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The Hydrogenation of 1,3-Butadiene over a Palladium Membrane

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The hydrogenation of 1,3-butadiene was carried out over a palladium membrane at 100 °C in two ways: (1) by hydrogen permeating the membrane, and (2) by hydrogen premixed in the gas phase. In the reactions using permeate hydrogen, hydrogenation at the higher pressures of butadiene was limited by the hydrogen permeation; namely, the rate was determined by the pressure of hydrogen upstream. The product composition was, at the same time, unchanged by the reaction rate. At the lower pressures of butadiene, the selectivity for butene formation was decreased with the decrease in the butadiene pressure, and the reaction rate was approximately equal to that when the premixed hydrogen was used over the β-phase membrane. The mechanism of the reaction using premixed hydrogen over the α-phase membrane was analyzed quantitatively by obtaining the dissolved hydrogen concentration from the measurement of the hydrogen-permeation rate from the reaction surface. It was elucidated that the reaction was limited by the hydrogen adsorption, the rate of which was affected by the presence of 1,3-butadiene, and that the reaction rate was much smaller than that when permeate hydrogen was used.

The catalytic hydrogenation of olefins is one of the reactions investigated most frequently. Palladium, among the metallic catalysts employed for hydrogenation, has the peculiar property of dissolving a large amount of hydrogen at room temperature and of making the hydrogen diffuse through it. It has been reported that the reaction of propylene by the hydrogen dissolved in palladium proceeds much faster than that by gaseous hydrogen.[1)] The present authors have also observed that the hydrogen permeating the palladium membrane enhanced the hydrogenation of 1,3-butadiene.[2)] For the hydrogenation of ethylene, however, no such enhancement could be observed.

The measurement of the hydrogen-permeation rate through the α-phase palladium membrane showed that the hydrogen permeation from the reaction surface was decreased by the reaction of 1,3-butadiene, not by the reaction of ethylene. It was considered, therefore, that the enhancement of olefin hydrogenation was related to the decrease in the hydrogen-permeation rate.[2)]

In a previous study,[3)] the present authors analyzed the kinetic mechanism of ethylene hydrogenation by means of permeate hydrogen. The hydrogen transport was considered to consist of three processes: (I) hydrogen adsorption or desorption on the membrane surface, (II) transfer into or out of the membrane through the interface, and (III) diffusion through the membrane. As for the hydrogenation of ethylene by means of permeate hydrogen, the reaction rate was found to be expressed by the mechanism assuming that the equilibrium was established for Processes (I) and (II) at the reaction surface of the membrane.[3)] In the case of 1,3-butadiene hydrogenation, the results of the hydrogen-permeation-rate measurement suggested that the equilibrium was not established.

In the present paper, the concentration of dissolved hydrogen in the vicinity of the reaction surface of the membrane was calculated from the permeation rate and the hydrogen sorption equilibrium data. Using the concentration thus calculated, the kinetic mechanism of 1,3-butadiene hydrogenation was investigated quantitatively based on the mechanism of hydrogen transport memtioned above.

Experimental

Materials. The palladium membranes purchased from the Tanaka Kikinzoku Kogyo Co. were 99.95% pure and 50 μm thick. The membrane was pretreated before the reaction as follows: Primarily, the membrane degreased with acetone was polished electrolytically in 0.5 M[†] H_2SO_4 aqueous solution, and palladium black was electrodeposited on both the surfaces of the membrane in 0.05 M of a $PdCl_2$ aqueous solution. Secondly, the membrane was oxidized in air at 600 to 700 °C.[4)] Then, the oxidized membrane which was set into the reactor was reduced by hydrogen at room temperature and heated in nitrogen stream to the reaction temperature in order to remove the hydrogen dissolved in the membrane.

The hydrogen contained in a cylinder was 99.99999% pure, and the other gases and reagents employed in the experiments were commercial-grade and were used without further purification.

Reactor and Procedure. The reactor, made of stainless steel, was separated into two compartments of equal volumes by the use of a palladium membrane pinched by reduced copper gaskets. Reactant gases were introduced into one compartment, called the reaction compartment, and hydrogen into the other, called the hydrogen compartment, for hydrogenation by means of permeate hydrogen. The effective area for hydrogen permeation was 4.9 cm². The details about the reactor was described elsewhere.[3)]

The hydrogenation of 1,3-butadiene was carried out by two different methods: (I) by the use of hydrogen permeating the palladium membrane from the hydrogen compartment, and (II) by the use of premixed hydrogen. The reaction system by Method (I) was named the permeation system; here, a mixture of 1,3-butadiene and a diluent gas such as nitrogen passed through the reaction compartment. The system by Method (II) was named the mixture system; here, a mixture of hydrogen, 1,3-butadiene, and nitrogen was passed through the reaction compartment, with nitrogen filling the hydrogen compartment.

