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Hydrogen recovery from cyclohexane as a chemical hydrogen carrier using a palladium membrane reactor

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Abstract

A palladium membrane reactor was applied to recover the hydrogen from cyclohexane as one of the promising chemical hydrogen carriers. The operation conditions of the palladium membrane reactor to obtain a higher hydrogen recovery were predicted by computer simulation. As a result, it was shown that the hydrogen recovery rate becomes higher as the pressure on the hydrogen permeation side is lowered below atmospheric pressure or as the reaction pressure increases. This was confirmed experimentally. As the perm-side pressure was lowered, the conversion as well as the hydrogen recovery rate at 573 K was found to increase. About 80% of the hydrogen contained in cyclohexane, depending on the operation condition was successfully recovered.

Keywords: Hydrogen carrier; Cyclohexane; Dehydrogenation; Membrane reactor; Palladium

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1. Introduction

Although great concern has been concentrated on hydrogen as a clean secondary energy, there are problems in its transportability and storability. Because hydrogen is gas and for liquefaction a temperature as low as 20 K is necessary, hydrogen carriers convenient for handling have been desired. In this sense, chemical carriers such as cyclohexane, methyl cyclohexane, etc., are considered suitable for hydrogen storage and transmission from the following viewpoints [1–3]. First, a higher hydrogen content (e.g., 7.1 wt.% of cyclohexane) is very attractive compared with metal hydrides (at most 3 wt.%). The dehydrogenated products, benzene and toluene, can be reversibly hydrogenated and reused, and those are all liquids at ordinary temperatures: these are technically important factors for establishing a hydrogen storage and transmission system. An additional advantage that there is no CO_2 emission in the dehydrogenation process will be rated highly in terms of environmental issues, whereas the steam reforming process of methanol produces not only hydrogen but also CO_2.

It is well-known that the dehydrogenation, limited by the thermodynamic equilibrium, can be enhanced very much by using a composite reactor incorporated with a membrane permselective for hydrogen [4–10]. For that, hydrogen separation membrane, which is stable under any reaction conditions is needed. Palladium is believed to be the best material for a hydrogen separation membrane because of its infinite

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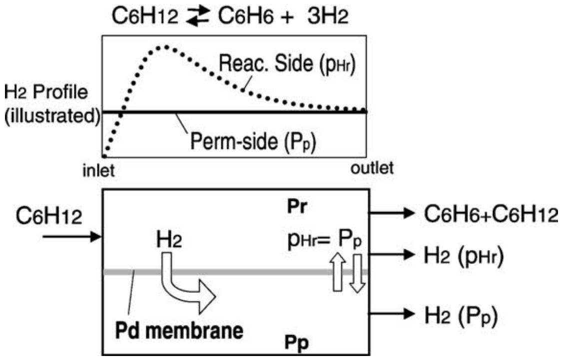

Fig. 1. Operation mode of the palladium membrane reactor for recovering pure hydrogen from the perm-side, where in principle the dehydrogenation of cyclohexane can proceed until $p_{Hr} = P_p$.

permselectivity for hydrogen and a comparatively large permeability over a wide range of temperatures. Here, it is considered that a membrane reactor using palladium should be operated as shown in Fig. 1 in order for hydrogen to be recovered in high purity. To ensure the driving force for hydrogen permeation through the membrane, the reaction pressure must be kept higher than that on the recovery-side, which is usually atmospheric pressure or less. Because such a complicated reaction system has many operating parameters, the operation conditions must be optimized to recover as much hydrogen as possible. As a matter of course, kinetic information on cyclohexane dehydrogenation at higher pressures, less in the literature is also necessary for parametric analysis.

This study is concerned with the recovery of hydrogen from cyclohexane as one of the promising chemical hydrogen carriers. First, the kinetic analysis of cyclohexane dehydrogenation under higher pressures was carried out to establish the rate expression necessary for the reactor analysis. The operation conditions of the palladium membrane reactor to obtain a higher hydrogen recovery rate were then predicted by computer simulation and followed by experiments.

