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Enhancement of Equilibriumshift in Dehydrogenation Reactions Using a Novel Membrane Reactor

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ABSTRACT

Electroless deposition of palladium thin-films on a surface of microporous ceramic substrate has been used to develop a new class of perm-selective inorganic membrane. In the last report, we presented a numerical method to analyze the stability in single-stage gas permeation. In this reporting period, we present our modeling work on dehydrogenation of cyclohexane in Pd-Ceramic membrane reactor. A model for studying dehydrogenation of cyclohexane in a membrane reactor is developed. Radial diffusion is considered to account for the concentration gradient in radial direction due permeation through the membrane. The model equations are derived for systems with reaction and without reaction. In the non-reaction case, a mixture of argon, benzene, cyclohexane, and hydrogen is used in the reaction side and argon is used as sweep gas in the separation side. Currently, we are working on the details of numerical solution of the model equations.

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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. In this work, we are currently studying the use of palladium-ceramic membrane in membrane reactor for separation and recovery of hydrogen from a dehydrogenation reaction. In our previous reports we presented models to describe permeation of hydrogen through single-stage palladium-ceramic composite membrane cell. Analysis of the model equations show that there exists a singular point when permeate hydrogen mole fraction equals to reject hydrogen mole fraction. At this condition, the numerical solution fails. To overcome this, a new method is proposed in this report. An example of a cocurrent single-stage permeation cell with three component system, without chemical reaction has been used to demonstrate the usefulness of the proposed new method.

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 FOR A MEMBRANE REACTOR

In order to develop a model for a membrane reactor, one needs to consider the reaction kinetics and the transport mechanism through the membrane as well as through the catalyst bed. In the present work, a palladium-ceramic membrane reactor is studied numerically for the dehydrogenation of cyclohexane to benzene and hydrogen. Pt/Al_2O_3 catalyst pellets are assumed inside the membrane tube, i.e. reaction side. The model is also investigated without reaction. In this case, a mixture of argon, benzene, cyclohexane, and hydrogen is considered in reaction side.

A number of rate expressions have appeared in the literature to describe the dehydrogenation of cyclohexane to benzene and hydrogen. Published expressions vary from empirical expression to that of more practical ones based on fundamentals. In Table 1, a summary of rate expressions is given that are pertinent to this work. In all cases, dehydrogenation reaction is considered to be catalytic and Pt/Al_2O_3 is used as the catalyst.

Derivation of Rate Expression for the Present Model

The dehydrogenation of cyclohexane on Pt/Al_2O_3 catalyst is a reversible reaction, which can be written as:

$$\begin{gathered} C_6H_{12} \Leftrightarrow C_6H_6 + 3H_2 \\ C \Leftrightarrow B + 3H \end{gathered} \tag{1}$$

TABLE 1. Rate expressions for dehydrogenation of cyclohexane proposed by different investigators.

Investigators (Year)	**Rate Expression**	**Comments**
Shinji et al. (1982)	$r_B = k\left(P_C - \frac{P_{H,e}^2}{K_P} P_B P_H\right)$	*Empirical *Basis: Homogeneous Reaction
Itoh et al. (1985)	$r_C = -k_0 e^{-E/RT}\left(P_C - \frac{P_B P_H^3}{K_P}\right)$	*Improved from the Previous Expression
Itoh (1987)	$r_C = \frac{-k\left(K_P P_C / P_H^3 - P_B\right)}{1 + K_B K_P P_C / P_H^3}$	*Adsorption Phenomena Considered *More Realistic

A reaction scheme according to Langmuir-Hinshelwood-Hougen-Watson mechanisms can be written as follows:

$$\begin{aligned} &\text{Adsorption:} && C + l \Leftrightarrow Cl \\ &\text{Surface Reaction:} && Cl + 3l \Leftrightarrow Bl + 3Hl \\ &\text{Desorption:} && Bl \Leftrightarrow B + l\ ;\quad 3Hl \Leftrightarrow 3H + 3l \end{aligned} \tag{2}$$

