A comparative evaluation of the hydrogen separation, purification and transport behavior of α-alumina membrane and γ-alumina membranes modified with AlOOH sol.

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A COMPARATIVE EVALUATION OF THE HYDROGEN SEPARATION, PURIFICATION AND TRANSPORT BEHAVIOR OF α-ALUMINA MEMBRANE AND γ-ALUMINA MEMBRANES MODIFIED WITH AlOOH Sol.

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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 showed 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 9.45×10^{-3} mol m^{-2} s^{-1} Pa^{-1} compared to 1.03×10^{-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 close to the theoretical Knudsen value of 3.73 which suggests a combined viscous and Knudsen flow transport mechanism.

Keywords: 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. Membrane filtration technology is a tried, tested, and proven method and is used in many industrial process streams, and now being adopted in applications such as biofuels production, integrated biorefineries, hydrogen production, purification, and integrated reactor systems. Membrane filtration technology shows promise to improve and facilitate carbon capture, storage, and utilization (CCUS) to help attain net-zero by 2050. Membranes are highly engineered, physical structured barriers that are used in processes for gas/gas, gas/liquid, liquid/liquid, and liquid/solid separation. They allow the passage of materials only within a window based on certain size, shape, or character. Today, particular attention is being paid to using membrane separation techniques that facilitate continuous, rather than batch, processes [1-11].

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 (Fig. 1). The tubes were dried at 65°C 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 similarly carried out through a multilayer deposition process using a dipping-drying-calcining method (Fig. 1). After each dipping, the support was dried for 10 hours at 65 °C and calcined at 873 K for 24 hours. Permeation tests were carried out in a membrane reactor module (Fig. 2) at 298, 323, 373, 473 and 573K.

RESULTS AND DISCUSSION

In Fig.3 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. 4 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 5, the maximum H_2/N_2 permselectivity of 3.07 was measured for the γ-alumina at 573 K while in Fig. 6, 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. 7 shows the α-Al_2O_3 structure increasingly open and flowery with more open pores layer wise going top, intermediate, and inner.
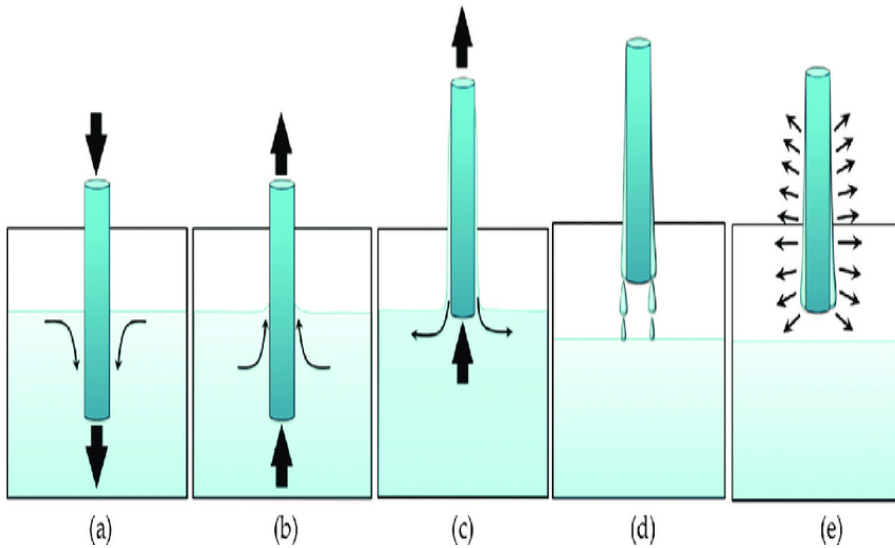

Fig. 1: Dip-coating stages: (a) immersion (b) start-up; (c) deposition; (d) drainage   and (e) evaporation
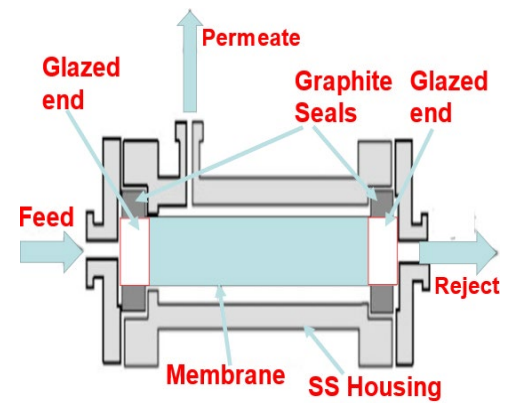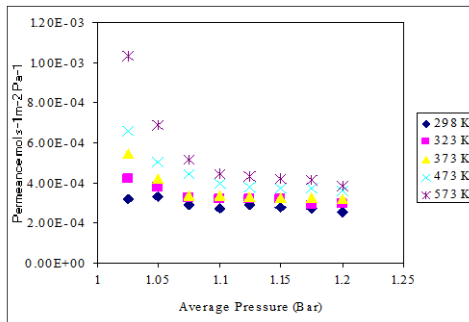

