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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 cocurrent flow configuration. Numerical simulation results show that the model under predicts reject composition and over predicts the product purity. These results suggest that the gas phase mass transfer resistance could be important. The difference between the predicted and actual hydrogen composition is less than 12%. Thus the model appears to be adequate for predicting the membrane module performance.

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EXECUTIVE SUMMARY

In recent years, there has been increased interest in developing robust membranes for in-situ separation of hydrogen to achieve equilibrium shift in membrane reactor-separator. To develop a new class of membrane, in our previous project funded by the US DOE, we developed a hydrogen selective palladium-ceramic composite membrane by electroless deposition palladium thin-film on microporous ceramic substrate. The same method will be used in fabricating composite membranes for membrane reactor. Before designing membrane reactor, it is important to understand the performance of a membrane module based on simple flow configurations with and without chemical reaction. In doing so, we started developing some computer models for cocurrent and countercurrent flow models for the palladium-ceramic composite membrane based modules using our previously obtained laboratory data. In this report we briefly review the cocurrent model.

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: Cocurrent Flow Membrane Module

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 [4]:

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

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 flow configuration with two permeable components and a non-permeable fraction in the feed and a sweep stream in the permeate.

Figure 1 illustrates a cocurrent flow pattern for a membrane-based gas permeator with plug flow on each side of the membrane. The model is based on a three component gas mixture with components a (more permeable), b (less permeable) and i (non-permeable). By considering a differential area element, dS , the following permeation rate equations can be obtained for the permeable gas components:

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

$$\frac{d}{dS}(Vy_a) = \frac{Q_a}{h}[(Px_a)^n - (py_a)^n] \quad (2)$$

$$\frac{d}{dS}(Vy_b) = \frac{d}{dS}[V(1 - y_a)] = \frac{Q_b}{h}[(Px_b)^n - (py_b)^n] \quad (3)$$

If we define the membrane permeability ratio as selectivity, $\alpha = Q_a / Q_b$, and ratio of pressures, $\beta = p / P$, Eqns. (2) and (3) are then expressed as:

$$dV = \frac{\alpha [x_a^n - (y_a)^n] + [x_a^n - (y_a)^n]}{\alpha (1 - y_a) [x_a^n - (y_a)^n] + y_a [x_a^n - (y_a)^n]} V dy_a \quad (4)$$

From a material balance of component, a , about differential area, dS , the differential local permeate flow rate may be expressed as:

$$dV = \frac{Ldx_a + Vdy_a}{x_a - y_a} \quad (5)$$

The overall component material balances between the inlet and an arbitrary point along the membrane for more permeable and non-permeable components are given by:

$$\begin{aligned} L_f + V_s &= L + V & L_f x_{af} + V_s y_{as} &= Lx_s + Vy_s \\ Lx_i &= L_f x_{if} & Vy_i &= V_{sy_{is}} \end{aligned} \quad (6)$$

If we define the ratio of the feed gas to sweep gas flow rates as F_f , and let $A = x_a^n - (y_a)^n$ and $B = x_b^n - (y_b)^n$, Eqns. (4)- (6) can be combined to give the following equation which relates changes in y_a with x_a :

$$\frac{dy_a}{dx_a} = \frac{y_a - x_{af} + F_f (y_a - y_{as})}{x_a - x_{af} + F_f (x_a - y_{as})} \times \frac{A(1 - y_a) - By_a}{A(1 - x_a) - Bx_a} \quad (7)$$

The dimensionless membrane area can be related to the actual membrane area by the following expression in differential form:

$$\frac{dR}{dS} = \frac{Q_a P^n}{hL_f} \quad (8)$$

Combining Eqns. (3), (5), (7) and (8), the differential equation which relates the changes in R with x_a can be obtained as:

$$\frac{dR}{dx_a} = \frac{1}{x_a - y_a} \frac{y_a - x_{af} + F_f (y_a - y_{as})}{A(1 - x_a) - Bx_a} \quad (9)$$

The solution of Eqns. (7) and (9) is an initial-value problem with the following initial conditions:

$$\begin{aligned} \text{at } R=0; \quad L &= L_f, \quad x_a = x_{af}, \quad \text{and} \quad x_i = x_{if} \\ \text{at } R=0; \quad V &= V_s, \quad y_a = y_{as}, \quad \text{and} \quad y_i = y_{is} \end{aligned} \quad (10)$$

Using Eqn. (9) and the mass balance equations, the local flowrate and non-permeable component composition on each side of the membrane can be computed using the following equations:

$$\begin{aligned}
 L &= \frac{Y_a - x_{af} + F_f (Y_a - Y_{as})}{Y_a - x_a} L_f \\
 V &= \frac{x_{af} - x_a + F_f (Y_{as} - x_a)}{Y_a - x_a} L_f \\
 x_i &= \frac{L_f x_{if}}{L} = \frac{x_{if} (Y_a - x_a)}{Y_a - x_{af} + F_f (Y_a - Y_{as})} \\
 Y_i &= \frac{V_s Y_{is}}{V} = \frac{Y_{is} F_f (Y_a - x_a)}{x_{af} - x_a + F_f (Y_{as} - x_a)}
 \end{aligned} \tag{11}$$

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 must be determined from the permeate rate equations, Eqns. (2) and (3), with initial conditions, Eqn. (10), where $V_s = 0$, and $Y_i = 0$. At the feed inlet point, Y_{as} can be expressed as:

$$\frac{Y_{as}}{1 - Y_{as}} = \frac{x_{af}^n - (Y_{as})^n}{x_{bf}^n - (Y_{bs})^n} \tag{12}$$

Thus, y_{as} may be solved from Eqn. (12) in terms of the feed conditions. It must be noted that Eqn. (7) appears to be indeterminate at the feed inlet because $V_s = 0$, and $x_a = x_{af}$. L'Hospital's rule, however, can be used to determine the derivative, $(dy_a/dx_a)_f$. After determining the values of Y_{as} and $(dy_a/dx_a)_f$, the integration of Eqn. (7) may be carried out.

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 Eqns. 7, 9 and 11. Therefore, one variable can be freely chosen for a parametric study. In this work, the differential equations (Eqns. 7 and 9 for cocurrent flow) were solved using the Runge-Kutta-Gill method. The cocurrent flow pattern problem was solved as an initial value problem, while the countercurrent flow problem was solved as a boundary value problem.

RESULTS AND DISCUSSION

Mathematical model for cocurrent flow pattern were 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 for cocurrent flow pattern. The model 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 μm film for cocurrent flow pattern.

CONCLUSIONS

A mathematical model is presented to describe the performance of a cocurrent permeation cell. In the coming months, we plan to include dehydrogenation reaction in the model and evaluate the performance membrane reactor-separator under cocurrent flow configuration. This information will be useful in planning our experiments on dehydrogenation of cyclohexane in membrane reactor-separator. As continuation of this modeling work, we would also investigate countercurrent flow configuration for this system.