A Membrane Reactor Using Palladium

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It is well known that a reversible reaction can never be complete under ordinary conditions because the conversion attainable is limited by the thermodynamics. However, an attractive method for dealing with such a limitation is proposed in this study.

Let us consider the following reversible gas-phase reaction as a model:

$$C_6H_{12} \rightleftharpoons C_6H_6 + 3H_2$$

If this reaction reaches a state of chemical equilibrium at any fixed conditions, no further change in the composition with time can occur; that is, the reaction does not go to completion. Nevertheless, if the products (both or either) can be separated from the reacting mixtures by employing a selective gas separation membrane, the reaction will advance in the forward direction and finally will go to completion.

Raymont (1975) has suggested a similar concept for increasing the decomposition yield of hydrogen sulfide, whose equilibrium conversion is quite low: only several percent at 1,000 K. Regrettably, his approach has never been attempted. Several years later, Kameyama et al. (1981) succeeded experimentally in improving the decomposition yield of hydrogen sulfide using a microporous Vycor glass membrane, through which one of the products, hydrogen gas, can pass more easily than other gaseous species. Still, by their method it was impossible to make the reaction complete because the undecomposed feed gas, hydrogen sulfide, also had passed through the porous membrane to the separation side. We have established by computer simulation that there is a limitation on the performance of such a microporous membrane reactor (Itoh et al., 1984, 1985a).

In the present study, a palladium membrane was selected because only hydrogen gas can permeate it—a phenomenon that has been known for more than 100 years. In the above model dehydrogenation, since the gases other than hydrogen can never pass through the palladium membrane, it is expected that the reaction will proceed without being limited thermodynamically. The aim of this note is to demonstrate that the model reaction is promoted beyond the thermodynamic limitations by employing a membrane reactor equipped with a palladium hollow tube.

Experimental Method

Details of a double-tube membrane reactor using a thin palladium tube, 200 μm thick, 17.0 mm OD, and 140 mm long, is shown in Figure 1. Inside the membrane tube (reaction side), cylindrical catalyst pellets (0.5 wt. % Pt/Al_2O_3, 3.3 mm OD, 3.6 mm high) were uniformly packed. The catalyst section was 140 mm long. A schematic diagram of the whole reactor system is given in Figure 2. A 19.7% saturated vapor of cyclohexane generated by flowing argon as a carrier gas through an evaporator was fed inside the catalyst packed bed. Also, argon was used as a purge gas to remove the hydrogen permeated to the shell side (separation side) through the membrane. The reactor was set in a thermostat whose temperature was kept at 473 K. Experiments were carried out at atmospheric pressure. The extent of conversion was determined by analyzing a concentration ratio of cyclohexane to benzene by means of a gas chromatograph. Neither cyclohexane nor benzene was detected in the gas mixtures exiting from the separation side.

Analysis

Isothermal, isobaric, and plug flow conditions within the membrane reactor were assumed in order to simplify the analysis of such a complicated problem. Furthermore, it was assumed that the amount of dehydrogenation taking place on the inner surface of the palladium tube was negligibly small compared to that on the catalyst pellets since the total active surface area of the Pt/Al_2O_3 catalyst pellets was generally considered to be much larger than that of the membrane. The permeation rate of hydrogen gas through the palladium membrane, Q_H, was assumed to obey the half-power pressure law (Bohmholdt and Wicke, 1967), i.e., it is proportional to the difference between the roots of the hydrogen partial pressures in the reaction and separation sides, p_H and p'_H:

$$Q_H = \alpha_H \left(\sqrt{\frac{p_H}{P_O}} - \sqrt{\frac{p'_H}{P_O}} \right)$$

$$\alpha_H = \frac{2\pi l_O}{\ln(r_O/r_i)} D C_O \qquad (1)$$

P_o is 1.013×10^5 Pa and D is Fick's diffusion coefficient of

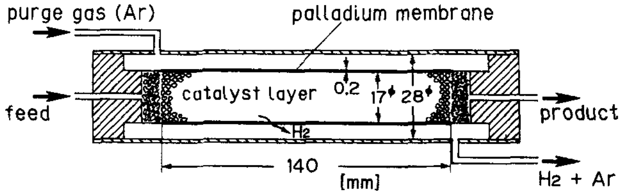

Figure 1. Details of membrane reactor using a palladium hollow tube.

