Propane Dehydrogenation over a Hydrogen Permselective Membrane Reactor

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The dehydrogenation of propane to propylene has been studied in an isothermal high-temperature shell-and-tube membrane reactor containing a Pd-coated γ-Al$_2$O$_3$ membrane and a Pt/K/Sn/Al$_2$O$_3$ packed catalyst. A tubular Pd-coated γ-Al$_2$O$_3$ membrane was prepared by an electroless plating method. This membrane showed high hydrogen to nitrogen permselectivities (P$_{H2/N2}$ = 10-50) at 400 °C and 500 °C with various transmembrane pressure drops. The employment of a membrane reactor in the dehydrogenation reaction, which selectively separates hydrogen from the reaction mixture along the reaction path, can greatly increase the conversion and enable operation of the reactor at lower temperatures. High hydrogen permselectivity has been confirmed as a key factor in determining the reactor performance of conversion enhancement.

Keywords : Pd-Composite membrane, Propane dehydrogenation, Hydrogen permselectivity.

Introduction

Many industrial catalytic reactions, including dehydrogenation of hydrocarbons, exhibit relatively low yields to olefins due to thermodynamic equilibrium limitations.[1] To overcome the thermodynamic constraints in the commercial dehydrogenation of hydrocarbons, high temperature and low pressure conditions are employed.[2] The dehydrogenation of propane is a typical example of such catalytic reactions, and it is a key step for producing propylene, a monomer for polypropylene, although most propylene is commercially produced by naphtha cracking. In these reactions, the thermodynamic equilibrium conversions are less than 20% even at 500 °C.[3,4] therefore, the high temperatures and low pressures that produce the acceptable olefin yields often create technical complications and require expensive process equipment or specialized catalysts.

The use of high temperature membranes for gas separation and catalytic processes is gaining attention in the chemical and petrochemical industry because it provides great promise for a wide range of reaction applications.[5-9] High-temperature catalytic membrane reactors, which combine reaction and separation in a single unit operation, may solve the yield problems of equilibrium-limited reactions.[9] In particular, the use of a hydrogen-permselective membrane reactor enables the supply of pure hydrogen product from a hydrogen-producing reaction and gives a high per-pass conversion by shifting the thermodynamic equilibrium.

In the present study, experiments have been carried out to assess the performances of Pd-coated γ-Al$_2$O$_3$ membrane and γ-Al$_2$O$_3$ membrane systems for propane dehydrogenation. The quantification of the effectiveness of Pd-coated membrane systems was accomplished through comparison with the operation of a fixed-bed reactor.

Experimental Section

Pd-coated γ-Al$_2$O$_3$ membrane (composite Pd membrane) was prepared by the electroless plating method, depositing Pd film onto the inner surface of an asymmetric mesoporous γ-alumina tube supplied by US Filters. The detailed process has been described previously.[10] The tube had an outer diameter of 10 mm, an inner diameter of 7 mm and length of 100 mm, and was composed of a multiple-layer alumina structure with a top layer of γ-Al$_2$O$_3$ having 5 nm pores. Pt/K/Sn/γ-Al$_2$O$_3$ catalyst was prepared by the sequential impregnation of aqueous solutions of SnCl$_2$, KCl, and H$_2$PtCl$_6$ onto a spherical γ-Al$_2$O$_3$ support (Kaiser Chemicals, S$_{BET}$ = 145 m^2/g, 1.2 mm diameter). The Pt content of the catalyst was 0.8 wt.%, and the molar ratio of Pt:K:Sn was 1.0:2.0:2.5. The prepared Pt/K/Sn/γ-Al$_2$O$_3$ catalyst was calcined in air at 500 °C for 2 h. Catalyst reduction was carried out *in-situ* under flowing 5% hydrogen in nitrogen at 400 °C for 5 h before the reaction. One g of the Pt/K/Sn/γ-Al$_2$O$_3$ catalyst was carefully packed into the tube to give a membrane area of about 22 cm^2/g$_{cat}$. The details of the experimental apparatus have been illustrated previously.[10] The apparatus consists of a reactant gas delivery system, a membrane reactor, and product collection and measurement devices. The membrane tube was placed within a wider quartz tube (30 mm outer diameter) to form the dehydrogenation membrane reactor. A gaseous mixture of propane (20 mol.%) and nitrogen at 30 mL/min was supplied in the inner compartment of the membrane reactor. Argon with a flow rate of 100 mL/min was used as a sweep gas to remove gases that permeated through the membrane. A detailed drawing of the catalytic membrane reactor for propane dehydrogenation is shown in Figure 1. The dehydrogenation of propane through the catalytic membrane system was studied at a temperature of 350-550 °C and a transmembrane pressure difference of 1 psi. The fixed bed operation without membrane, in which the shellside inlet and exit of γ-Al$_2$O$_3$