If we assume that the desorption of benzene is rate limiting step and other steps are fast and are in dynamic equilibrium, then the following rate expressions can be derived for cyclohexane:

$$r_C = \frac{-k\left(K_P \frac{P_C}{P_H^3} - P_B\right)}{1 + K_P K_B \frac{P_C}{P_H^3}} \tag{3}$$

Here it is assumed that the adsorption equilibrium constants for cyclohexane, K_C, and for hydrogen, K_H, are very small compare to that for benzene, K_B. For benzene, we write the rate expression as:

$$r_B = \frac{k\left(K_P \frac{P_C}{P_H^3} - P_B\right)}{1 + K_P K_B \frac{P_C}{P_H^3}} \tag{4}$$

Itoh (1987) used this expression in the analysis of membrane reactor using palladium. The expressions for the constants are:

$$\begin{aligned} k &= 0.211\exp(-4270/T) && (\mathrm{mol/m^3 \cdot Pa \cdot s}) \\ K_B &= 2.03\times10^{-10}\exp(6270/T) && \mathrm{Pa^{-1}} \\ K_p &= 4.89\times10^{35}\exp(3190/T) && \mathrm{Pa^{3}} \end{aligned} \tag{5}$$

Transport Mechanism through Palladium-Ceramic Membrane

Palladium-ceramic membrane is nonporous. No pore space is available for diffusion. The transport of gases through nonporous membranes occurs by a solution-diffusion mechanism. The gas molecules dissolve in the membrane surface on the high-pressure side of the membranes. The gas molecules then diffuse through the membrane phase and desorb at the low-pressure side.

The studies describing the mechanism of hydrogen transport through the palladium membrane (Hulbert and Konecny, 1961; Sieverts and Danz, 1936) and palladium-ceramic membrane (Fan, 1996) have been studied by different investigators. Observations have generally been expressed as

$$N_H = \frac{Q_H}{t}\left(P_H^n - p_H^n\right) \tag{6}$$

where P_H and p_H are the hydrogen partial pressures of feed side and separation side, Q_H is the permeability and t is the membrane thickness. The values for n range from 0.5 to 1. The value of 0.5 implies that the transport of hydrogen through the bulk of metal is rate determining and that equilibrium is established at the surface, i.e. an equilibrium between hydrogen molecules in gas phase and hydrogen atoms dissolved in the metal. The hydrogen concentration is proportional to the square root of hydrogen pressure, which is known as Sivert's law. The result is expressed as:

$$N_H = \frac{Q_H}{t}\left(P_H^{0.5} - p_H^{0.5}\right) \tag{7}$$

A value of n equaling 1, implies a slow, rate determining surface reaction of hydrogen with palladium.

According to Fan (1996), hydrogen transport through palladium-ceramic membrane does not follow the Sivert's law because the value of n is different from 0.5. Thus, it is necessary to develop a generalized model for all values of n, $0.5 \le n \le 1$.

Transport Mechanism through Catalyst Bed

There are two types of models to describe the transport mechanism through the catalyst bed: pseudo-homogeneous and heterogeneous. Pseudo-homogeneous models do not account explicitly for the presence of catalyst, in contrast with heterogeneous models, which lead to separate conservation equations for fluid and catalyst.

Two-Dimensional Pseudo-Homogeneous Membrane Reactor Model

Figure 1 shows the schematic of the membrane reactor. Pt-Al_2O_3 catalyst pellets are assumed inside the palladium-ceramic membrane tube. Hydrogen produced by the reaction permeates through the membrane into the shell side. Argon is used as the carrier gas in the feed side and as sweep gas in the shell side to remove the permeated hydrogen. Concentration of hydrogen near the membrane wall is depleted due to permeation. Hence a concentration gradient occurs in the radial direction. From the discussion of different reactor models, it can be concluded that a two-dimensional model is suitable to describe the transport mechanism through the catalyst bed.

