



Composite DD3R-Alumina hollow fiber for CO₂/CH₄ separation

Renan Fraga Barbosa^{a,*} Alberto Claudio Habert^a, Cristiano Piacsek Borges^a,

^a Chemical Engineering Program, COPPE, Federal University of Rio de Janeiro, Rio de Janeiro, Brazil

*renan@peq.coppe.ufrj.br

Abstract

More efficient and durable membranes are required to produce gas permeation modules with high area/volume for CO₂ removal from natural gas. Therefore, this research focused on developing zeolite DD3R-alumina composite hollow fibers with high performance for CO₂/CH₄ separation. A porous hollow fiber support was prepared from low-cost alumina via phase inversion and thermal treatment. A selective layer was formed by implanting DD3R zeolite seeds onto the surface of these fibers via hydrothermal synthesis. The thickness of this layer was controlled by the seed concentration, which affected the membrane performance. A reduced-diameter composite DD3R-alumina hollow fiber was therefore obtained showing a typical selectivity of 203 and a CO₂ permeance of $5.4 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ at a pressure of 2 bar. The technique shows excellent indications for obtaining new efficient and stable hollow fiber membranes for CO₂ removal

Introduction

Polymeric membranes have been used for CO₂ removal from natural gas since the mid-80's. However, these membranes have operational limitations, including reduced selectivity owing to CO₂-induced plasticization, decreased permeance due to membrane compaction, aging, and susceptibility to rupture at high pressures. As an alternative to polymeric materials, zeolite membranes are excellent candidates for CO₂/CH₄ separation because of their high selectivity and permeance, attributed to the strong affinity of zeolites for CO₂, combined with the molecular sieving separation provided by the microporous zeolite structure. [1–3]

Among the zeolites used for membrane production, decadodecasil 3 rhombohedral (DD3R) zeolite stands out because of its unique pore opening (0.36×0.44 nm), resulting in an effective pore diameter of 0.36 nm, which is in the range of the kinetic diameters of CO₂ (0.33 nm) and CH₄ (0.38 nm), allowing to produce membranes with selectivity above 200. However, large-scale production remains a challenge because of issues associated with the fabrication process. These include the formation of competitive phases, like Dodecasil-1H (DOH) and Sigma-2 (SGT) zeolites [4], and the development of intercrystalline defects.

The purpose of this investigation was to prepare and characterize a DD3R zeolite composite membrane selective for CO₂ in a hollow-fiber configuration. There are not many reports in the literature on such a single channel selective hollow fiber. The 2 steps fabrication technique involves the preparation of an affordable alumina microporous support to be coated with a locally synthesized DD3R zeolite layer. The evaluation of the permeability of these membranes provides preliminary criteria for the effectiveness of the technique and its potential use in permeation modules for gas separation processes.

Experimental

Low-cost alumina hollow fiber supports were produced using phase inversion and sintering techniques. The precursor hollow fibers were sintered in a tubular electric furnace using a three-stage temperature procedure. The temperature was increased from room temperature to 200 °C at a rate of 2 °C min⁻¹ and held for 1 h, then to 600 °C at a rate of 2 °C min⁻¹ and held for 2 h before heating to 1550°C at a rate of 5°C min⁻¹ and held for 4 h, after that the furnace was cooled slowly to 25 °C.

DD3R zeolite coated layers were synthesized using a secondary growth method. The precursor hollow fibers were immersed in a suspension to insert the crystals onto their external surface. They were then placed in a stainless-steel autoclave containing the synthesis gel, 1SiO₂:0.056 ADA:0.056 KF:52 H₂O (molar ratio), at 140 °C for 24h. The recently prepared DD3R-alumina hollow fibers were calcined in a tubular oven in an ozone environment for the detemplation of zeolite pores, following the methodology described by Wang et al. [4]. The calcination process was carried out at 200 °C, maintaining a continuous oxygen flow rate of 1 L/min, containing 56 mg/L ozone, for a time period ranging from 120-192h.

