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Membrane reactor application to hydrogen production

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Abstract

Selective removal of hydrogen in a membrane reactor enables the hydrogen production by steam reforming at lower reaction temperatures than conventional processes. We invented a composite membrane consisting of thin palladium layer deposited on the outer surface of porous ceramics by electroless-plating. The palladium layer could completely cover the surface, so that only hydrogen could permeate through the membrane with a 100% selectivity. By use of this kind of membrane, Tokyo Gas and Mitsubishi Heavy Industries have developed a membrane reformer applicable to the polymer electrolyte fuel cell system. Our current approach is the application of a CVD technique to deposit non-Pd metals, such as Pt, to overcome the limitations caused by Pd membranes, such as hydrogen embrittlement. The permeability and permeation selectivity of these metal-ceramic composite CVD membranes were investigated in a comparison with electroless-plating palladium membranes, as well as the performance in membrane reactors applied to steam reforming of methane. The permeation of hydrogen through the CVD membranes is not based on the solution-diffusion transport mechanism but on the surface diffusion mechanism. Although the CVD membranes gave higher conversion of methane than thermodynamic equilibrium, their performance became similar to electroless-plating membranes, only when the membranes showed high H_2/N_2 separation factors. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: CVD membranes; Electroless-plating membranes; Solution-diffusion transport mechanism; Surface diffusion mechanism; Steam reforming; Hydrogen

1. Introduction

Hydrogen and syngas (a mixture of CO and H_2) are most economically produced nowadays by steam reforming, a reaction between steam and hydrocarbons, using supported nickel catalysts. As CH_4 is a stable hydrocarbon, extremely high reaction temperatures, around 800°C, are required for endothermic reaction (1). Carbon monoxide is further reformed with steam to CO_2 and H_2 by exothermic reaction (2).

$$CH_4 + H_2O = CO + 3H_2 \tag{1}$$

$$CO + H_2O = CO_2 + H_2 \tag{2}$$

If H_2 is selectively removed from the reaction system, thermodynamic positions of these reactions are shifted to the product sides, and highly efficient conversion of CH_4 to H_2 and CO_2 can be attained and it can be accomplished even at low temperatures.

Actually, enhanced performance of steam reforming with a real membrane catalytic system was firstly reported by Oertel et al. [1], in accordance with a computer simulation study. An absolute selectivity of Pd-based membranes for hydrogen separation based on the solution-diffusion transport mechanism had already been demonstrated by the pioneering works of Professor Gryaznov and his group on a number of examples for membrane catalysis using Pd membranes in the forms of spirals offering high surface area [2].

The membrane employed by Oertel et al. [1] was a Pd disk with a thickness of 100 μm, which effectively

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enhanced hydrogen production, but at very high temperatures, like 700 or 800°C. According to the calculation by Shu et al. [3], membrane separation can result in the greatest improvement on the CH_4 steam-reforming equilibrium at a lower temperature range of 500–600°C. At such moderate temperatures, commercially available Pd membranes are too thick to work effectively.

The critical features of membrane for successful membrane reactors are not only high separation selectivity, but also high permeability, namely the rate of permeation should be comparable to the rate of catalytic reaction. Another important feature is stability. This article mainly describes our approach to highly efficient membranes by electroless-plating of Pd and our more recent approach by CVD of precious metals with their application to H_2 production by steam reforming of CH_4.

2. Electroless-plating Pd membranes

The most effective way to increase the permeability of H_2 through Pd membranes is the reduction in the membrane thickness. In order to reduce the thickness of Pd membrane without reducing permselectivity and mechanical strength, we [4] have proposed a composite membrane consisting of thin Pd layer deposited on the outer surface of asymmetric porous ceramics by an electroless-plating technique. The Pd layer having a thickness larger than 4.5 μm was empirically proved sufficient to attain a 100% selectivity for hydrogen permeation. The rate of hydrogen permeation was inversely proportional to the thickness of membrane. This indicates that the rate-determining step is involved in diffusion of hydrogen in the bulk of Pd even when the thickness of membrane is reduced to this range, and that hydrogen can diffuse without resistance through the pore support [5].

With the development of our composite membrane as a starting point, much effort has been devoted to the preparation of various excellent Pd-based composite membranes not only by electroless-plating [6–9], but also by chemical vapor deposition, CVD [10], sol–gel method [11,12], spray pyrolysis [13], and sputtering [14,15]. Among these deposition techniques, electroless-plating was successfully employed to obtain membranes without pinholes and cracks. Other techniques have not wholly proven to give membranes where transport of hydrogen is completely controlled by the deposit of Pd.