2. Experimental

First, the kinetic analysis of cyclohexane dehydrogenation was carried out at 523–573 K and 1–4 bar to establish the rate expression. An integral reactor (8 mm$^{i.d.}$ × 75 mm long) packed with 5.18 g of 0.5 wt.% Pt/Al_2O_3 catalyst pellets (supplied by N.E. CHEMCAT Ltd., Japan) was used. To regulate the feed concentration, argon as an inert gas was added through a mass-flow controller.

The palladium membrane reactor used is shown in Fig. 2. The palladium membrane with a thickness of about 4 μm was prepared on an α-alumina tube (2 mm in outer diameter, 1.6 mm in inner diameter, 100 mm long, void fraction of 0.43, average pore size of 0.15 μm) by a metallorganic chemical vapor deposition (MOCVD) technique [11]. To prevent any damage due to direct contact between the membrane tube and the catalyst pellets, a porous sintered tube (of stainless steel) was placed inside the reactor. In the annular space around the sintered tube, 51.9 g of 0.5 wt.% Pt/Al_2O_3 catalyst pellets were uniformly packed. The membrane reactor was placed inside a thermostat as shown in Fig. 3. Cyclohexane was fed to an evaporator with a high-pressure syringe pump, vaporized and sent to the catalyst bed of the reactor. The reaction pressure was controlled in the range of 2–4 bar with a back-pressure regulator while the perm-side (recovery-side) pressure was controlled in the range of 0.1–1 bar with a vacuum controller.

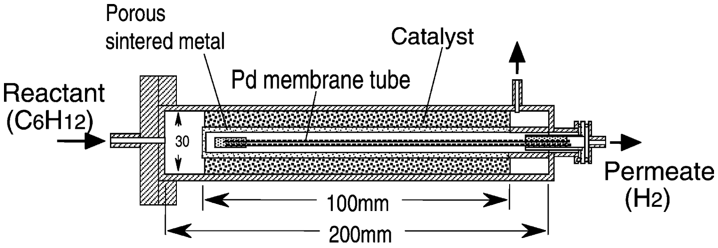

Fig. 2. Cross-sectional view of the palladium membrane reactor used.

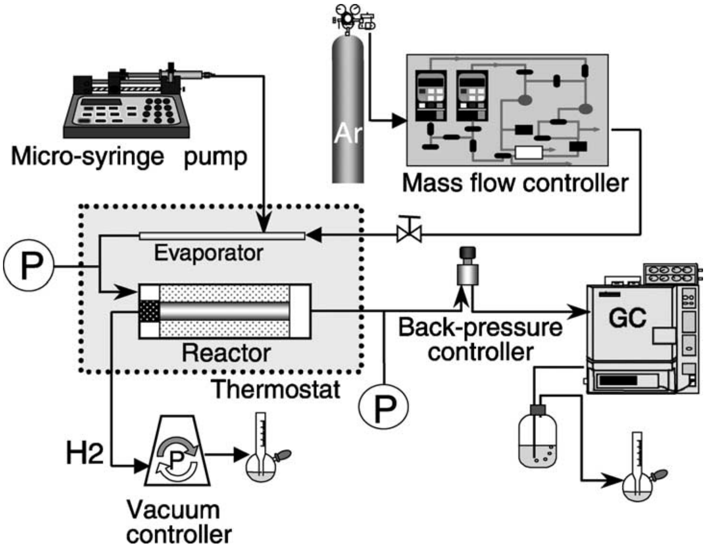

Fig. 3. Experimental set-up.

