/85 HA) and the ashes were dissolved in concentrated nitric acid (67 wt%) for 24 h at 50 °C, then, the samples were diluted with 5 wt% nitric acid and the Al content determined using a Microwave Plasma Atomic Emission Spectroscopy (MP-AES) (Agilent, 4210).

Water adsorption test was used to investigate the change of hydrophilicity in the pores of CMSMs, support-free CMSMs samples were weighted and left in 100% RH in a custom-made climate chamber for one week, after one week, the samples were left for 24 h at 20 °C and 30% RH to remove the bulk water on the surface of the samples in the climate chamber (Mem- mert HCP 50). Then, the samples were weighed again and normalized percentage of increase in weight compared to the sample without any Al(acac)3 in the dipping solution.

Permeation characterization
Single gas permeation tests were performed in the permeation setup shown in Fig. 1. The setup has 3 main sections, a) gas feeding, equipped with multiple mass flow controllers (MFCs). b) the tubular oven equipped with 3 thermocouples located along the membrane. c) the back pressure regulator, safety valve, and the bubble flow meter (Horiba SEC VP1 and VP3). Before permeation measurement, the CMSM was kept at N2 atmosphere for 24 h at 45 °C and 1 bar pressure difference (between permeate and retentate streams) for stabilization. H2 and N2 single gas permeation measurements were carried out at various pressure differences and temperatures. The ideal H2/N2 selectivity (perm-selectivity) is the ratio of H2 and N2 flow rates at given temperature and pressure. The CMSM with the best performance in terms of H2/N2 perm-selectivity was tested for 720 h; at 150 °C and 6 bar pressure difference; H2 and N2 flux were measured every day.

Perm porosimetry tests
The measurements of average active pore size in CMSMs were performed with a custom-made (Figure S1) capillary condensation perm porosimeter; details of the equipment and the perm-porosimetry test could be found in the supplementary information section.

Results and discussions
SEM images of a CMSM obtained with dipping solutions without Al(acac)3 (M0) and with 0.7 wt% Al(acac)3 (M0.7) are shown in Fig. 2. It can be observed that a continuous layer ~1.5 μm thick of carbon without defects is deposited on a porous alumina support. It was observed by SEM that the thickness of the membrane increases (~2 μm for M0.7) with the concentration of Al(acac)3 in the dipping solution as shown in Fig. 3. To explain this behaviour, the viscosity of the dipping solutions was measured, and the results are also plotted in the same figure. It can be seen that the thickness of the CMSM increases with the viscosity of the dipping solution following the Landau-Levich equation (Eq. (1)):

| Membrane | Novolac | Al(acac)3 | NMP | Formaldehyde | Oxalic acid |
|----------|---------|----------|-----|--------------|-------------|
| M0       | 20      | 0        | 78  | 1.6          | 0.4         |
| M0.7     | 19.3    | 0.7      | 78  | 1.6          | 0.4         |
| M2       | 18      | 2        | 78  | 1.6          | 0.4         |
| M4       | 16      | 4        | 78  | 1.6          | 0.4         |
| M6       | 14      | 6        | 78  | 1.6          | 0.4         |
\[ h_0 = c \left( \frac{\eta U_0}{g} \right)^{2/3} \gamma^{1/6} \rho^{1/3} \]  

(1)

where \( h_0 \), \( \rho \), \( g \), \( U_0 \), \( \eta \) and \( \gamma \) are the wet film thickness, solution density, gravitational constant, withdrawal speed of the ceramic support from dipping solution, viscosity of the dipping solution and surface tension, respectively. \( c \) is related to the curvature of the dynamic meniscus and could be calculated experimentally [33–35].

From M0 to M2, the increase in the viscosity is small, while for higher Al(acac)₃, the viscosity increases sharply. This could be due to the formation of complexes between Al (III) with the OH- groups of the phenolic resin behaving as a metal chelating crosslinker. This complex formation and the increase in the viscosity of the dipping solution will hinder the movement of Al(III), avoiding the formation of poly aluminium compounds such as alumina (Al₂O₃) and boehmite (γ-AlO(OH)). As a result the AlO(OH) could be synthesized without attaching together and this will enhance the hydrophilicity of the CMSM. Moreover, XRD spectra of the samples presented in Fig. 4 do not show the corresponding peaks of γ-Al₂O₃/boehmite (γ-AlO(OH)) [31] meaning after carbonization, the CMSMs resulted in a uniform dispersion of AlO(OH) in their amorphous carbon matrix.

