Comparison of ceramic α-alumina and modified γ-alumina membranes for H2 separation.

ORAKWE, I., ALKALI, A., SHEHU, H. and GOBINA, E.

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An investigation into the Hydrogen separation, purification and transport behavior of a ceramic α-alumina membrane and its comparison with a γ-alumina membrane modified with AlOOH sol.

[1] Ifeyinwa Orakwe, [1]Abubakar Alkali, [1] Habiba Shehu and [1] Edward Gobina*

Robert Gordon University, Sir Ian Wood Building, Garthdee Road, Aberdeen, AB10 7GJ, United Kingdom.

*Corresponding Author (email: e.gobina@rgu.ac.uk; tel: +441224262348)

***Abstract*- The main purpose of this work is to investigate the hydrogen permeation behavior of a commercial ceramic alumina membrane and compare same with that of a γ-alumina membrane graded with an AlOOH sol using the dip coating method. The permeance of hydrogen and 5 other single gases (He, N_2, CH_4, CO_2 and Ar) were investigated at high temperatures. Mixed gas permeation tests for a H_2 gas mixture were also carried out. Results show that the permeance of H_2 increased with increasing temperature for the graded γ- Al_2O_3 membrane while it decreased for the α-Al_2O_3 support. For the single gas tests, the α-Al_2O_3 support show higher permeance of up to 9.45 x 10^{-3} mol m^{-2} s^{-1} Pa $^{-1}$ compared to 1.03 x 10^{-3} mol m^{-2} s^{-1} Pa^{-1} for the γ-Al_2O_3 but the graded substrate was permeable to only H_2 at fifth coating. The mixed gas tests for a gas mixture (H_2= 50%, CO= 28%, CO_2=10% CH_4=8%, N_2=4%) show lower H_2 permeance which was attributed to the inhibition effect of CO_2 in the gas mixture. The H_2/N_2 permselectivity for both membranes was lower than the theoretical Knudsen value of 3.73 which suggests a viscous flow transport mechanism.**

***Index Terms*: Hydrogen, Alumina, Membranes, Dip-coating, Permeance.**

***Introduction*:** Membrane technology for hydrogen separation and production processes is becoming an important and enabling technology in the current global decarbonisation efforts aimed at combating climate change and ensuring energy security. It is still 'work in progress' before H_2 is fully adopted as the global energy carrier to replace fossil fuels. During this transition period from fossil fuels to H_2, research into several H_2 separation and purification processes is gaining increased attention. One of these processes is membrane technology which offers several advantages in hydrogen processes including energy efficiency, cost effectiveness and infinite selectivity to hydrogen for dense palladium membranes when defect free. Alumina membranes are thermally and chemically stable and can withstand harsh operating conditions.

***Experimental*:** The experiment was carried out for a macroporous α- alumina support with a 30 nm pore size and i.d= 7mm, o.d= 10 mm, effective length= 0.34 m. Another 30 nm α-alumina support was graded with AlOOH sol and converted to γ-alumina by 5 sequential dippings using the dip coating method. The objective was to investigate the hydrogen permeation and selectivity at high temperature including the gas transport mechanisms. The tubes were dried at 65 ^oC for 2 hours in an oven to remove any water vapor or moisture and sealed at both ends. The modification of the α-Al_2O_3 support was carried out through a multilayer deposition process using a dipping-drying-calcining method. After each dipping, the support was dried for 10 hours at 65 ^0C and calcined at 873 K for 24 hours. Permeation tests were carried out in a membrane reactor module at 298, 323, 373, 473 and 573K.

***Theoretical Considerations*:** The permeance, $\boldsymbol{F}_o$ of a gas through the multilayered inorganic membrane is the gas flux, $\boldsymbol{Q}$ (i.e., the gas flowrate, of divided by the membrane area, A) divided by the pressure drop, P_1-P_2 across the membrane. In the simplest approximation the permeance is the sum of a Viscous and Knudsen contribution and can be described by equation 1:

$$F_0 = F_{Knudsen} + F_{Viscous}\left(\frac{mol}{m^2 s}\right) \qquad (1)$$

where $F_{Knudsen}$ and $F_{Viscous}$ are the Knudsen and viscous contributions respectively and are defined by:

$$F_{Knudsen} = \frac{8r_p(P_1 - P_2)}{3\delta(2\pi MRT)^{\frac{1}{2}}}\left(\frac{mol}{m^2 s}\right) \qquad (2)$$

$$F_{Viscous} = \frac{r_p{}^2(P_1^2 - P_2^2)}{16\delta\mu RT}\left(\frac{mol}{m^2 s}\right) \qquad (3)$$

Substituting equations (2) and (3) into equation (1) gives equation 4:

$$F_0 = \frac{8r_p(P_1 - P_2)}{3\delta(2\pi MRT)^{1/2}} + \frac{r_p{}^2(P_1^2 - P_2^2)}{16\delta\mu RT} \qquad (4)$$