3. Results and discussion

3.1. Limiting hydrogen recovery

Referring to Fig. 1, it is easily understood that dehydrogenation of cyclohexane can in principle proceed until the partial pressure of hydrogen on the reaction side, p_{Hr}, becomes identical with the pressure on the perm-side, P_{p}, as long as the reactor length is sufficient for the reaction to reach such a dynamic equilibrium state. Here, let us define the limiting hydrogen recovery rate, RH, on the basis of 1 mol/s of cyclohexane, corresponding to 3 mol/s of hydrogen as follows:

$$\mathrm{RH} = \frac{Q_{\mathrm{t}} - Q_{\mathrm{r}}}{3} \tag{1}$$

where Q_{t} (mol/s) is the total amount of H_2 produced and Q_{r} (mol/s) is the amount of H_2 remaining on the reaction side. It has already been shown from the standpoint of dynamic equilibrium consideration that the first term, Q_{t}, can be given by the following equation [12]:

$$Q_{\mathrm{t}} = \frac{3K_{\mathrm{p}}/P_{\mathrm{p}}^3}{1 + K_{\mathrm{p}}/P_{\mathrm{p}}^3} \tag{2}$$

where K_{p} (Pa^3) is the equilibrium constant. The second term, Q_{r}, is derived from the dynamic equilibrium condition at the outlet of the reactor, $p_{\mathrm{Hr}} = P_{\mathrm{p}}$, as follows:

$$P_{\mathrm{r}} \frac{Q_{\mathrm{r}}}{1 + Q_{\mathrm{i}} + Q_{\mathrm{r}}} = P_{\mathrm{p}} \tag{3}$$

where P_{r} is the total pressure on the reaction side and Q_{i} (mol/s) is the amount of inert gas added. Rearranging Eqs. (1)–(3), the next expression for RH is obtained:

$$\mathrm{RH} = \frac{K_{\mathrm{p}}/P_{\mathrm{p}}^3}{1 + K_{\mathrm{p}}/P_{\mathrm{p}}^3} - \frac{(P_{\mathrm{p}}/P_{\mathrm{r}})(1 + Q_{\mathrm{i}})}{3(1 - P_{\mathrm{p}}/P_{\mathrm{r}})} \tag{4}$$

Based on the above equation, the limiting hydrogen recovery rate, RH, was calculated and is presented in Fig. 4 when $Q_{\mathrm{i}} = 0$. It is clear that the hydrogen recovery rate increases with increasing reaction pressure and decreasing perm-side pressure. In particular, decreasing the perm-side pressure is found to be very effective. Also, it is presumed that 100% of RH will be realized at $P_{\mathrm{p}} = 0$. Increasing the reaction pressure makes the recovery rate large but the increment rate becomes small at reaction pressures higher than 4 bar.

3.2. Kinetic equation for cyclohexane dehydrogenation

To obtain higher hydrogen recovery, the above result suggests that the dehydrogenation is preferably

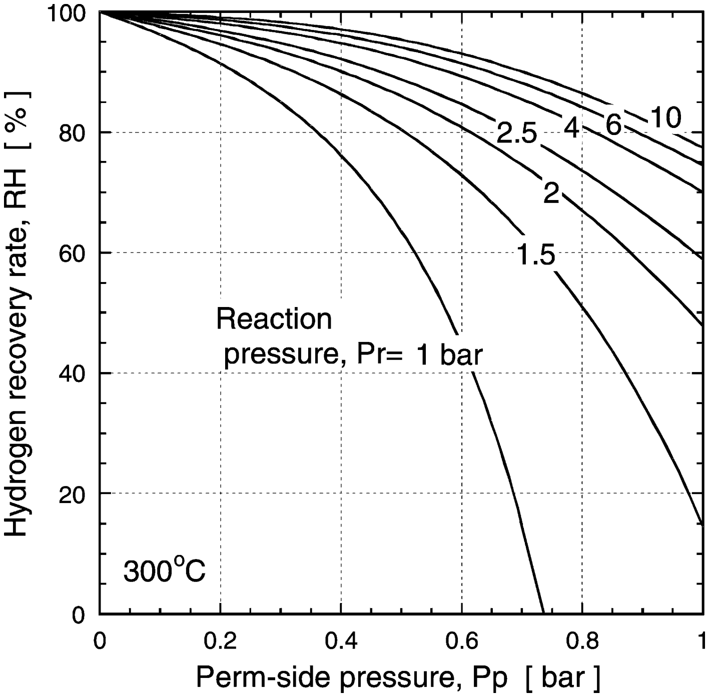

Fig. 4. Limiting hydrogen recovery rate calculated using Eq. (4), RH, when cyclohexane dehydrogenation is carried out in a palladium membrane reactor.

