ELSEVIER

Catalysis Today 56 (2000) 75–81

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Steam reforming of methane in membrane reactors: comparison of electroless-plating and CVD membranes and catalyst packing modes

E. Kikuchi [a,*], Y. Nemoto [a], M. Kajiwara [b], S. Uemiya [b], T. Kojima [b]

[a] Department of Applied Chemistry, School of Science and Engineering, Waseda University,
3-4-1 Okubo, Shinjuku, Tokyo 169-8555, Japan

[b] Department of Industrial Chemistry, Faculty of Engineering, Seikei University,
3-3-1 Kichijojikita-machi, Musashino, Tokyo 180-8633, Japan

Abstract

Steam reforming of methane was studied at 773 K using a membrane reactor containing two types of supported precious metal membranes: one is an electroless-plating palladium membrane, and the others are CVD palladium, platinum, and ruthenium membranes. A CVD platinum membrane having a H_2/N_2 separation factor as high as 280 gave an excellent performance comparable to the electroless-plating palladium membrane. The advantages of the CVD platinum membrane versus the electroless-plating palladium membrane are lower metal loading and lower cost as well as a lower tendency toward hydrogen embrittlement. It is also shown in this study based on a computer simulation that compared with thermodynamic equilibrium, the non-palladium CVD membranes produced a high conversion of methane similar to an electroless-plating palladium membrane only when showing high hydrogen permselectivity. The catalyst packing in front of the membrane zone enhances the membrane reactor efficiency. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Methane; Steam reforming; Membrane reactor

1. Introduction

Steam reforming of hydrocarbons using supported nickel catalysts has been used industrially to produce hydrogen or syngas [1]. Actually, about 50% of the hydrogen demand are supplied via the steam reforming of methane due to an increase in the production of natural gas consisting mainly of methane. The steam reforming of methane follows the following sequential reactions:

$$CH_4 + H_2O = CO + 3H_2 \quad (1)$$

$$CO + H_2O = CO_2 + H_2. \quad (2)$$

As methane is chemically stable, extremely high reaction temperatures, around 1073 K, are required for this endothermic reaction (1). The produced carbon monoxide is further converted with steam to carbon dioxide and hydrogen by the slightly exothermic reaction (2). The overall reaction is endothermic; therefore, higher temperatures enable the higher conversion of methane to hydrogen.

If hydrogen is selectively removed from the reaction system, for instance, using a hydrogen permselective membrane, the thermodynamic positions of these reactions are shifted to the product side, and a high conversion of methane to hydrogen and carbon dioxide can be attained even under mild reaction conditions such as low temperatures and a low steam/carbon ratio. If the permselectivity of the membrane is perfect,

---

* Corresponding author. Fax: +81-3-5286-3203.
E-mail address: ekikuchi@mn.waseda.ac.jp (E. Kikuchi).

PII: S0920-5861(99)00264-3

the produced hydrogen is free of carbon monoxide, so that it can be applied to a low temperature fuel cell like the polymer electrolyte-type.

Many researchers including us have studied the applicability of membrane reactors to the steam reforming of methane [2–16]. The first attempt using a palladium membrane reactor was done by Oertel et al. [2], who used a commercially available palladium membrane with a thickness of 100 μm. Unfortunately, their palladium membrane was so thick that the effect of the membrane reactor could be observed at the thermodynamically favorable high temperature of 1073 K. Based on the simple thermodynamic calculations, Shu et al. [11] emphasized that a great improvement in the shift of the thermodynamic equilibrium can be observed by hydrogen separation at moderate temperatures of 773–873 K, and a high hydrogen separation efficiency of more than 90% is required to express the satisfactory effect of the membrane reactor below these temperatures.