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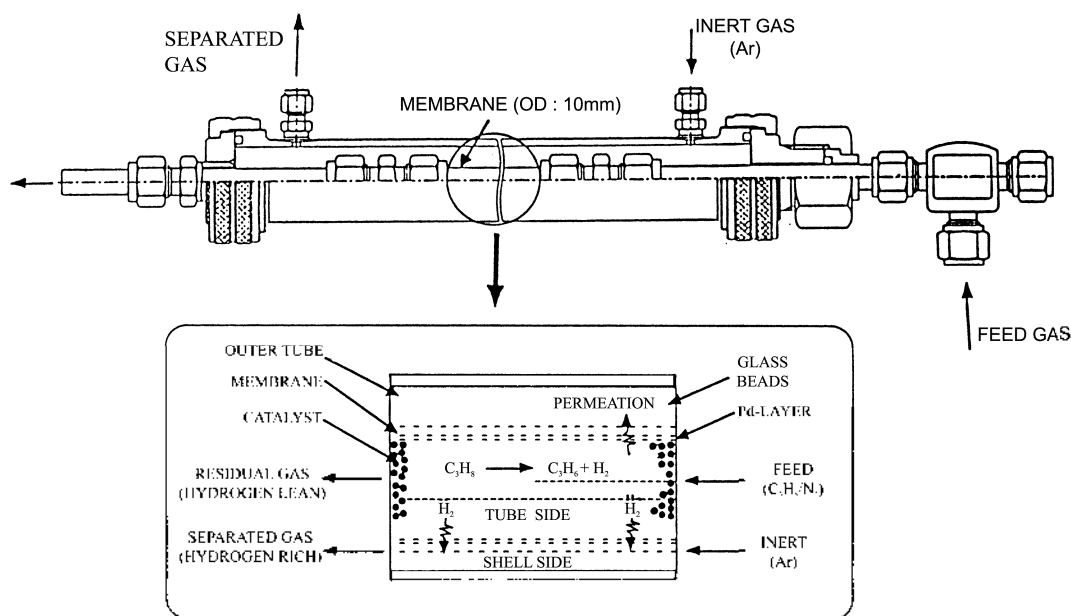krict.re.kr

Figure 1. Catalytic membrane reactor set-up for propane dehydrogenation.

membrane were closed, was used to evaluate the effectiveness of the membrane system. Effluent gases from the reactor were analyzed by a FID gas chromatograph (Chrompack, model 9001), using a capillary column (Chrompack Carbo-PLOT P7, 25 m × 0.53 mm). Theoretical equilibrium conversion of the propane dehydrogenation was calculated, using HSC Chemistry for Windows (Version 3.0) software from Outokumpu corporation. Before the reactor performance test in the membrane reactor, gas permeability measurements were carried out first using hydrogen and then nitrogen to evaluate the permeation behavior of the composite Pd membrane. The permeated gas flow rates were measured at a constant pressure difference across the membrane, using a soap bubble flow meter while varying the dosing pressure in the inner compartment of the reactor. The permeabilities of these gases were obtained at transmembrane pressure difference in the range of 0-7 psi. The permselectivity for hydrogen at a given temperature was then obtained by dividing the hydrogen permeability by that of nitrogen.

