

SIMULATION OF BIFUNCTIONAL PALLADIUM MEMBRANE REACTOR

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Key Words: Membrane Reactor, Palladium Membrane, Dehydrogenation, Oxidation of Hydrogen, Hydrogen Permeation, Reactor Model

A bifunctional membrane reactor using palladium was proposed by taking advantage of its catalytic and hydrogen-permeable functions and then by coupling dehydrogenation and oxidation. Isothermal and adiabatic reactor models were developed and simulated.

Under an isothermal condition, the dehydrogenation taking place in a catalyst packed bed was enhanced owing to continuous removal of the hydrogen produced in the course of reaction through the membrane. The amount of hydrogen removable was remarkably increased by the subsequent oxidation of hydrogen on the palladium surface of the permeation side. In addition to such effects, it was shown by the adiabatic model that transfer of heat by oxidation to the dehydrogenation side across the membrane can lead to further enhancement of dehydrogenation.

Introduction

Application of a palladium membrane to a dehydrogenation process was attempted by the author⁴⁾, where selective removal of hydrogen through the membrane was expected to yield a remarkable equilibrium shift of dehydrogenation. As expected, almost 100% conversion could be obtained under a chosen operating condition for dehydrogenation of cyclohexane to benzene.

At that time, palladium was only considered to be a hydrogen-permeable membrane. However, there is another possibility, taking advantage of its catalytic activities for hydrogenation, dehydrogenation and oxidation. If palladium can function not only as a hydrogen separation membrane but also as a catalytic membrane, a hybrid type of reactor completely different from conventional reactors can be realized. We call such a reactor a "bifunctional palladium membrane reactor". In this reactor two types of reaction, such as dehydrogenation and either hydrogenation or oxidation, occur on the two sides of the palladium membrane separately but simultaneously. A series of such studies with regard to the dehydrogenation-hydrogenation system has been made by Gryatznov *et al.*²⁾ Some interesting results, in particular the improvement of selectivity, were obtained. However, when one aims at improvement of reaction yield, their results seemed not to be necessarily good. This is thought to be due to too small a rate of the reactions per unit volume. Namely, the place in which reactions can occur was limited to

the surface of the palladium membrane since no catalyst but the palladium membrane itself was used in their so-called "catalytic membrane reactor".

In this study, therefore, a different type of reactor system, which can raise the productivity of dehydrogenation with catalyst packed on the dehydrogenation side of the reactor, is considered. The purpose of this study is to determine what kind of effects and how much advantage can be expected. Isothermal and adiabatic reactor models are proposed for a dehydrogenation-oxidation system. Further, the experimental results reported in the previous note⁵⁾ are compared with those calculated using a model developed in this study.

1. Concept of Bifunctional Palladium Membrane Reactor

Figure 1 shows the concept of a bifunctional palladium membrane reactor schematically. Since catalyst pellets are packed uniformly on the reaction side, dehydrogenation can proceed at sufficient speed. Then the hydrogen produced can permeate to the separation side through the palladium membrane. On the separation side, oxygen or a gas stream containing it will react easily with the hydrogen permeated on the active surface of the palladium membrane. The oxidation of hydrogen using oxygen is selected as the hydrogen-consuming reaction because it is known as a rapid reaction accompanied by a large amount of exothermic heat^{1,6)}.

By combining such two contrastive reactions, more favorable conditions for both reactions will be established. Hence, the following effects can be expected.

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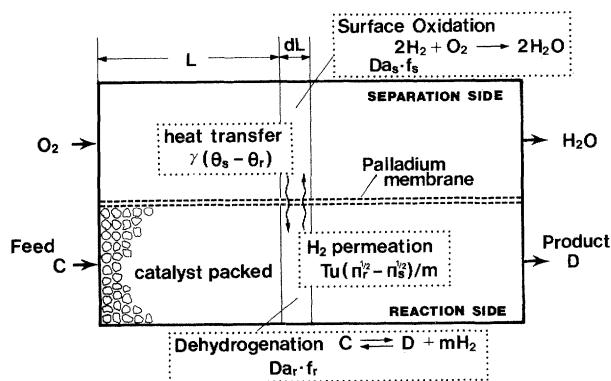