To obtain the highly efficient effect of the membrane reactor around such moderate temperatures, the best way is to decrease the thickness of the palladium membrane. We have proposed composite membranes consisting of a thin palladium layer (thickness, 4.5–22.5 μm) deposited on the outer surface of porous materials by an electroless-plating technique [17,18]. The palladium layer could completely cover the surface, so that only hydrogen could permeate with a 100% selectivity. In fact, the membrane reactor embodied with these composite membranes gave 100% conversion of methane to hydrogen and carbon dioxide even at the relatively low temperature of 773 K [3,4].

Although the electroless-plating technique gives membranes with excellent permeability of hydrogen to enable an efficient membrane reactor performance, some drawbacks have been pointed out; one is the embrittlement of palladium due to the formation of the hydrogen-rich β-PdH phase during the heating and cooling cycles, while the other is the high cost of palladium metal.

To overcome these drawbacks, the following two countermeasures were examined in this study. First, a CVD technique was used to deposit precious metals such as platinum and ruthenium on the surface or inside the pores (average size, 200 nm) of an alumina tube at atmospheric pressure [19]. The permeability and permselectivity of these CVD membranes were investigated and compared with electroless-plating palladium membranes, as well as the performance in membrane reactors used for the steam reforming of methane.

Second, the effect of the catalyst packing mode was investigated to save the sectional area of the membrane or to reduce membrane cost. The catalyst bed in a reactor was split into the hydrogen-permeation part and non-permeation part (in front). It can be expected that this configuration will give a higher conversion of methane with the same amount of catalyst and the same membrane area than the normal way of catalyst packing. Promotion of the membrane reactor efficiency with the variation in catalyst packing is discussed in terms of a computer simulation where a commercial-scale membrane reactor is postulated.

2. Experimental

2.1. Membrane preparation

The procedures for preparation of the composite membranes by CVD [19] and electroless-plating [17,18] techniques were previously reported in detail. In the case of CVD, precious metals such as palladium, platinum and ruthenium were thermally deposited on the surface or inside the pores of a commercially available alumina tube with an average pore size of 200 nm on the outer side using vaporized acetylacetonato-complexes of the corresponding metal. The CVD was conducted at atmospheric pressure on the outside of the alumina tube, keeping inside at a reduced pressure using an evacuating pump. Sublimation of the complexes was done at 433 K for palladium and at 473 K for ruthenium and platinum. The decomposition was carried out at 543 K for palladium and ruthenium, and at 493 K for platinum. Deposition of the metallic layer was restricted to the central part (628 mm^2) of the supporting tube.

Electroless-plating palladium membranes were prepared as follows: prior to the electroless-plating, palladium nuclei as catalysts for the reduction of palladium ions to palladium were deposited on the outer surface of the supporting tube by the traditional activation treatment using palladium chloride and stannous chloride solutions. Palladium was autocatalytically deposited from a bath containing the palladium tetraammine complex, EDTA, ammonium hydroxide and hydrazine.

The resulting membranes were characterized using scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX). Hydrogen permeability and ideal permselectivity over nitrogen were examined using a conventional gas separator under the conditions of temperature, 473–773 K, pressure difference, 0.05–0.25 MPa, and without use of any sweep gas.

2.2. Membrane reactor and operation

A laboratory-scale double tubular type membrane reactor was employed in this study. The detailed structure was described in our previous paper [3,4]. The membrane reactor was composed of a hydrogen-permselective membrane (o.d. 10 mm) as the inner tube and a commercial non-porous quartz tube (i.d. 18 mm) as the outer one. Between them, a weighted amount of supported nickel catalyst active for low temperature steam reforming to produce the substituted natural gas (SNG, mainly methane) from naphtha, supplied from Tokyo Gas, was packed. Hydrogen permeation was allowed at the wall of the catalyst bed (628 mm^2). Steam reforming was conducted at a temperature of 773 K, a steam/methane molar ratio of three and atmospheric pressure. Permeated hydrogen was evacuated using a rotary pump with a sufficient evacuation performance. Flue gases from the reaction and permeation sides were analyzed using gas chromatography.