Results and Discussion

Morphologies of Membranes. Scanning electron microscopy measurements showed that Pd layers on porous alumina wall, which was coated four times by the electroless plating method, were very thin with a thickness of about 5 μm, as has been illustrated previously.[10] A tubular membrane of γ-Al$_2$O$_3$ from US Filter corporation was a composite or graded structure having three different layers of Al$_2$O$_3$ particles. The first layer consisted of large and irregular α-Al$_2$O$_3$ particles that play a role in the mechanical support of the membrane. A thin γ-Al$_2$O$_3$ layer of selective membrane (thickness: 5-10 μm, pore size: 40-50 Å) was superimposed on the mechanical support. An intermediate layer consisting

of medium sized α-Al$_2$O$_3$ (thickness: ~40 μm, pore size: ~0.8 μm) was sandwiched between the support and the γ-Al$_2$O$_3$ layer. The pore size of the γ-Al$_2$O$_3$ membrane was determined by the γ-Al$_2$O$_3$ particle size. A Pd layer of about 5 μm was coated uniformly on the inner surface of the γ-Al$_2$O$_3$ membrane.

Permeability Characteristics of Membranes. The composite Pd membrane used was shown to be almost impermeable to nitrogen but permselective toward hydrogen, implying an atomic-hydrogen diffusion mechanism (solution diffusion mechanism). To confirm whether the membrane is permselective to hydrogen, the permeation flux of hydrogen and nitrogen were measured and plotted as a function of the pressure difference at various temperatures (Figure 2). The
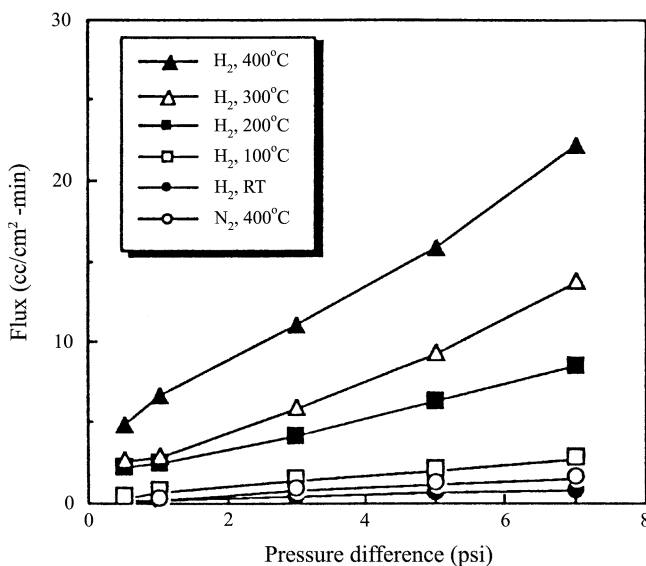

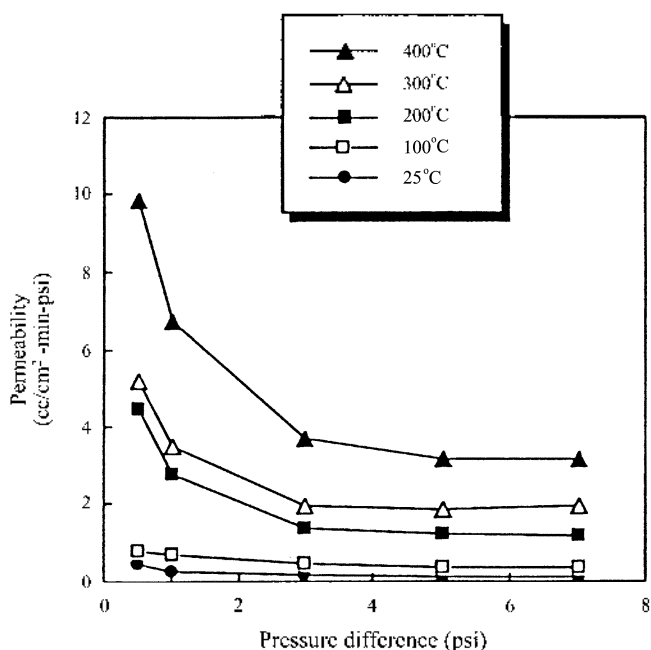**Figure 2.** The effect of temperature on H$_2$ and N$_2$ flux over Pd/γ-Al$_2$O$_3$ membrane.

Figure 3. The effect of temperature on H₂ permeability over Pd/γ-Al₂O₃ membrane.

