Development of Membrane Reactors for Dehydrogenating Organic Chemical Hydrides to Supply High-purity Hydrogen

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This review describes recent developments in the field of membrane reactors for obtaining high-purity hydrogen from organic chemical hydrides using hydrogen-selective amorphous silica membranes prepared by chemical vapor deposition. The application of such membrane reactors for hydrogen production reactions enables us to achieve higher conversion because of equilibrium shifts and to obtain high-purity hydrogen in one step, thus accomplishing an effective hydrogen supply. The most important issue in developing membrane reactors is the selection and preparation of appropriate hydrogen-selective silica membranes for each dehydrogenation reaction. Initially, the pore-size control method was developed by changing chemical structures of silica precursors in the chemical vapor deposition step. Using these membranes, membrane reactors for dehydrogenating cyclohexane or methylcyclohexane were developed and equilibrium shifts were achieved under various reaction conditions. High-purity hydrogen (>99.9 %) was stably attained by operating the membrane reactors with neither carrier gas nor sweep gas.

Keywords
Membrane reactor, Silica membrane, Chemical vapor deposition, Hydrogen, Organic chemical hydride, Methylcyclohexane

1. Introduction

Hydrogen has attracted much attention as one of the cleanest energy sources that will be able to replace the fossil energy sources. Coupled to this, the establishment of technology for hydrogen storage and transport is urgently required. Subsequently, many types of hydrogen storage and transport systems, including hydrogen carrier materials, have been proposed and examined. Among these, the organic chemical hydrides system as hydrogen carriers has emerged as one of the most promising candidates for the purpose (1)~(18).

The organic chemical hydrides are saturated cyclic hydrocarbons such as cyclohexane, methylcyclohexane and decalin, which can produce hydrogen via a dehydrogenation reaction. Furthermore, once these hydrides are dehydrogenated to utilize the hydrogen, they can again be converted into the organic chemical hydrides via a hydrogenation reaction. When hydrogen that is produced by using natural energy, such as by the electrolysis of water by natural energy, is used in this hydrogenation step, a very clean and safe production-transportation-utilization system of hydrogen will be established.

However, the dehydrogenation reactions are endothermic and limited by thermodynamic equilibrium. Therefore an effective system for hydrogen production from the organic chemical hydrides needs to be developed. One of the candidate systems is membrane reactors with hydrogen-selective membranes (19)~(30). When using membrane reactors with hydrogen-selective membranes for such dehydrogenation reactions, the equilibrium shift required to obtain higher conversion is easily achieved by extracting the produced hydrogen from the reaction side to the permeation side. This then also means that high-purity hydrogen can be obtained in one step, without the requirement for any post-treatment for separation, such as pressure swing adsorption (PSA) or thermal swing adsorption (TSA). In other words, the membrane reactor can make the hydrogen production system more compact and efficient, compared with conventional processes. Much literature is available on the development of membrane reactors for dehydrogenating the organic chemical hydrides with hydrogen-selective membranes. Furthermore, the effectiveness of utilizing membrane reactors has also been demonstrated in other hydrogen production systems, such as the steam reforming reaction of hydrocarbons (31)~(40) or the decomposing reaction of hydrogen.
sulfide. The most important issue in determining the performance of membrane reactors is the hydrogen-selective membranes. In general, the performance of a hydrogen-selective membrane is determined in terms of the following two values: (1) hydrogen permeance and (2) separation factors of hydrogen compared with other gases that are to be separated. Higher values are preferable in both cases. When applying hydrogen-selective membranes to membrane reactors for hydrogen production reactions such as the dehydrogenation of organic chemical hydrides, steam reforming of hydrocarbons or decomposition of hydrogen sulfide, generally a high hydrogen permeance is preferable for realizing a larger equilibrium shift, and a higher hydrogen separation factor is preferable for obtaining high-purity hydrogen. There are three different types of membrane material available for hydrogen separation: polymeric membranes, palladium or its alloyed membranes, and microporous ceramic membranes. Polymeric membranes cannot be used at temperatures above 200°C. Therefore the utilization of a membrane reactor with such membranes is unsuitable for hydrogen separation. In the case of palladium or its alloyed membranes, the hydrogen separation mechanism is the “solution-diffusion mechanism,” which means that only hydrogen can dissociate into atomic H on the membrane surface from the feed side, which then diffuses to the permeation side where it reassociates to molecular hydrogen. Therefore this type of membrane shows excellent hydrogen-selective performance. However, when such membranes are applied to the dehydrogenation reaction of organic chemical hydrides, the membranes have to be used in the temperature range 473-573 K, where the palladium would become brittle after repeated use. The fact that such metals are expensive is a further disadvantage. On the other hand, in the case of microporous ceramic membranes, such as amorphous silica membranes, the hydrogen separation mechanism is a “molecular sieve mechanism,” which means that only those gases with sizes smaller than the pore sizes of the membrane can permeate, and other larger gases cannot permeate through the membrane. Compared with palladium or its alloyed membranes, the hydrogen brittleness cannot be raised. Furthermore, the cost of preparing these membranes is lower.