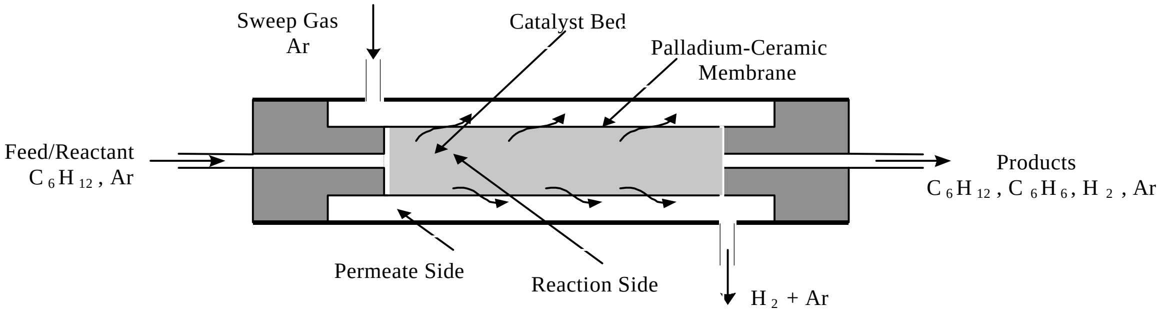

Figure 1. Pd-Ceramic Membrane Reactor

Two-dimensional heterogeneous model requires the knowledge of effectiveness factor. For a first-order reaction it can be evaluated easily. Dehydrogenation of cyclohexane is a complex reaction and defining the effectiveness factor is complicated. In order to avoid this complexity, two-dimensional pseudo-homogeneous model is assumed to describe the transport mechanism through the catalyst bed.

Model Assumptions:

1. Isothermal, isobaric and steady-state flow through the whole reactor (both the packed-bed and separation sides).
2. Plug flow is assumed through the shell side or separation side.
3. Ideal gas law is applicable
4. Flat concentration profile is assumed in separation side
5. Partial pressure gradient of hydrogen in the radial direction, caused by the permeation of hydrogen through the palladium-ceramic membrane, is taken into account.
6. Axial diffusion is negligible
7. The amount of dehydrogenation taking place on the palladium-ceramic tube is negligibly small compared to that on the catalyst pellet surface.

The permeation rate of hydrogen gas through the palladium-ceramic membrane (Fan, 1996), N_H, can be expressed as

$$N_H = \frac{Q_H}{t}\left(P_H^n - p_H^n\right) \tag{8}$$

where n is different from one-half, i.e. $0.5 < n < 1.0$

Using the assumptions, the continuity equations for different components become

$$u\frac{\partial C_A}{\partial z} = (D_{er})_A\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_A}{\partial r}\right)\right] \tag{9}$$

$$u\frac{\partial C_B}{\partial z} = (D_{er})_B\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_B}{\partial r}\right)\right] - r_C \tag{10}$$

$$u\frac{\partial C_C}{\partial z} = (D_{er})_C\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_C}{\partial r}\right)\right] + r_C \tag{11}$$

$$u\frac{\partial C_H}{\partial z} = (D_{er})_H\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_H}{\partial r}\right)\right] - 3r_C \tag{12}$$

with boundary conditions

$$\text{at } r = 0, \quad 0 \le z \le l_0 \qquad \left\{\begin{array}{ll} \dfrac{\partial C_A}{\partial r} = 0 & \dfrac{\partial C_B}{\partial r} = 0 \\ \dfrac{\partial C_C}{\partial r} = 0 & \dfrac{\partial C_H}{\partial r} = 0 \end{array}\right. \tag{13}$$

$$\text{at } r = r_1, \quad 0 \le z \le l_0 \qquad \left\{\begin{array}{ll} \dfrac{\partial C_A}{\partial r} = 0 & \dfrac{\partial C_B}{\partial r} = 0 \\ \dfrac{\partial C_C}{\partial r} = 0 & (D_{er})_H\dfrac{\partial C_H}{\partial r} = \dfrac{Q_H}{t}\left(P_H^n - p_H^n\right) \end{array}\right. \tag{14}$$

and initial conditions for cocurrent flow configuration

Reaction side:

$$\text{at } z=0,\quad 0\le r\le r_1 \quad \begin{cases} C_A = C_A^0 & C_B = 0 \\ C_C = C_C^0 & C_H = 0 \end{cases} \tag{15}$$