Figure 4. Arrhenius plot of H₂ permeability on Pd/γ-Al₂O₃ membrane.

experimental results show that the permeation flux of hydrogen was proportional to the pressure drop and increased with increasing temperature. However, the permeation flux of nitrogen was almost negligible, even at 400 °C. Thus, it was clearly established that the prepared Pd composite membrane in this study is permselective to hydrogen.

Permeability is defined as gas permeation flux over the average pressure drop across the membrane. This property has been used conventionally to describe gas permeation through porous membranes.[10] For the present study, calculated results of permeability at various temperatures with a pressure drop across the membrane are given in Figure 3. Hydrogen permeability at each temperature of operation decreased with increasing pressure drop and this tendency became pronounced above 200 °C, excluding the existence of either macropores or mesopores in the membrane.[9,10] In the case of macropores, the mechanism of gas transport through the membrane is viscous flow and/or Knudsen flow. If viscous flow is involved, P_L would be expected to increase with pressure.[9] Membranes with cracks have been shown to exhibit such behavior. Gas permeation through mesopores, on the other hand, occurs primarily by Knudsen diffusion, and in this case, gas permeability has been shown to be independent of pressure drop.[9] The possible influence of mesopores on the hydrogen permeation flux could also be excluded by considering the observed temperature effect on permeability. Hydrogen permeation through zeolite membranes has been found to fall into the micropore diffusion regime. However, in such a case, hydrogen permeability has been found to decrease with increasing temperature,[9] which is different from the present hydrogen permeation through a thin Pd membrane.

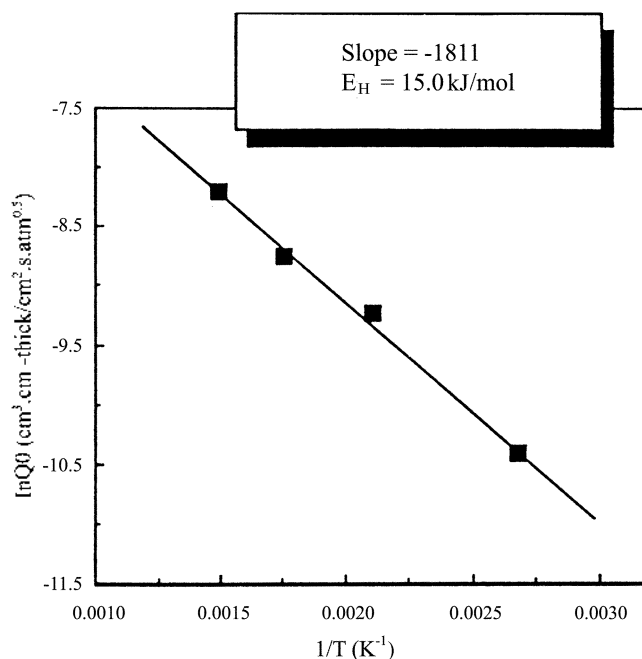Hydrogen permeates through a dense Pd membrane *via*

the atomic diffusion mechanism.[11] The rate of hydrogen permeation can therefore be expressed as a function of the difference in the square root of hydrogen partial pressures.[11] Since the membrane thickness was effectively invariant, the rate of hydrogen permeation, J, can be expressed as J = $QA[p_1^{0.5}-p_2^{0.5}]/d$,[11] where Q is the permeation coefficient, A is the cross sectional area, d is Pd membrane thickness. p_1 is inlet pressure and p_2 is outlet pressure.

The permeation coefficient of hydrogen is a strong function of temperature and can be described by an Arrhenius-type equation, as below:[12,13]

$$Q_H = Q_{H0}\exp[-E_H/RT],$$

where Q_{H0} is the pre-exponential factor in the Arrhenius relationship, E_H is the apparent activation energy of hydrogen permeability, T is the absolute temperature and R is the universal gas constant. Arrhenius plot of the permeability data over the composite Pd membrane is shown in Figure 4. The thickness of the Pd film of this membrane was about 5 μm from SEM imaging.[10] From the linear relation of permeability with temperature, an apparent activation energy was calculated to be 15.0 kJ/mol, which is similar to the literature values of 15.7 kJ/mol[12] and 17 kJ/mol,[13] cited for an ultrathin Pd membrane (2 μm) on mesoporous γ-Al₂O₃ ceramic tube.