SEM-EDX analysis of M2 reveals that Al, C and O are well distributed in the membrane (Figure S2) uniformly and no clusters could be found. Further, C, H and O elemental composition of the membranes obtained by organic elemental analysis and SEM-EDX, and Al composition determined by
MP-AES are listed in Table 2. All techniques lead to comparable results, whereas the elemental analysis is more accurate.

As expected, the amount of oxygen in the samples increases with the Al content in the CMSMs. A similar trend is observed with the amount of H, suggesting that the increment is caused by the presence of OH groups in the membrane. Thus, together with the absence of the corresponding XRD peaks (Fig. 4), this finding supports the conclusion that Al₂O₃ is not present in the membrane. Instead, Al could be in the form of aluminium hydroxides (AlO(OH) and/or Al(OH)₃) bounded to the carbon matrix. Since both compounds are hydrophilic, the hydrophilicity of the membrane should increase with the Al content in the membrane. This is assessed in Fig. 5, where the ratio between the weight after hydration to that of the dry sample is plotted as a function of the Al wt (%) present in the membrane. In line with expectation, the relation is almost linear.

Next, the pore size and pore size distribution of the CMSMs are assessed, as they are very important properties for gas permeation through these membranes. The effect of aluminium hydroxides on the average pore size of the CMSMs was analysed by perm-porosimetry. In this method, the condensation of water in the pores will gradually block them.
to the passage of other gases, starting from the smallest to the biggest pores as the ratio of water vapor to non-condensable gas (N₂) increases. The kinetic diameter of N₂ (i.e., the permeating gas in this experiment) is 0.364 nm, so this method only measures pores bigger than around 0.4 nm. The effect of Al(acac)₃ on the pore size distribution of the CMSMs calculated by porosimetry is presented in Fig. 6. First, it is evident that CMSM, M0, which does not have Al(acac)₃, has

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**Fig. 5** – Water adsorption in function of the Al wt% content in the membrane for determination of the change in hydrophilicity of CMSMs.

**Fig. 6** – Pore size distribution measured with perm porosimetry of the supported CMSMs at various Al(acac)₃ content in the dipping solution and the change of the pore size distribution.
the biggest pores among all the samples tested, with the highest percentage of pores at around 0.72 nm and the largest pores at around 1.2 nm. Larger pores were not observed. With an introduction of the Al(acac)₃, the pore size distribution shifts towards narrower pores, with the smallest detected pores around 0.6, 0.55 and 0.49 nm for M0.7, M2 and M4, respectively. The M4 only shows one peak, denoting a very narrow pore size distribution (i.e., 66% of the pores are below 0.5 nm) which will result in the higher ideal selectivity for H₂/N₂ gases. When even more Al(acac)₃ is added, as in M6, bigger pores start to appear. Thus, the predominance of smallest pores in the membrane shows a volcano shape against the addition of Al(acac)₃, with a maximum at M4.

**CMSMs permeation tests**

N₂ permeation tests were conducted for qualitative assessment of the potential defects in the membranes, hereby considered as pores bigger than 50 nm. The N₂ permeance of a CMSM can be considered to be the result of the contribution of several transport mechanisms: Knudsen diffusion (in pores of 2–50 nm) and viscous flow (in pores >50 nm). Since the flux in the micropores (<2 nm) is low, their contribution can be neglected. Thus, the observed permeance (Permₐₜₜ) can be expressed according to Eq. (2), as the sum of the permeation by Knudsen (PermKnudsen) and that by viscous flow (Permviscous), the latter being a function of pressure difference (P):

\[
\text{Permeance}_{\text{obs}} = \text{Permeance}_{\text{Knudsen}} + \text{Permeance}_{\text{viscous}} = \alpha + \beta P
\]

where \(\alpha\) and \(\beta\) are independent of the pressure difference.

Fig. 7 shows the results of N₂ permeances of the CMSMs vs. applied pressure difference between retentate and permeate (P). According to Eq. (2), a positive slope (\(\beta > 0\)) would indicate a significant contribution of viscous flow and therefore the presence of defects (pores >50 nm). However, the trend in Fig. 7 (i.e., \(\beta = 0\) for all membranes) reveals that the membranes do not contain defects. Besides, the permeances of all membranes is in agreement with the pore size distribution shown in Fig. 6 (i.e., with M0 and M4 showing the highest and the lowest permeances, as well as the biggest and smallest pores, respectively).