Based on these considerations, we developed membrane reactors for dehydrogenating organic chemical hydrides with hydrogen-selective amorphous silica membranes. First of all, hydrogen-selective silica membranes with controlled pore sizes and pore size distributions appropriate for extracting hydrogen from organic chemical gases were prepared using the one-sided diffusion chemical vapor deposition (CVD) method or the counterdiffusion CVD method. Then the effectiveness of the membrane reactors was demonstrated for the cyclohexane-benzene system and methylcyclohexane-toluene system. Finally, the stable operation of the membrane reactors to produce high-purity hydrogen without the requirement for carrier gas nor sweep gas, which enables us to supply the produced hydrogen directly to fuel cells, was demonstrated.

2. Pore Size Control in the Preparation of Silica Membranes by the Chemical Vapor Deposition Method

To achieve high separation factors, the membrane pore size should be larger than hydrogen and simultaneously smaller than the gases that should be separated from hydrogen. In our previous studies we developed hydrogen-selective silica membranes with tetramethoxysilane (TMOS) as silica precursor, and reported that the membranes showed a higher hydrogen permeance and hydrogen separation factor at 773-873 K. Based on the permeation behaviors of several gas species, the membrane prepared with TMOS was estimated to have a pore size of around 0.3 nm. However, the activation energy for hydrogen permeation is rather high, which results in lower hydrogen permeance in the lower temperature range of 473-573 K. Therefore it is important to develop a technique to control the pore sizes of the silica membranes in order to obtain a high hydrogen permeance and hydrogen separation factor, even at 473-573 K.

In this study we prepared hydrogen-selective silica membranes that could be used in membrane reactors for dehydrogenating organic chemical hydrides. The kinetic diameters of cyclohexane, benzene, methylcyclohexane and toluene are 0.60, 0.59, 0.60 and 0.59 nm, respectively, while that of hydrogen is 0.289 nm. Thus, the pore size of the hydrogen-selective silica membrane should be set at around 0.5-0.55 nm, if unfavorable side reactions do not occur. There are a few reports on the pore size control of amorphous silica membrane by the CVD method. Among these, Sea et al. reported on the preparation of silica membranes by the pyrolysis of ethoxysilane, phenyltriethoxysilane or diphenyldiethoxysilane, and indicated that a looser structure was formed and the pore sizes of the silica membranes increased as the number of phenyl groups in the silica precursor increased. The amorphous silica layer is supposed to be fabricated by an oligomerization reaction; thus, the bulky phenyl group would result in steric hindrance in the oligomerization reaction. Viewed in this light, the finding can be understood qualitatively. However, analysis of the membranes or of the mechanism of micropore formation has hardly been discussed.