Plots of the hydrogen permselectivities at 400 °C over the composite Pd membrane and γ-Al₂O₃ membrane as a function of trans-membrane pressure drop with respect to nitrogen are shown in Figure 5. The permselectivity over the composite Pd membrane is much larger than the Knudsen ratio, (H₂/N₂) = 3.74, and increases sharply with decreasing pressure drop below 3 psi. This result suggests a primarily solution diffusion mechanism for hydrogen gas on this
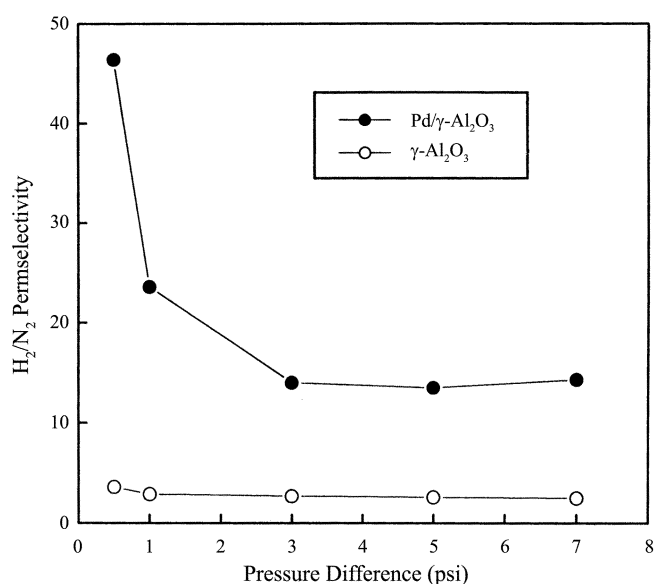
Figure 5. Permselectivities of hydrogen-to-nitrogen at 400 °C on Pd/γ-Al₂O₃ and uncoated γ-Al₂O₃ membranes.

membrane. On the other hand, the permselectivity over γ-Al₂O₃ membrane is close to the Knudsen ratio and is independent of the pressure drop. The change of hydrogen permselectivity with pressure drop at 500 °C over the composite Pd membrane is presented in Figure 6. The general trend is similar to that at 400 °C. However, the permselectivity at this temperature was much higher than that at 400 °C. This result indicates that hydrogen can be activated at higher temperatures, resulting in high solubility of hydrogen in the Pd membrane. This is more evidence that the Pd composite membrane permeates hydrogen via a solution-diffusion mechanism.[9]

The permselectivity over the composite Pd membrane in this study is rather different from that over the dense Pd
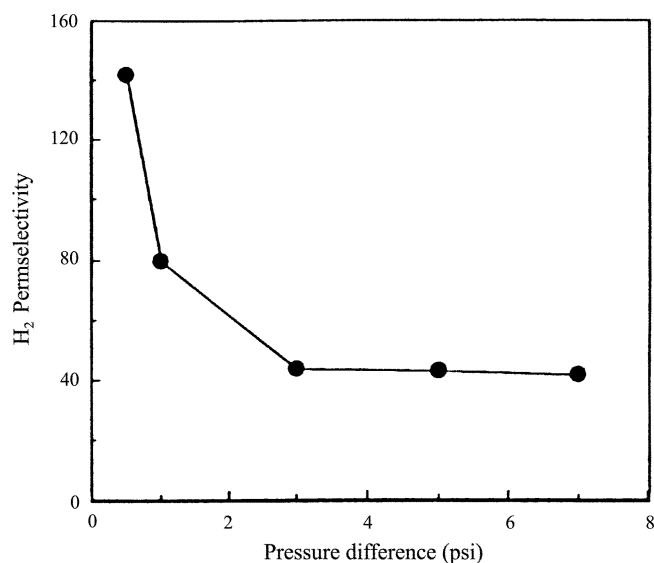

Figure 6. Permselectivities of hydrogen-to-nitrogen at 500 °C on Pd/γ-Al₂O₃ membrane.

membranes, which yield perfect permselectivity of hygrogen in some cases. This is mainly due to the presence of pinholes and microchasms in the Pd layer formed during the deposition of the palladium. According to the results of Hughes and co-workers,[14] a perfectly continuous Pd layer without pinholes cannot be prepared because microchasms and pinhole formation are inevitable during the palladium coating onto the alumina wall. Therefore, some pinholes in the palladium layer are expected, which could not be seen in the SEM image.