Separation side:

$$\text{at } z=0,\quad r_2\le r\le r_3 \quad \begin{cases} C_A = C_A^0 \\ C_H = 0 \end{cases} \tag{16}$$

Assuming ideal gas behavior, we replace C_i by $\frac{P_i}{R_g T}$ and obtain Eqns. (9) – (12) as:

$$u\frac{\partial P_A}{\partial z} = \left(D_{er}\right)_A\left[\frac{1}{r}\frac{\partial P_A}{\partial r} + \frac{\partial^2 P_A}{\partial r^2}\right] \tag{17}$$

$$u\frac{\partial P_B}{\partial z} = \left(D_{er}\right)_B\left[\frac{1}{r}\frac{\partial P_B}{\partial r} + \frac{\partial^2 P_B}{\partial r^2}\right] - r_C R_g T \tag{18}$$

$$u\frac{\partial P_C}{\partial z} = \left(D_{er}\right)_C\left[\frac{1}{r}\frac{\partial P_C}{\partial r} + \frac{\partial^2 P_C}{\partial r^2}\right] + r_C R_g T \tag{19}$$

$$u\frac{\partial P_H}{\partial z} = \left(D_{er}\right)_H\left[\frac{1}{r}\frac{\partial P_H}{\partial r} + \frac{\partial^2 P_H}{\partial r^2}\right] - 3r_C R_g T \tag{20}$$

Boundary Conditions:

$$\text{at } r=0,\quad 0\le z\le l_0 \quad \begin{cases} \dfrac{\partial P_A}{\partial r} = 0 & \dfrac{\partial P_B}{\partial r} = 0 \\ \dfrac{\partial P_C}{\partial r} = 0 & \dfrac{\partial P_H}{\partial r} = 0 \end{cases} \tag{21}$$

$$\text{at } r=r_1,\quad 0\le z\le l_0 \quad \begin{cases} \dfrac{\partial P_A}{\partial r} = 0 & \dfrac{\partial P_B}{\partial r} = 0 \\ \dfrac{\partial P_C}{\partial r} = 0 & \dfrac{\partial P_H}{\partial r} = \dfrac{R_g T Q_H}{\left(D_{er}\right)_H t}\left(P_H^n - p_H^n\right) \end{cases} \tag{22}$$

Initial conditions on the reaction and separation sides are:

Reaction side:

$$\text{at } z=0,\quad 0\le r\le r_1 \quad \begin{cases} P_A = P_A^0 & P_B = 0 \\ P_C = P_C^0 & P_H = 0 \end{cases} \tag{23}$$

<u>Separation side:</u>

$$\text{at } z=0, \quad r_2 \le r \le r_3 \quad \begin{cases} P_A = P_A^0 \\ P_H = 0 \end{cases} \tag{24}$$

To make the governing equations and boundary conditions dimensionless, we may introduce the following dimensionless variables:

$$\begin{array}{lll} Z = \dfrac{z}{l_0} & U = \dfrac{u}{u_0} & R = \dfrac{r}{r_1} \\ \Phi_i = \dfrac{P_i}{P_0} = \dfrac{X_i}{\sum X_i}\dfrac{P_r}{P_0} & & f_i = \dfrac{p_i}{P_0} = \dfrac{x_i}{\sum x_i}\dfrac{p_s}{P_0} \\ & & (i = A, B, C, \text{and } H) \end{array} \tag{25}$$

It should be noted that P_0 , the atmospheric pressure, is reference pressure. If the system pressure is atmospheric pressure, then Φ_i and f_i are mole fractions in reaction and separation sides respectively i.e.,

$$\sum \Phi_i = 1 \qquad \text{and} \qquad \sum f_i = 1 \tag{26}$$

Now the differential equations and the boundary conditions in terms of dimensionless variables can be expressed as:

$$\frac{\partial (U\Phi_A)}{\partial Z} = \frac{d_P l_0}{(Pe_r)_A r_1^2}\left(\frac{1}{R}\frac{\partial \Phi_A}{\partial R} + \frac{\partial^2 \Phi_A}{\partial R^2}\right) \tag{27}$$