Equation (4) can be normalized to take into consideration the separating layer thickness. This is

achieved by multiplying both the L.H.S. and R.H.S. of equation 4 by $\frac{\delta}{(P_1 - P_2)}$ to give equation (5):

$$\frac{F_0\delta}{(P_1 - P_2)} = F_T = \frac{8r_p}{3(2\pi MRT)^{1/2}} + \frac{r_p{}^2(P_1 + P_2)}{16\mu RT}\left(\frac{molm}{m^2 sPa}\right) \quad \textbf{(5)}$$

where F_T is the normalized permeance or permeability of the multilayered membrane.
Equation (5) can also be written in the more convenient form of equation 6:

$$F_T = \frac{8r_p}{3(2\pi MRT)^{1/2}} + \frac{r_p{}^2}{8\mu RT}\left(\frac{(P_1 + P_2)}{2}\right)\left(\frac{molm}{m^2 sPa}\right) \quad \textbf{(6)}$$

Equation (6) can be written in a more compact form as:

$$F_T = K_0 + B_0 P_{Average} \quad \textbf{(7)}$$

where:

$$K_0 = \frac{8r_p}{3(2\pi MRT)^{1/2}}\left(\frac{molm}{m^2 sPa}\right), \quad B_0 = \frac{r_p{}^2}{8\mu RT}\left(\frac{molm}{m^2 sPa^2}\right), \text{ and}$$

$$P_{Average} = \left(\frac{(P_1 + P_2)}{2}\right)(Pa)$$

Equation (7) is straight line of F_T is plotted against $P_{Average}$ resulting in a slope equal to B_0 and an intercept on the F_T axis equal to K_0. The nature of the straight line will indicate the extent of the F_T relative contributions of Viscous and Knudsen flow.

If the graph plotted is of the form $F_T = B_0 P_{Average}$ then the flow is characterised by viscous flow. If, however, the graph plotted is of the form $F_T = B_0 P_{Average} + K_0$, then both the Knudsen flow and viscous flow contribute to the transport characteristics. Analysis of the intercept and the slope will then yield the values of an K_0 and B_0, which upon substitution into equation (6) will enable estimation of the pore radius of the multilayered membrane.

Examination of equations (2) and (3) shows that several possibilities exist.
(i) For Knudsen flow:

$$\frac{F_{0,A}}{F_{0,B}} = \sqrt{\frac{M_B}{M_A}} \quad \textbf{(8)}$$

(ii) For Viscous flow:

$$\frac{F_{0,A}}{F_{0,B}} = \frac{\mu_B}{\mu_A} \quad \textbf{(9)}$$

The mean free path of a gas molecule is given by equation (10):

$\lambda = 2r_p$.Knudsen Coefficient (m) **(10)**

In the equation (7), both B_0 and K_0 depend on the membrane material characteristics such as thickness of the separating layer, the porosity, tortuosity, and pore radius. Temperature and type of gas also influence B_0 and K_0 as described by equation (11):

$B_0 \sim 1/\mu T$ and $K_0 \sim 1/MT$ **(11)**

where μ is the viscosity, T the temperature and M the gas molecular weight. Viscosities of most gases are relatively close to each other and therefore it is obvious that the gas separation will mainly depend on the difference in the molecular weight, and this will be determined by the Knudsen flow contribution of equation (6) as shown in equation (8) for a gas mixture containing components A and B.

Equation (7) is only a simple approximation where the pressure difference is the driving force for gas transport through the multilayered membrane and does not consider other transport mechanism such as surface flow, multilayer diffusion, capillary condensation, and molecular sieving. It however gives a good indication of the performance and quality of the membrane provided that the necessary precautions are achieved to before and during gas transport measurements.

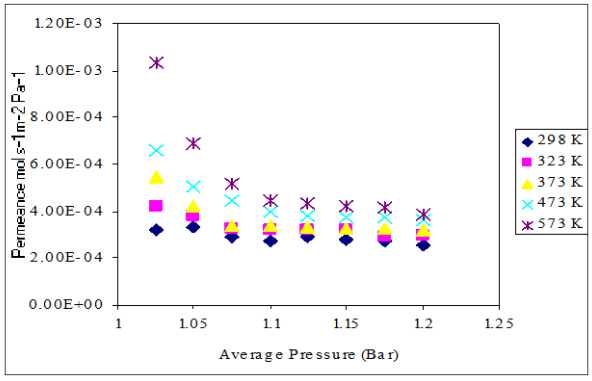

Fig.1. H_2 permeance as a function of average pressure at different temperature for the γ-Al_2O_3 membrane at first coating.