Results and discussion

The alumina hollow fiber support showed a uniform sponge-like structure with a mean pore diameter of 0.7 μm, achieving a high nitrogen permeance of $4.6 \times 10^{-5} \text{ (mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1})$. These membranes exhibited an impressive flexural strength of $177.5 \pm 27 \text{ MPa}$, as confirmed by a three-point bending test. This mechanical robustness can be attributed



to the sponge-like morphology resulting from the wide particle size distribution of alumina, ranging from 0.2 to 10 μm . Additionally, high sintering temperatures contributed significantly to material densification and the subsequent reduction in pore diameter.

DD3R selective layers were produced over the alumina hollow fibers using the secondary growth method. The thickness of the selective layer in the DD3R-alumina membrane was controlled by the number of seeds deposited over the alumina hollow fiber surface by adjusting the seed concentration in the suspension and the dip coating time, as shown in Table 1. Notably, a smaller quantity of seeds implanted in the membrane support led to reduced crystal intergrowth in the DD3R selective layer, and consequently, to the formation of a thinner selective layer.

Table 1- Synthesis condition and average thickness for DD3R selective layers

Batch	Seed concentration (%)	Dip coating time (s)	DD3R layer thickness (μm)
C1-DD3R	0.50	30	9.2
C2-DD3R	0.25	30	8.1
C3-DD3R	0.25	15	6.4

Table 2 presents the performances of the membranes produced from the C1-DD3R and C2-DD3R batches. In the C1-DD3R batch, higher selectivity was observed owing to the larger DD3R crystal intergrowth, resulting in fewer defects and lower permeance. Conversely, C2-DD3R membranes were formed with fewer seeds in the support, leading to reduced crystal intergrowth, resulting in a higher permeance; however, in this case, membranes had more defects in their selective layers resulting in a decrease in selectivity. For both batches, variations in the performance of the membrane were provoked by irregularities in the thickness of the selective layer as well as the formation of an impermeable competitive phase of DD3R zeolite, known as zeolite SGT. For batch C3, permeation tests were not performed because it was noticed that the reduced crystal intergrowth produced defective selective layers, leading to membranes without selectivity.

Table 2- Separation performance* of DD3R-alumina hollow fiber.

Membrane	Permeance $\text{CO}_2 \times 10^{10} (\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1})$	Selectivity CO_2/CH_4
C1-DD3R-1	134	277
C1-DD3R-2	74	150
C1-DD3R-3	7	208
C2-DD3R-1	660	27
C2-DD3R-2	807	33
C2-DD3R-3	536	203
C2-DD3R-4	114	294
C2-DD3R-5	315	84

*Permeation conditions: 23°C; pressure difference: 1 bar (C1-DD3R permeation) and 2 bar (C2-DD3R permeation).

Conclusions

High-performance hollow fiber membranes with reduced size single channel were obtained with typical selectivities of 203 and a CO_2 permeances of $5.4 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ at a pressure of 2 bar. These results clearly indicate the potential of DD3R-alumina hollow fibers as candidates for use in permeation modules with a high packing density for CO_2/CH_4 separation.

References

- Martin-Gil V, Ahmad MZ, Castro-Muñoz R, Fila V. Economic Framework of Membrane Technologies for Natural Gas Applications. *Separation & Purification Reviews* [Internet]. 2018;00(00):1–27. Available from: <https://doi.org/10.1080/15422119.2018.1532911>
- Himeno S, Tomita T, Suzuki K, Nakayama K, Yajima K, Yoshida S. Synthesis and permeation properties of a DDR-type zeolite membrane for separation of CO_2/CH_4 gaseous mixtures. *Ind Eng Chem Res*. 2007;46(21):6989–97.
- Wang L, Zhang C, Gao X, Peng L, Jiang J, Gu X. Preparation of defect-free DDR zeolite membranes by eliminating template with ozone at low temperature. *J Memb Sci* [Internet]. 2017;539(May):152–60. Available from: <http://dx.doi.org/10.1016/j.memsci.2017.06.004>
- Gücüyener C, Van Den Bergh J, Joaristi AM, Magusin PCMM, Hensen EJM, Gascon J, et al. Facile synthesis of the DD3R zeolite: Performance in the adsorptive separation of buta-1,3-diene and but-2-ene isomers. *J Mater Chem*. 2011;21(45):18386–97.