Fig 2: Membrane permeator

Fig.3. H_2 permeance as a function of average pressure at different temperature for the γ-Al_2O_3 membrane
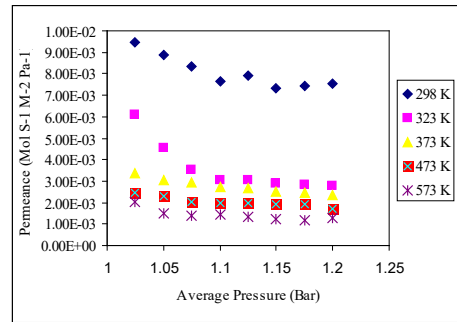
Fig. 4. H_2 permeance as a function of average pressure at first coating. at various temperature for the α-Al_2O_3 membrane.
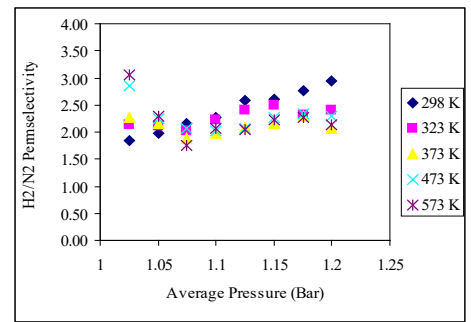
Fig. 5. H_2/N_2 permselectivity for the γ-alumina membrane at different temperature.
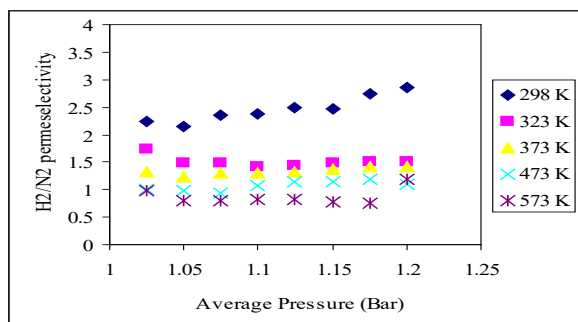
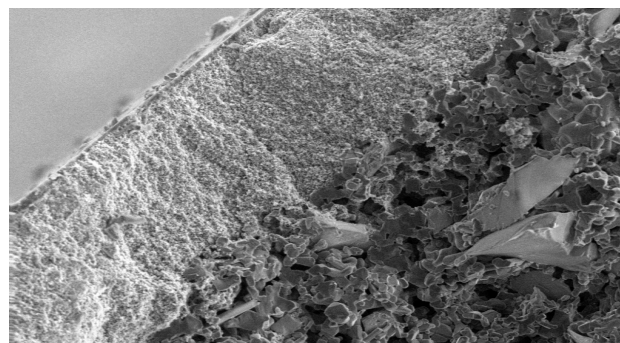Fig. 6. H$_2$/N$_2$ permselectivity for the α-alumina membrane at different temperature.

Fig. 7: SEM image of cross-sectional area of the macroporous α-alumina support (resolution 1000 x)

CONCLUSION

A commercial Al$_2$O$_3$ support was graded with Boehmite sol using the repeat dip-coating method and its hydrogen permeation behaviour and H$_2$/N$_2$ permeslectivity investigated. The results for the graded γ-Al$_2$O$_3$ substrate were compared with those of a macroporous α-Al$_2$O$_3$ support. The results show that H$_2$ permeance increases with temperature for the γ-Al$_2$O$_3$ membrane while it decreases for the α-Al$_2$O$_3$ substrate. The measured H$_2$/N$_2$ separation ratios indicate a combination of Knudsen and viscous flow mechanisms. The templated membranes provide the core-shell structured membrane for various applications in catalytic processes. The pores could be easily impregnated with catalytic materials to form catalytic membrane reactors because they have a high BET surface area, hierarchical porosity, and good permeability. In catalytic reactors membrane is fabricated using metal-dispersed nanoparticle-embedded pores and was successfully used for membrane catalysis in which the reactants could easily penetrate the wall of the membrane to contact the active metal nanoparticles, resulting in the high catalytic activity. The catalysts loaded in the membrane are not restricted to the nanoparticle. Various metal catalytic species such as Ag, Pt, Pd can be immobilized in the micro- and mesopores of the membrane and can be further modified with specific functional groups through post reaction, to provide specific binding sites for other active components of interest.

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