hydrogen dissolved in the palladium. C_o is defined as a standard concentration of hydrogen in the palladium, which is at equilibrium with the gas-phase hydrogen at pressure P_o. The α_H is defined as a permeation rate constant of hydrogen gas. When literature values, i.e., 9.23×10^{-10} m$^2 \cdot$ s^{-1} for D (Nagamoto and Inoue, 1985) and 1,280 mol $\cdot$ m^{-3} for C_o (Sieverts and Danz, 1936) at 473 K, were used, α_H calculated was 4.47×10^{-5} mol $\cdot$ s^{-1}.

Figure 3 shows the flow model of component gases in the reactor. The quantitative represention for this was developed by taking a material balance of each component in a dimensionless differential section of the reactor dL. Hence,

$$\frac{du_C}{dL} = r_C V_r \tag{2}$$

$$\frac{du_H}{dL} = -3r_C V_r - \alpha_H \left(\sqrt{P_{Tr} \frac{u_H}{\Sigma u_i}} - \sqrt{P_{Ts} \frac{v_H}{\Sigma v_i}} \right) \tag{3}$$

$$\begin{aligned} \Sigma u_i &= u_C + u_B + u_H + u_A \\ \Sigma v_i &= v_A + v_H \\ u_B &= u_C^o - u_C \end{aligned} \tag{4}$$

$$v_H = u_H - 3(u_C^o - u_C) \tag{5}$$

$$u_A = u_A^o, \quad v_A = v_A^o, \quad v_C = v_B = 0 \quad \text{(constant)} \tag{6}$$

where the u_i and v_i (i = C, H, B, and A) are the flow rates of component i in the reaction and separation sides, respectively. Vr is the gross volume of the reaction section. P_{Tr} and P_{Ts} are the total pressures in the reaction and separation sides, respectively. The disappearance rate of cyclohexane, r_C, can be expressed by (Itoh et al., 1985b),

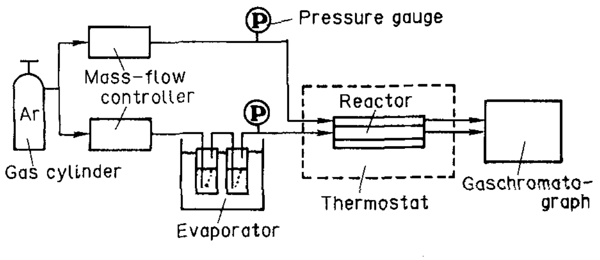

Figure 2. Experimental apparatus.

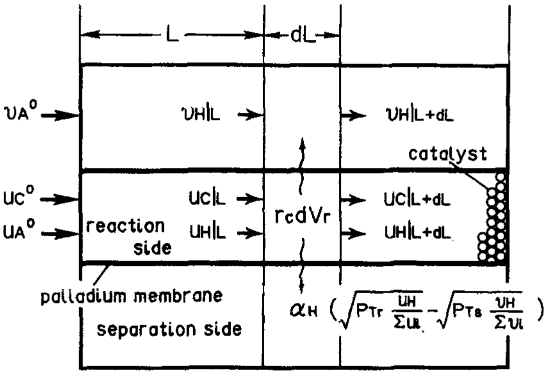

Figure 3. Flow model in palladium membrane reactor.

$$r_C = \frac{-k(K_p p_C / p_H^3 - p_B)}{1 + K_B K_p p_C / p_H^3}$$

$$\begin{aligned} k &= 0.221 \exp(-4{,}270/T) && (\text{mol} \cdot \text{m}^{-3} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}) \\ K_B &= 2.03 \times 10^{-10} \exp(6{,}270/T) && (\text{Pa}^{-1}) \\ K_P &= 4.89 \times 10^{35} \exp(3{,}190/T) && (\text{Pa}^3) \end{aligned} \tag{7}$$

where p_i is the partial pressure of component i in the reaction side. Equations 2–7 were numerically integrated by the Runge-Kutta-Gill method with initial conditions

$$\begin{aligned} L = 0 : u_C = u_C^o, \quad u_B = 0, \quad u_H = 0 \\ u_A = u_A^o, \quad v_H = 0, \quad v_A = v_A^o \end{aligned} \tag{8}$$

Results and Discussion

Figure 4 shows experimental results and the corresponding calculated curves. Since they are almost in agreement, the simple analytical method proposed above is found to be useful for analysis of such a complex reactor.

