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Enhancement of Equilibriumshift in Dehydrogenation Reactions Using a Novel Membrane Reactor

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ABSTRACT

A mathematical model is developed to describe the permeation of hydrogen through thin-film palladium ceramic composite membrane in countercurrent flow configuration. Numerical simulation results were compared with the cocurrent flow model. The results show that due to high perm-selectivity of the new Pd-ceramic composite membrane, flow configurations have marginal effect on the product purity and recovery. Both the cocurrent and counter current model neglect the gas phase mass transfer resistance. When compared with the experimental hydrogen flux data, the difference between the predicted and actual hydrogen composition was less than 12%. The models appear to adequate for predicting the membrane module performance and may be used as in developing the membrane reactor-separator model to study the equilibriumshift in dehydrogenation reactions.

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EXECUTIVE SUMMARY

In recent years, there has been increased interest in developing inorganic and composite membranes for in-situ separation of hydrogen to achieve equilibrium shift in catalytic membrane reactors. However, the productivity of these membrane reactors is severely limited by the poor permeability and selectivity of currently available membranes. To develop a new class of permselective inorganic membranes, we have used electroless plating to deposit a thin palladium film on a microporous ceramic substrate. The work was funded by a grant from the U.S. DOE. Test results indicate that the new membrane has both a high permeability and selectivity for hydrogen. This new membrane has the potential to find application in high temperature hydrogen separations and membrane reactors.

In this work, we propose to study at least one of the industrially significant catalytic dehydrogenation reactions to demonstrate the application of the newly developed thin-film palladium composite membranes for hydrogen separation and equilibrium shift in a membrane reactor. Specifically, we plan to study the enhancement of equilibrium shift in the dehydrogenation of cyclohexane to benzene using our new membrane in a novel membrane reactor-separator.

In this report, we present a mathematical model that describes the performance of cocurrent and countercurrent permeation cells. Although the model neglects mass transfer resistance in the gas phase, the results show that the model is adequate in predicting the performance of the membrane module. We plan to include dehydrogenation reaction in the model and evaluate the performance of the membrane reactor-separator under cocurrent and countercurrent flow configuration. This will be useful in designing the experiments on dehydrogenation of cyclohexane in membrane reactor-separator by equilibrium shift.

INTRODUCTION

The overall objective of this project is to develop inorganic and composite membranes for in-situ separation of hydrogen and equilibrium shift in catalytic membrane reactors. The specific objectives of this research are to:

1. Design and fabrication of catalytic membrane reactor using thin film palladium-composite membrane for dehydrogenation of cyclohexane to benzene
2. Conduct dehydrogenation reaction experiments to study the equilibrium shifts and hydrogen permeation characteristics
3. Develop a theoretical foundation for equilibrium shifts and hydrogen transport in the membrane reactor

Mathematical Model: Countercurrent Flow Membrane Module

In our previous report we presented a cocurrent flow model to describe the permeation of hydrogen through palladium-ceramic composite membrane in a membrane module. In this report, we extend the work to a membrane module with countercurrent flow.

The permeation of hydrogen through a palladium film is a complex process. The process begins with sorption of hydrogen molecules on the film surface and ends with hydrogen desorption from the ceramic substrate. It is believed that the hydrogen molecule dissociates into hydrogen atoms on one side of the film. The hydrogen atoms then diffuse through the film and reassociate on the other side. Since the reaction kinetics for the formation of hydrogen atoms from molecules and the reverse reaction are assumed to be very fast, the permeation of the hydrogen atoms through the film is the rate limiting step. Permeability can be considered as product of solubility and diffusivity. The permeation rate of hydrogen can be given by:

$$J_a = \frac{Q_a}{h} \left[(P X_a)^n - (P Y_a)^n \right] \quad (1)$$

If diffusion through the bulk metal is the rate limiting step and hydrogen atoms form an ideal solution in the metal, then Sievert's law holds for hydrogen solubility dependence and n is equal to 0.5. The hydrogen flux is inversely proportional to the palladium film thickness, (h) when the bulk diffusion is the rate limiting step. For polymeric membrane, where selective transport of a gas is by a solution-diffusion process, the index n is 1. For thin-film Pd-ceramic composite membrane, since n lies between 0.5 to 1. The new design of membrane module requires detailed analysis of the flow patterns for gas separations using Eqn. (1). A unified model was formulated to study membrane dependent index n varying from 0.5 to 1. for cocurrent and countercurrent flow configurations with two permeable components and a non-permeable fraction in the feed and a sweep stream in the permeate.