3. Simplified simulation model for membrane reactor on commercial scale

One of the effects of a membrane reactor is the shift in thermodynamic equilibrium to the product side. If a sufficient amount of catalyst to establish a thermodynamic equilibrium is packed before the reactant stream reaches the entrance of the hydrogen permeation part, an enhanced membrane reactor effect can be expected. From this point of view, the effect of the catalyst packing mode was semi-quantitatively investigated in a commercial-scale membrane reactor, anticipating to save the sectional area of the membrane or to reduce the cost of the membrane.

A differential flow model in a commercial-scale palladium membrane reactor is shown in Fig. 1, where the differential equations derived from material balances are also written. Here, reactor geometry (effective palladium area and catalyst amount) and reaction conditions for the calculations are almost the same as those of a commercial-scale membrane reactor developed by the Tokyo Gas and Mitsubishi Heavy Industries [20]. The model and calculations were simplified based on the following assumptions:

- methane and steam are converted only to carbon dioxide and hydrogen with a negligible carbon monoxide formation ($\mathrm{CH_4 + 2H_2O = CO_2 + 4H_2}$);
- catalyst bed is isothermal and isobaric;
- no radial gas concentration gradient exists in the catalyst bed;
- hydrogen permeation coefficient for hydrogen separation from any multi-component gas mixture is the same as that obtained for pure hydrogen;
- the partial pressure of hydrogen in the permeation side is maintained at zero.

The following rate equation for the steam reforming of methane, reported by Quach and Rouleau [21], was employed.

$$r = \mathrm{ks} K_{\mathrm{CH_4}} \left(\frac{P_{\mathrm{CH_4}} P_{\mathrm{H_2O}}^2 - P_{\mathrm{CO_2}} P_{\mathrm{H_2}}^4 / K}{1 + K_{\mathrm{CH_4}} p_{\mathrm{CH_4}}} \right),$$

$$\mathrm{ks} = 2.04 \times 10^{-13}\,\mathrm{m^3\,cat\text{-}kg^{-1}\,s^{-1}\,Pa^{-2}},$$

$$K_{\mathrm{CH_4}} = 4.50 \times 10^{-5}\,\mathrm{Pa^{-1}},$$

where r, ks, $K_{\mathrm{CH_4}}$, K and P_i are the reaction rate, rate constant, adsorption constant for methane, equilibrium constant, and the partial pressure of component i, respectively.

The rate of hydrogen permeation through a dense palladium membrane, J, was estimated as follows from our reported results for electroless-plating membranes [3,17,18]:

$$J = \left(\frac{QA}{t} \right) \left(P_{\mathrm{H_2}}^{0.5} - {P'_{\mathrm{H_2}}}^{0.5} \right),$$

$$Q = 7.04 \times 10^{-8}\,\mathrm{Nm^3\,m^{-2}\,m\,s^{-1}\,Pa^{-0.5}}.$$

Here, Q, A, t, $P_{\mathrm{H_2}}$, $P'_{\mathrm{H_2}}$ are the hydrogen permeation coefficient, the area and thickness of the membrane, and the partial pressures of hydrogen on the reaction

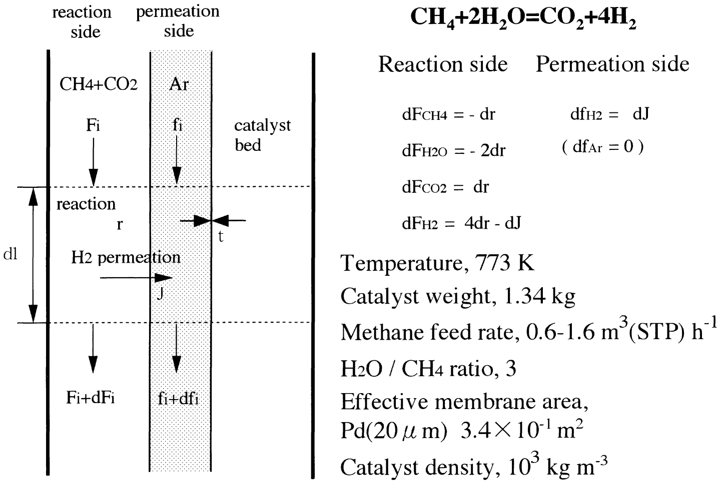

Fig. 1. Flow model of palladium membrane reactor for simplified simulation.

side (high pressure side) and permeation side (low pressure side), respectively. It has already been determined that the rate of hydrogen permeation is inversely proportional to the thickness of the palladium film when the palladium film has a thickness greater than several micrometers.

