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Limiting conversions of dehydrogenation in palladium membrane reactors

Naotsugu Itoh *

National Institute of Materials and Chemical Research, 1–1 Higashi, Tsukuba 305, Japan

Abstract

The limiting conversions of dehydrogenation in four palladium membrane reactors (cocurrent, countercurrent, one-side uniform and bifunctional models) are discussed both theoretically and experimentally and compared with that in a conventional catalytic reactor, which corresponds to the thermodynamic equilibrium conversion.

1. Introduction

It has been demonstrated both experimentally and theoretically that membrane reactors, inside which dense palladium or palladium alloy membranes — permeable only to hydrogen — are equipped to remove the hydrogen produced, can provide a very high performance for dehydrogenation even in a single stage [1,2]. The next concern is to make clear whether there exists a limitation or not in the performance of palladium membrane reactors, and if so, how much it is.

As fundamental reactor models for evaluating the performance, cocurrent, countercurrent and one-side uniform models as shown in Fig. 1 are selected from the viewpoint of practical significance. Ideal mathematical descriptions for the three reactor models have been already made and solved numerically [3,4], taking dehydrogenation of cyclohexane to benzene as a model reaction. In the cocurrent and countercurrent models, the hydrogen passing from the reaction side through the palladium membrane is removed by a sweep gas flowing under isobaric conditions. In the one-side uniform model, the driving force for hydrogen permeation is obtained by lowering the separation-side pressure to a greater extent than that on the reaction side, ultimately by maintaining a vacuum. In this case, it is advantageous in terms of obtaining highly pure hydrogen from the exhaust on the separation side. As a result, in the cocurrent [5] and the one-side uniform [4] (OSU) models, the dehydrogenation proceeds until the partial pressures of hydrogen in both side streams become identical. In other words, limited conversions exist, and 100% conversion can be

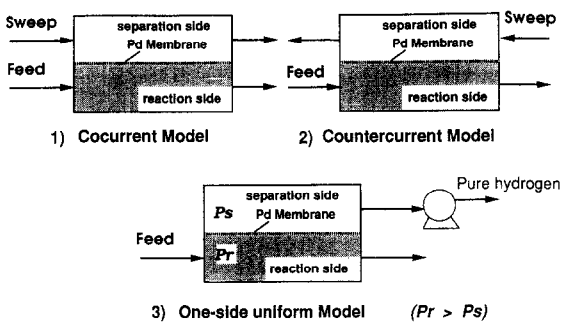

Fig. 1. Reactor models.

* Corresponding author.

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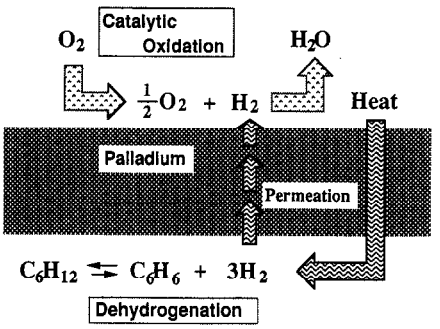

Fig. 2. Reaction coupling accompanying heat reflux in a bifunctional membrane reactor.

achieved only if the pressure on the separation side is kept at zero in the OSU model or an infinite flow-rate of sweep gas is used in the cocurrent model. On the other hand, in the countercurrent model [5], there is no limitation in possible conversion, that is, the dehydrogenation can be completed with a finite flow-rate of sweep gas.

As a way of more efficiently completing the reaction, coupling of dehydrogenation and oxidation in the palladium membrane reactor as illustrated in Fig. 2 can offer an outstanding advantage [6,7]. The hydrogen produced during the dehydrogenation easily passes through the membrane, and then reacts readily with oxygen on the palladium surface and evolves considerable heat. If the reactor is isolated from the exterior thermally (adiabatic condition), such heat can flow backward to the dehydrogenation side immediately, so that it is not necessary to supply the endothermic heat required for the dehydrogenation from outside the reactor. Simultaneously the dehydrogenation will go to completion. This bifunctional membrane reactor will lead to a 'fuel-less reaction system'.