Fig. 1. Concept of bifunctional membrane reactor using palladium

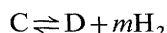
- 1) Equilibrium shift
- 2) Mutual compensation of heats of reaction
- 3) Enhancement of reaction rate

This reaction process is advantageous in view of chemical equilibrium because equilibrium shifts of both reactions become possible by removing hydrogen from one of the dehydrogenation products on the reaction side, and by supplying it for oxidation on the separation side. Further, there is the possibility of compensating their reaction heats with each other; i.e., while dehydrogenation is an endothermic reaction, oxidation is exothermic. This means that the oxidation can become a source of heat for the dehydrogenation. In addition to these merits, of course, kinetic effects are also expected. A decrease in partial pressure of hydrogen in the dehydrogenation will cause a decrease in the rate of its backward reaction. Also, an increase in reaction temperature will enhance the reaction rate.

2. Development of Reactor Models

Isothermal and adiabatic reactor models, which are important from the viewpoint of practical application, are presented. The basic equations to describe the mass and heat balances in the reactor, into whose separation side an oxygen-containing gas is introduced co-currently, are derived with the following assumptions: 1) plug flow; 2) no axial or radial dispersion of gaseous components; 3) ideal gas behaviour; and 4) no pressure drop.

Dehydrogenation is in general represented as



This reaction scheme can include not only reactions of hydrocarbons but also decomposition reactions of H_2S , HI , H_2O and the like.

2.1 Isothermal reactor model

The isothermal reactor model is so simple that it is a very convenient means of obtaining a basic understanding of the bifunctional membrane reactor. Referring to Fig. 1, the equations governing the change

in flow rate of each component, U_i [—], along the reactor length on the reaction (dehydrogenation) side are as follows.

$$dU_C/dL = -Da_r^0 f_r \quad (1)$$

$$dU_H/dL = Da_r^0 f_r - Tu^0(\sqrt{\pi_{Hr}} - \sqrt{\pi_{Hs}})/m \quad (2)$$

$$U_D = 1 - U_C \quad (3)$$

$$U_I = U_I^0 \text{ (constant)} \quad (4)$$

The permeation rate of hydrogen through palladium is assumed to obey the Sieverts law, as was introduced in the previous study⁴; that is, it is proportional to the difference between the roots of the dimensionless partial pressures of hydrogen on the reaction and separation sides, $\sqrt{\pi_{Hr}} - \sqrt{\pi_{Hs}}$.

On the other hand, the changes in flow rate of the respective components on the separation side, V_i [—], accompanying the hydrogen-oxygen reaction, $2H_2 + O_2 \rightarrow 2H_2O$, are described by the following equations.

$$dV_O/dL = -Da_s^0 f_s \quad (5)$$

$$V_W = 2(V_O^0 - V_O) \quad (6)$$

$$V_H = 1 - U_C - U_H - 2(V_O^0 - V_O)/m \quad (7)$$

$$V_I = V_I^0 \text{ (constant)} \quad (8)$$

Concrete expressions are necessary for f_r [—] in Eq. (1) and f_s [—] in Eq. (5) in practical calculations. In this study, the dehydrogenation of cyclohexane to benzene is taken as the model reaction and the following rate equation, which was experimentally determined by the authors,³ is used.

$$f_r = \frac{K_P \pi_C / \pi_H^3 P_0^3 - \pi_D}{(P_r/P_0)(1 + K_P K_D \pi_C / \pi_H^3 P_0^2)} \quad (9)$$

On the other hand, the following expression for f_s (Appendix Eq. (A2)) is used.

$$f_s = \pi_O \pi_H^2 / (P_s/P_0)^3 \quad (10)$$

The above set of simultaneous ordinary differential equations can be numerically solved only if the following inlet conditions are given.

$$L=0: U_C=1, \quad U_D=U_H=V_H=V_W=0 \quad (11)$$

2.2 Adiabatic reactor model

In this model, internal heat exchange between the endothermic dehydrogenation and the exothermic oxidation is taken into account with an assumption of adiabatic condition, that is, no heat transfer between the reactor and its exterior. However, there is a resistance to heat transfer between the separation and reaction sides. Although strictly a temperature profile in the radial direction must be considered, a one-dimensional model was applied for the sake of simplicity. Hence, the heat transfer rate between the two sides, q , is assumed to be given by using the

overall heat transfer coefficient, h_o , as follows.

