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Performance of palladium-coated α-alumina tubular membranes for gas separation

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Abstract

Currently, the use of membrane separation processes is rising in the industry, aiming to enhance or replace classical separation processes. Gas separation is a specific area of Membrane Technology that needs high-efficiency and specially tailored membranes to achieve a helpful separation. Composite inorganic membranes in gas separation have become a promising alternative. This work aimed to separate CO_2 and CH_4 using Pd-coated ceramic membranes with different Pd layers deposited. The Pd layers were deposited by the sol-gel and electroless plating methods. The membranes were evaluated for CO_2 and CH_4 permeability. Those with thinner Pd layers showed higher gas permeability. According to the size and molar mass of the gas molecules, the membranes showed a higher CH_4 permeability than CO_2, regardless of the number of Pd layers deposited. The membranes showed a greater chemical affinity with CH_4 than CO_2, having the potential to be used in gas separation processes, especially CH_4 separation and purification.

Introduction

When coated with palladium, ceramic supports combine the metallic layer's high selectivity with the porous support's high permeability [1]. The principal applications of ceramic membranes encompass the catalytic recovery of hydrogen, tar cracking, and the separation of different gases, such as carbon dioxide (CO_2) and methane (CH_4), oxygen (O_2), and nitrogen (N_2) [1-2].

However, the gas flux is inversely related to the active layer thickness. In this sense, a coating thickness that maximizes the separation factors without sacrificing too much flux is necessary to obtain efficient and useful membranes [1]. For metal-coated ceramic membranes, catalytic reactions involving hydrogen and metallic surfaces promote gas transport due to the interaction of the gas atoms with the metal. The transport mechanism of hydrogen across the Pd-coated membrane occurs mainly by adsorption of H_2, followed by dissociation, and the H atoms react catalytically with the Pd in the coating, forming hydrides. After crossing the selective layer, the H atoms reassociate as H_2 [3].

H_2 can be obtained by steam reforming of CH_4, which produces H_2 and CO. Also, biomass pyrolysis can yield CO, CO_2, H_2S, CH_4, and H_2 [4]. In this context, Pd-coated ceramic membranes can promote the separation of CO_2 and CH_4, decreasing the emission of these gases to the atmosphere and possibly recovering H_2 from gaseous mixtures [2-3].

Given the above, this work aimed to assess the performance of Pd-coated α-alumina tubular membranes in the permeation of CH_4 and CO_2, with the permeability of the gases evaluated according to the number of Pd layers deposited.

Materials and methods

The gas permeation tests using CH_4 and CO_2 were conducted individually with a gas permeation system. The system was composed of an inlet hose gas (1), inlet (2) and outlet (6) pressure regulating valve, input (3) and output (5) manometer for pressure measurement, tubular shell (4), rotameter (7) to check the retentate gas flow, and an outlet hose gas (8). A simplified scheme of the test unit is shown in Fig.1.

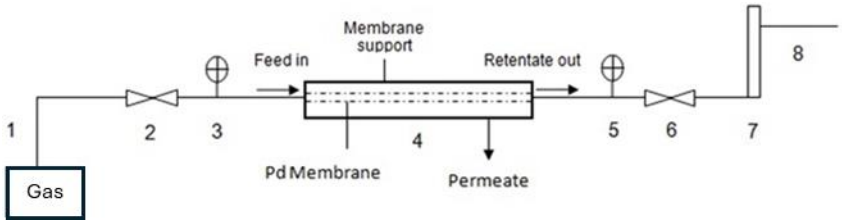

Fig. 1 – Scheme of the gas permeation unit used in the experiments.

The tests were performed using the α-alumina ceramic tube and with the coated membranes, operating crossflow. The rotameter measured the retentate gas flow. All experiments were carried out at 150 kPa. The permeate flux (*Jw*) values were calculated according to Equation 1.

$$J_w = \frac{V}{A \times t} \quad (1)$$

Where *V* is the permeate volume (L), *A* is the membrane area (m^2), and *t* is the permeation time (h).

Results and discussion

The transmembrane fluxes for CH_4 and CO_2 with the tested membranes are shown in Table 1.

Table 1 – CH_4 and CO_2 transmembrane fluxes (*Jw*) with α-alumina tubular membranes coated with increasing layers of Pd, produced by the sol-gel and electroless plating methods.

Number of Pd layers deposited	Pd coating thickness (μm)	CO_2 permeate flux ($L \cdot m^{-2} \cdot h^{-1}$)	CH_4 permeate flux ($L \cdot m^{-2} \cdot h^{-1}$)	Separation factor (J_w CH_4/J_w CO_2)
-	-	189.5	282.4	1.49
1	80	137.0	218.6	1.59
2	170	9.5	19.4	2.04
3	310	7.4	12.9	1.74

According to the results at 150 kPa (Table 1), the permeate fluxes of both gases in the Pd-coated membranes decreased relative to the non-coated α-alumina tube. This increase in gas retention shows a better efficiency of the α-alumina-Pd membranes, with the Pd layers acting as an active layer for the retention and differential separation.

Also, according to the calculated separation factor, a two-layer Pd coating yielded the greatest ratio between the CH_4 and CO_2 fluxes, suggesting that a thicker coating would reduce membrane efficiency by excessively reducing CH_4 permeability. At 150 kPa, the CH_4 and CO_2 permeabilities for the membrane with two Pd layers deposited were 0.13 $L \cdot m^{-2} \cdot kPa^{-1} \cdot h^{-1}$ and 0.06 $L \cdot m^{-2} \cdot kPa^{-1} \cdot h^{-1}$, respectively.

In addition, the membranes had greater CH_4 fluxes, showing that the Pd coating had more affinity with the CH_4 molecules than with CO_2. Such a behavior can result from several factors, ranging from the intrinsic affinity between H and Pd, and the formation of smaller pores within the coating, which allowed the permeation of CH_4 relative to CO_2 since smaller molecules can diffuse faster throughout the membranes.

Conclusion

The membranes had greater chemical affinity with CH_4, probably due to the smaller molecule size and molar mass. A thicker Pd layer increased CO_2 retention at the expense of reducing CH_4 permeability. These preliminary results show an interesting possibility of using such membranes to separate natural gas and CH_4-rich mixtures.

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