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Application of a microchannel to catalytic dehydrogenation of cyclohexane on Pd membrane

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Abstract

A microreactor was constructed by inserting a stainless-steel rod into a Pd membrane tube reactor to investigate the effects of microchannel size on the dehydrogenation of cyclohexane to benzene. The Pd membrane, having selective permeability for hydrogen, was coated onto the surface of an α-alumina porous tube. The dehydrogenation of cyclohexane was carried out at 573 K and atmospheric pressure. The yield of benzene was affected by varying the diameter of the stainless-steel rod, and the yield with the thickest rod was approximately two times higher than that without any rods. The application of the microchannels apparently increased the surface area per volume of the Pd membrane, and thus increased the catalytic reaction on the Pd membrane. The present results indicate that the dehydrogenation of cyclohexane is accelerated by applying microchannels.

Keywords: Microreactor; Channel size effect; Palladium membrane; Dehydrogenation; Cyclohexane

1. Introduction

Attempts at the practical use of hydrogen as a secondary source of clean and recyclable energy have been extensive [1–3]. Practical use, however, involves solving problems such as storage and transport of the hydrogen [3]. Among various methods for the storage of hydrogen [4–6], storage as liquid organic hydrides is a preferable candidate for practical use [7–10]. It is especially attractive that the liquid organic hydrides are transportable in pipelines with no change in status [11]. In terms of weight and volume for storage, this method is comparable to other methods such as storage in metal hydrides [11,12]. In a previous study, we studied on Pd membranes to apply to chemical processes in which hydrogen species participate in certain reactions, and found that a Pd membrane plays a role in permeating hydrogen selectively and generating active species to improve reaction efficiency, as well as a role of a reaction catalyst [13,14]. These advantages of a Pd membrane can be utilized in hydrogen storage processes with liquid organic hydrides.

Here, microchemical processes have attracted significant interest in the fields of chemical industry and science, resulting in extensive research into these processes [15–20]. These processes are at the sub-micrometer to sub-millimeter scale, and the space and/or the process itself is called a microreactor [21,22]. The extremely short distance for heat transfer and material transfer in a microreactor results in beneficial effects on various reactions, namely, efficient conversion, high reaction selectivity, and ease of reaction control [23,24]. The application of a micro chemical process is expected to enhance the performance of a Pd membrane reactor used in hydrogen storage processes.

The purpose of this study is to demonstrate that narrowing a reaction channel is a potential method to improve efficiency of the hydrogen storage process. Such narrow channels mean that a microreactor must be constructed for these processes. This study is the first known application of a microreactor to a heterogeneous gaseous reaction on a Pd membrane.

In this study, the effects of microchannel size on the dehydrogenation of cyclohexane in the gaseous phase utilizing a Pd membrane were studied; this reaction is half of the following hydrogen storage process [25].

$$C_6H_{12} \rightleftharpoons 3\,H_2 + C_6H_6 \qquad (1)$$

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First, a microreactor was constructed. Then, cyclohexane conversion, benzene yield, hydrogen recovery and benzene selectivity were measured for various channel widths.