Formulation of a Countercurrent Flow Model

The countercurrent flow model is shown schematically in Figure 1. For this case, the feed gas and sweep gas flow in opposite directions. For this model, the material balances are taken between the reject end and any point along the membrane. For this case, L and V have opposite mathematical signs. The feed flow direction was arbitrarily selected to be positive. The differential equations which relate changes in Y_a and R with x_a can be expressed as:

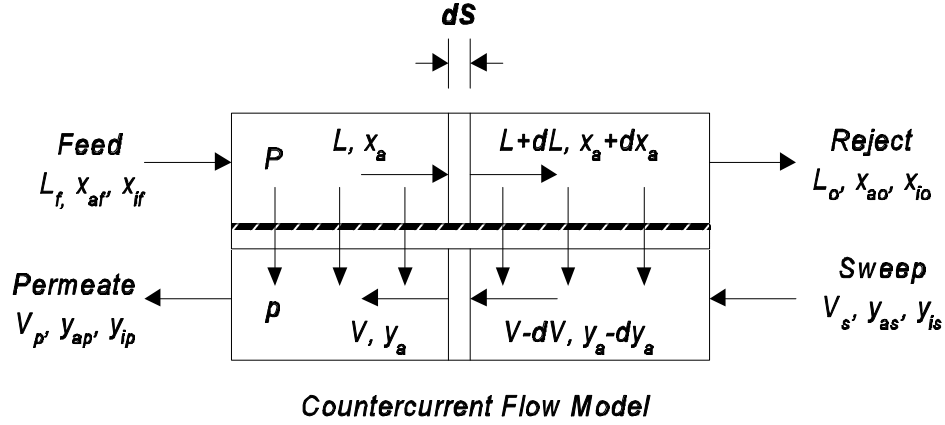


Figure 1: Schematic diagram of single-stage membrane module with countercurrent flow pattern.

$$\frac{dy_a}{dx_a} = \frac{y_a - x_{ao} + F_o (y_a - y_{as})}{x_a - x_{ao} + F_o (x_a - y_{as})} \times \frac{A(1 - y_a) - By_a}{A(1 - x_a) - Bx_a} \quad (2)$$

$$\frac{dR}{dx_a} = \frac{y_a - x_{ao} + F_o (y_a - y_{as})}{y_a - x_a} \frac{L_o}{L_f} \frac{1}{A(1 - x_a) - Bx_a} \quad (3)$$

where F_o is defined as the ratio of sweep gas to feed gas flowrates. Defining R_o as the total dimensionless area, the boundary conditions are given as:

$$\begin{aligned} \text{at } R=0; & \quad L=L_f, \quad x_a=x_{af}, \quad \text{and} \quad x_i=x_{if} \\ \text{at } R=R_o; & \quad V=V_s, \quad y_a=y_{as}, \quad \text{and} \quad y_i=y_{is} \end{aligned} \quad (4)$$

Following the analysis as for the cocurrent flow model, the local flowrates and nonpermeable component composition on each side of the membrane can be calculated by the following equations:

$$\begin{aligned}
 L &= \frac{Y_a - X_{ao} + F_o (Y_a - Y_{as})}{Y_a - X_a} L_o \\
 V &= \frac{X_{ao} - X_a + F_o (Y_{as} - X_a)}{Y_a - X_a} L_o \\
 X_i &= \frac{L_o X_{io}}{L} = \frac{X_{io} (Y_a - X_a)}{Y_a - X_{ao} + F_o (Y_a - Y_{as})} \\
 Y_i &= \frac{V_s Y_{is}}{V} = \frac{Y_{is} F_o (Y_a - X_a)}{X_{ao} - X_a + F_o (Y_{as} - X_a)}
 \end{aligned} \tag{5}$$

For the special case of no sweep gas on permeate side, the composition of component a in the permeate side (Y_{as}) cannot be specified and is related to the reject state. At the reject point, Y_{as} can be expressed as:

$$\frac{Y_{as}}{1 - Y_{as}} = \frac{X_{ao}^n - (Y_{as})^n}{X_{bo}^n - (Y_{bs})^n} \tag{6}$$

Using Eqn. (6), Y_{as} can be solved in terms of the reject conditions. Eqn. (2) appears to be indeterminate at the reject state because $V_s = 0$, and $Y_a = Y_{as}$, but L'Hospital's rule can be used to determine the derivative, $(dy_a/dx_a)_o$. After determining the values of Y_{as} and $(dy_a/dx_a)_o$, Eqn. (2) can be solved. The method of calculation is the same as for the corresponding case with purging, but it is better to start solving Eqn. (2) from the reject end using the initial value of $(dy_a/dx_a)_o$.