At a fixed feed rate of cyclohexane u_C^o, it can be seen that increasing flow rate of purge gas v_A^o results in higher conversion, that is, a noticeable increase in promotion of the reaction. This is due to the increasing removal rate of hydrogen passed through the membrane from the reaction side. On the other hand, when v_A^o is fixed, the conversion increases with decreasing u_C^o, that is, increasing residence time of the reactant in the reactor. It is generally accepted that a higher conversion can be obtained with an

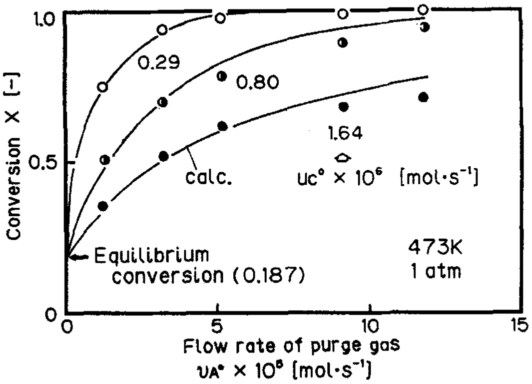

Figure 4. Experimental and calculated results.

increase in the reaction time unless the reaction proceeds to completion or reaches a state of chemical equilibrium.

When $u_C^o = 2.90 \times 10^{-7}$ mol · s^{-1} and $v_A^o = 11.8 \times 10^{-5}$ mol · s^{-1}, the conversion attained was 99.7%; this value is much higher than that at equilibrium, 18.7%, which is the maximum conversion obtained by using an ordinary catalytic reactor. On the basis of such results, it is expected that if the operation conditions are properly chosen, 100% conversion will be attainable by using the membrane reactor. In this case, as only benzene leaves from the outlet of the reaction side, no additional separation apparatus between benzene and cyclohexane will be needed; this may lead to reduced operating costs. Instead of using a purge gas as described above, there is an alternative method for removing the permeated hydrogen. The pressure on the separation side can be maintained at a reduced level or vacuum. In such a case, very pure hydrogen can be obtained from the outlet of the separation side, so that direct hydrogen production in the course of the reaction would be possible.

Notation

C_o – concentration of hydrogen dissolved in palladium, mol · m^{-3}
D – Fick's diffusion coefficient of hydrogen, m^2 · s^{-1}
k – apparent rate constant, Eq. 7, mol · m^{-3} · Pa^{-1} · s^{-1}
K_B – adsorption equilibrium constant of benzene, Pa^{-1}
K_P – equilibrium constant, Pa^3
L – dimensionless length of reactor
l_o – entire length of reactor, m
p'_H – partial pressure of component *i* on separation side, Pa
p_i – partial pressure of component *i* on reaction side, Pa
P_r – total pressure on reaction side, Pa
P_S – total pressure on separation side, Pa
P_o – standard pressure, 1.013×10^5 Pa
Q_H – permeation rate of hydrogen through palladium, mol · s^{-1}
r_C – dehydrogenation rate of cyclohexane, mol · m^{-3} · s^{-1}
r_i – inner radius of palladium tube, m
r_o – outer radius of palladium tube, m
T – absolute temperature, K
u_A^o – flow rate of argon at reaction-side inlet, mol · s^{-1}
u_C^o – flow rate of cyclohexane at reaction-side inlet, mol · s^{-1}
u_i – flow rate of gas *i* in reaction-side stream, mol · s^{-1}
v_A^o – flow rate of argon at separation-side inlet, mol · s^{-1}
v_i – flow rate of gas *i* in separation-side stream, mol · s^{-1}
α_H – permeation rate constant of hydrogen, mol · s^{-1}

Subscripts

A – argon
B – benzene
C – cyclohexane
H – hydrogen
i – component *i*

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