$$q = h_o A (\theta_s - \theta_r) \quad (12)$$

Therefore, the heat balances for the two sides are respectively given by
(Reaction side)

$$\frac{d(\sum C_{pi} U_i \theta_r)}{dL} = -Da_r^0 \exp\left\{\frac{E_r}{RT}\left(1 - \frac{1}{\theta_r}\right)\right\} \left(\frac{\Delta H_r}{c_{pc}^0 T_0}\right) f_r + \gamma(\theta_s - \theta_r) \quad (13)$$

(Separation side)

$$\frac{d(\sum C_{pi} V_i \theta_s)}{dL} = -Da_s^0 \exp\left\{\frac{E_s}{RT}\left(1 - \frac{1}{\theta_s}\right)\right\} \left(\frac{\Delta H_s}{c_{pc}^0 T_0}\right) f_s - \gamma(\theta_s - \theta_r) \quad (14)$$

On the other hand, the mass balance for this case can also be given by Eqs. (1)–(8). Since the permeability also has a temperature dependency as well as the Damköhler numbers, Da_r^0 and Da_s^0 , Tu^0 must be replaced by Tu as follows.

$$Tu = Tu^0 \exp\left\{\frac{E_p}{RT}\left(1 - \frac{1}{\theta_r}\right)\right\} \quad (15)$$

The set of the differential equations thus obtained can be solved simultaneously with an additional inlet condition with regard to temperature:

$$L=0: \theta_r=1, \quad \theta_s=1 \quad (16)$$

3. Simulation

Various values used in simulation are summarized in **Table 1**. Numerical calculations were carried out by the Runge-Kutta-Gill method.

3.1 Isothermal model

Figure 2 shows the conversion curves for the dehydrogenation with varying V_{sw}^0 , where the Damköhler number, Da_s^0 , relating the reaction rate of oxygen-hydrogen is selected as a parameter. When $Da_s^0=0$, although no reaction takes place on the separation side, the dehydrogenation is found to be increased beyond the equilibrium conversion of 18.2%. This is caused by the removal of hydrogen to the separation side through the palladium membrane, as has already been shown mathematically and experimentally in the previous study⁴⁾. Such an effect becomes large with increasing V_{sw}^0 , that is, higher conversion is obtainable owing to the increasing amount of hydrogen removable. On the other hand, when the permeated hydrogen reacts catalytically with oxygen on the membrane surface, the chemical change of the hydrogen to water lowers the hydrogen concentration in the separation-side stream extremely compared with the case using only inert gas as the sweep gas. As a result, since a larger amount of hydrogen can be removed, much higher conversion is

Table 1. Parameters used in calculations

$E_r = 35.5^{(3)}$	$E_s = 41.8^{(*)}$	$E_p = 12.7^{(*)}$	[kJ/mol]
$\Delta H_r(473 \text{ K}) = 214.7$			[kJ/mol-benzene]
$\Delta H_s(473 \text{ K}) = -243.6$			[kJ/mol-water]
$K_D = 2.03 \times 10^{-10} \exp(6270/T)^{3)}$			[Pa ⁻¹]
$K_P = 4.89 \times 10^{3.5} \exp(-26490/T)$			[Pa ³]
$m = 3$	$P_r = P_s = 1.013 \times 10^5$		[Pa]
$T_0 = 473$			[K]

Each value of c_{pi} was given by the form $a + bT + cT^2$.

^{*)} Assumed value.