For the purpose of investigating the effect of the catalyst packing mode, the catalyst bed in a reactor was split into the hydrogen-permeation part and non-permeation part.

4. Results and discussion

4.1. Comparison of hydrogen permeance between CVD and electroless-plating membranes

SEM photographs of the surface and cross-section morphology of membranes prepared by the CVD (platinum) and electroless-plating (palladium) techniques are shown in Fig. 2. Here, the platinum or palladium intensities along with the cross-sectional depth of the

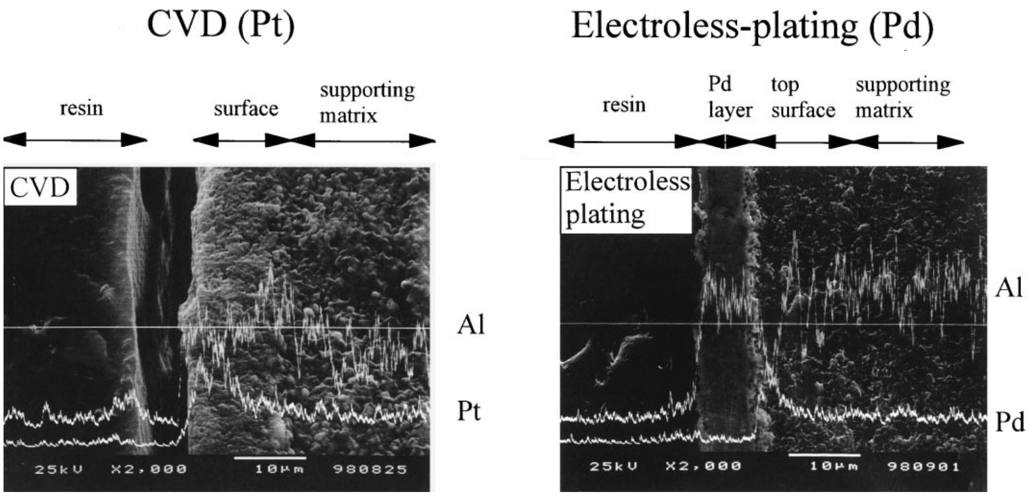

Fig. 2. SEM photographs of cross-section of CVD platinum membrane and electroless-plating palladium membrane.

surface vicinity are also shown on the corresponding SEM photographs. The resulting membranes had a surface morphology similar to the metallic layer formed near the surface, but with different metal distributions. In electroless-plating, a dense palladium film was formed on the surface of the supporting porous alumina. On the other hand, platinum was mainly deposited inside the pores of the support in the CVD. Effective deposition of a precious metal into the pores can lead to a decrease in the formation of a metal membrane maintaining sufficient permselectivity with a lower amount of metal, thus resulting in the fabrication of a cheaper membrane than depositing the metal on the outer surface of the support. Furthermore, such non-palladium membranes may endure hydrogen embrittlement, though it has not been experimentally confirmed yet.

Table 1 compares the hydrogen permeance among the platinum, ruthenium and palladium membranes prepared by CVD and a palladium membrane having a thickness of 8 μm prepared by electroless-plating. Note that although the diffusivity of hydrogen is very small in the bulk of platinum, the CVD platinum membranes have a hydrogen permeance comparable to the electroless-plating palladium membrane. Furthermore, other CVD metal membranes also showed similar hydrogen permeance. It has been concluded that the permeation of hydrogen through CVD membranes is not based on the solution–diffusion transport mechanism, but on the surface diffusion mechanism. The details of the hydrogen permeation mechanism are presented in our previous paper [19].

