Effects of Micro Channel Size in a Pd Membrane Reactor on Dehydrogenation of Cyclohexane to Benzene in Gaseous Phase

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To confirm the effects of microreactor on cyclohexane dehydrogenation, we have narrowed the reaction channel of Pd membrane reactor to micro scale. We show that the application of micro channel improves the performance of Pd membrane reactor. The experimental results indicate that the improvement in cyclohexane dehydrogenation with applying the micro channel is attributable to the enhancement of a heterogeneous catalytic reaction due to increasing the surface area per volume of Pd membrane.

Micro chemical processes attract a great deal of interest in the fields of chemical industry and science, thus many researches on these processes have been conducted.[1] These processes are handled in the spaces of sub-micrometer to sub-millimeter scale; the space and/or the process itself is called a microreactor. The extremely short distance for transfers of materials and heat in microreactor leads to efficient conversion, high reaction selectivity, ease of reaction control, etc.

Here, examinations for the practical use of hydrogen as a secondary source of clean and recyclable energy have been carried out. Storage and transportation of hydrogen are important issues on the practical use. Among various methods for the storage of hydrogen, storing as liquid organic hydrides is one of the preferable candidates.[2] We have studied on Pd membrane to apply for the chemical processes in which hydrogen species participate.[3] The Pd membrane plays a role to permeate hydrogen selectively as well as a role of catalyst. The advantages of the Pd membrane are effectively offered in the hydrogen-storage process with liquid organic hydrides.[4]

The application of a microreactor is expected to enhance the performance of a Pd membrane reactor on the hydrogen-storage process. In this study, we have investigated the effects of micro channel size on dehydrogenation of cyclohexane with a Pd membrane in gaseous phase; this reaction is the one-half of the hydrogen-storage process as follows.

$$C_6H_{12} \rightleftarrows 3H_2 + C_6H_6. \quad (1)$$

The purpose of this study is to demonstrate that narrowing a reaction channel to micrometer scale is a potential method to improve efficiency of the hydrogen-storage process. To the best of our knowledge, there are no precedents for applying a microreactor to a heterogeneous gaseous reaction on Pd membrane through the manner of this study.

The reactor used for our experiments was of flow type and composed of Pd membrane coated on the surface of an α-alumina porous tube by chemical vapor deposition. In addition, we devised inserting a stainless-steel rod in the membrane reactor to construct a microreactor. The illustration of the microreactor is shown in Figure 1. Nitrogen bubbled through cyclohexane and the vapor (ca. $3\,\text{mol}\,\text{m}^{-3}$) was flowed in the rate range of 2–$10\,\text{mL}\,\text{min}^{-1}$ at inside of the reactor tube (react-side). Flow rate of N_2 at the outside (perm-side) was constantly $5\,\text{mL}\,\text{min}^{-1}$ as carrier gas to sweep permeated hydrogen. We carried out dehydrogenation of cyclohexane at 573 K and atmospheric pressure. The microreactors, Micro-1, Micro-2, and Micro-3, were prepared by employing the various stainless-steel rods of 0.80, 1.00, and 1.26 mm as diameters, respectively. These three microreactors and the normal membrane reactor were 600, 500, 370, and 2000 µm as each average width of fluid channel. We have conformed in a supplemental experiment that the change in the local pressure in reaction channel with the channel width is negligibly small.

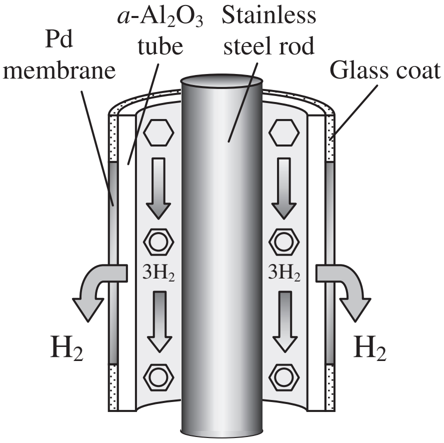

Figure 1. Microreactor with Pd membrane for dehydrogenation of cyclohexane to benzene. A stainless-steel rod was inserted in a Pd membrane tube reactor to prepare a micro channel.

Cyclohexane conversion and benzene selectivity during dehydrogenation in the microreactors are shown in Figure 2a. The selectivity has been defined as the production rate of benzene divided by the reduction rate of cyclohexane. The conversion increased with the decrease in the reaction channel width at a given retention time. The equilibrium constant of dehydrogenation of cyclohexane to benzene in gaseous phase, K_p, is given as follows.[5]

$$K_p = 4.70 \times 10^{20} \exp(-26490/T). \quad [\text{atm}^3] \quad (2)$$

The equilibrium conversion at 573 K is calculated to be 91.2% from Eq 2; thus the dehydrogenation of cyclohexane in our reactors does not achieve the equilibrium. In addition, the reaction rate of homogeneous dehydrogenation of cyclohexane is negligibly small, because the rate constants calculated theoretically[6] are extremely lower than those obtained as our results. Thus, the observed dehydrogenation of cyclohexane is consid-