[†] 1 M=1 mol dm^{-3}.

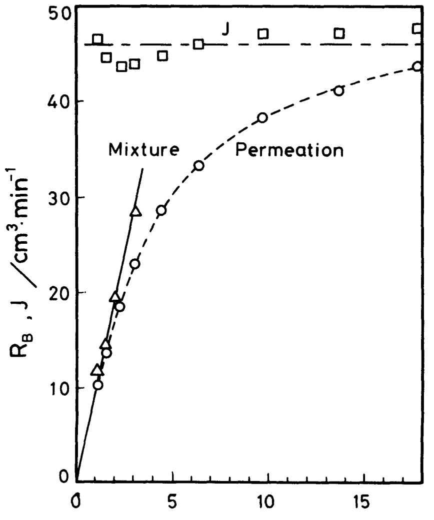

Fig. 1. Hydrogenation rates of 1,3-butadiene over a 0.005 cm palladium membrane and hydrogen permeation rate, *J*, at 100 °C and at the upstream hydrogen pressure of 100 kPa. Triangles represent the rates of the reaction by premixed hydrogen of 47 kPa.

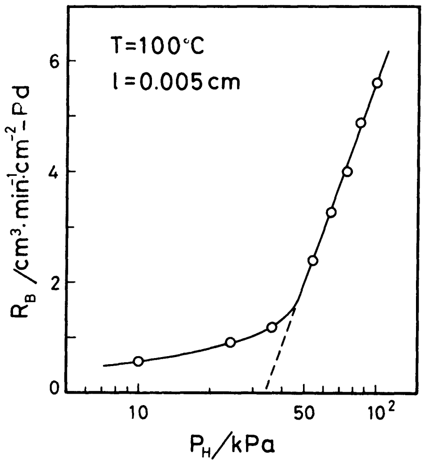

Fig. 2. Hydrogenation rate of 1,3-butadiene by permeate hydrogen through a 0.005 cm Pd membrane at the butadiene pressure of 40 kPa and at 100 °C as a function of the upstream hydrogen pressure.

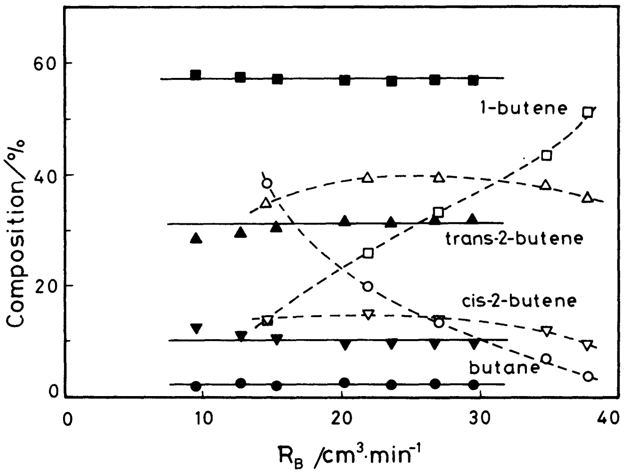

Fig. 3. Product distribution in the hydrogenation of 1,3-butadiene by permeate hydrogen at 100 °C. Filled symbols represent the compositions under the hydrogen permeation limitation and open symbols otherwise.

The molar fractions of the component gases were determined with a gas chromatograph equipped with a TC detector. The column packings were VZ-7 for the analysis of hydrocarbons and Molecular Sieve 13X for hydrogen.