carried out at pressures of several bars. Therefore, it was examined regarding whether the following rate equation that was determined at atmospheric pressure [13] was available at even higher pressures:

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

(C : cyclohexane, B : benzene, H : hydrogen) (5)

where k_r (mol/(m^3 s Pa)) is the rate constant, K_B (1/Pa) the adsorption equilibrium constant with benzene, and p_i the partial pressure of component i. Analytically, the conversion was obtained by integrating the rate equation numerically, where an ideal flow reactor with isothermal and isobaric conditions was assumed. Fig. 5 shows the experimental results and the comparisons with the analytical results over the range of 514–546 K and 1–4 bar. Both are in a good agreement; therefore, it is considered that the rate equation (5) can be applied at least up to 4 bar of the reaction pressure.

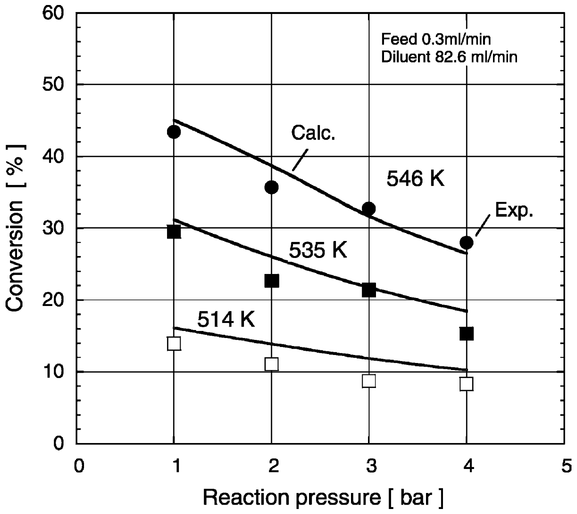

Fig. 5. Comparison of the conversions observed (symbols) with varying temperatures and pressures with the calculated lines.

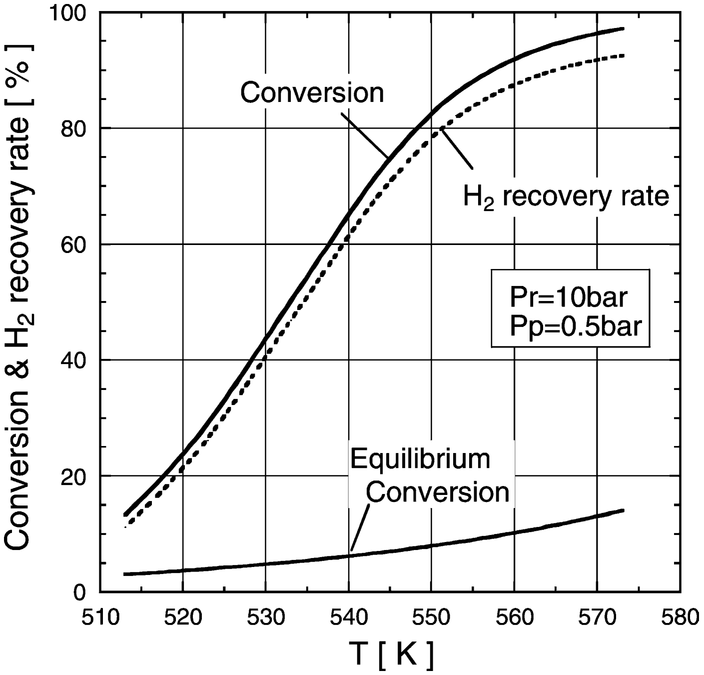

Fig. 6. Effects of the reaction temperature on the conversion and the hydrogen recovery rate simulated.

