Modelling of a Pd-Ag Membrane Reactor for the Production of Ultrapure H_2 from the Dry Reforming of Methane

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Introduction

The endothermic dry reforming reaction is favored at high temperatures. Through the use of membrane reactors (MR), it is possible to operate at lower temperatures while increasing the H_2 yield. As a bonus, pure H_2 is obtained in a single vessel. To predict the influence of key process variables on conversion and product composition, a good reactor model is required. A mathematical model is proposed here to simulate the membrane reactor using a palladium-silver membrane with 100% hydrogen selectivity. This study uses the kinetic equations reported by Múnera et al. [1,2] for the dry reforming on Rh/La_2O_3 and Rh/La_2O_3-SiO_2 catalysts and those for the water gas shift reaction (WGSR) we obtained for the modelling.

Materials and Methods

A tube and shell reactor configuration was used; the catalyst was placed in the shell side. The following assumptions were incorporated to the mathematical model:

1. The internal mass transfer resistance of the packed catalyst had no limiting effect due to the small size of the catalyst particles.
2. One–dimensional tubular reactor with no radial concentration and temperature gradient and axial dispersion on both the tube and shell sides, and no gas film resistance to heat and mass transfer at the membrane walls. The validity of this assumption was checked applying the criterion reported by Mears [3] for laboratory reactors.

Mass balance for a differential reactor volume along the z-axis in the MR:

Reaction zone (shell side) *Permeation zone (tube side)*

$$\frac{dQ_i}{dz} = \frac{W_C}{V_r}\sum_{j=1}^{2} \upsilon_i r_i + 2\frac{N_i R_1}{(R_3^2 - R_2^2)} \qquad \frac{dQ'_i}{dz} = 2\frac{N_i}{R_2 - R_1}$$

Where Qi and Q'$_i$ are the axial molar flow rate of the ith species in both membrane sides, W_C is catalyst weight, V_r is reactor volume, υ_i and r_i are stoichiometric coefficients and reaction rate for dry reforming and the RWGS reactions, R_1 and R_2 are inner radius of the sweep gas tube and of the permeation tube, respectively; R_3 is inner radius of the shell and N_i the permeation flux of hydrogen. The system of differential equations was solved using the Bulirsch-Stoer (Bulstoer) method available in the 1997 Mathcad Professional package.

Results and Discussion

An important parameter which influences the performance of the MR is the sweep gas flow rate. Fig 1a shows its effect on both methane conversion and permeated H_2/methane fed ratio for the Rh catalysts. At higher flow rates, the reactant conversion increases due to the reduction of hydrogen partial pressure in the permeate side. The increase of both quality parameters becomes relatively small between 30 and 40 ml/min. This could be due to the small membrane area used and the low hydrogen permeation flux. We have compared the results from the mathematical models of dry reforming reaction in the membrane reactor with the experimental results for different sweep gas flow rates [4]. No similar comparison has been previously published for this reaction. The simulation results fit the experimental values fairly well under all conditions.

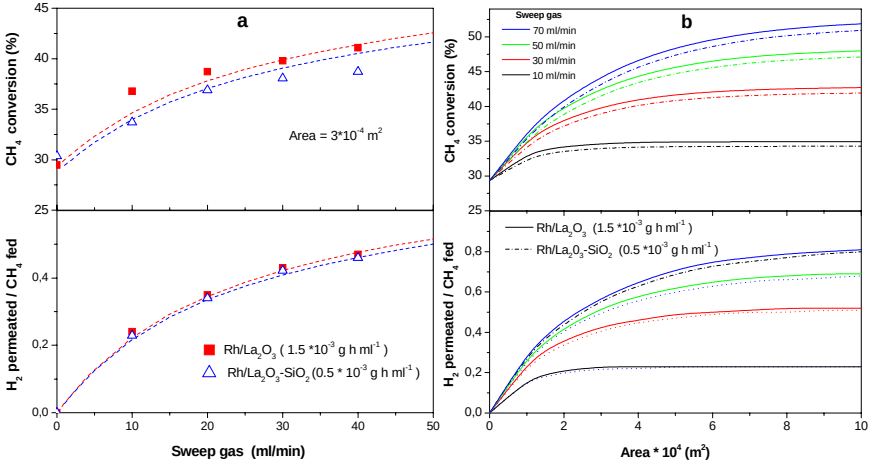

Figure 1. a) Effect of sweep gas flow rate (Comparison of theoretical and experimental results) and b) Effect of permeation area and sweep gas flow rate, on methane conversion and permeated hydrogen. Theoretical results, T= 823 K, P=1Atm.

Fig. 1b shows the simulated values of both methane conversion and permeated H_2. Note that at any given sweep gas flow rate, both parameters reach plateau values with the size of the permeation areas. Increasing the permeation area above ca. 8 x 10^{-4} m^2 and the flow rate above 70 ml/min has little effect upon the reactor performance. The differences in performance of both catalysts are minimal in agreement with the similar kinetic parameters (not shown) of both systems.

Significance

The good fit is an indication of the ability of the model to predict the membrane reactor behavior when reliable kinetic data are employed.

References

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