Stability of ceramic supported PdAg membranes for hydrogen production in a fluidized bed membrane reactor

Palladium membrane, fluidized bed membrane reactor, Membrane stability, membrane sealing, steam methane reforming.

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STABILITY OF CERAMIC SUPPORTED PD/AG MEMBRANES IN A FLUIDIZED BED MEMBRANE REACTOR FOR METHANE STEAM REFORMING

Introduction

The development of membrane reactors for the production of hydrogen has received significant research attention in the last decade. With the integration of membranes in the reactor a high degree of process intensification can be achieved. The excellent permeation properties of the Pd-based membranes, i.e. very high permeation fluxes combined with very high perm-selectivities, makes them particularly attractive for integration in membrane reactors. The application of these membranes in packed-bed membrane reactor configurations have shown difficulties due poor heat and mass transfer rates [1], which has initiated research on fluidized bed membrane reactors with their more favourable heat and mass transfer properties. However, experiments in fluidized bed membrane reactors have shown a significant decrease in perm-selectivity with time-on-stream [3][4]. The purpose of this work is to identify the main parameters that contribute to this decrease in perm-selectivity. A better understanding of the origin of the decrease in selectivity can help the further development of more stable membranes and selection of durable operation conditions.

Experimental

In this study ceramic supported Pd-based membranes have been used, that were produced by electroless plating. The membranes were sealed using a Swagelok sealing method with graphite ferrules, presented by Fernandez et al. [5]. Supports with different diameter and thickness have been tested which allowed varying the torque applied on the sealing. Both open-end and finger like membranes have been used and compared. A picture of the membranes has been provided in Figure 1. All the membranes were tested in a multitubular reactor, where the feed, temperature and pressure were controlled and monitored. In such a way, all membranes have experience the same temperature ramps and pressures, making easier a direct comparison between membranes. The flux through the membrane was measured with a Horiba film flow meter. Post-characterization was carried out using an ethanol leak test, SEM and XRD in order to identify the main causes for the decrease in perm-selectivity.

Results and discussion

The different membranes were first stablized using pure hydrogen for over 1000 h at 500 °C. For all the tested membranes, initially ideal H_2/N_2 perm-selectivities of around 10,000 were obtained. However, the perm-selectivity decreased in time, as shown in Figure 2, which is attributed to an increase in the nitrogen leakage, in the worst case up to 8 times the initial nitrogen permeance. After the stabilization period, the membranes were immersed in a fluidized bed. The effect of different particle sizes, temperatures and reactive/inert conditions on the membrane peformance was investigated, where the rate of hydrogen and nitrogen flux increase or decrease is used to compare the different membranes and the different conditions.

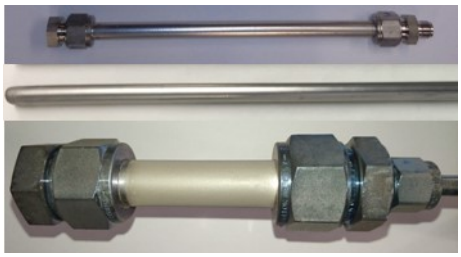

Fig. 1. Membranes from top to bottom, 7 Nm sealed swagelok, finger like and 14 Nm sealed swagelok membrane.

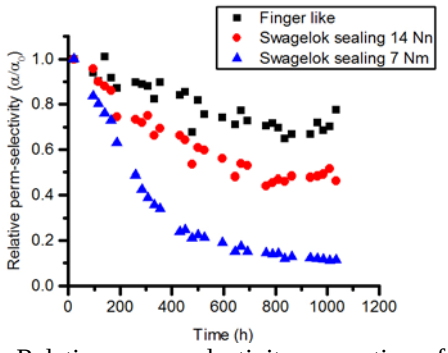

Fig. 2. Relative perm-selectivity over time for three differently sealed membranes (T=500 °C)

Conclusions

The experimental results will show that under gas separation conditions the decline in perm-selectivity can be mainly attributed to the sealing technique. The decrease in selectivity can be significantly improved by finger like membranes. The stability of the membranes is affected by the presence of the fluidized gas-solid suspension. Further studies on the stability of the membranes under fluidizing conditions is ongoing. The results of this study will provide further insights on the parameters contributing to the loss of selectivity during operation.

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