Hydrogen permeation through Pd-based membranes is a complex process that includes hydrogen chemisorption, dissolution in the Pd lattice, diffusion in the bulk driven by the concentration gradient and, finally, desorption from the opposite surface.[9,11] The measured hydrogen permeability was found to be proportional to the difference in permeation pressures by a power larger than 0.5 at elevated temperatures. The atomic hydrogen dissolved in cavities or microcracks within the membrane may combine to form molecular hydrogen species. The square-root dependence of permeation flux on pressure originates from Sievert's law of hydrogen solubility. When diffusion through the bulk metal is the rate-limiting step and hydrogen atoms form an ideal solution in the metal, Sievert's law predicts that n equals 0.5. However, a value of n greater than 0.5 may be obtained when surface processes influence the permeation rate or when Sievert's law is not followed.[12]

Propane Dehydrogenation Using a Membrane Reactor. The major advantage of the membrane reactor is conversion enhancement of an equilibrium-limited reversible reaction. Such an enhancement using the composite Pd membrane reactor is confirmed from the results shown in Figure 7, which plots propane conversion and propylene yield with respect to reaction temperatures. Upon applying the membrane to the propane dehydrogenation, the conversion is
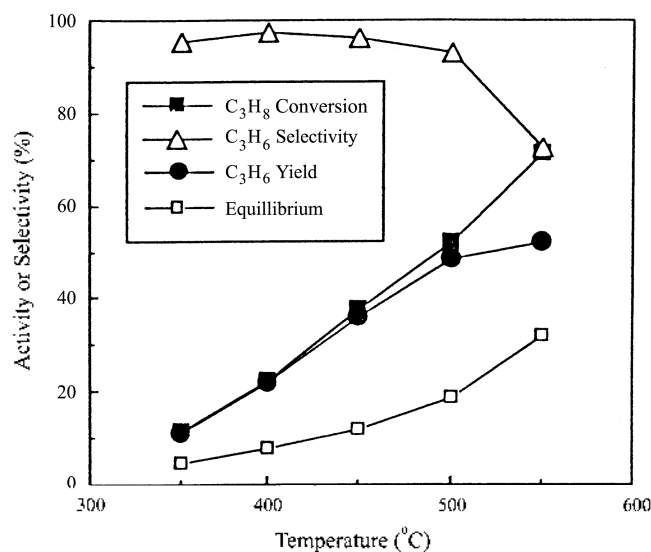
Figure 7. Propane dehydrogenation using Pd/γ-Al₂O₃ membrane according to reaction temperature: packed bed catalyst. Pt/Sn/γ-Al₂O₃; contact time, 2 sec; partial pressure of C₃H₈, 20 kPa; flowrate of sweep gas (Ar), 100 mL/min.

greatly increased above the equilibrium value at 350-550 °C to a large extent; at 500 °C the propane conversion is 52.0% compared with 28% at equilibrium level. Propane conversion increases linearly with reaction temperature. The selectivity to propylene is more than 90% below 550 °C. This significant improvement is mainly due to the effective removal of hydrogen gas from the product mixture and the significant decrease of the reaction temperature compared with a conventional reaction. To clarify the membrane effect, the propane dehydrogenation was executed within γ-Al₂O₃ membrane and a non-membrane reactor at 500 °C. A conventional quartz reactor was employed as a non-membrane reactor. All the reaction conditions were the same as those of the membrane reactor. According to the theoretical calculation, the obtainable conversion of propane at 500 °C is 27.9%. In the case of the non-membrane reactor, the conversion was only 8.4%. However, 28.4% conversion, which is similar or a little higher than theoretical, was obtained using γ-Al₂O₃ membrane. By contrast, when Pd/γ-Al₂O₃ membrane was applied to the reaction, 52.0% conversion was reached, which is about 2 times higher than theoretical. Thermodynamically, 52.0% conversion can be obtained at 580 °C, implying that the reaction temperature can be stepped down by 80 °C with the employment of the Pd composite membrane. The propylene selectivity was 87.2% in a non-membrane reactor, and it increased to 93.2% in a Pd-composite membrane reactor. This is due to the alleviation of reaction temperature and continuous removal of the produced hydrogen gas, resulting in an impeding side reaction. In the non-membrane system, hydrogen produced from the dehydrogenation reaction can cause a side reaction, such as hydrogenolysis, at high temperature. However, in the membrane system, side reactions associated with hydrogen gas can be reduced by selective removal of hydrogen and lowering the reaction temperature.