The reaction was carried out at 100 °C for both systems. The partial pressures of 1,3-butadiene ranged from 1 to 41 kPa. The hydrogen partial pressures ranged from 10 to 100 kPa for the permeation system and from 1 to 47 kPa for the mixture system. The flow rate in the reaction compartment was kept at 500—600 cm^3 min^{-1} in order to avoid limiting the reaction rate by mass transfer in the gas-boundary film.[5]

Results

Hydrogenation by Permeate Hydrogen. Figure 1 shows the hydrogenation rate and the hydrogen permeation rate as a function of the 1,3-butadiene pressure at the upstream hydrogen pressure of 100 kPa. The behavior of the reaction rate was different from that for ethylene hydrogenation, which showed that the dependence of the reaction rate on the ethylene pressure could be expressed approximately by two straight lines.[5]

At the butadiene pressures higher than 20 kPa, the hydrogenation rate was approximately constant and almost identical with the hydrogen-permeation rate. The hydrogenation rate at the butadiene pressure of 40 kPa is shown in Fig. 2 as a function of the upstream hydrogen pressure. The rate was varied linearly with ln P_H when the hydrogen pressure was higher than 35 kPa, which approximately corresponds to the minimum pressure for forming the β-phase at the reaction temperature.[6] While the reaction rate was changed by the upstream hydrogen pressure, the composition of the products was substantially unchanged, and the selectivity for butene formation was more than 0.98 (Fig. 3).

At the butadiene pressures lower than 20 kPa, the hydrogenation rate was dependent on the butadiene pressure. At a pressure as low as 1 kPa, the rate was very close to that obtained for the mixture system at the hydrogen pressure of 47 kPa, where the membrane formed the β-phase. However, the pressure of the unreacted hydrogen in the reaction compartment was much lower than the minimum pressure for forming the β-phase. Since the hydrogen-permeation rate under a reaction was approximately independent of the reaction rate or the butadiene pressure, the pressure of the unreacted hydrogen increased as the reaction rate decreased. With the increase in the unreacted hy-

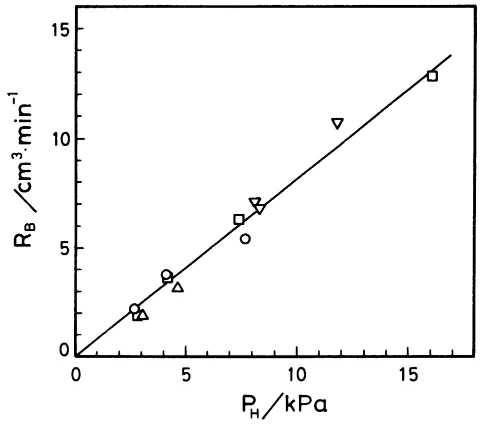

Fig. 4. Hydrogenation rate of 1,3-butadiene by premixed hydrogen over an α-phase Pd membrane of 0.005 cm at 100°C. 1,3-Butadiene pressure (kPa)----- ○: 1.0, □: 2.5, △: 5.0, ▽: 7.0.

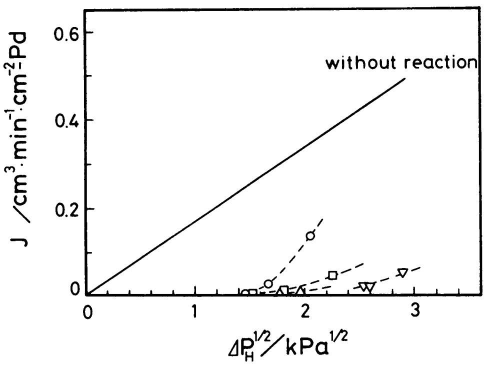

Fig. 5. Hydrogen permeation rate from the reaction surface of a 0.005 cm Pd membrane at 100°C. Keys are the same as in Fig. 4.

drogen pressure, the product composition was remarkably changed, as is shown in Fig. 3.

Hydrogenation by Premixed Hydrogen. The hydrogenation was performed over the palladium membrane of two different phases. When the membrane consisted of the β-phase, i.e., when the hydrogen pressure was over 30 kPa, the hydrogenation rate was proportional to the butadiene pressure, as is shown in Fig. 1. In the case of the α-phase membrane, the rate was proportional to the hydrogen pressure and independent of the butadiene pressure, as is shown in Fig. 4.

As for the latter case, the hydrogen-permeation rate from the reaction side to the other side of the membrane was also measured; it is shown in Fig. 5. The permeation rate was strongly dependent on the butadiene pressure. The hydrogen-permeation rate after the butadiene feed to the reactor had been stopped was well recovered to the initial permeation rate. The concentration of the dissolved hydrogen in the vicinity of the reaction surface, n, was calculated from the permeation rate by the use of Eq. 1:

$$n = \frac{P_H}{K_H} + \frac{J}{\kappa D_\alpha / l} \qquad (1)$$

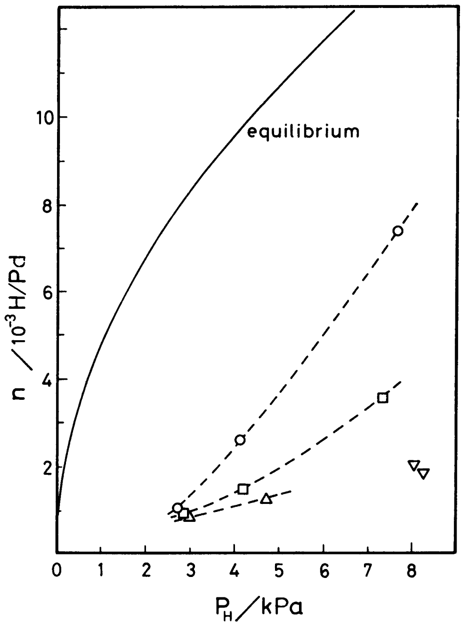

Fig. 6. Dissolved hydrogen concentration in the vicinity of the reaction surface under reaction at 100°C as a function of hydrogen pressure. Keys are the same as in Fig. 4.

P_H is the hydrogen pressure in the compartment to which hydrogen diffuses, and J is the hydrogen permeation rate. K_H is Sieverts' constant; l, the membrane thickness; κ, the hydrogen concentration at $n=1$, and D_α, the hydrogen-diffusion coefficient through the α-phase palladium. The calculated values of the hydrogen concentration under the reaction, shown in Fig. 6, were lower than those in equilibrium with the gaseous hydrogen and decreased as the butadiene pressure increased.

Discussion

Hydrogenation by Permeate Hydrogen. The previous kinetic analysis of reaction by permeate hydrogen[3] obtained the following results. When the adsorption constant of hydrogen is much larger than the value determined by the operational condition, the reaction rate increases in proportion to the olefin-surface coverage until the rate becomes equal to the hydrogen-diffusion rate, and thereafter the rate is limited by the diffusion rate. This case was observed in the hydrogenation of ethylene. When the hydrogen-adsorption constant is as large as the value determined by the operational condition, the reaction rate increases, but not in proportion to the olefin surface coverage.

Based on the analysis presented above, the behavior of the hydrogenation of 1,3-butadiene shown in Fig. 1 can be explained either by the small adsorption constant of hydrogen affected by butadiene, or by the nonlinear adsorption isotherm of butadiene and the large hydrogen-adsorption constant. The hydrogenation rate by permeate hydrogen at a butadiene pressure of less than 3 kPa was found to be smaller than that by premixed hydrogen over the β-phase membrane, where the hydrogen surface coverage was considered to be unity. The adsorption constant of hydrogen under the reaction of 1,3-butadiene, therefore, was not so large as that under the reaction of ethylene. It was concluded that the presence of 1,3-butadiene affected the hydrogen adsorption. This conclusion was supported by the change in the butene selectivity caused by the butadiene pressure, as is shown in Fig. 3.

At a butadiene pressure as high as 40 kPa, it was observed that the hydrogenation rate for the permeation system was over ten times larger than that for the mixture system at the same hydrogen pressure as low as 0.2 kPa.[2] This suggested that the rate-determining step was different between the two systems. For the permeation system, the reaction rate was limited by the hydrogen permeation through the membrane, since the rate was varied linearly with ln P_H and since its slope was in good agreement with that predicted for the hydrogen permeation limitation.[6] Thus, it is reasonable to consider that the permeate hydrogen is ready to react with the adsorbed butadiene after reaching the reaction surface when butadiene is adsorbed in a sufficient amount.

Rate Process over α-Phase Membrane for the Mixture System. The hydrogenation rate equation over the α-phase membrane was expressed as:

$$R = kP_{\mathrm{H}}^{1.0}P_{\mathrm{B}}^{0}. \tag{2}$$

This equation for the α-phase is different from that for the α-phase, but is often met with in the hydrogenation of olefins. Sato et al.[7] analyzed the kinetic mechanism of ethylene hydrogenation over various metallic catalysts, including palladium, and reached the conclusion that the rate-determining step lies on the hydrogen adsorption. Since it was found that 1,3-butadiene affects the hydrogen adsorption, as has been discussed above, it is reasonable to assume that the hydrogenation of butadiene proceeds under the hydrogen-adsorption limitation.