Next, the permeation properties of these membranes for hydrogen separation are assessed by measuring hydrogen permeance and H₂/N₂ ideal selectivity at a given temperature and pressure. The H₂ and N₂ permeances of the CMSMs are as a function of the permeation temperature and the content of Al(acac)₃ in the dipping solution are illustrated in Figures S3 and S4. Since the thickness of the CMSMs depends on the viscosity of the dipping solution, the permeances standardized with the thickness (i.e., permeabilities) are shown in Figures S5 and S6. Fig. 8 represents the H₂/N₂ ideal selectivity

![Fig. 7](image1)

**Fig. 7** – N₂ permeance vs. applied pressure on CMSMs at 45 °C in order to verify the defect free top selective layer.

![Fig. 8](image2)

**Fig. 8** – Effect of temperature of operation on H₂/N₂ ideal selectivity of the CMSMs at 6 bar ΔP to validate the effect of temperature on the type of transport mechanisms for the gas molecules.

![Fig. 9](image3)

**Fig. 9** – Comparison of CMSMs prepared in this with polymeric membranes according to the Robeson’s upper bound limit and the CMSMs synthesized from different polymeric precursors.
of CMSM at various Al(acac)₃ contents at 6 bar pressure difference as a function of the temperature of permeation. It is evident that M₄, the membrane with the narrowest pore size distribution, also shows the highest selectivity at all the temperatures, with a maximum of ca. 400 at around 150 °C.

In general, the H₂/N₂ ideal selectivities at a given temperature follow the order M₀ < M₀.₇ < M₂ < M₆ < M₄, in line with the volcano shape for the smallest pore size distribution (Fig. 6) and N₂ permeance (Fig. 7).

It is clear from Fig. 8 that the temperature and the added Al(acac)₃ have an effect on the H₂/N₂ selectivity. According to Figures S3 and S4, H₂ and N₂ permeances present a sharp increase at temperatures higher than 300 °C, which is an indication of unstable CMSMs performance. This is attributed to the change in the carbon matrix and, as a result, a change in the pore size and pore size distribution. The sharp increase in the permeances of both gases leads to a significant decrease in H₂/N₂ ideal selectivity (Fig. 8) due to the increase in the average pore size in CMSMs.

Fig. 9 compares the H₂/N₂ permeation performance of the CMSMs of this work with polymeric membranes and other carbon membranes from the literature by introducing the H₂ permeability and H₂/N₂ ideal selectivity in a Robeson plot. All the CMSMs of this work are well above the Robeson upper limit, which increases the potential of CMSMs to be implemented in H₂ separation processes. In addition to polymeric membranes, CMSMs performance in this work are compared to the performance of CMSMs found in literature which are fabricated with Phenolic Resin (PR) [36] or different precursors such as PR/PAA [37] and PDMS [38]. The membrane’s perm-selectivities are indicated in Fig. 9 and the CMSMs with Al(acac)₃ loading more than 0.7 wt%, performed higher in terms of ideal H₂/N₂ selectivity. As the content of Al(acac)₃ increases, the performance of the CMSMs increases, reaching the maximum at M₄ membrane that surpasses the reported values for the CMSMs and polymeric membranes in the literature. Finally, long term stability of the optimal CMSM (M₄) was tested by analysing the H₂ permeance and H₂/N₂ ideal selectivity for 720 h at 150 °C and 6 bar pressure difference. Fig. 10 shows that M₄ is stable during the entire test with maximum 5.7% SD variation in H₂/N₂ ideal gas selectivity and 7.04% SD variation in H₂ permeability.

Conclusions

CMSMs made from Novolac and various contents of Al(acac)₃ on the outside porous asymmetric alumina support (100 nm pore size) without defects were successfully prepared. The thickness of the CMSM layers depends on the content of Al(acac)₃ in the dipping solution which is related to the increase of the viscosity of the solution, attributed to the formation of complexes between Al(III) with the OH- groups of the phenolic resin behaving as a metal chelating crosslinker. Elemental analysis shows that the O and H content in the CMSM increases with the Al content which suggest the presence of hydrophilic aluminium compounds containing hydrophilic groups, as demonstrated by water adsorption studies. The formation of complexes of Al with the OH of the phenolic groups have influence in the pore size distribution of the membrane; M₀ (without Al), has the biggest pores, and the pores became smaller with the addition of Al(acac)₃. M₄ has the smallest pores and the narrowest pore size distribution, which is reflected in the permeation properties of this membrane: it has the highest H₂/N₂ selectivity in the 50–350 °C range of temperature permeation. All the membranes prepared are well
above the upper bond limit for polymeric membranes. The M4 membrane was stable for H2 permeation for 720 h at 150 °C and 6 bar ΔP.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijhydene.2022.02.198.

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