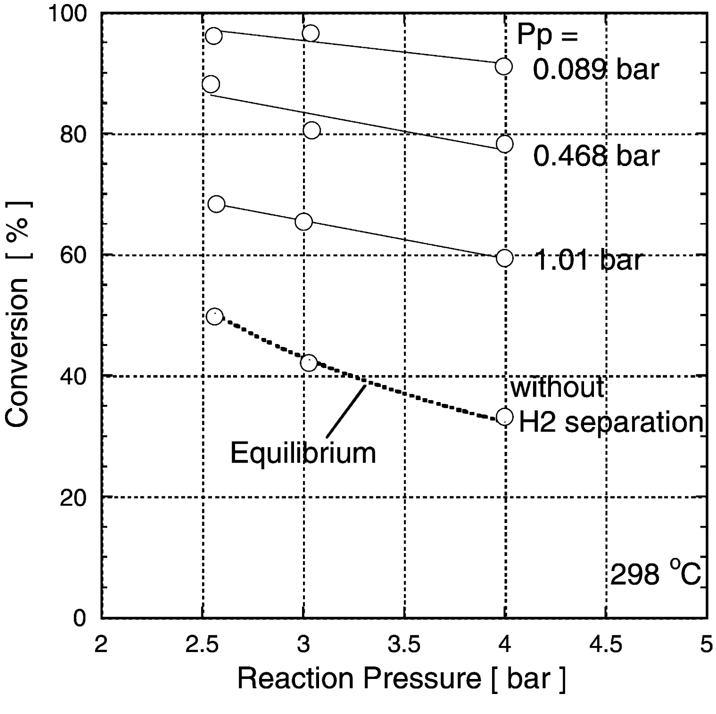

Fig. 7. Changes in conversion obtained experimentally with varying reaction and perm-side pressures.

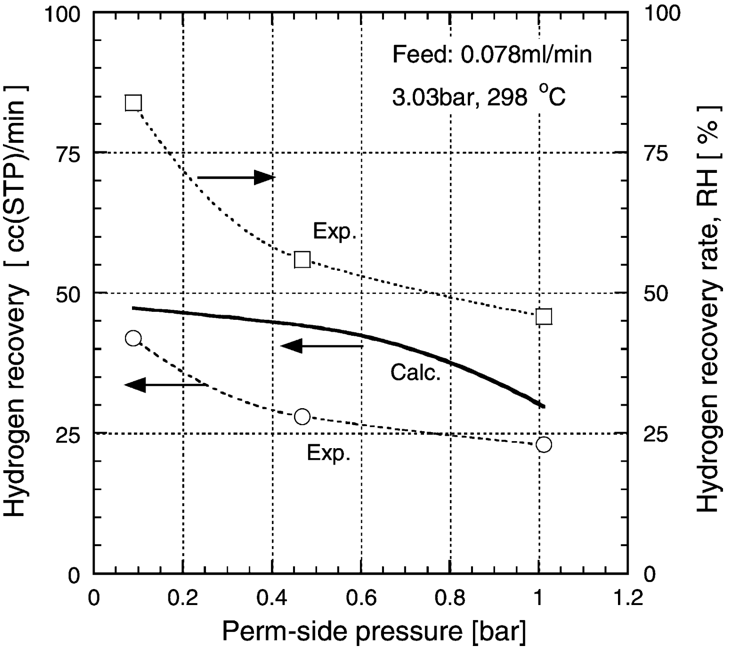

Fig. 8. Effects of the reaction pressure on the hydrogen recovery rate when the reaction side is kept at 3.03 bar (symbols: experimental, solid line: calculated).