The ideal hydrogen selectivity, defined as the ratio of the molar fluxes of hydrogen to nitrogen, is also summarized in Table 1. Just after preparation, the leaking of nitrogen through the CVD membranes was negligible. However, the selectivity, particularly those of the palladium and ruthenium membranes decreased with time on stream, probably due to insufficient thermal stability (sintering of fine metal particles and grains) during the activation procedure of the catalyst. Further studies, including the reproducibility during preparation, are necessary for improvement of the CVD membranes.

4.2. Membrane reactor performance with CVD and electroless-plating membranes

As previously mentioned, the CVD and electroless-plating membranes gave similar hydrogen permeances, but different hydrogen selectivities. Among the CVD membranes, platinum gave the highest level of methane conversion, 83.4% (equilibrium conversion in a normal reactor, 43.9%) and showed a comparable effect to the electroless-plating membrane as indicated in Table 1. These results prompt us to conclude that the membrane reactor effect depends on the permselectivity as well as the permeance of an embodied membrane.

The distribution of products on the reaction and permeation sides of the CVD membrane reactor is shown in Fig. 3. A similar composition of methane, carbon monoxide and carbon dioxide was formed in either side of the platinum membrane reactor. On the other hand, there was less methane and more carbon dioxide and monoxide on the permeation side than on the reaction side of the ruthenium and palladium membrane reactors. It has been proved in a

Table 1
Effects of CVD and electroless-plating membranes on steam reforming of methane[a]

Membrane	Permeance (mol m^{-2} s^{-1} atm^{-1})	Selectivity H_2/N_2	CH_4 conversion (%)	Permeated dry-gas composition (vol.%)			
				H_2	CO	CO_2	CH_4
CVD							
Pd	0.35	13.0	70.8	95.4	0.4	3.9	0.3
Ru	0.30	6.5	47.0	85.7	1.4	12.3	0.6
Pt	0.33	280	83.4	99.0	0.3	0.3	0.4
Electroless-plating Pd (8 μm)	0.35	∞	86.4	100	0	0	0

[a] Temperature, 773 K; pressure, 1 atm; catalyst weight, 0.7 g; methane feed rate, 25 cm^3 (STP) per min; H_2O/CH_4 ratio, 3.

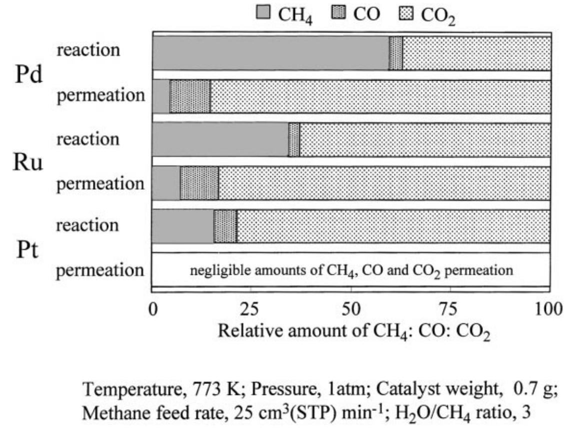

Fig. 3. Comparison in gas composition between reaction and permeation sides reaction conditions: temperature, 773 K; catalyst, Ni/Al_2O_3 0.7 g; methane feed rate, 25 cm^3(STP) per min; H_2O/CH_4 molar ratio, 3.

previous paper [17] that all gases except for hydrogen can permeate through the CVD membranes via the Knudsen diffusion mechanism. In this mechanism, carbon dioxide cannot permeate faster than methane. Therefore, it can be presumed that methane was converted into carbon oxides in the pore of these membranes which worked as the catalyst. The catalytic activities of these metals were in the order: ruthenium > palladium > platinum. Chai et al. [9] reported a similar result using the catalytic membrane reactors prepared by the sol–gel technique. They claimed that a rhodium- or ruthenium-dispersed alumina membrane produced high levels of methane conversion.