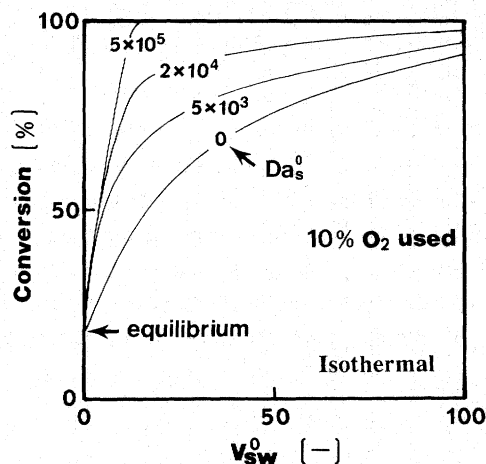


Fig. 2. Relation between conversion and V_{sw}^0 with varying Da_s^0 (Isothermal, $Da_r^0 = 100$, $Tu^0 = 45$, $U_l^0 = 4$)

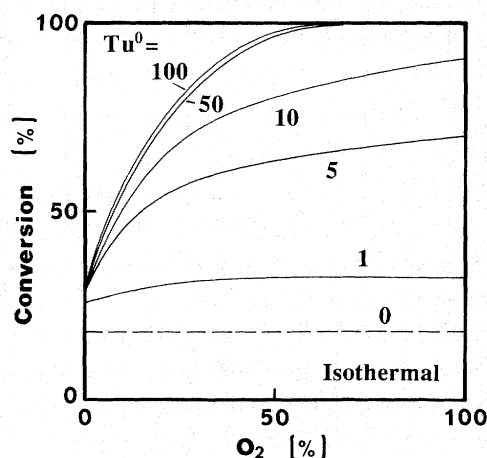


Fig. 3. Effects of initial oxygen concentration in the separation-side stream on conversion with varying Tu^0 (Isothermal, $Da_r^0 = 100$, $Da_s^0 = 5 \times 10^3$, $U_l^0 = 4$, $V_{sw}^0 = 5$)

found to be attainable. Furthermore, it is clear from **Fig. 2** that the conversion obtained increases with increasing Da_s^0 .

Figure 3 shows the effects of the initial oxygen concentration in the sweep gas being sent to the separation side on the conversion of the dehydrogenation, where the ratio of the hydrogen permeability to the feed rate, Tu^0 , is used as a parameter. As the oxygen concentration and Tu^0 increase, higher conversion can be obtained. It is also found that the

difference between the conversion for $Tu^0=50$ and that for $Tu^0=100$ is very small. This indicates that when Tu^0 becomes large, the rate of the dehydrogenation is not affected very much by the hydrogen permeability, Tu^0 , but is limited by the oxidation rate, Da_s^0 .

3.2 Adiabatic model

1) In the case where γ is infinite First, the calculated result for the special case where the heat exchange between the reaction and separation sides is complete ($\gamma = \infty$) and thereby the temperatures on the two sides are identical, is shown in Fig. 4. This figure shows the conversion and temperature profiles in the reactor when the oxygen concentration in the sweep gas is varied. It is found that the reactor temperature begins to drop as soon as the reactant enters the reactor. This is because initially the dehydrogenation is so predominant that the resulting endothermic heat is larger than the exothermic heat due to the oxidation. Then, as the evolution of heat due to the surface oxidation (combustion) of the hydrogen permeating from the reaction side gradually becomes larger than the endothermic heat, the temperature begins to rise. Because both the dehydrogenation and the oxidation are accelerated with increasing temperature, it can be seen that the temperature also rises very rapidly. Correspondingly to this temperature behavior, the conversion curves represent a drastic change as found in Fig. 4. Of course, the reactor length necessary to complete the reaction becomes shorter as the oxygen concentration is increased.

On the other hand, when the oxygen concentration equals zero, i.e., no oxidation occurs, the conversion obtained is found to be very low. This is due to a self-cooling effect, which means that the reaction temperature drops due to the endothermic heat of the dehydrogenation itself.

2) In the case where γ is finite Figure 5 shows the conversion and temperature profiles in the reactor using a parameter γ . At $\gamma=10^4$, there is no clear difference between the respective temperatures on the reaction and separation sides, θ_r and θ_s . As γ decreases, the difference increases and further the reactor length needed to obtain 100% conversion becomes shorter; that is, the reaction proceeds faster with decreasing heat transfer rate. Although this appears unusual at first sight, the reason can be explained as follows. As the heat transfer rate (or coefficient) becomes small, the heat evolved by the oxidation on the separation side is more difficult to transfer to the reaction side. Namely, since the heat is mainly consumed to heat up the separation-side stream itself and to make the rate of oxidation larger, the temperature will increasingly rise, with an accompanying increase of the temperature difference between the separation and reaction sides, $\theta_s - \theta_r$. This affects the heat transfer