Propane conversion and propylene selectivity in the propane dehydrogenation reaction can be increased considerably with the use of a Pd-coated ceramic membrane. Therefore, the reaction temperature could be lowered via the alleviation of chemical equilibrium. As expected, high hydrogen permselectivity is confirmed as a key factor in determining reactor performance in terms of conversion enhancement.

Conclusion

The dehydrogenation of propane to propylene was studied in an isothermal high-temperature shell-and-tube membrane reactor containing a Pd-coated γ-Al₂O₃ membrane and a Pt/K/Sn/Al₂O₃ packed catalyst. The employment of a mem-

brane reactor in the dehydrogenation reaction, which selectively separates hydrogen from reaction mixture along the reaction path, can greatly increase reactant conversion and may permit lower temperature operation of the reactor. Thus, Pd composite membrane leads to conversion twice as high as equilibrium conversion and 6 times as high as conversion with a conventional reaction system at 500 °C. High hydrogen permselectivity has been confirmed as a key factor in determining reactor performance in terms of conversion and selectivity. Therefore, it is confirmed that the reaction temperature in the propane dehydrogenation reaction can be lowered *via* the alleviation of chemical equilibrium.

Nomenclature

A	: the cross sectional area
δ	: the thickness of the membrane
J	: the rate of permeation
p_1	: the inlet partial pressure of hydrogen
p_2	: the outlet partial pressure of hydrogen
Q	: the permeation coefficient
Q_H	: the permeation coefficient of hydrogen
Q_{H0}	: the pre-exponential factor of hydrogen

References

1. Saracco, G.; Specchia, V. *Catal. Rev.-Sci. Eng.* **1994**, *36*, 305.
2. Ziaka, Z. D.; Minet, R. G.; Tsotsis, T. T. *AIChE J.* **1993**, *39*, 526.
3. Armor, J. N. *Appl. Catal.* **1989**, *49*, 1.
4. Armor, J. N.; Farris, T. S. *Stud. Surf. Sci. Catal.* **1992**, *75*, 1363.
5. Ha, H. Y.; Nam, S. W.; Lim, T. H.; Oh, I.-H.; Hong, S.-A. *J. Membr. Sci.* **1996**, *111*, 81.
6. Nam, S.-E.; Lee, K.-H. *J. Membr. Sci.* **1996**, *170*, 91.
7. Mohan, K.; Govind, R. *AIChE J.* **1988**, *34*, 1493.
8. Park, S.-E.; Lee, S. H.; Chang, J.-S.; Park, J. T. *Membrane J.* **1995**, *5*, 97.
9. Park, S.-E.; Chang, J.-S.; Roh, H.-S.; Jung, K. S. *Membrane J.* **1998**, *8*, 177.
10. Roh, H.-S.; Park, M. S.; Chang, J.-S.; Park, Y.-K.; Park, S.-E. *J. Ind. Eng. Chem.* **1999**, *5*, 198.
11. Kikuchi, E. *Cattech* **1997**, *1*, 67.
12. Shu, J.; Grandjean, B. P. A.; Kaliaguine, S.; Giroir-Fendler, A.; Dalmon, J.-A. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 2745.
13. Koffler, S. A.; Hudson, J. B.; Ansell, G. S. *Trans. AIME* **1969**, *245*, 1735.
14. Yildirim, Y.; Gobina, E.; Hughes, R. *J. Membr. Sci.* **1997**, *135*, 107.