It is generally difficult to determine the rate equation of the surface reaction under the adsorption limitation. In the 1,3-butadiene hydrogenation, however, there have been many studies which provide some knowledge about the reaction mechanism. The mechanism neglecting the conformations of the adsorbed butadiene and butenes can be described as follows[8]:

$$\mathrm{C_4H_6(gas)} \rightleftharpoons \mathrm{C_4H_6(ads)} \underset{2}{\overset{1}{\rightleftharpoons}} \mathrm{C_4H_7} \xrightarrow{3} \mathrm{C_4H_8(ads)}.$$

The half-hydrogenated species, C_4H_7 may change back to diene and to butene. Since it has been reported that the ratio of hydrogen to deuterium atoms on the palladium surface is low,[9] the reverse reaction of the half-hydrogenation (Step 2) can be considered to be a slow-step. When the reaction of half-hydrogenated species

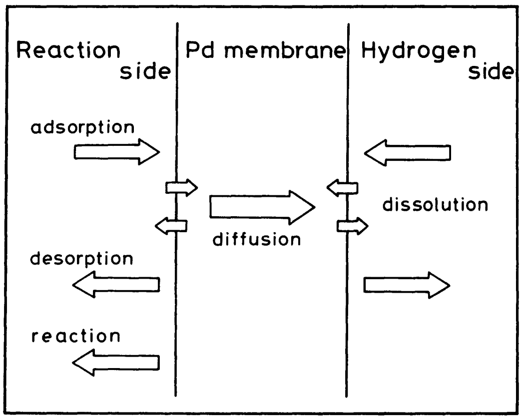

Fig. 7. Illustration of mass transfer process of hydrogen.

with hydrogen (Step 3) proceeds faster than the reverse reaction, the rate equation is expressed as:

$$R = k_{\mathrm{B}}\theta_{\mathrm{H}}\theta_{\mathrm{B}}. \tag{3}$$

When the hydrogenation occurs on the palladium membrane, hydrogen is, at the same time, dissolved into the membrane and diffuses through the membrane. These processes are shown schematically in Fig. 7. The rate equations of these processes may be presented as:

$$\text{dissolution: } r_{\mathrm{s}} = k_{\mathrm{i}}\theta_{\mathrm{H}} - k_{\mathrm{o}}n \tag{4}$$

$$\text{diffusion : } r_{\mathrm{d}} = k_{\mathrm{d}}(n-n_{\mathrm{o}}) \doteqdot k_{\mathrm{d}}n \tag{5}$$

The hydrogen adsorption rate is:

$$\text{adsorption: } r_{\mathrm{a}} = k_{\mathrm{a}}P_{\mathrm{H}} \tag{6}$$

Where k_i and k_o are the rate constants for hydrogen transfer into a membrane and out of a membrane respectively. k_d is equal to $\kappa D_\alpha/l$, as has been noted previously. k_a is the rate constant of hydrogen adsorption.

From Eqs. 4 and 5, the concentration of the dissolved hydrogen atom, n, in the steady-state is expressed as:

$$n = \frac{k_{\mathrm{i}}}{k_{\mathrm{o}}+k_{\mathrm{d}}}\theta_{\mathrm{H}} \tag{7}$$

and:

$$r_{\mathrm{s}} = r_{\mathrm{d}} = \frac{k_{\mathrm{d}}k_{\mathrm{i}}}{k_{\mathrm{o}}+k_{\mathrm{d}}}\theta_{\mathrm{H}}. \tag{8}$$

Since the hydrogen-adsorption rate is equal to the sum of the reaction rate and the diffusion rate, then:

$$r_{\mathrm{a}} = \left(k_{\mathrm{B}}\theta_{\mathrm{B}} + \frac{k_{\mathrm{d}}k_{\mathrm{i}}}{k_{\mathrm{o}}+k_{\mathrm{d}}}\right)\theta_{\mathrm{H}}. \tag{9}$$

From Eqs. 6, 7, and 9, the following expression is obtained:

$$n = \frac{k_{\mathrm{a}}P_{\mathrm{H}}}{(k_{\mathrm{o}}+k_{\mathrm{d}})k_{\mathrm{B}}\theta_{\mathrm{B}}/k_{\mathrm{i}}+k_{\mathrm{d}}}. \tag{10}$$

The reaction rate was much larger than the hydrogen-permeation rate, as is shown in Fig. 5, and the next expression can be derived:

$$k_B\theta_B \gg k_1k_d/(k_o+k_d). \tag{11}$$

Finally, n is expressed as:

$$n = \frac{k_1k_a}{k_B(k_o+k_d)}\frac{P_H}{\theta_B}. \tag{12}$$

Equation 12 shows that the concentration of the dissolved hydrogen is dependent on the butadiene surface coverage as well as the hydrogen pressure. It was found that the behavior of the hydrogen concentration shown in Fig. 6 can be qualitatively explained by Eq. 12.