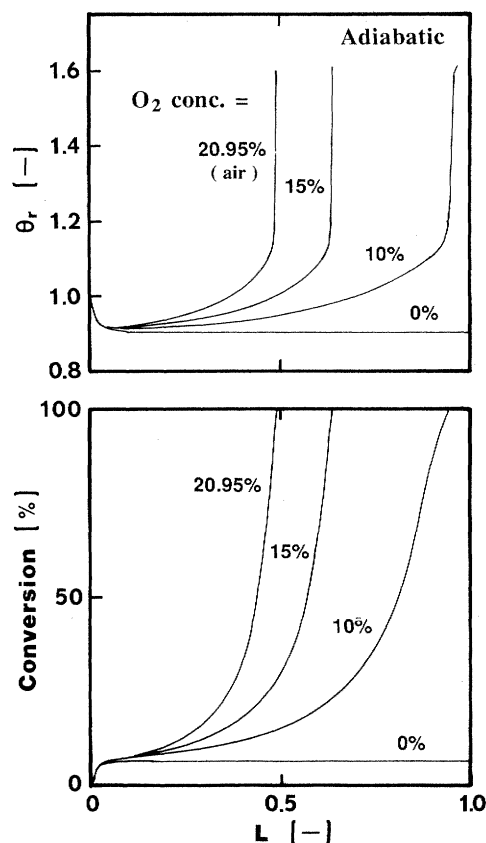


Fig. 4. Conversion and temperature profiles along the reactor length with varying oxygen concentration ($\gamma = \infty$, $Da_r^0 = 100$, $Da_s^0 = 5 \times 10^3$, $Tu^0 = 45$, $U_I^0 = 4$, $V_{sw}^0 = 5$)

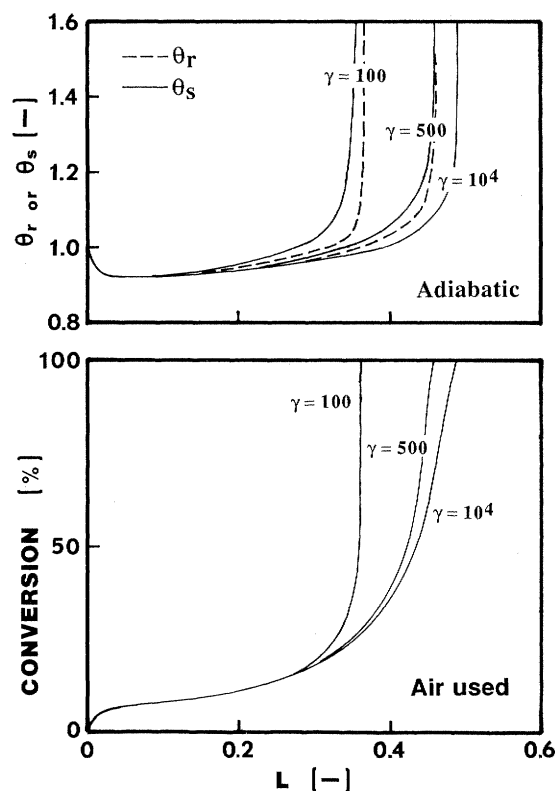


Fig. 5. Conversion and temperature profiles when γ is large ($Da_r^0 = 100$, $Da_s^0 = 5 \times 10^3$, $Tu^0 = 45$, $U_I^0 = 4$, $V_{sw}^0 = 5$)