We therefore first investigated the preparation of hydrogen-selective amorphous silica membranes by the CVD method with oxygen and TMOS, phenyltrime-
thoxysilane (PTMS) or dimethoxydiphenylsilane (DMDPS). These silica membranes were then deposited onto a γ-alumina-coated α-alumina tube. The pore size of the γ-alumina-coated substrate was found to be about 4 nm by permporometry measurement. A schematic diagram of the CVD apparatus is shown elsewhere\textsuperscript{45}). The CVD was conducted at 873 K. **Figure 1** shows the permeances of several gases through the TMOS-, PTMS- and DMDPS-derived membranes at 573 K. The TMOS-derived membrane was prepared by the counterdiffusion CVD method and the other membranes were prepared by the one-sided diffusion CVD method. In the case of the TMOS-derived membrane, the permeance of H\textsubscript{2} was much higher than that of any other molecules. Molecules larger than oxygen were estimated to permeate the membrane by the Knudsen diffusion mechanism. In the case of the PTMS-derived membrane, a similar trend to that of the TMOS-derived membrane was observed, except for the selectivity of oxygen and nitrogen. The selectivity of oxygen/nitrogen was 3.0, and this value exceeded the selectivity of 0.94 estimated by the Knudsen mechanism. Furthermore, the permeances of all the gases through the PTMS-derived membrane were higher than those through the TMOS-derived membrane. This was because the PTMS-derived membrane had larger pores. In the case of the DMDPS-derived membrane, molecular sieving was observed, not only for hydrogen/oxygen and oxygen/nitrogen but also between the other gases. The permeances of the gases through the DMDPS-derived membrane were the highest. This was because the DMDPS-derived membrane had much larger pores, a looser structure and a wider pore-size distribution than the PTMS- and TMOS-derived membranes. **Figure 2(a)** shows the Arrhenius plots of permeances through the TMOS-derived membrane. The activation energy for hydrogen permeation was 19 kJ/mol. The permeances of the other gases showed hardly any dependency on the permeation temperature. This probably results from the TMOS-derived membrane having suitable pores to separate hydrogen from other gases effectively, i.e., having an estimated size of around 0.3 nm, on the basis of kinetic diameters. **Figure 2(b)** shows the Arrhenius plots of permeation results in the case of the PTMS-derived membrane. The activation energy for hydrogen permeance decreased from 19 to 11 kJ/mol. On the other hand, a dependency of the oxygen permeance on the permeation temperature appeared. **Figure 2(c)** shows the Arrhenius plots...
of permeation results in the case of the DMDPS-derived membrane. Only the permeance of CF₄ showed a high activation energy of 23 kJ/mol. This means that the DMDPS-derived membrane has large micropores, approximately 0.30-0.47 nm, which was estimated on the basis of the kinetic diameter of CF₄. Judging from the results mentioned above, the pore size of amorphous silica precursors being zero (TMOS), one (PTMS) or two (DMDPS).

Furthermore, the CBS-QB3 quantum chemical calculation method was employed to explain why the different molecular structures of the silica precursors have a great effect on the enlargement of the pore size of amorphous silica membranes. The resultant bond energies indicated that whether or not the intermediate contains phenyl groups has a great effect on the permeance of gases. The activation energy of H₂ was around 23 kJ/mol. This means that the difference between the one-sided and counter-diffusion methods had no effect on the performance of the DMDPS-derived membranes.

3. Consideration of a Membrane Reactor Model from a Chemical Engineering Point of View

From a chemical engineering point of view, a 1-D membrane reactor model has been developed to predict and discuss the performances of the membrane reactors. The membrane reactor was composed of a cylindrical stainless steel tube and tubular silica membrane. The membrane was coaxially fixed inside the cylindrical tube. The reaction took place inside the membrane, into which catalyst particles were loaded. The outer side of the silica membrane was the permeation side. This simulation model was based on the following assumptions. (1) The reactor is isothermal. (2) All gas components on both the reaction side and the permeation side are subject to plug flow. (3) There is no radial distribution of pressure in the membrane reactor. (4) The effect of diffusion is negligible, both radially and axially. (5) The gas permeation through the membrane is proportional to the difference between the partial pressures on the reaction side and permeation side. (6) The dehydrogenation reaction occurs only on the reaction side.

The mass balance of the reaction side and permeation side is described by the following equations:

\[
\frac{dN_{rk}}{dt} = v_i r_0 S_{rk} - 2\pi r_0 Q_i (P_{r} - P_{y_i}) \quad (1)
\]

\[
\frac{dN_{rp}}{dt} = 2\pi r_0 Q_i (P_{r} - P_{y_i}) \quad (2)
\]