Model Solution Methodology

A typical design problem is to determine the states of the permeate and reject streams and the membrane area requirement for given feed and sweep gases conditions. Thus, the flowrates (L_f and V_s), compositions (x_{af} , y_{if} , y_{as} , and Y_{is}) of feed and sweep gases and three model parameters (n , α , and β) are given. Thus, there are seven unknown variables to be determined by six equations (Eqns. 2, 3 and 4). Therefore, one variable can be freely chosen for a parametric study. In this work, the differential equations, Eqns. 2 and 3 were solved using the Runge-Kutta-Gill method as a boundary value problem.

RESULTS AND DISCUSSION

The hydrogen flux data were used to estimate the value of n in Eqn. (1) using Marquardt-Levenberg non-linear least squares method. For the $8.5 \mu\text{m}$, $9.77 \mu\text{m}$, and $12 \mu\text{m}$ films, the average values of n were estimated as 0.778, 0.513 and 0.501, respectively for pure hydrogen. From this analysis, it appears that a palladium film of $12 \mu\text{m}$ thickness approaches the limiting definition of a dense Pd-film according to Sievert's law. Flux data for pure gases (He, Ar, and CO_2) were also analyzed. The values of index n were found to be 1.1 for helium, and 1.81 for both carbon dioxide and argon. The results show that the hydrogen flux increases with increasing temperature for a given driving force.

Mathematical model for countercurrent flow patterns was used to predict the experimental data for H_2/N_2 mixture gas at 573 K. In the computer simulation, the selectivity (α) and the power index (n) were taken as 800 and 0.623, respectively. The stage-cuts were determined from the experimental data. Hydrogen composition data in the permeate and reject streams are compared to model predictions in Figure 2(a,b) for the cocurrent and countercurrent flow patterns. The two models gave very similar results due to the high selectivity of the membrane. Both models over predicted the product purity and underpredicted reject composition. These results indicate that the gas phase mass transfer resistance restricts hydrogen diffusion. The difference between the predicted and actual hydrogen composition is less than 12%. Therefore, the models accurately predicted membrane module performance.

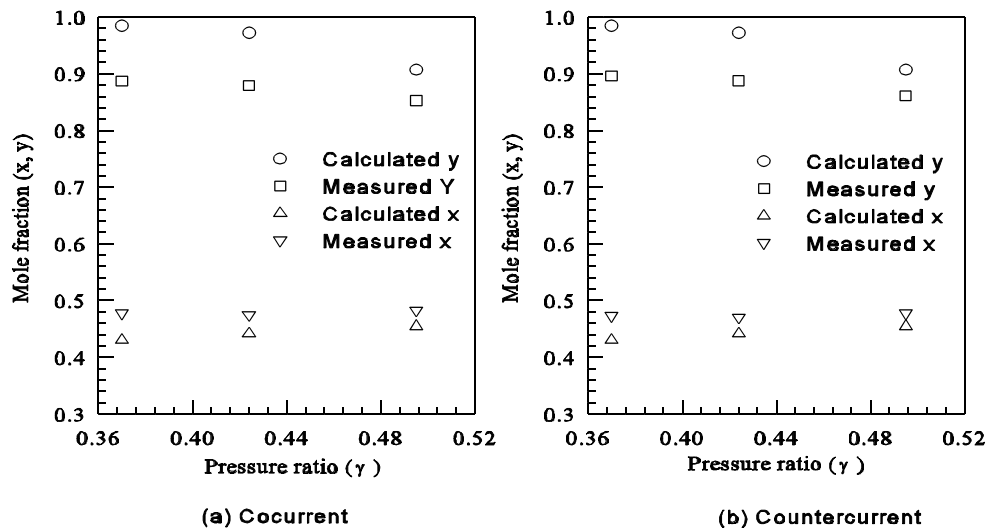


Figure 2: Effect of pressure ratio on permeate and reject compositions at 573 K compared to model predictions for Pd-ceramic composite membrane with $9.77 \mu\text{m}$ film: (a) cocurrent, and (b) countercurrent flow models.

CONCLUSIONS

A mathematical model is developed to describe the performance of cocurrent and countercurrent permeation cells. Although the model neglects mass transfer resistance in the gas phase, the results show that the model is adequate in predicting the performance of the membrane module. We plan to include dehydrogenation reaction in the model and evaluate the performance of the membrane reactor-separator under cocurrent and countercurrent flow configuration. This will be useful in designing the experiments on dehydrogenation of cyclohexane in membrane reactor-separator by equilibriumshift.