2. Experimental

The reactor (Fig. 1) was a flow-type reactor composed of a Pd membrane (1 μm thickness, 100 mm effective length, 2 mm o.d.) supported on the surface of an α-alumina porous tube (2 mm o.d., 300 mm length, 0.2 mm thickness, 0.15 μm average pore size, 43% porosity) [13,14]. The Pd membrane was made by a chemical vapor deposition method with $(CH_3COO)_2Pd$, and the permeability of hydrogen through the membrane was approximately 1.3 ml min^{-1} mm^{-2} $atm^{-0.5}$ at 573 K. The Pd membrane shields effectively against gas molecules except hydrogen, H_2/He permeation selectivity is $>10^4$ at 573 K. The microreactor was constructed by inserting a stainless-steel rod into the membrane reactor. Three microreactors were constructed by inserting different diameter stainless-steel rods into the membrane reactor: Micro-1 had a 0.80-mm-diameter rod, Micro-2 had 1.00-mm, and Micro-3 had 1.26-mm. The average width of the fluid channel was 600 μm for Micro-1, 500 μm for Micro-2, 370 μm for Micro-3, and 2000 μm for a ‘‘normal’’ membrane reactor (i.e., no inserted stainless-steel rod). The membrane reactor was then enclosed within a stainless-steel tube (7.5 mm i.d.) to isolate the outside and inside of the reactor so that certain gases could be fed also to the outside of the reactor. Fig. 2 shows a flow diagram of experimental apparatus. Nitrogen was bubbled through cyclohexane in flow rate range of 2–10 ml min^{-1}, and the vapor (ca. 14 vol.% at 313 K) was flowed at the inside of the reactor (react-side). The flow rate of nitrogen outside the reactor (perm-side) as a carrier gas to sweep permeated hydrogen was kept constant at 5 ml min^{-1}. We carried out the dehydrogenation of cyclohexane at 573 K and atmospheric pressure. Flow rates were measured at four points in the apparatus: the inlet of the react-side, the inlet of the perm-side, the outlet of the react-side, and the outlet of the perm-side. Then, we analyzed the composition of each gas flow; the analyses for hydrocarbons (i.e., cyclohexane and benzene) were performed at the inlet of the react-side and the outlet of the react-side with gas chromatography-flame ionization detector (GC-FID), and the analyses for hydrogen were at the inlet of the perm-side, the outlet of the react-side and the outlet of the perm-side with gas chromatography-thermal conductivity detector (GC-TCD), and other inorganic compounds (i.e., carbon dioxide, nitrogen, water, etc.) were analyzed at all four points with GC-TCD.

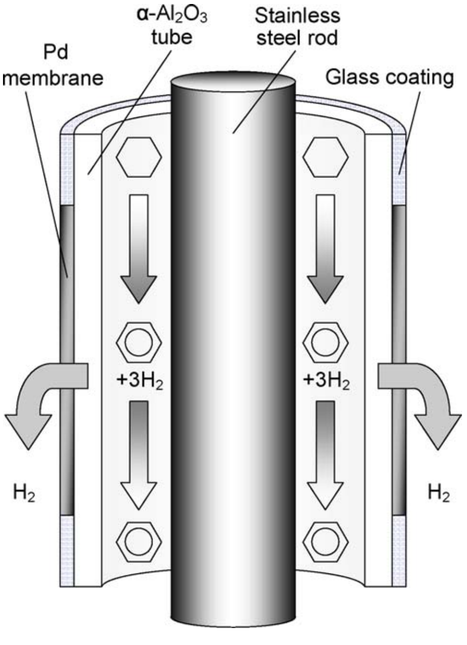

Fig. 1. Microreactor with a Pd membrane for dehydrogenation of cyclohexane to benzene. A stainless-steel rod was inserted in a Pd membrane reactor supported by an α-alumina porous tube.

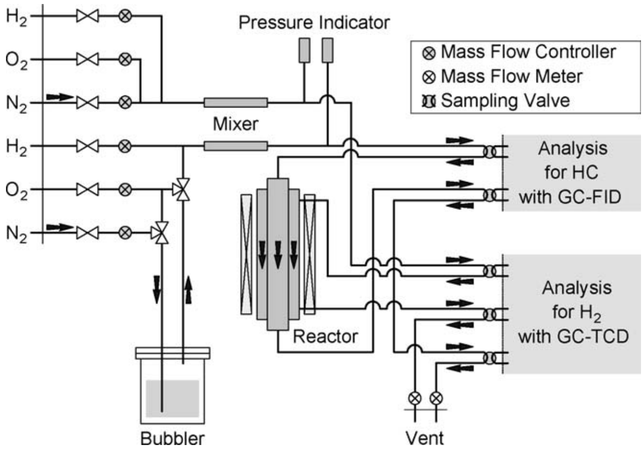

Fig. 2. Flow diagram of experimental apparatus. Nitrogen containing vaporized cyclohexane was introduced into the inside of the reactor (react-side), and nitrogen flowed over the outside (perm-side) to sweep permeated hydrogen. Dehydrogenation of cyclohexane was carried out at 573 K and atmospheric pressure.