In this paper, the results of some experiments based on the four models will be presented and compared with those predicted.

2. Experimental

Details of the palladium membrane reactor used in the present study are shown in Fig. 3. A one-end closed membrane tube composed of 77% palladium and 23% silver (191 mm long, 200 mm thick and 10.4 mm in outer diameter) was employed. Inside the membrane tube, a 1/8-inch stainless tube was inserted to take out the sweep gas containing permeated hydrogen. Spherical 0.5

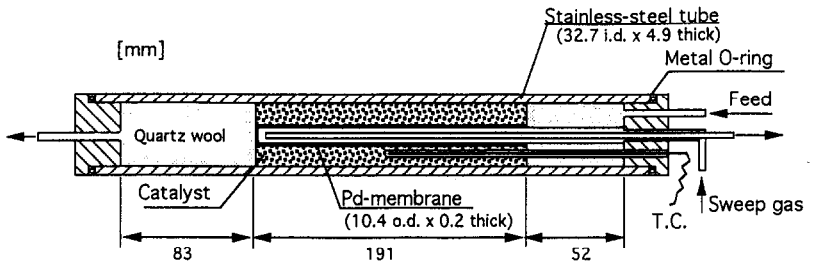

Fig. 3. A sectional view of the palladium membrane reactor.

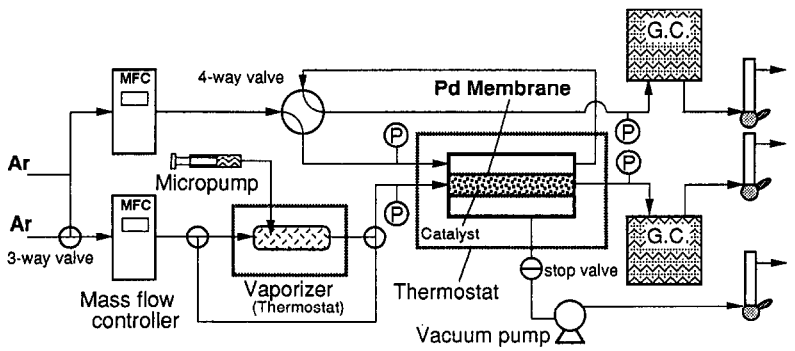

Fig. 4. Flow diagram of the whole reactor system.

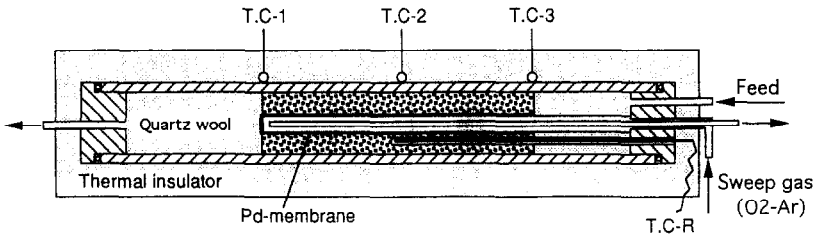

Fig. 5. The membrane reactor covered with thermal insulator.

wt.-% Pt/Al_2O_3 pellets (2.0 mm in average diameter) were uniformly packed in the concentric annulus around the membrane tube.

Fig. 4 shows the schematic diagram of the apparatus used. Cyclohexane injected to a vaporizer by a micro-syringe pump at a constant rate is vaporized and then is sent to the reaction side of the membrane reactor accompanied by inert gas (argon), the flow-rate of which is regulated by a mass-flow controller. Argon used as sweep gas is introduced to the separation side in the cocurrent and countercurrent runs. In the reduced-pressure runs (the one-side uniform model), the sweep-gas inlet line is off and the separation side of the reactor is connected to a vacuum pump through a vacuum controller, by which the separation side can be kept at any pressure below atmospheric pressure. Experiments were carried out at 473 K under atmospheric pressure. After a steady state is reached, the concentrations of components at the outlets are measured by means of a gas chromatograph. Simultaneously, the pressures at the inlets and outlets of both sides are recorded, and the flow-rates of effluent gases from both outlets are measured by using a soap-film flowmeter.