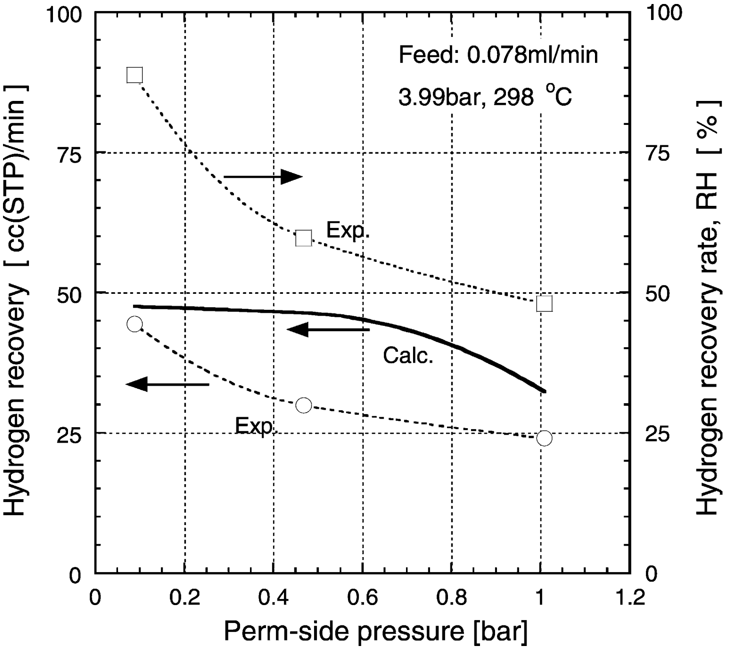

Fig. 9. Effects of the perm-side pressure on the hydrogen recovery rate when the reaction side is kept at 3.99 bar (symbols: experimental, solid line: calculated).

3.3. Hydrogen recovery by the membrane reactor

First, a computer simulation based on the mathematical model describing the mass balance within the reactor [12] was done to seek the better conditions for operating the palladium membrane reactor with the highest performance possible. As a result, it becomes clear that the reaction temperature significantly affects the improvement in the conversion as shown in Fig. 6. Based upon this simulated result, the reaction was carried out at 573 K.

The conversions obtained are plotted in Fig. 7 when the reaction and the perm-side pressures were varied. It is obvious that the conversions without removing hydrogen are in good agreement with the equilibrium ones calculated thermodynamically. As the perm-side pressure is lowered, the conversion is found to increase. This is because the amount of hydrogen removed increases with decreasing pressure on the perm-side, thereby increasing the driving force for hydrogen permeation, which is proportional to the difference between the square root of the partial pressure of hydrogen on the reaction side and that on the perm-side. Next, the results with respect to the hydrogen recovery are shown in Figs. 8 and 9. It is clearly seen that the flow rate of the hydrogen recovered increases with a decrease in the perm-side pressure. Because the feed rate of cyclohexane (78 μl/min) is determined so as to be 50 cm^3/min in terms of the total hydrogen evolution rate, a high recovery rate exceeding 80% is obtained near 0.1 bar of the perm-side pressure but around 25% at atmospheric pressure. Also, in Figs. 8 and 9, the results predicting the hydrogen flow rate are presented for comparison with the experimental results. The difference between these is found to be large in the range 0.4–0.8 bar, but the reason is unclear at the moment. According to the prediction, because there is a possibility that a high recovery rate of near 80% can be attained even at near 0.6 bar, further study is necessary to improve the performance.

4. Conclusion

The recovery of hydrogen from cyclohexane as one of the promising chemical hydrogen carriers was examined using a palladium membrane reactor. First, the rate expression for the cyclohexane dehydrogenation under higher pressures, necessary for the reactor design and analysis was established. The operation conditions of the palladium membrane reactor to obtain a higher hydrogen recovery were then predicted by computer simulation. As a result, it was shown that the hydrogen recovery rate becomes higher as the pressure on the hydrogen permeation side is lowered below atmospheric pressure or as the reaction pressure increases. Also, it was found that the reaction temperature significantly affects the conversion of cyclohexane to benzene, and preferably, the temperature should be around 573 K for accomplishing a higher recovery rate of hydrogen.

Based upon the simulated results, the reaction was carried out at 573 K and 1–4 bar while the perm-side pressure was kept in the range 0.1–1 bar. It was clearly shown that as the perm-side pressure is lowered, the conversion as well as the hydrogen recovery rate increases. Near 0.1 bar of perm-side pressure, about 80% of the hydrogen contained in cyclohexane was successfully recovered.

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