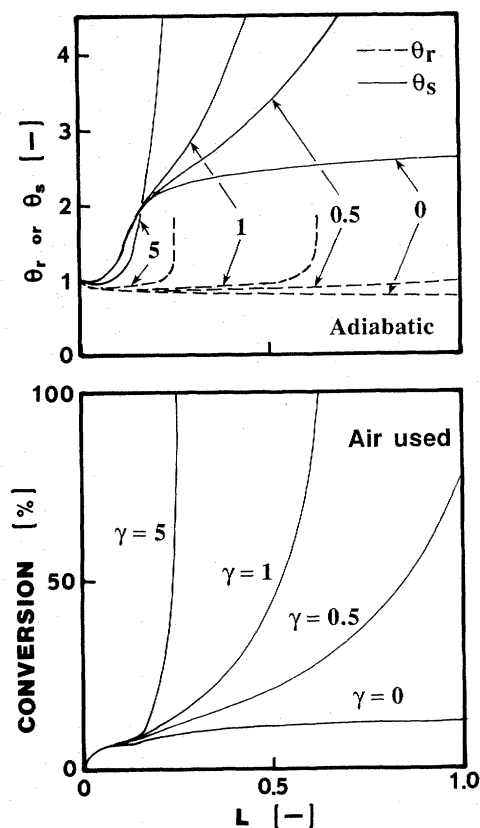


Fig. 6. Conversion and temperature profiles when γ is small ($Da_r^0 = 100$, $Da_s^0 = 5 \times 10^3$, $Tu^0 = 45$, $U_I^0 = 4$, $V_{SW}^0 = 5$)

rate, causing the product of the heat transfer coefficient and the temperature difference to be larger. That is why the reaction with a small γ value proceeds more rapidly than that with a large γ value.

Such a tendency holds until γ reaches about 5, for the same reason as seen in Fig. 6. It can be found that as γ falls below 5, the progress of the reaction becomes slower. This is understandable by considering that the heat transfer coefficient is so small that the heat supply from the separation side to the reaction side is no longer enough to maintain a sufficient speed of dehydrogenation. In addition, as the rate of dehydrogenation becomes small, the amount of hydrogen produced becomes small: this leads not only to a decrease in the amount of hydrogen permeable to the separation side but also to a decrease in the heat evolved by the oxidation. As a result of these synergistic effects, the rate of the reaction can be decreased extremely.

In Fig. 7, the reactor length, L_e [—], necessary to complete the dehydrogenation with varying γ is calculated. Although L_e rapidly decreases with increasing γ , it reaches a minimum for some γ in the range 10 – 10^2 . Then L_e attains a saturated value more than $\gamma = 10^4$. It is evident that there is a minimum value for L_e under a given condition. This condition can be said to be optimum for operating the membrane

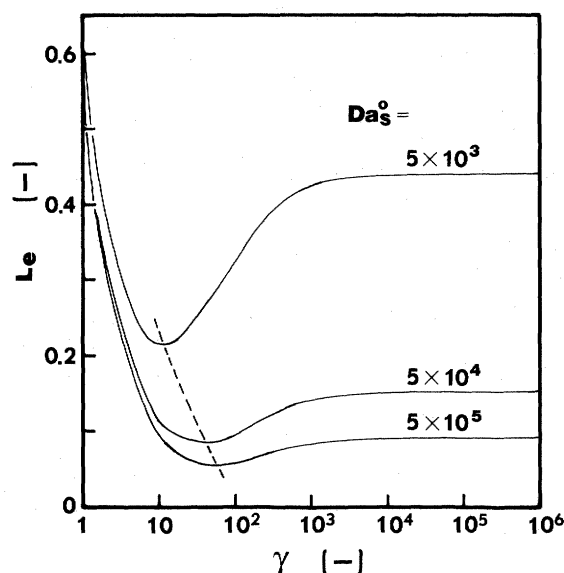


Fig. 7. Reactor length required to attain 100% conversion ($Da_r^0 = 100$, $Tu^0 = 45$, $U_I^0 = 4$, $V_{SW}^0 = 5$)

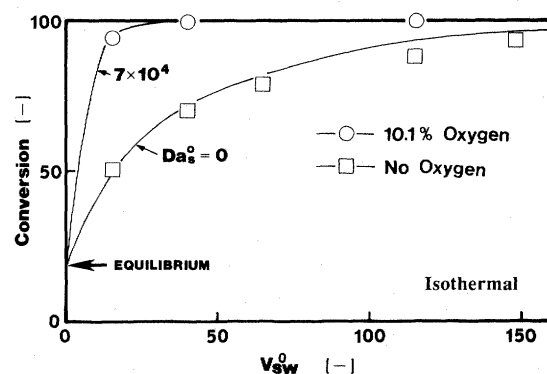


Fig. 8. An example of application of the isothermal model to experimental results ($Da_r^0 = 107$, $Tu^0 = 45.1$, $U_I^0 = 4.05$, 473 K)

reactor adiabatically. It is also found that increasing Da_s^0 results in a decrease of L_e ; this is because the evolution rate of heat due to the oxidation is increased.