3. Steam reforming in Pd-based membrane reactor

Using a single membrane tube, we set up a membrane reactor and tested the effects on promotion of various reactions, such as steam reforming [16–19], CO_2 reforming [19,20], water–gas shift reaction [21,22], dehydrogenation of isobutane [23], and dehydrocyclization of propane [24,25].

In the study of steam reforming of CH_4, we used a catalyst which had already been developed by Tokyo Gas for production of substituted natural gas (SNG) by steam reforming of LPG or naphtha at around 500°C. Sufficient conversion of CH_4 could be accomplished at temperatures as low as 500°C, in the Pd membrane reactor, without any deactivation of either catalyst or membrane [16]. Under the same conditions, porous Vycor glass membrane was useless, that is no promotive effect being brought about by this kind of membrane.

The Ni catalyst for the SNG process worked enough at these temperatures for H_2 production. A thermodynamic equilibrium could be established among CH_4, CO, CO_2, H_2O, and unpermeated H_2 remaining in the reaction system [17]. Increasing reaction pressure, which is a thermodynamically unfavorable condition, accelerated hydrogen permeation, resulting in the increase of CH_4 conversion [18].

This membrane was applied by Tokyo Gas and Mitsubishi Heavy Industries to a membrane reformer on a larger scale to develop a practical apparatus and to confirm the applicability to a fuel processor for a polymer electrolyte fuel cell (PEFC) [26]. As the operating temperature of PEFC is below 120°C, then the Pt electrodes are seriously poisoned by CO. The concentration of CO must be below 10 ppm, and hence pure hydrogen is indispensable.

The reformer, as depicted elsewhere [27], has a burner in the center surrounded by a catalyst bed, in which 24 supported Pd membrane tubes are aligned circumferentially. The catalyst particle size is 20 mm. The membrane was first prepared by electroless-plating a 20-μm thick layer of Pd

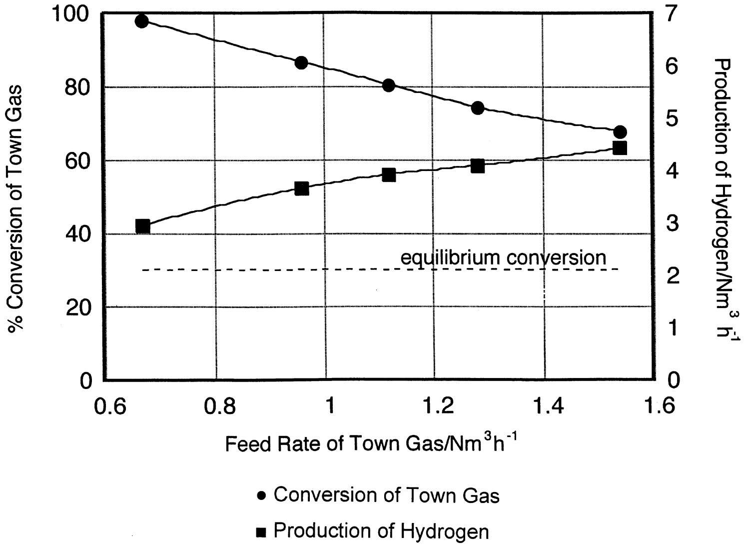

Fig. 1. Conversion of town gas and hydrogen yield in the membrane reformer [28] as a function of the feeding rate of town gas at 550°C and 6.2 atm, with a steam/carbon ratio of 2.4.

on the surface of a porous metal tube. Nowadays, they employ alloy casting and rolling (hot press) for use in more general purpose. They use steam as a sweep gas with an adjusted flow rate so as the fraction of hydrogen in the permeate gas being 0.5–0.6.

Here, are shown a few results reported by Tokyo Gas and Mitsubishi Heavy Industries with their membrane reformer [28]. Fig. 1 shows the effect of feeding rate of town gas on the conversion level of town gas and hydrogen yield, at 550°C and 6.2 atm with a steam/C ratio of 2.4, and 14.5 kg catalyst. Under these conditions, the equilibrium conversion was ca. 30%, while more than 60% of town gas was converted. The composition of the permeated gas was only hydrogen and that of the unpermeated gas from the reformer is shown in Table 1. More than 90% of the unpermeated gas was CO_2. The spent gas is used as the burner fuel for the reformer.

They operated the membrane reformer in the temperature range of 500–600°C and in the pressure range of 270–610 kPa. Thermodynamically unfavorable condition of increasing reaction pressure rather increased the town gas conversion and H_2 yield, due to the increase in driving force of hydrogen permeation through the membrane.

These results well reproduced our experimental results taken in our single membrane tube reactor, already reported [16–19].