4.3. Effect of catalyst packing on membrane reactor effect

Two configurations were investigated here, as shown in Fig. 4; one is a normal packing mode (Type 1), where the catalyst-bed is placed with the same length along with the gas flow (membrane part), while in the other packing mode (Type 2), a part of the catalyst is packed in the membrane part and the other part is in front of the membrane part. In the former mode, both the catalytic reaction and hydrogen permeation simultaneously occur only in the catalyst-packed section, while in the latter mode, steam reforming is advanced before the gas stream reaches the entrance of the membrane part. Calculations were done using the same amount of catalyst and the same membrane area.

Fig. 4 shows a comparison of the two catalyst packing modes on the level of methane conversion and the rate of hydrogen that permeated through a palladium

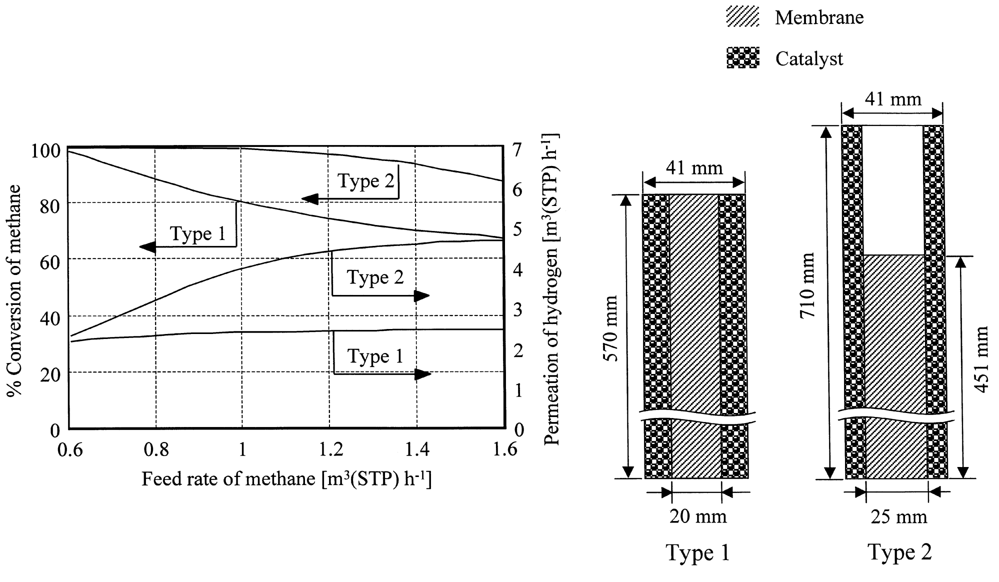

Fig. 4. Simulation study on effect of catalyst packing on membrane reactor effect; Type 1, catalyst is packed in the same length as membrane part; Type 2, catalyst is packed in front of membrane part as well as in membrane part.

membrane. As properly expected, the Type 2 mode gives enhanced hydrogen permeation and production, irrespective of the feed rate of methane. Namely, packing of the catalyst in front of the membrane part like Type 2 serves to reduce the membrane area needed to achieve the same level of hydrogen yield required for the normal packing mode (Type 1) for the same methane feed rate.

5. Conclusion

The non-palladium CVD membranes gave higher conversions of methane than the thermodynamic equilibrium one attainable in a normal reactor without a hydrogen separation function. However, as the permeation of hydrogen through the CVD membranes is not based on the solution–diffusion transport mechanism but on the surface diffusion mechanism, they gave a high conversion similar to the electroless-plating membranes only when they showed high hydrogen selectivities. A computer simulation study demonstrated that catalyst packing in front of the membrane part gives enhanced membrane reactor efficiency, i.e., higher levels of methane conversion and permeated, pure hydrogen production with the same amount of catalyst and the same membrane area than the normal way of catalyst packing.