The reaction kinetics is also important to develop the membrane reactor model. For the dehydrogenation reaction of cyclohexane, the reaction kinetics and parameters applied in this simulation were taken from the literature, as reported by Itoh et al.\(^{51}\), as follows:

\[
r_d = \frac{k \left( K_{eq} P_{CH}/P_H^3 - P_{\text{BEN}} \right)}{1 + \left( K_{\text{BEN}} K_{eq} P_{CH}/P_H^3 \right)} \quad (3)
\]

\[
k = 0.221 \exp(-4270/T) \quad (4)
\]

\[
K_{eq} = 4.89 \times 10^{-15} \exp(-26490/T) \quad (5)
\]

\[
K_{\text{BEN}} = 2.03 \times 10^{10} \exp(6270/T) \quad (6)
\]

For the dehydrogenation reaction of methylcyclohexane, the expression of reaction rate was taken from Ali and Bailer\(^{54}\), as follows:

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In addition, the parameter $k_1$ was determined by the dehydrogenation reaction experiments conducted by us in the temperature range 473-553 K, and under the pressure condition of 0.1 MPa. The derived equation for the $k_1$ was as follows:

$$k_1 = \exp \left(11.4 - \frac{112000}{RT}\right)$$  \hspace{1cm} (8)

Hereinafter, the experimental results on the membrane reactors are compared with the simulation results.

4. Dehydrogenating Cyclohexane Using the Membrane Reactors with Silica Membranes\textsuperscript{55,56)

A SUS tube and TMOS- or DMDPS-derived membrane were used for the reactor. The SUS tube was nonporous, and therefore no gas could permeate to the permeation side. On the other hand, hydrogen can permeate selectively through the TMOS- or DMDPS-derived membranes. Pt/Al$_2$O$_3$ particles were used as a catalyst and were loaded into the SUS tube or the hydrogen-selective silica membranes.  

Figure 4 shows the relationship between the reactor temperature and the conversion of cyclohexane for the three reactors operated at 1 atm. In all the reactors, the conversion of cyclohexane increased as the reactor temperature increased. This is because this dehydrogenation reaction is endothermic. In the case of the reactor with a SUS tube, the conversion of cyclohexane coincided with the equilibrium one predicted by thermodynamics. In this case, the produced hydrogen is not extracted from the reaction side, and hence in principle the conversion of cyclohexane never exceeds the equilibrium conversion. This result also indicated that the residence time was sufficient to reach the equilibrium conversion. In the case of the reactor with a TMOS-derived membrane, the conversion of cyclohexane exceeded the equilibrium one. This equilibrium shift was because of the extraction of the produced hydrogen through the TMOS-derived membrane. In the case of the reactor with a DMDPS-derived membrane, the conversions of cyclohexane exceeded those achieved in the case of the membrane reactor with the TMOS-derived membrane. The reason for this greater equilibrium shift achieved with the reactor with a DMDPS-derived membrane was the higher hydrogen permeance. The extent of the equilibrium shift coincided with the hydrogen permeance through the membranes. 

The simulation results are also shown in Fig. 4. They indicated that, in both cases, the relationship between reaction temperature and conversion as predicted by this simulation model corresponded well with results obtained experimentally. It was also confirmed that the extraction of the produced hydrogen from the reaction side to the permeation side made it possible to shift the thermodynamic equilibrium, and that the extent of the equilibrium shift was determined by the hydrogen permeance of the membranes. It can therefore be said that both a higher hydrogen permeance and a higher separation factor of hydrogen (compared with other gases) are crucial factors for the efficient performance of the membrane reactors.