In the adiabatic runs, the membrane reactor is fully covered with ca. 25 mm thick ceramic wool as a thermal insulator for preventing heat loss from the reactor to the outside. The experimental procedure is as follows: Beforehand, a cocurrent run is conducted as mentioned above until the conversion obtained becomes steady. Then, the analysis is started by changing the gas flowing on the separation side from argon to 15.1% O_2–Ar. Three thermocouples are attached to measure the temperature changes at the outer wall of the reactor tube as shown in Fig. 5.

3. Limiting conversions for the cocurrent, countercurrent and one-side mixing reactor models

3.1. Cocurrent model

When the hydrogen permeation rate is large enough to attain a state of dynamic equilibrium, the hydrogen concentrations on the reaction and separation sides become identical and therefore the reaction cannot further proceed. This can be described mathematically as follows [5].

$$K_p = P_r^m \frac{m^m X_l^{m+1}}{(1-X_l)(1+U_I^0+V_I^0+mX_l)^m} \qquad (1)$$

where K_p is the equilibrium constant, P_r is the total pressure on the reaction side, m is the stoichiometric number, X_l is the limiting conversion, U_I^0 is the dilution ratio, and V_I^0 is the ratio of sweep-gas flow-rate to feed rate. Eq. (1) means that the limiting conversion, X_l, achievable by the cocurrent membrane reactor is identical with the equilibrium conversion, X_e, by a conventional catalytic reactor when the dilution ratio is taken as $U_I^0 + V_I^0$. To avoid confusion, let us designate X_e as $X_{e.sys}$, which represents the inclusive equilibrium conversion for the entire reactor system. Clearly from Eq. (1), it is impossible to get the conversion to exceed $X_{e.sys}$ in the cocurrent type of the membrane reactor, and an infinite flow-rate of sweep gas is needed to accomplish 100% conversion.

This shows that there is no particular advantage in utilizing the membrane reactor from the standpoint of shifting the reaction equilibrium. However, the membrane reactor has another profitable feature of making the overall reaction rate itself

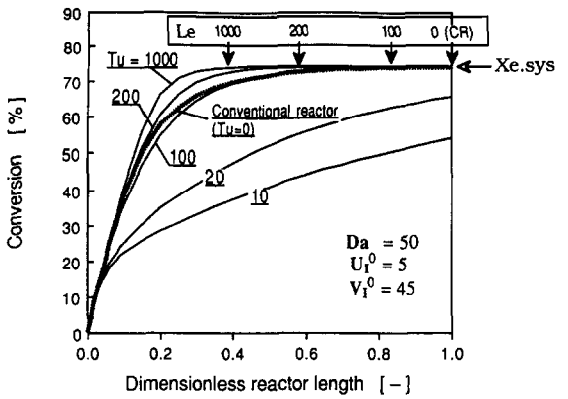

Fig. 6. Comparison of conversion curves in the reactor when varying *Tu* (*Le* is the length required to attain the equilibrium conversion).

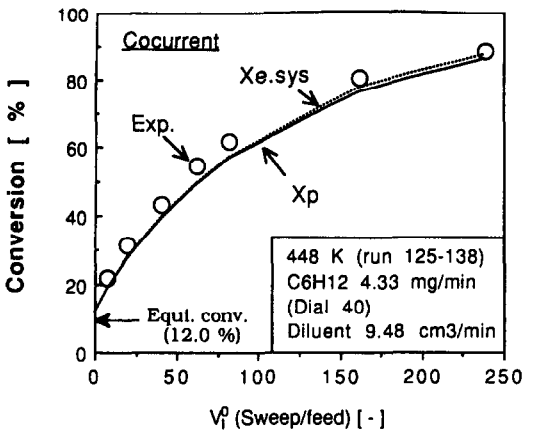

Fig. 7. Experimental and calculated results (concurrent model).

