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Silica Ceramic Membranes for Selective Separation of CO_2 in Natural Gas Processing

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Abstract

In the exploration and production activities within the petroleum industry, the presence of corrosive gases, such as CO_2 and H_2S, in hydrocarbon reservoirs poses significant challenges. Depending on their concentrations, these gases can jeopardize worker safety, cause equipment damage, and potentially render a project economically unviable. In the Santos Basin, Brazil, there is a notable presence of wells with concentrations of CO_2 exceeding 5 %, even reaching up to 80 % in certain areas [1]. Among the various techniques employed for CO_2 separation, ceramic membranes have emerged as a promising technology for upstream applications. These membranes exhibit unique structural and functional properties, offering a viable alternative to conventional methods like amine-based systems [2-3].

Ceramic membranes, characterized by their multilayered structure, encompassing macroporous support, mesoporous intermediate, and microporous separation layers, provide an attractive solution for selective CO_2 removal. The advantages of ceramic membranes lie in their high permeation rates and molecular sieving, allowing smaller gas molecules to pass through while obstructing larger ones. This unique property contributes to the membranes' high selectivity and relatively high permeability. Furthermore, the fabrication of ceramic membranes through processes like sol-gel ensures versatility in tailoring the pore sizes and structures, enhancing the membranes' efficiency for CO_2 separation from natural gas [2].

Ceramic membranes were developed at Federal University of Minas Gerais (UFMG) for CO_2 separation in natural gas, emphasizing tailored properties for high pressure processing. UFMG ceramic membranes were produced by depositing sol-gel silica solutions onto α-Al_2O_3 mono-channel tubular supports (OD ≈ 9 cm), followed by the appropriate thermal treatment. The alumina ceramic mass of the supports received additions of TiO_2 (1 %, 3 %, and 5 % wt.) to enhance the mechanical strength of the ceramic membranes.

Single-gas permeation tests (CO_2, N_2, and CH_4) were performed at room temperature to determine the permeance of UFMG ceramic membranes using Eq. (1), where V_P is the permeate flow rate ($cm^3_{(STP)}/s$), A_m is the membrane separation area (cm^2), P_F and P_P are the pressure (cm·Hg) in feed and permeate side, respectively. The ideal selectivity or ideal permselectivity ($\alpha^*_{A/B}$) was calculated by the ratio of permeances for gas pairs as per Eq. (2). The mechanical strength of the membranes was assessed through three-point bending tests (30 mm span) using a universal mechanical testing machine (Instron, EMIC 2310) with a compression rate of 0.5 mm/min.

$$\rho_A = V_P/(A_m \cdot (P_F - P_P)) \quad (1)$$

$$\alpha^*_{A/B} = \rho_A/\rho_B \quad (2)$$

According to the single-gas permeation tests, the UFMG ceramic membranes exhibited a high flux of carbon dioxide. A CO_2 permeance of 1.1 x 10^{-6} mol/m^2·s·Pa was achieved at a feed pressure of 9 bar (9.0 x 10^5 Pa) with a ΔP of 2.1 bar (2.1 x 10^5 Pa). The CO_2 permeance of the UFMG ceramic membrane is significantly higher than that of polymeric membranes commonly employed in gas separations, exceeding a typical polymeric membrane with a permeance of 1,500 Barrer (10^{-7} mol/m^2·s·Pa) by one order of magnitude. For this same condition the nitrogen and methane permeance were 1.5 x 10^{-7} mol/m^2·s·Pa and 1.1 x 10^{-7} mol/m^2·s·Pa respectively.

The results of ideal permselectivity for the gas pairs CO_2/N_2 and CO_2/CH_4 of UFMG ceramic membranes are presented in Tab. 1. The UFMG ceramic membrane showed a CO_2/CH_4 permselectivity of 9.7, indicating its efficiency in CO_2 separation from natural gas. Also, the results showed that the permselectivity obtained for the pair CO_2 and CH_4 is higher when compared to the CO_2 and N_2 ($\alpha^*_{CO_2/CH_4}$ = 7). This occurs due to the larger difference in size between carbon dioxide and methane, when comparing to carbon dioxide and nitrogen, which confirms sieving effect present in the membranes due to its pore sizes.

Tab. 1 - Ideal permselectivity for the gas pairs CO_2/N_2 and CO_2/CH_4 of UFMG ceramic membranes.

P_{feed} [bar]	ΔP [bar]	$\alpha^*_{CO_2/N_2}$	$\alpha^*_{CO_2/CH_4}$
2	1.0	3.1	4.5
4	1.3	4.7	6.7
6	1.6	5.8	8.2
8	1.9	6.7	9.3
9	2.1	7.0	9.7

The ceramic support plays a pivotal role in providing mechanical strength to ceramic membranes, directly influencing their robustness. It is evident that the mechanical strength of the support is directly correlated with the mechanical strength of the UFMG ceramic membranes derived from it. The mechanical strength of UFMG ceramic membranes, manufactured from ceramic supports with different chemical compositions and thermal treatments, are shown in Tab. 2. The findings indicate that the mechanical properties of UFMG ceramic membranes can be tailored through the introduction of TiO_2 and variations in the thermal treatment temperature of the supports. These adjustments facilitate the optimization of the mechanical characteristics of the membranes, enhancing their strength and durability. The results suggest that UFMG ceramic membranes exhibit a remarkable capacity to withstand high loads. This implies that these membranes can be successfully employed in gas separation processes, even under extremely high-pressure conditions, reaching up to 2900 bar. This study makes a contribution to the understanding and enhancement of the mechanical performance of ceramic membranes, expanding their potential applications in gas separation processes within the oil and gas industry.

Tab. 2 - Mechanical strength of UFMG ceramic membranes according to the composition and sintering temperature of the support.

TiO_2 loading	**Ceramic support mechanical strength [MPa]**			
	1,300 °C	**1,400 °C**	**1,500 °C**	**1,600 °C**
0 % wt.	11.9 ± 7.1	34.6 ± 7.3	54.4 ± 22.9	73.3 ± 19.4
1 % wt.	48.2 ± 4.9	109.6 ± 27.8	133.8 ± 20.4	206.8 ± 85.4
3 % wt.	62.7 ± 19.1	142.5 ± 15.0	207.0 ± 10.2	234.5 ± 128.7
5 % wt.	55.8 ± 32.5	136.1 ± 8.7	192.4 ± 20.2	296.3 ±24.1

References

[1] Almeida, K. S., Vilela, P. C., Cardoso, R. A., Fernandes, R. F., Souza, M. F. F. Ocorrência de CO_2 em campos petrolíferos na margem leste brasileira. Empresa de Pesquisa Energética – EPE, Ministério de Minas e Energia. Rio de Janeiro, Brasil, 2018.

[2] Kamio, E., Tomohisa, Y., Hideto, M. Recent advances in carbon dioxide separation membranes: A review. Journal of Chemical Engineering of Japan, 56, 2222000, 2023.

[3] Pasichnyk, M., Stanovsky, P., Polezhaev, P., Zach, B., Šyc, M., Bobák, M., Jansen, J. C., Přibyl, M., Bara J. E., Friess, K., Havlica, J., Gin, D. L., Noble, R. D., Izák, P. Membrane technology for challenging separations: Removal of CO_2, SO_2 and NO_x from flue and waste gases. Separation and Purification Technology, 323, 124436, 2023.