Figure 5 shows the relationship between the reactor pressure and the conversion of cyclohexane for the three reactors operated at 503 K. The pressures ranged from 1 to 8 atm. This dehydrogenation reaction produces 3 mol H$_2$ and 1 mol benzene from 1 mol cyclohexane. From a thermodynamics point of view, lower pressure conditions are preferable for the production of hydrogen. As is shown in Fig. 5, in the case of the packed bed reactor with the nonporous SUS tube, the conversion decreased monotonically with reaction pressure. On the other hand, in the case of the membrane reactor with hydrogen-selective membranes, we should also take into consideration that higher pressure conditions are preferable for the equilibrium shift, because of a greater driving force for hydrogen extraction. Therefore, the effect of pressure on the performance of the membrane reactors depends on the operating conditions and the membrane performance. In the case of the membrane reactor with the TMOS-derived membrane, the conversion exceeded the equilibrium ones under all pressure conditions used in the experiment. The conversion decreased with pressure and became...
almost constant above 0.3 MPa. In the case of the membrane reactor with the DMDPS-derived membrane, the conversion also exceeded the equilibrium conversion and that of the membrane reactor with the TMOS-derived membrane under all pressure conditions used. Furthermore, the conversions were similar, regardless of the pressure conditions. These results are similar to those shown in Fig. 4. The order of the equilibrium shift coincided with that of hydrogen permeance. We can say that the reason why the conversions did not decrease under higher pressure condition was an offset by larger amount of hydrogen extraction due to larger driving force for permeation, in the case of the membrane reactors. However, in a strict sense, agreement between the experiments and the simulations was not observed in Fig. 5. The conversions obtained experimentally were somewhat lower than those predicted by the simulation studies, where the gas permeances of fresh membranes were used. This was probably because of the effect of the reaction temperature. When the membrane reactors were operated under lower temperature conditions, other gas species such as benzene might be adsorbed onto the surface of the pores of the membrane, resulting in the exclusion of hydrogen extraction. This would result in a lower equilibrium shift compared with the membrane reactors with fresh membranes. Actually, the measurement of hydrogen permeance through the DMDPS-derived membrane (after all the pressure-dependent experiments) indicated that it decreased to \(2.7 \times 10^{-7}\) mol m \(^{-2}\) s \(^{-1}\) Pa \(^{-1}\). The prediction line obtained from the simulation study using this low permeance is also shown in the Fig. 5. It was lower as a result of the decrease in hydrogen permeance, and the difference between experimental and calculation values became rather small. The extent of the difference was, however, acceptable. These results indicate that it is not simple to operate the membrane reactor under such low-temperature conditions because the adsorption is inevitable. More detailed studies on this point should be conducted.

Figure 6 shows the time courses of conversion of cyclohexane (measured by gas chromatography), reaction pressure, hydrogen purity, hydrogen production rate and hydrogen permeance before and after each series of runs. It should be noted that in this experiment the membrane reactor with the DMDPS-derived membrane was operated with no carrier gas nor sweep gas. The hydrogen produced from the membrane reactor was of high purity and could be used directly for any purpose, without the requirement for any posttreatment. This is a very important point, particularly when considering practical applications. There are as yet no reports on membrane reactors (other than a few reports of palladium membrane reactors) using silica membranes that were successfully operated at a pressure \(>1\) atm without the requirement for carrier or sweep gases.

This experiment was initially carried out over a period of 6 h each day, followed by cooling to room temperature overnight and then recommencing it the following day. This cycle continued for 3 days (1st day, 2nd day, 3rd day). Four days later (7th day), a 3 h reaction experiment was conducted and the reactor was cooled to room temperature. After another 4 days (11th day), a final 3 h reaction test was performed. The reaction temperature was 583 K, and the pressure on the reaction side was 0.3 MPa. As is shown in the 1st day’s result, the conversion of cyclohexane was around 0.8, and the purity of the produced hydrogen was around 99.9 %. These values were stable during the 6 h operation. Furthermore, when the membrane reactor was operated the following day (2nd day), the conversion and the purity were almost the same as on the 1st day. The reason for the stable performance of this membrane reactor is that the DMDPS-derived silica membrane maintained a high permeance of H\(_2\) and high hydrogen selectivity. To the best of our knowledge this is the first successful membrane reactor operating with a hydrogen-selective amorphous silica membrane with a feed of pressurized materials and with neither a carrier nor sweep gas.

A detailed determination of the purity of the produced hydrogen was carried out by quantitative analysis of the permeate gas on the 11th day of operation, using a vacuum ultraviolet single-photon ionization mass spectrometer. In this technique, the sample gases are photoionized at 10.5 eV, and the limit of detection of benzene and cyclohexane is a few ppbv. Figure 7 shows the results of the mass spectrometric measurement of the gas on the permeation side, diluted with ni-
Two strong peaks at $m/z$ 78 and 84 were observed, which correspond with benzene and cyclohexane, respectively. Other gas species such as cyclohexadiene or cyclohexene were not detected in the permeate gas. Quantitative analysis indicated that the concentrations of the impurities were 0.118 % benzene and 0.043 % cyclohexane. The hydrogen purity determined from these values was in good agreement with that determined from the gas chromatography measurement, as mentioned above.