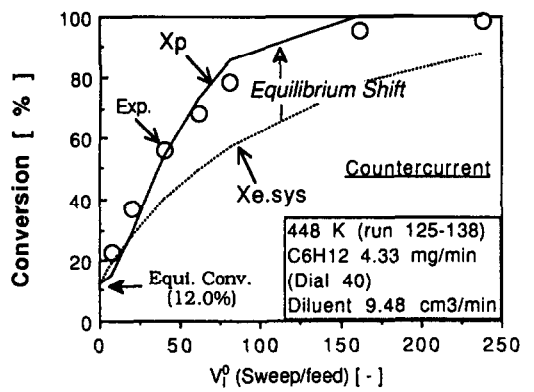

Fig. 8. Experimental and calculated results (countercurrent model).

larger by removing the hydrogen from the reaction field. Such a kind of 'kinetic effect' will result in making the reactor length requirement small. Fig. 6 proves this, where *Tu* is used as a parameter representing a ratio of hydrogen permeation rate to reaction rate. Consider the case that a conventional reactor requires its whole reactor length to attain inclusive equilibrium conversion (dotted line). Obviously, the membrane reactor can proceed the reaction to the equilibrium with a shorter reactor length although a larger value of *Tu* is demanded. As *Tu* is more than 100, the attainment to the equilibrium conversion is recognized to become faster in the membrane reactor. Namely the cocurrent-type membrane reactor can be still said to be superior to a conventional catalytic one.

Fig. 7 shows the experimental results together with the inclusive equilibrium conversion, $X_{e.sys}$ ($=X_I$), calculated using Eq. (1) and the predicted conversion, X_p, which can be obtained by numerically solving the simultaneous differential equations governing the material balance along the reactor length [3]. It is found that the conversions obtained experimentally are very close to the calculated $X_{e.sys}$ line, whereas slightly higher experimental conversions than the $X_{e.sys}$ and X_p curves are thought to be due to experimental errors.

3.2. Countercurrent model

In this case, it has been already made clear in a previous study [5] that there is no limitation in a rise of conversion, that is, 100% conversion is attainable since the complete removal of hydrogen becomes possible if *Da* (Damkohler number), *Tu* and V_I^0 are sufficiently large to accomplish it. It is not necessary that V_I^0 is infinitely different from the cocurrent model.

Fig. 8 shows the experimental results together with the inclusive equilibrium conversion, $X_{e.sys}$ ($=X_I$), calculated using Eq. (1). The measured conversions are found to be much higher than the $X_{e.sys}$ and X_p lines except in a low range of V_I^0. This is no doubt caused by the equilibrium shifting.

3.3. One-side uniform model

Similarly to the cocurrent model, in the one-side uniform model, the reaction can continue to proceed until the partial pressure of hydrogen on the reaction side becomes equal to that on the separation side. When such a dynamic equilibrium

is established, the reaction can no longer proceed. The limiting conversion, X_l, can be given by the following relation [4].

$$X_l = \frac{K_p/P_s^m}{1+K_p/P_s^m} \quad (2)$$

where P_s is the hydrogen pressure on the separation side. This equation represents that X_l is determined only by the P_s value regardless of P_r and U_l^0.

Fig. 9 shows the experimental results together with the limiting conversion, X_l, calculated using Eq. (2) and the predicted conversion, X_p [4]. In this case, similarly to the cocurrent model, it is also possible to accomplish the conversions up to X_l with a shorter reactor length. As an additional advantage, highly pure hydrogen can be taken out from the exhaust of the vacuum pump.