$$\frac{\partial (U\Phi_B)}{\partial Z} = \frac{d_P l_0}{(Pe_r)_B r_1^2}\left(\frac{1}{R}\frac{\partial \Phi_B}{\partial R} + \frac{\partial^2 \Phi_B}{\partial R^2}\right) + j \tag{28}$$

$$\frac{\partial (U\Phi_C)}{\partial Z} = \frac{d_P l_0}{(Pe_r)_C r_1^2}\left(\frac{1}{R}\frac{\partial \Phi_C}{\partial R} + \frac{\partial^2 \Phi_C}{\partial R^2}\right) - j \tag{29}$$

$$\frac{\partial (U\Phi_H)}{\partial Z} = \frac{d_P l_0}{(Pe_r)_H r_1^2}\left(\frac{1}{R}\frac{\partial \Phi_H}{\partial R} + \frac{\partial^2 \Phi_H}{\partial R^2}\right) + 3j \tag{30}$$

where,

$$j = \frac{R_g T l_0}{u_0 P_0} \frac{k\left(K_P \Phi_C - P_0^3 \Phi_H^3 \Phi_B\right)}{P_0^2 \Phi_H^3 + K_B K_P \Phi_C}$$

$$\left(Pe_r\right)_A = \frac{u_0 d_p}{\left(D_{er}\right)_A} \qquad \left(Pe_r\right)_B = \frac{u_0 d_p}{\left(D_{er}\right)_B} \tag{31}$$

$$\left(Pe_r\right)_C = \frac{u_0 d_p}{\left(D_{er}\right)_C} \qquad \left(Pe_r\right)_H = \frac{u_0 d_p}{\left(D_{er}\right)_H}$$

Boundary conditions in dimensionless form

$$\text{at } \mathrm{R} = 0, \quad 0 \le Z \le 1 \qquad \begin{cases} \dfrac{\partial \Phi_A}{\partial r} = 0 & \dfrac{\partial \Phi_B}{\partial r} = 0 \\ \dfrac{\partial \Phi_C}{\partial r} = 0 & \dfrac{\partial \Phi_H}{\partial r} = 0 \end{cases} \tag{32}$$

$$\text{at } \mathrm{R} = 1, \quad 0 \le Z \le 1 \qquad \begin{cases} \dfrac{\partial \Phi_A}{\partial r} = 0 & \dfrac{\partial \Phi_B}{\partial r} = 0 \\ \dfrac{\partial \Phi_C}{\partial r} = 0 & \dfrac{\partial \Phi_H}{\partial r} = b\left(P_H^n - p_H^n\right) \end{cases} \tag{33}$$

where,

$$b = \frac{r_1}{r_2 - r_1} \frac{R_g T Q_H}{P_0^{1-n} \left(D_{er}\right)_H}$$

Initial conditions in dimensionless variables are then given as:

Reaction side:

$$\text{at } \mathrm{Z} = 0, \quad 0 \le R \le 1 \qquad \begin{cases} \Phi_A = \Phi_A^0 & \Phi_B = 0 \\ \Phi_C = \Phi_C^0 & \Phi_H = 0 \end{cases} \tag{34}$$

Separation side:

$$\text{at } Z = 0, \quad \text{for any position} \qquad \begin{cases} \Phi_A = \Phi_A^0 \\ \Phi_H = 0 \end{cases} \tag{35}$$

Above equations can not be solved analytically. Finite difference method is used to solve these equations.

RESULTS AND DISCUSSIONS

A two-dimensional pseudo-homogenous reactor model is presented to describe the dehydrogenation of cyclohexane to benzene in a membrane-reactor. The governing equations and boundary conditions are derived in dimensionless form for numerical solution. In the next semi-annual report we plan to present some numerical results. This numerical experimentation will be used in designing our membrane reactor experiment to study the equilibrium shift of the dehydrogenation reaction.

CONCLUSIONS

A mathematical model is presented to describe the dehydrogenation of cyclohexane to benzene and hydrogen in a membrane-reactor. The model considers the radial diffusion due to selective permeation of hydrogen through the membrane wall. The model equation derived can be used to study both reactive and non-reactive systems in a membrane-reactor.

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