Finally, the permeate gas produced by the membrane reactor was supplied directly to a commercial fuel cell, and stable electric power generation was confirmed. Thus we can conclude that our membrane reactor can supply hydrogen, with sufficient purity, directly to a fuel cell under normal pressure, and it can work stably.

5. Dehydrogenating Methylcyclohexane Using the Membrane Reactors with Silica Membranes

Compared with the cyclohexane–benzene system, the methylcyclohexane–toluene system holds several advantages for the application of the dehydrogenation reaction using the membrane reactors with hydrogen-selective silica membranes, as described below. First, methylcyclohexane and toluene are liquids at standard temperature and pressure, and they have sufficiently low melting points, which means that they do not freeze in cold regions. Second, the equilibrium conversion of methylcyclohexane as predicted by thermodynamics is higher than that of cyclohexane, which means that hydrogen could be produced from methylcyclohexane at lower temperature. Third, the carcinogenic material benzene, detected in small amounts on the permeation side in the case of a membrane reactor for the dehydrogenation of cyclohexane, as mentioned above, is not produced in principle as it is in the case of the dehydrogenation of methylcyclohexane. Thus this organic chemical hydride system is preferable. Here, a SUS tube or the DMDPS-derived membrane was used for the reactor. Pt/Al$_2$O$_3$ particles, loaded into the SUS tube or the hydrogen-selective silica membrane, were used as catalyst.

Figure 8 shows the relationship between the reactor temperature and the conversion of methylcyclohexane for the two reactors operated at 1 atm. In both the reactors, the conversion of methylcyclohexane increased as the reactor temperature increased. This is because...
this dehydrogenation reaction is endothermic, similar to the case of the cyclohexane–benzene system. When using the packed bed reactor, the conversions recorded at all temperatures in the experiments coincided well with those predicted by the thermodynamic equilibrium. When using the membrane reactor, the equilibrium shift was successfully observed because of hydrogen extraction through the membrane. Figure 9 shows the relationship between the reactor pressure and the conversion of methylcyclohexane for the two reactors operated at 533 K. In the case of the packed bed reactor, the conversion decreased monotonically and this profile coincided with the equilibrium. In the case of the membrane reactor, a conversion as high as 0.99 was maintained under the experimental conditions used. This is because the effect of hydrogen extraction offset the effect of thermodynamics, which can be explained by the simulation results, which are also shown in Fig. 9. This means that the membrane reactor with sufficient hydrogen extraction has an advantage when it is operated under higher pressure, namely achieving higher conversion than the equilibrium conversion.

Figure 10 shows the time courses of methylcyclohexane conversion, reaction pressure, hydrogen purity, production rate of hydrogen, and hydrogen permeance for the DMDPS-derived membrane reactor during the dehydrogenation of methylcyclohexane. In this experiment, and as was also described for Fig. 6, the dehydrogenation reaction of methylcyclohexane was carried out in a membrane reactor without using carrier gas nor sweep gas. After the 1st day’s run, the conversion was about 0.8 and hydrogen purity was as high as 99.95 %. These values were mostly stable for 6 h. In the simulation study, the conversion and hydrogen purity were predicted to be 0.86 and 99.98 %, respectively. These values are in good agreement with the experimental results. It is significant that hydrogen gas with 99.9 % purity can be produced simply by using the membrane reactor, without any special posttreatment. As is shown in Fig. 10, this stable performance of the membrane reactor was maintained on the 2nd day’s run and the 3rd day’s run, which is similar to what was observed in the case of the cyclohexane–benzene system.

To the best of our knowledge, these successful operations of membrane reactors with hydrogen-selective amorphous silica membranes, using neither carrier gas nor sweep gas, are the first in the world. It is considered significant to be able to demonstrate the effective-
ness of this membrane reactor for hydrogen production by dehydrogenating organic chemical hydrides.

6. Conclusion

This review describes our recent developments of hydrogen-selective amorphous silica membranes and their use in membrane reactors for the production of high-purity hydrogen from organic chemical hydrides. Membranes with both higher hydrogen permeance and higher hydrogen selectivity are required in membrane reactors for efficient hydrogen production. Therefore, pore-size control technique appropriate for application to the membrane reactor was developed by changing the chemical structure of silica precursors. The pore size of the silica membrane was significantly increased when the number of phenyl groups on the silica source increased from zero (as in TMOS) or one (as in PTMS) to two (as in DMDPS). The DMDPS-derived membrane was found to be the most suitable membrane for this application.