3.4. Bifunctional membrane reactor model

Palladium can function not only as a hydrogen purification membrane but also as a catalytic membrane. Therefore, it can be realized that the dehydrogenation of cyclohexane coupled with oxidation of permeating hydrogen as illustrated in Fig. 2 is enhanced much more than the simple hydrogen removal system using inert sweep gas such as the cocurrent and countercurrent models. The reactor performance of such a bifunctional membrane reactor has been simulated under isothermal and adiabatic conditions [7].

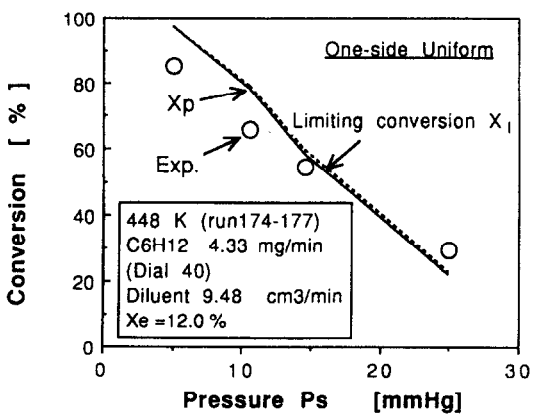

Fig. 9. Experimental and calculated results (one-side uniform model).

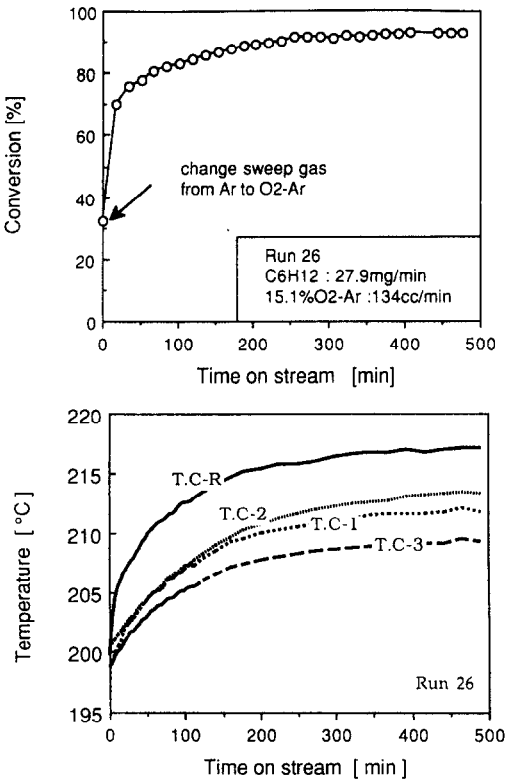

Fig. 10. Changes in temperatures and conversion (bifunctional model).

In spite of incomplete adiabatic conditions, that is, there is inevitably some heat flow from the reactor wall to the exterior through the ceramic-wool insulator, an increase in temperatures at different positions and conversion can be observed as shown in Fig. 10. The rise in the temperature inside the reactor follows the dramatic increase in conversion. This confirms that the exothermic heat evolved by oxidation of permeating hydrogen by oxygen is made reflux to the dehydrogenation side. If this system, possibly called the 'fuel-less system', works perfectly, it will be no longer necessary to supply the process heat to maintain the dehydrogenation because the hydrogen combustion heat of -729 kJ/mol cyclohexane ($3H_2$) is much larger than the dehydrogenation heat of 215 kJ/mol cyclohexane.

4. Conclusion

The limiting conversion in the cocurrent model was found to be identical with the inclusive equi-

librium conversion calculated taking into account the sweep gas used on the separation side. However, a kind of kinetic effect by removal of hydrogen, one of the dehydrogenation products, could result in a smaller reactor length requirement than that of a conventional catalytic reactor. The countercurrent model was evidenced to be the only reactor model which could realize perfect conversion. The limiting conversion of the one-side uniform model was determined by the hydrogen pressure on the separation side connected to a vacuum pump. In the bifunctional model, coupling of dehydrogenation with oxidation of permeating hydrogen through the membrane showed a good possibility of realizing a 'fuel-less dehydrogenation system'.

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