From Eq. 12, the butadiene coverage is expressed by the following equation:

$$\theta_B = \frac{k_1k_a}{k_B(k_o+k_d)}\frac{P_H}{n} \tag{13}$$

Since the Langmuir-type adsorption isotherm has a wide applicability, it was assumed that the adsorption of butadiene obeys the Langmuir-type isotherm under the present experimental conditions; namely:

$$\frac{P_B}{\theta_B} = \frac{1}{K_B} + P_B \tag{14}$$

Therefore, a quantitative examination of Eq. 12 can be made by a cross plotting of nP_B/P_H against P_B, as is shown in Fig. 8. Since the relationship between nP_B/P_H and P_B was described fairly well by a straight line, Eq. 12 was considered to be reasonable. In addition, the result that the calculated value of the butadiene adsorption constant, 0.23 kPa^{-1}, was larger than that of 1-butene[3] at 100 °C was consistent with the result obtained by other investigators.[9] It was concluded that, for the present mixture system, the reaction was limited by the hydrogen adsorption and that the hydrogen adsorption was affected by the adsorption and/or the reaction of 1,3-butadiene.

Comparison of Reaction Rates for the Mixture and Permeation Systems. Based on the above considerations, the reason for the difference in the reaction rates for the permeation and mixture systems at the same composition of reactant gases may be explained as follows.

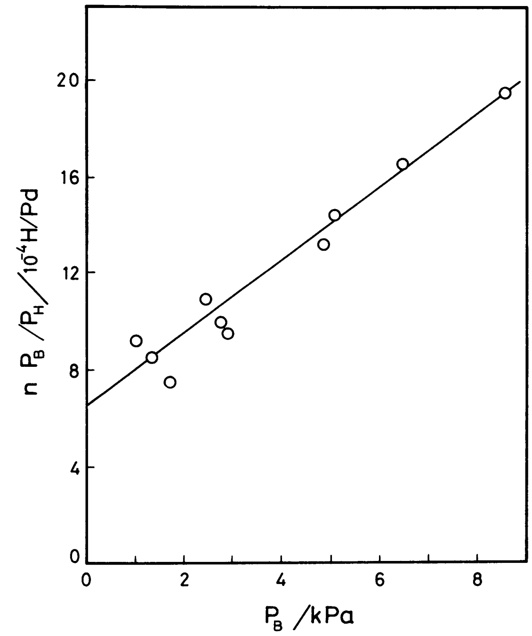

Fig. 8. Plot of nP_B/P_H against P_B for the hydrogenation of 1,3-butadiene at 100°C.

For the mixture system, the concentration of hydrogen atoms on the catalyst surface is very small because the hydrogen adsorption is strongly affected by the butadiene adsorption and/or the reaction. For the permeation system, on the other hand, hydrogen atoms are supplied from the dissolved phase in palladium, and the hydrogen-transfer process through the interface is scarcely affected at all since the reaction was not limited by this process, but by the diffusion process in bulk. Therefore, the surface coverage of hydrogen for the permeation system can considerably exceed that for the mixture system, even at the same hydrogen pressure. Thus, the reaction proceeded much faster for the permeation system than for the mixture system.

References

1) R. J. Rennard, Jr., and R. J. Kokes, *J. Phys. Chem.*, **70**, 2543 (1966).

2) H. Nagamoto and H. Inoue, *Chem. Eng. Commun.*, **34**, 315 (1985).

3) H. Nagamoto and H. Inoue, *J. Chem. Eng. Jpn.*, **14**, 377 (1981).

4) H. Nagamoto and H. Inoue *Nippon Kagaku Kaishi*, **1977**, 1264.

5) H. Nagamoto and H. Inoue, *Nippon Kagaku Kaishi*, **1979**, 327.

6) E. Wicke and G. H. Nernst, *Ber. Bunsenges. Physik. Chem.*, **68**, 224 (1964).

7) S. Sato and K. Miyahara, *Shokubai*, **18**, 153 (1976).

8) E. F. Meyer and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **85**, 2881 (1963).

9) G. C. Bond and P. B. Wells, *Advances Catalysis*, **15**, 91 (1964).