4. Simulation for Experimental Results

Simulation for the results experimentally obtained in the previous note⁵⁾ was done using the isothermal model. Application of this model is considered to be valid since the membrane reactor used is placed in a thermostat to keep the overall temperature uniform, the feed is diluted with argon, and further the feed rate is small enough to ignore the heat of reaction produced to be a constant, i.e., $u_c^0 = 6.9 \times 10^{-7}$ mol/s.

The other parameters except the Damköhler number with respect to the oxidation, Da_s^0 , in the model equations have already been evaluated on the basis of the experimental results, etc. as shown in Fig. 8. Figure 8 shows a comparison of the experimental results with the calculated curves which were drawn by obtaining good agreement between the two by using

Da_s^0 as the parameter in calculations. When $Da_s^0 = 0$, it means that the sweep gas includes no oxygen. Although further basic study is considered to be required to determine whether the mechanism of the oxidation proposed is valid or not, it seems that the newly developed reactor model could explain the experimental results well.

Conclusion

A bifunctional membrane reactor using palladium, which can function both as a hydrogen-permeable membrane and as a catalyst for oxidation, was proposed. This type of reactor makes possible the selective removal of hydrogen produced by dehydrogenation through the palladium membrane and the subsequent reaction on its opposite surface between the hydrogen permeated and oxygen. Therefore, effects will be expected such as equilibrium shift, compensation of heats of reaction and improvement of reaction rate. In this study, analytical models for the dehydrogenation-oxidation system necessary to evaluate the performance of such a reactor, i.e., isothermal and adiabatic models, were developed and were solved numerically.

By the isothermal model, it was shown that a remarkable drop in the concentration of hydrogen on the separation side due to its consumption by catalytic oxidation leads to an increase in the net permeation rate of hydrogen and thereby higher conversion compared with that at an equilibrium attainable by a conventional catalytic reactor. On the other hand, by the adiabatic models, taking into account the heat balance, it was found that the rate of the dehydrogenation is greatly affected by the magnitude of γ , a dimensionless number related to the heat transfer rate.

Finally, the experimental results reported in the previous note, where the dehydrogenation of cyclohexane to benzene and the hydrogen-oxygen reaction were combined, was found to be largely explained by applying the isothermal model developed in this study.

Appendix

Kinetic model for the hydrogen-oxygen reaction on the palladium membrane surface

Although investigations of the catalyzed reaction between hydrogen and oxygen (so-called surface combustion) on platinum have appeared in the literature, there are few studies employing palladium as the catalyst. Especially, no kinetics applicable to this case can be found. Therefore, the following kinetic model based on the Langmuir-Hinshelwood mechanism was postulated.

- 1) $O_2 + \delta \rightleftharpoons O_2^*$ (equilibrium)
- 2) $2H^* \rightleftharpoons H_2 + 2\delta$ (equilibrium)
- 3) $O_2^* + 4H^* \rightarrow 2H_2O^* + 3\delta$ (slow)
- 4) $2H_2O^* \rightleftharpoons 2H_2O + 2\delta$ (equilibrium)

where δ shows active positions on the surface. It was assumed that

adsorption equilibrium is maintained at all times, and that the rate-controlling step is the chemical reaction between the adsorbed oxygen molecule and the dissociated hydrogen atoms on the catalyst surface. Accordingly, the net rate of reaction becomes

$$-r_O = \frac{k_s(p_O p_H^2 - p_W^2/K_{P_w})}{(1 + \sqrt{K_H p_H} + K_O p_O + \sqrt{K_W p_W})^5} \quad (A1)$$

In this equation, since the value of the equilibrium constant for water decomposition, K_{P_w} , is very large⁸⁾, i.e., 3.03×10^{58} atm at 400 K, 1.82×10^{37} atm at 600 K and 3.80×10^{26} atm at 800 K, and p_W is expected to be not large under the usual operating conditions, the term p_W^2/K_{P_w} may be negligible. In addition, at present a meaningful evaluation of the adsorption term is impossible, so that this term is also neglected. Thus, a simpler power form of the rate equation is obtained as

$$-r_O = k_s p_O p_H^2 \quad (A2)$$

This form is similar to that proposed by F. Leder and J. B. Butt for a platinum catalyst⁷⁾.