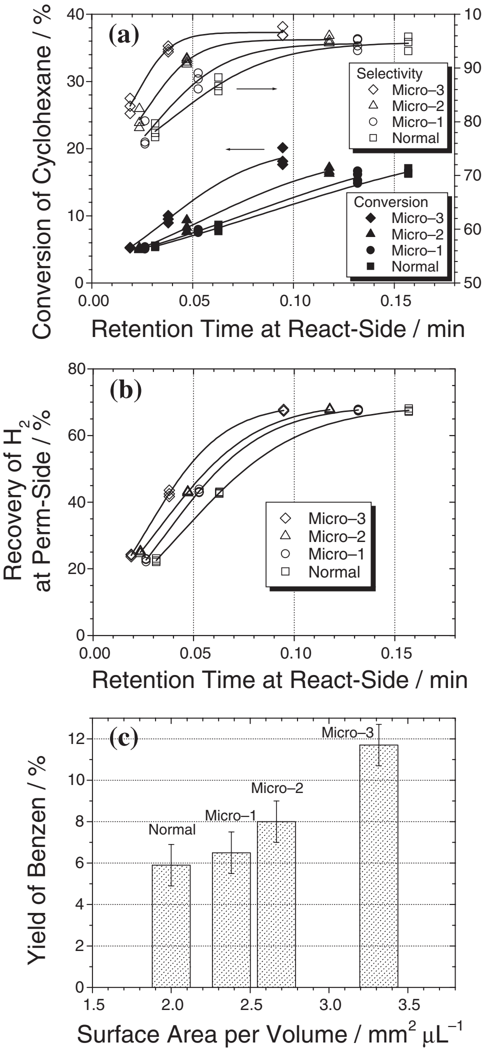

Figure 2. (a) Dependence of cyclohexane conversion, selectivity to benzene and (b) hydrogen recovery at perm-side on retention time at react-side, and (c) dependence of benzene yield on Pd membrane surface area per volume (retention time: 0.05 min) during dehydrogenation of cyclohexane in microreactors. Micro-1, Micro-2, Micro-3, and normal had each fluid channel of 600, 500, 370, and 2000-μm width.

ered mainly caused by heterogeneous catalytic reaction on the Pd membrane. The improvement in cyclohexane conversion with decreasing channel size is, therefore, attributable not to the transition of thermodynamic equilibrium due to hydrogen segregation but to the enhancement of catalytic dehydrogenation due to increasing the surface area per volume of Pd membrane.

For all four reactors, more than 98% of the molecular balances of carbon and hydrogen were obtained form benzene, hydrogen gas, and cyclohexane at outlet flow. However, the values of selectivity below 80% were observed (Figure 2a). It is supposed that the insufficiency of produced benzene is caused by deposition of some carbon compounds on the surface of Pd membrane. Actually, slight decreases in cyclohexane conversion and hydrogen recovery with time were observed through a repetition of dehydrogenation reaction, and this reduction in reaction efficiency was restored by a treatment with oxygen flow at 573 K. As shown in Figure 2a, the selectivity has increased with narrowing the reaction channel at a given retention time, and thus the application of micro channels can prevent the reduction in reaction efficiency due to the coking on the surface of Pd membrane.

We investigated the recovery of hydrogen at perm-side (Figure 2b). The recovery has been defined as permeation amount of hydrogen divided by all amount of produced hydrogen. The application of micro channels increased these values at a given retention time, despite an increase in produced hydrogen due to the enhancement of cyclohexane conversion. This result is attributable to an increase in hydrogen distribution ratio at perm-side due to decreasing the volume at react-side. The increase in hydrogen recovery is another advantage arising from narrowing a reaction channel.

Narrowing a reaction channel extends the surface area per volume of Pd membrane. Micro-1, Micro-2, Micro-3, and the normal reactor have each surface area per volume of 2.4, 2.7, 3.3, and 2.0 $\mathrm{mm^2\,\mu L^{-1}}$, respectively. The yield of benzene was affected by varying the surface area per volume of Pd membrane, and these values enhanced approximately two times as compared to the value with normal reactor at 0.05 min as retention time (Figure 2c). This result evidently indicates one of the advantages of microreactor for dehydrogenation of cyclohexane, namely, the increase in catalytic reaction on Pd membrane due to the increase in the surface area per volume of Pd membrane, as discussed above.

In this study, the significant effects of applying micro channels have been found on dehydrogenation of cyclohexane in the simple manner; despite constructing a microreactor has been conventionally regarded difficult and/or expensive. The improvement in cyclohexane dehydrogenation with decreasing channel size is mainly caused by catalytic reaction on the Pd membrane. The dehydrogenation efficiencies should be able to further increase by a combination of any other catalysts and/or pressure control in the reactors. We anticipate some advantages of the micro channels to benzene hydrogenation.

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