N_2, He AND CO_2 DIFFUSION MECHANISMS THROUGH NANOPOROUS YSZ/γ-AL$_2$O$_3$ LAYERS AND THEIR USE IN A PORE-FILLED MEMBRANE FOR MEMBRANE REACTORS

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Introduction

Application of Pd-based membranes in membrane reactors can decrease the operating temperature of the reactor while maintaining the reactant conversion and obtain benefits in terms of energy efficiency and reduction of material and volumes. However, the cost of Pd-based membranes could increase dramatically if large scale applications are foreseen, especially due to the resource scarcity of Pd [1]. This problem could be circumvented by producing very thin Pd layers which would bring two benefits: i) increase in permeation rates (decrease of membrane area required), and ii) decrease in the amount of Pd required (decrease of costs). Nevertheless, thin Pd layers would easily be damaged by contact with catalyst particles. In this work we investigate the possibility to produce Pd-based pore-filled membranes, i.e. membranes where the Pd layer is in the pores of a porous structure such that the layer can be very thin but still protected against any damage due to interaction with catalysts [2]. The nanoporous layers were obtained by deposition of YSZ/γ-Al$_2$O$_3$ nanoparticles (from 50% to 90% of YSZ) on top of ceramic supports (α-Al$_2$O$_3$) with initial pore size of 100 nm by dip-coating technique and followed by calcination at 550ºC in air during 3 hours. The pores are filled with palladium and a protective layer is added in order to avoid surface attrition when the membranes are integrated in (fluidized bed) membrane reactors.

Experimental and results

The diffusion mechanisms of N_2, He and CO_2 have been studied in a temperature range of 50-400 ºC with a pressure difference of 0,3-1,0 bar. The effect of layer composition, temperature and pressure on permeation and selectivity were analyzed (Figures 1 to 6).

GAS PERMEATION PROPERTIES

Effect of layer composition

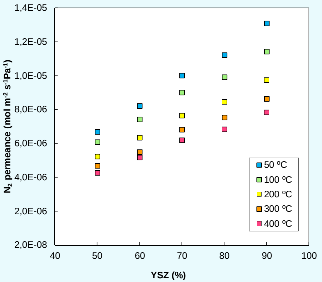

Fig. 1. N2 permeance at 1 bar of pressure difference as a function of YSZ content for different operating temperatures.

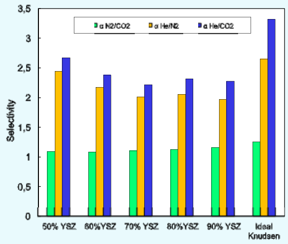

Fig. 4. Selectivity at 1 bar of pressure difference and 400°C as a function of YSZ content.

Effect of temperature

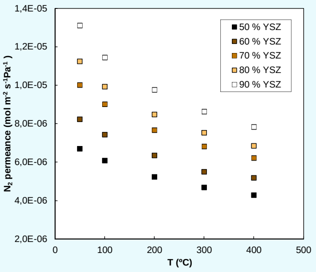

Fig. 2. N2 permeance at 1 bar of pressure difference as a function of operating temperature for mesoporous layers with different YSZ content.

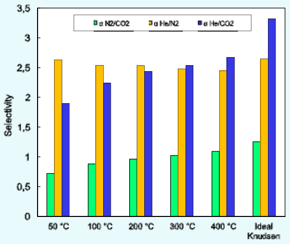

Fig. 5. Selectivity at 1 bar of pressure difference as a function of operating temperature for mesoporous layers with different YSZ content.

Effect of pressure

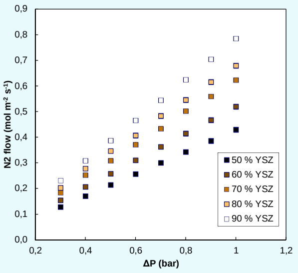

Fig. 3. N2 molar flow at 400°C as a function of pressure difference for mesoporous layers with different YSZ content.

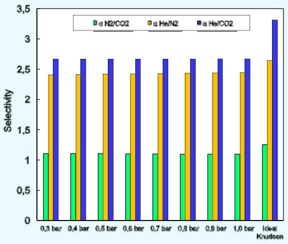

Fig. 6. Selectivity at 400°C as a function of pressure difference for nanoporous layer with 50 wt.% YSZ.

MICROSTRUCTURAL ANALYSIS

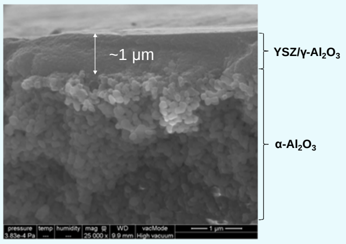

Fig.7. SEM cross section images of PF-A64 with 70 wt% YSZ

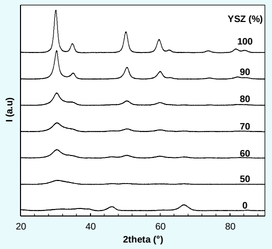

Fig. 8. XRD pattern of samples calcined at 550° in air for 3 h.

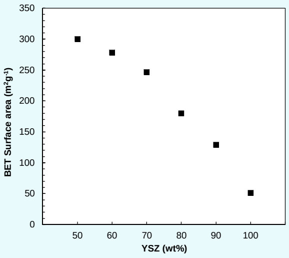

Fig. 9. Surface area of samples calcined at 550° in air for 3 h.

Conclusions

- The pore size of nanoporous layers decreases as the amount of γ-Al$_2$O$_3$ increases, (lower number of defects and viscous flow contribution)
- At 400 ºC as the content in γ-Al$_2$O$_3$ increases the selectivity increases from ~2,2 (10 wt% γ-Al$_2$O$_3$) to 2,7 (50 wt% γ-Al$_2$O$_3$).
- The He/CO_2 separation factor decreases as the operation temperature decreases. Nanoporous layers with 50 wt% γ-Al$_2$O$_3$ represent the best option for formation of pore-filled membranes.

References

[1] A. Helmi et al, International Journal of Hydrogen Energy , 39 (2014) 10498-10506 [2] D.A. Pacheco Tanka et al, Journal Membrane Science, 320 (2008) 436-441

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