Cyclohexane conversion was calculated as the reduction rate of cyclohexane divided by the feed rate of cyclohexane, benzene yield was calculated as the production rate of benzene divided by the feed rate of cyclohexane, hydrogen recovery was calculated as the permeation rate of hydrogen to perm-side divided by the total production rate of hydrogen, and benzene selectivity was calculated as the production rate of benzene divided by the reduction rate of cyclohexane. Additionally, carbon balance was calculated as the amount of carbon contained in outlet flow of react-side divided by that contained in inlet flow of react-side.

To determine whether the catalytic activity of the inserted stainless-steel rod or the α-alumina porous tube influenced the cyclohexane dehydrogenation, cyclohexane was fed into an α-alumina porous tube coated only with glass (i.e., without a Pd membrane) with an inserted stainless-steel rod. The experiment was done under the same conditions as those for cyclohexane dehydrogenation. No conversion of cyclohexane was detected, confirming that neither the stainless-steel rod nor the α-alumina porous tube affected the cyclohexane dehydrogenation.

3. Results and discussion

3.1. Channel size effect on cyclohexane conversion

Fig. 3 shows the conversion of cyclohexane during dehydrogenation in the microreactors. For all four reactors, the conversion increased with mean residence time at the react-side. Here, the mean residence time was used as an indicator of reaction time in the microreactors, and was defined as the inverse of the space velocity, namely, the volume of the react-side divided by the feed rate of the reaction gas. The increase in conversion increases continuously with mean residence time because of its low level, whereas that in selectivity tapers off because this value achieves almost 100% as shown in Fig. 6. Therefore, a further increase in conversion is expected with a longer mean residence time. At a given mean residence time, the conversion increased with decreasing width of the react-side fluid channels. This increase in conversion owing to the narrowing reaction channel observed with a fixed mean residence time, suggests an improvement in reactor performance. The theoretical value of equilibrium conversion at 573 K is approximately 91% [26]. The dehydrogenation of cyclohexane in the four reactors apparently did not achieve equilibrium. Furthermore, the reaction rate of the homogeneous dehydrogenation of cyclohexane is considered negligibly small at 573 K, because the theoretical rate constant is significantly lower than those obtained in our results; the theoretical rate constant of cyclohexane to cyclohexene is approximately 10^{-16}–10^{-15} s^{-1} [27–29], cyclohexene to cyclohexadiene is 10^{-11} s^{-1} [30] and cyclohexadiene to benzene is 10^{-10} s^{-1} [31]. Consequently, the observed conversion of cyclohexane is considered primarily caused by heterogeneous catalytic reactions on the Pd membrane. The improvement in conversion with decreasing channel size is, therefore, due to the increase in catalytic dehydrogenation reactions caused by an increase in surface area per volume of the Pd membrane.

3.2. Improvement in benzene yield by surface area per volume of the Pd membrane

Fig. 4 shows that the benzene yield during the dehydrogenation increased with increasing surface area per volume of the Pd membrane owing to the decreasing width of the reaction channels. The surface area per volume was 2.4 mm^2 μl^{-1} for Micro-1, 2.7 mm^2 μl^{-1} for Micro-2, 3.3 mm^2 μl^{-1} for Micro-3, and 2.2 mm^2 μl^{-1} for the normal reactor. At mean residence times of 0.05 and 0.095 min, the benzene yield with Micro-3 was approximately twice higher than that with the normal reactor (i.e., without an inserted stainless-steel rod). This higher yield demonstrates one of the advantages of a microreactor for the cyclohexane dehydrogenation, namely, improvement in the catalytic dehydrogenation on the Pd membrane owing to increasing surface area per volume of the Pd membrane, as discussed in Section 3.1. More importantly, the increase rate in the benzene yield was higher than that proportional to the surface area per volume, suggesting that the increase in the surface area of the catalyst is not the only contributor to the improvement in cyclohexane dehydrogenation. Another possible contributor is that the temperature in the microreactor is more uniform and/or the supply of reactant to the surface of the catalyst is larger, owing to the short distance for heat transfer and material transfer in the microreactor. Another possibility is the change of mass transfer velocity owing to inserting the stainless-steel rod. For all four reactors, a theoretical calculation reveals that the flow pattern at react-side is laminar flow independently of the channel width. The mass transfer velocity in laminar flow depends on molecular diffusion. The proportion of α-alumina porous layer to the total reactor volume increases due to the inserted stainless-steel rod. The average pore size of an α-alumina porous tube is 0.15 μm, and the estimated mean free path of the reaction gas is approximately 0.1 μm, and thus the molecular diffusion mechanism in the α-alumina porous layer belongs to the