Membrane reactors for dehydrogenating cyclohexane or methylcyclohexane were also developed. Using a hydrogen-selective amorphous silica membrane such as the TMOS-derived or the DMDPS-derived membrane, an equilibrium shift was successfully achieved under various temperature and pressure conditions. These performances were well predicted with the simple model developed. The extent of the equilibrium shift was greater when a membrane with higher hydrogen permeance was used. Furthermore, it is noteworthy that we have successfully operated these membrane reactors.

Fig. 10  Time Courses of Methylcyclohexane Conversion, Reaction Pressure, Hydrogen Purity, Hydrogen Production Rate and Hydrogen Permeance through the DMDPS-derived Membrane during the Operation of the Membrane Reactor with no Carrier Gas or Sweep Gas
with no carrier gas or sweep gas, for the first time in the world. This means that high-purity hydrogen at atmospheric pressure can be obtained in a one-step procedure, and the produced hydrogen can then be directly supplied to a fuel cell. High-purity hydrogen, with purity >99.9%, was stably obtained using the membrane reactors. This stable performance was achieved because of the stable performances of the hydrogen-selective membranes and the catalysts.

For practical applications, the long-term durability of membrane reactors should be determined by their continuous operation for at least several months. We are currently engaged in commencing these tests.

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Nomenclatures

\[ k \] : apparent rate constant \( [\text{mol} \cdot \text{s}^{-1} \cdot \text{m}^{-3} \cdot \text{Pa}^{-1}] \)

\[ k_i \] : reaction rate \( [\text{mol} \cdot \text{s}^{-1} \cdot \text{kg} \cdot \text{cat}^{-1} \cdot \text{Pa}^{-1}] \)

\[ E_{\text{eq}} \] : equilibrium constant \( [\text{Pa}] \)

\[ i \] : reactor length \( [\text{m}] \)

\[ N_{i,r} \] : molar flow rate of component \( i \) on the reaction side \( [\text{mol} \cdot \text{s}^{-1}] \)

\[ N_{i,p} \] : molar flow rate of component \( i \) on the permeation side \( [\text{mol} \cdot \text{s}^{-1}] \)

\[ P_i \] : partial pressure of component \( i \) on the reaction side \( [\text{Pa}] \)

\[ P_R \] : total pressure on the reaction side \( [\text{Pa}] \)

\[ P_P \] : total pressure on the permeation side \( [\text{Pa}] \)

\[ Q_i \] : permeance of component \( i \) \( [\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}] \)

\[ r \] : outer radius of membrane \( [\text{m}] \)

\[ r_i \] : dehydrogenation rate of cyclohexane or methylcyclohexane \( [\text{mol} \cdot \text{s}^{-1} \cdot \text{kg}^{-1}] \)

\[ R \] : gas constant \( [\text{m}^2 \cdot \text{kg} \cdot \text{s}^{-2} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}] \)

\[ S_R \] : sectional area of the reaction side \( [\text{m}^2] \)

\[ x_i \] : mole fraction of component \( i \) on the reaction side \( [—] \)

\[ y_i \] : mole fraction of component \( i \) on the permeation side \( [—] \)

\(<\text{Greek}>>\)

\[ \nu_i \] : stoichiometric coefficient \( [—] \)

\[ \rho \] : bulk density of catalyst \( [\text{kg} \cdot \text{m}^{-3}] \)

\(<\text{Subscript}>\)

BEN : benzene

CH : cyclohexane

MCH : methylcyclohexane

TOL : toluene

H : hydrogen

\( i \) : component \( i \)

References


要 旨

高純度水素供給を可能にする有機ハイドライド脱水素膜反応器の開発

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CVD 法を用いて調製した水素分離アルファシリカ膜を搭載した水素引き抜き型膜反応器を開発し、水素キャリアーとして期待されている有機ハイドライドの脱水素反応系に適用した。脱水素反応は平衡反応であるが、水素分離シリカ膜を反応系に組み込むことで、選択的に水素を引き抜き、これにより平衡シフトによる高転化率の達成と高純度水素の安定供給を同時