6. Nomenclature

A	the area of membrane (m^2)
J	the rate of hydrogen permeation through a dense palladium membrane ($Nm^3\,s^{-1}$)
ks	rate constant (m^3 cat-kg^{-1} s^{-1} Pa^{-2})
K_{CH_4}	adsorption constant for methane (Pa^{-1})
Kp	equilibrium constant (Pa^2)
P_i	the partial pressure of component i, on reaction side (high pressure side) (Pa)
p_i	the partial pressure of component i, on permeation side (low pressure side) (Pa)
Q	hydrogen permeation coefficient ($m^3\,m^{-2}\,m\,s^{-1}\,Pa^{-0.5}$)
r	reaction rate (m^3 cat-kg^{-1} s^{-1})
t	thickness of membrane (m)

Acknowledgements

This work was partly supported by the Simple Chemistry Program from New Energy and Industrial Technology Development Organization (NEDO), and Japan Chemical Industry Association. Uemiya gratefully acknowledges the financial support by the Sasakawa Scientific Research Grant from The Japan Science Society.

References

[1] J.R. Rostrup-Nielsen, J.-H. Bak Hansen, L.M. Aparicio, Sekiyu Gakkaishi 40 (1997) 366.

[2] M. Oertel, J. Schmitz, W. Weirich, D. Jendryssek-Neumann, R. Schulten, Chem. Eng. Technol. 10 (1987) 248.

[3] S. Uemiya, N. Sato, H. Ando, T. Matsuda, E. Kikuchi, Appl. Catal. 67 (1991) 223.

[4] E. Kikuchi, S. Uemiya, T. Matsuda, Stud. Surf. Sci. Catal. 61 (1991) 509.

[5] J. Shu, B.P.A. Grandjean, A. Van Neste, S. Kaliaguine, Can. J. Chem. Eng. 69 (1991) 1036.

[6] A.M. Adris, S.S.E.H. Elnashaie, R. Hughes, Can. J. Chem. Eng. 69 (1991) 1061.

[7] S.I. Prokopiev, Y.I. Aristov, V.N. Parmon, N. Giordano, Int. J. Hydrogen Energy 17 (1992) 275.

[8] A.M. Adris, C.J. Lim, J.R. Grace, Chem. Eng. Sci. 49 (1994) 5833.

[9] M. Chai, M. Mochida, K. Eguchi, H. Arai, Appl. Catal. A 110 (1994) 239.

[10] S. Laegagaard Jorgensen, P.E. Hojlund Nielsen, P. Lehrmann, Catal. Today 25 (1995) 303.

[11] J. Shu, B.P.A. Grandjean, S. Kaliaguine, Catal. Today 25 (1995) 327.

[12] E. Kikuchi, Sekiyu Gakkaishi 39 (1996) 301.

[13] E. Kikuchi, CATTECH 1 (1997) 67.

[14] A.M. Adris, C.J. Lim, J.R. Grace, Chem. Eng. Sci. 52 (1997) 1609.

[15] G. Barbieri, F.P. Di Maio, Ind. Eng. Chem. Res. 36 (1997) 2121.

[16] G. Barbieri, V. Violante, F.P. Di Maio, A. Criscuoli, E. Drioli, Ind. Eng. Chem. Res. 36 (1997) 3369.

[17] S. Uemiya, N. Sato, H. Ando, Y. Kude, T. Matsuda, E. Kikuchi, J. Membr. Sci. 56 (1991) 303.

[18] E. Kikuchi, S. Uemiya, Gas Separat. Purificat. 5 (1991) 261.

[19] S. Uemiya, M. Kajiwara, T. Kojima, AIChE J. 43 (1997) 2715.

[20] Y. Shirazaki, Proceedings of the 27th Annual Meeting of Japan Petroleum Institute (in Japanese), 1997, p. 247.

[21] T.Q.P. Quach, D. Rouleau, J. Appl. Chem. Biotechnol. 25 (1975) 445.