4. CVD non-Pd membranes

Hydrogen permselective membranes are often fabricated from Pd due to its very high selectivity. There are, however, some limitations in Pd membranes. The inherent hydrogen permeance of pure Pd membrane requires an ultrathin, continuous layer of Pd for high H_2 flux. Moreover, Pd has a strong tendency to

Table 1
Typical composition of the effluent gas from the membrane reformer operating at 550°C and 6.2 atm, with a steam/carbon ratio of 2.4[a]

Component	Volume (%)
H_2	6
CO	1
CO_2	91
CH_4	2

[a] Feeding rate of town gas, 0.67 $Nm^3 h^{-1}$; temperature, 823 K; S/C, 2.4; pressure, 608 kPa.

hydrogen embrittlement, and consequently, insufficient mechanical stability against temperature or hydrogen pressure cycles. Furthermore, Pd is a costly metal and its price is occasionally subject to unpredictable market force. Poor resistances against sulfur poisoning and carbon deposition are also problems for practical application.

Several countermeasures to cope with these problems have been proposed. To reduce the amount of costly Pd and the price of membranes, novel preparation techniques were reported, combining electroless deposition and osmotic pressure [8], and a two-step deposition procedure [29].

Mitsubishi Heavy Industries has energetically been searching various binary and ternary Pd-based alloy ingots for better hydrogen permeance. Some alloy elements of VI, VII and VIII groups in the periodic table, particularly Ag [30], are known to cause an increase in hydrogen permeability of Pd membrane. More important is that alloying with Ag is effective to reduce the Pd embrittlement.

Metals such as Nb, Ta, V, and Zr or their alloys, particularly V–Ni, have greater hydrogen permeability than Pd, while they have greater surface resistance to hydrogen transport. Although the surface resistance can be improved by coating precious metals, the stability of these metals, particularly in the oxidizing atmosphere remains questionable.

Our current approach is a membrane based on the surface diffusion of hydrogen assisted by non-Pd metals, such as Pt. We applied a chemical vapor deposition (CVD) technique for preparation of metal/ceramic composite membranes. The CVD technique applied to preparation of metal membranes, so far reported, is mostly restricted to Pd membranes.

Yan et al. [10] reported metal organic CVD (MOCVD) using Pd acetate, which has a low vapor pressure, so that CVD was performed at reduced pressures. Due to the first-order dependence of hydrogen permeance on the partial pressure difference, they concluded that the diffusion of dissolved hydrogen is not the rate-determining step. More recently, Xomeritakis and Lin [31] reported on Pd/alumina composite membranes using Pd acetylacetonate. They showed that hydrogen permeance increased with the Pd crystal grain size, indicating that the surface adsorption/desorption appears to be rate-limiting. These authors consider the hydrogen permeation through these CVD membranes is based on the solution-diffusion transport mechanism.

Using the same technique, quite different membranes with Pt and Ru as well as Pd were reported by Uemiya et al. [32]. Their findings show that Pt and Ru as well as Pd, when deposited on a porous Al_2O_3 support, gave comparable hydrogen permeability. Therefore, the permeation of hydrogen through these membranes cannot commonly be explained by the solution-diffusion transport mechanism as is the case for Pd membranes. Our recent result [33] on the sulfur poisoning of the Pt membrane show that the permeation of only H_2 is promoted by Pt, and that other gases permeate through this membrane by the Knudsen diffusion. These results suggest that the hydrogen permeation through the CVD metal membranes is related to the surface diffusion of spillover hydrogen, with a little contribution of Knudsen diffusion.

CVD membranes have an advantage over electroless-plating membranes in the lesser amount of metal coating or lower membrane cost. The disadvantage of CVD membranes is, of course, less selectivity for H_2. We employed these CVD membranes for steam reforming of CH_4 [34]. With a similar permeance for H_2, the Pt membrane prepared by CVD gave relatively high selectivity for H_2 against N_2 and showed a level of CH_4 conversion comparable to the electroless-plating Pd membrane. This means that the applicability of CVD membranes for membrane reactor depends not only on the H_2 permeance, but also on the permselectivity for H_2.

5. Conclusion

Electroless plating of thin Pd layer on asymmetric porous ceramics successfully led to Pd membranes with high permeance and a 100% selectivity for H_2. The membrane could be applied to steam reforming of natural gas in the PEFC system. Steam reforming is one of the most promising reactions to which the membrane reactor can be applicable, since the reaction is highly suppressed thermodynamically at moderate temperatures. Appropriate catalysts have already been developed and high thermal efficiency can be expected, and particularly when ultra-pure hydrogen is required. Chemical vapor deposition gave non-Pd membranes, like Pt membranes, having advantages such as lesser amounts of metal coating or cheaper membrane cost and less tendency for hydrogen embrittlement against electroless-plating membranes, although the disadvantage is less selectivity for hydrogen permeation.

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