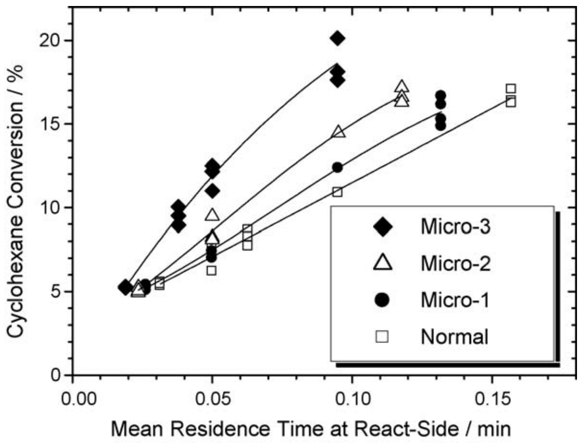

Fig. 3. Conversion of cyclohexane during cyclohexane dehydrogenation in three microreactors (with an inserted stainless-steel rod) and in a "normal" reactor (without an inserted stainless-steel rod). The width of the fluid channels was 600 μm for Micro-1, 500 μm for Micro-2, 370 μm for Micro-3, and 2000 μm for the normal reactor.

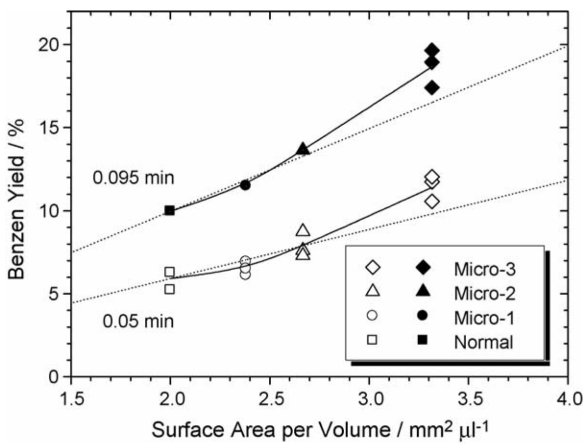

Fig. 4. Dependence of benzene yield during cyclohexane dehydrogenation on the surface area per volume of the Pd membrane at mean residence times of 0.05 and 0.095 min for the three microreactors and the normal reactor. Surface area per volume was 2.4 mm^2 μl^{-1} for Micro-1, 2.7 for Micro-2, 3.3 for Micro-3, and 2.0 for the normal reactor.

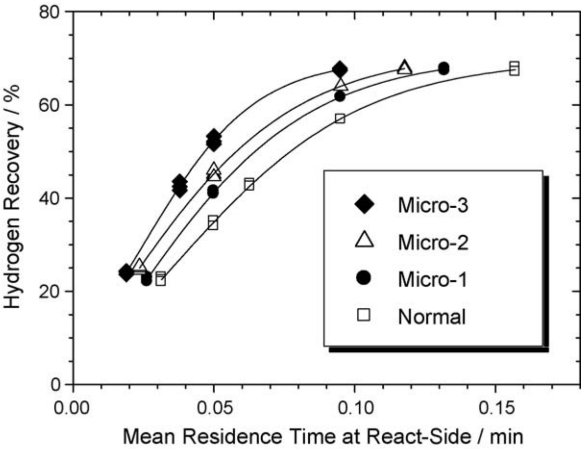

Fig. 5. Dependence of hydrogen recovery at the perm-side on mean residence time at the react-side. Recovery was defined as the permeated amount of hydrogen divided by the total amount of produced hydrogen.

transition region between the Knudsen region and the continuum-flow region. The mass transfer velocity in the porous layer differs from that at interior part of the alumina tube, in which molecular diffusion should be in continuum-flow region.