Nomenclature

A	= membrane area	[m ²]
$c_{P_c}^0$	= specific heat of reactant	[J · mol ⁻¹ · K ⁻¹]
c_{P_i}	= specific heat of gas i at a temperature T	[J · mol ⁻¹ · K ⁻¹]
C_{P_i}	= $c_{P_i}/c_{P_c}^0$	[—]
C_O	= concentration of hydrogen dissolved in palladium membrane at a temperature T_0 and a pressure P_0	[mol · m ⁻³]
D	= diffusion coefficient of hydrogen through palladium membrane	[m ² · s ⁻¹]
Da_r^0	= Damköhler number for reaction side at T_0 and P_0 , $k_r V_r P_r / u_C^0$	[—]
Da_s^0	= Damköhler number for separation side at T_0 and P_0 , $k_s A P_s^3 / u_C^0$	[—]
E_j	= activation energy	[kJ · mol ⁻¹]
f_j	= rate expression	[—]
h_o	= overall heat transfer coefficient	[kJ · m ⁻² · s ⁻¹ · K ⁻¹]
ΔH_j	= heat of reaction	[kJ · mol ⁻¹]
k_r	= rate constant of dehydrogenation	[mol · m ⁻³ · s ⁻¹ · Pa ⁻¹]
k_s	= rate constant of oxidation	[mol · m ⁻² · s ⁻¹ · Pa ⁻³]
K_i	= adsorption equilibrium constant of gas i	[Pa ⁻¹]
K_P	= equilibrium constant for dehydrogenation	[Pa ³]
L	= dimensionless reactor length	[—]
L_e	= dimensionless reactor length required to complete dehydrogenation	[—]
m	= stoichiometric number	[—]
p_i	= partial pressure of gas i	[Pa]
P_r	= total pressure on reaction side	[Pa]
P_s	= total pressure on separation side	[Pa]
P_0	= reference pressure, 1.01325×10^5	[Pa]
R	= gas constant	[J · mol ⁻¹ · K ⁻¹]
t_m	= thickness of membrane	[m]
T	= absolute temperature	[K]
T_0	= absolute temperature at inlet of reactor	[K]
Tu	= dimensionless number representing a ratio of hydrogen permeation rate to feed rate, $DC_O A / (t_m u_C^0)$	[—]
Tu^0	= Tu value at T_0 and P_0	[—]
u_i	= flow rate of gas i in reaction-side stream	[mol · s ⁻¹]
u_i^0	= flow rate of gas i at reaction-side inlet	[mol · s ⁻¹]
U_i	= dimensionless flow rate of gas i in reaction-side stream, u_i / u_C^0 , $u_H / (m u_C^0)$	[—]

v_i	= flow rate of gas i in separation-side stream	$[\text{mol} \cdot \text{s}^{-1}]$
v_i^0	= flow rate of gas i at separation-side inlet	$[\text{mol} \cdot \text{s}^{-1}]$
V_i	= dimensionless flow rate of gas i in separation-side stream, $v_i/u_C^0, v_H/(mu_C^0)$	$[-]$
V_r	= reaction-side volume	$[\text{m}^3]$
V_{SW}^0	= total flow rate of sweep gas at separation-side inlet, $V_I^0 + V_O^0$	$[-]$
γ	= $h_s A / c_{Pc} u_C^0$	$[-]$
θ_j	= dimensionless temperature, T_j/T_0	$[-]$
π_i	= dimensionless pressure, p_i/P_0	$[-]$

<Subscripts>

C	= reactant of dehydrogenation
D	= dehydrogenated product
H	= hydrogen
i	= gas i
j	= either reaction or separation side
I	= inert gas
O	= oxygen
p	= permeation

r	= reaction side
s	= separation side
SW	= sweep gas
W	= water
<Superscript>	
0	= indicates inlet value

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