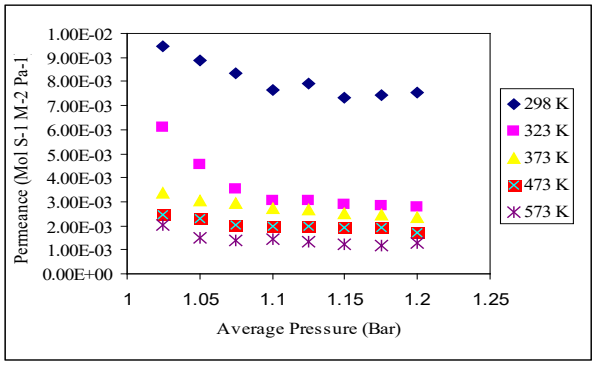

Fig. 2. H_2 permeance as a function of average pressure at different temperature for the α- Al_2O_3 membrane.

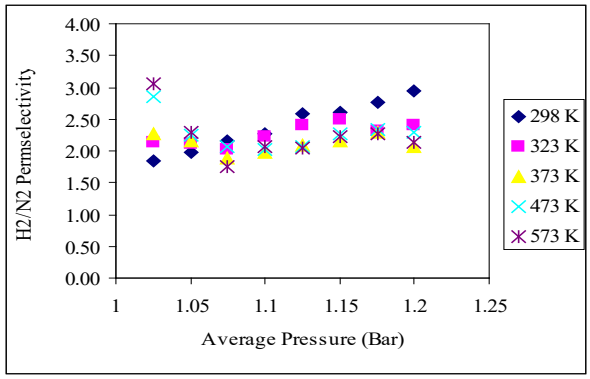

Fig. 3. H_2/N_2 permselectivity for the γ-alumina membrane at different temperature.

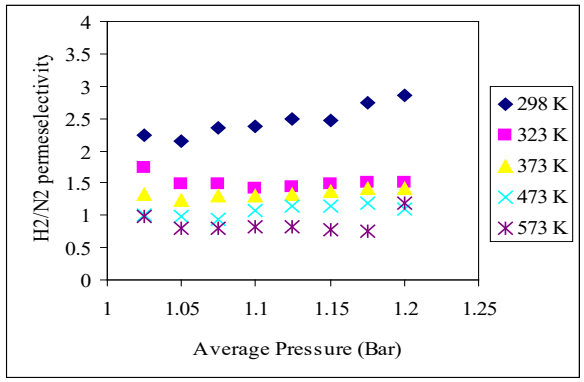

Fig. 4. H_2/N_2 permselectivity for the α-alumina membrane at different temperature.

Results and Discussion: In Fig.1 the H_2 permeance increased with temperature but decreased with the number of coatings as more layers of the Boehmite sol were deposited. This decrease in permeance is in conformity with the principle that the higher the membrane thickness, the higher the resistance to permeation and therefore the lower the permeance. The γ-Al_2O_3 substrate was only permeable to H_2 at fifth coating. In Fig. 2 the decrease in H_2 permeance with increasing temperature for the α-Al_2O_3 support indicates low mobility of the gas molecules in the pores and suggests that surface adsorption was inversely proportional to temperature hence high temperature negates surface diffusion of hydrogen in the α-alumina support while low temperature enhances it. In Fig 3, the maximum H_2/N_2 permselectivity of 3.07 was measured for the γ-alumina at 573 K while in Fig. 4, it was 2.9 for the α-alumina support at 298 K and both are lower than the Knudsen value of 3.73 which suggests the existence of viscous flow mechanism. The slightly higher H_2/N_2 permselectivity of the γ-alumina substrate at 3.07 indicates less dominance of viscous flow and more closeness to Knudsen diffusion.

The SEM image in Fig. 5 shows the α-Al_2O_3 structure increasingly open and flowery with more open pores layer wise going top, intermediate, and inner.

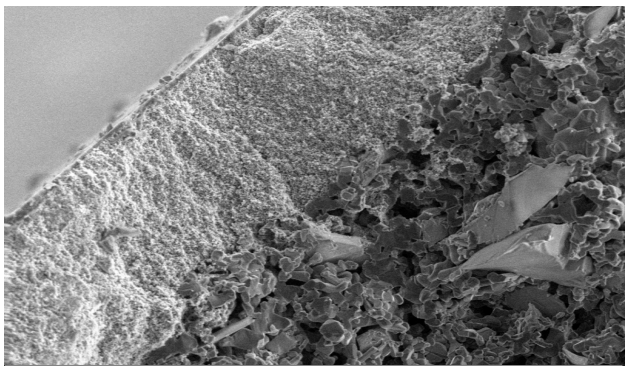

Fig. 5 SEM image of cross-sectional area of the macroporous α-alumina support (resolution 1000 x)

Conclusion: A commercial Al_2O_3 support was graded with Boehmite sol using the dip coating method and its hydrogen permeation behaviour and H_2/N_2 permeslectivity investigated. The results for the graded γ-Al_2O_3 substrate were compared with those of a macroporous α-Al_2O_3 support. The results show that H_2 permeance increases with temperature for the γ-Al_2O_3 membrane while it decreases for the α-Al_2O_3 substrate. The measured H_2/N_2 separation ratios indicate a viscous flow mechanism.

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