3.3. Behavior of hydrogen recovery at perm-side of the microreactor

Fig. 5 shows the recovery of hydrogen at perm-side of the microreactor. At a given mean residence time, the application of microchannels increased the hydrogen recovery. This increase in hydrogen recovery is attributable to a decrease in the volume at react-side by applying the microchannels, leading to the increase in hydrogen amount permeating from react-side to perm-side. The improvement in hydrogen recovery is another advantage arising from narrowing a reaction channel. For all four reactors, the amount of hydrogen obtained at the perm-side per unit time increased with mean residence time at the react-side, whereas the production rate of hydrogen via dehydrogenation decreased probably owing to a reduction in the feed rate of the cyclohexane. This increase in hydrogen at the perm-side is because the concentration of hydrogen at the perm-side relatively decreased with decreasing flow rate at the react-side. Thus, the increase in hydrogen recovery with the mean residence time depends on the ratio between flow rate at react-side and that at perm-side.

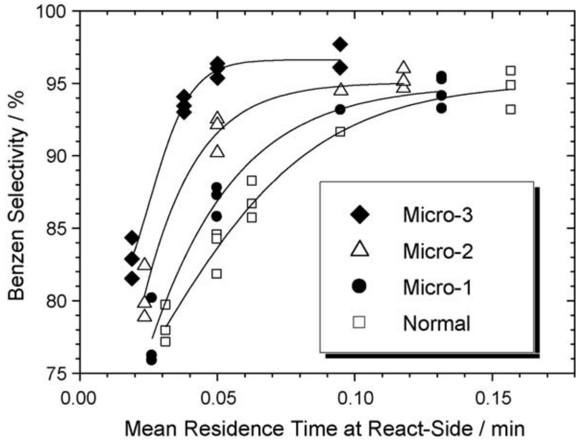

Fig. 6. Selectivity of benzene during cyclohexane dehydrogenation in the three microreactors and the normal reactor. Selectivity was defined as the production rate of benzene divided by the reduction rate of cyclohexane.

3.4. Improvement in selectivity to benzene and prevention of reduction in reaction efficiency

More than 98% of the molecular balances of carbon and hydrogen were obtained from benzene, hydrogen gas, and cyclohexane at the outlet flow for all four reactors. Fig. 6 shows the selectivity of the microreactors to benzene. However, the values of selectivity to benzene below 80% were observed. This low level of selectivity might be due to coking (i.e., deposition of carbon compounds such as oligomer of benzene) on the surface of the Pd membrane. Actually, although slight decreases in conversion and in hydrogen recovery with time were observed in replicate experiments of the dehydrogenation reaction, this reduction in reaction efficiency could be restored by treatment with oxygen flow at 573 K. Furthermore, the carbon dioxide equivalent to the insufficient benzene was detected through the oxygen treatment, and approximately 100% of carbon balance was achieved by adding the detected carbon dioxide. These results support the above supposition for the low level of selectivity. The increase in selectivity with mean residence time should arise from decreasing deposition of carbon compounds on surface of the Pd membrane. We consider that complete dehydrogenation from cyclohexane to benzene is not achieved with a short residence time, resulting in the deposition of carbon compounds. As shown in Fig. 6, at a given mean residence time, the selectivity to benzene increased with decreasing microchannel size, and thus the reduction in reaction efficiency due to the coking on the surface of the Pd membrane can be prevented by applying microchannels. This efficiency of the microchannel would be rationalized with a suitable reaction mechanism of the coking, although we have not arrived at a rational explanation.

4. Conclusion

This study revealed the advantages of applying a microreactor for the dehydrogenation of cyclohexane by using a Pd membrane. The application of microchannels was performed in a simple manner, despite the construction of a microreactor having been conventionally regarded as difficult and/or expensive. Results from this study showed that the dehydrogenation of cyclohexane primarily occurred on the Pd membrane as heterogeneous catalytic reactions. In conclusion, an improvement in cyclohexane dehydrogenation by applying microchannels is due to the increase in heterogeneous catalytic reactions caused by an increase in surface area per volume of the Pd membrane.

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