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Palladium/ceramic membranes for selective hydrogen permeation and their application to membrane reactor

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Abstract

Plating thin Pd or Pd–Ag alloy film on the outer surface of a porous alumina ceramic tube enables very rapid hydrogen permeation with an absolute selectivity based on the solution–diffusion transport mechanism. Effectiveness, such as displacement of thermodynamic equilibrium, selectivity enhancement, is brought forth by incorporating the metal/ceramic composite membrane in the catalytic reactor, as demonstrated in concrete examples of steam and CO_2 reforming of methane and dehydrogenation of isobutane. It is also shown that the membrane reactor occasionally requires its own catalyst which is different from conventional ones.

1. Introduction

A membrane reactor in which the permselective characteristic of the membrane is used to remove product from the reaction zone as it forms, can be beneficial to an equilibrium-limited process by allowing higher one-pass reactor conversions to be achieved and/or by decreasing reaction temperature if it is endothermic, as well as by simplifying downstream recovery and purification steps. Based on this concept, many works have been reported on hydrogen-permselective reactors, as recently reviewed by Armor [1] or Saracco and Specchia [2].

The application of a membrane reactor to heterogeneous gas phase reactions requires thermally stable inorganic membranes. These are classified into two groups according to the separation mechanisms: (a) porous membranes mainly made of ceramic; (b) dense metallic membranes, particularly Pd and its alloys. Porous membranes provide relatively low selectivity for hydrogen separation because of the separation mechanism based on Knudsen diffusion, compared with dense Pd-based membranes which exhibit extremely high selectivity for hydrogen permeation, due to the solution–diffusion transport mechanism. The metal membrane, however, gives only a small hydrogen flux as a result of the thickness required for mechanical durability. In practice, commercial Pd-based membranes are usually at least as thick as 150 μm, so that hydrogen permeation is not very fast.

For the purpose of improving the hydrogen-permeability of Pd membrane, we have proposed a composite membrane consisting of thin Pd film (4.5–13 μm) supported on porous ceramic tube having minute and controlled pores of 200–300 nm in size [3–6]. An electroless plating technique has successfully been applied to the preparation of this composite membrane.

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Using the composite membrane as a separation medium, a membrane reactor was set up. Several advantages gained by the use of a membrane reactor instead of conventional reactors have been proven in some heterogeneous catalytic reactions, such as in hydrogen-producing reactions of steam reforming [7,8] and in the water-gas shift reaction [9,10], as well as in the dehydrogenation of isobutane [11] and in the dehydrocyclization of propane to aromatics [12]. The present paper describes the characteristic features of catalysis in the hydrogen-permselective membrane reactor, particularly thermodynamic and kinetic effects, demonstrated by our studies, with a brief description of the preparation and hydrogen permeability of the composite membrane, and of the structure of the catalytic reactor.

2. Composite membranes of thin Pd and Pd–Ag film on porous ceramic

The rate of permeation (J) of hydrogen, if the rate determining step is involved in the diffusion of atomic hydrogen through the bulk of Pd, is expressed as follows:

$$J = [Q(P_{0.5} - P_{0.5}) \cdot A]/t \qquad (1)$$

where P_1 and P_2 represent the partial pressures of hydrogen in the high- and low-pressure sides, and A and t are the area and thickness of the Pd membrane, respectively. The hydrogen permeation coefficient Q is the product of the hydrogen diffusion coefficient (D) and the hydrogen solubility constant (S).

The hydrogen flux can be enhanced by reducing the thickness of the membrane. For this purpose, we used a composite membrane by supporting a thin film of Pd on the asymmetric outside layer of a porous alumina ceramic cylinder, by a technique of electroless (chemical) plating which allowed a complete coating of the outer surface with Pd without any pinholes. Prior to plating, Pd nuclei were deposited only on the outer surface of the cylinder by successive immersion procedures consisting of repeated sensitization and activation treatments with Sn(II) chloride and Pd(II) chloride solutions, respectively.

The hydrogen permeability of the Pd membrane can also be improved by increasing Q. Alloy formation between Pd and Ag is effective in increasing S, while it reduces D, making an optimum Ag content at around 23 wt.-%. Pd–Ag alloy membranes were prepared in the manner of consecutive electroless plating of Pd and Ag, followed by thermal treatment at 1173 K for 12 h in a stream of Ar.

Fig. 1 compares the rates of hydrogen permeation through thus prepared composite membranes and typical commercial membranes. The Pd–Ag (23 wt.-%) membrane gave a rate of hydrogen permeation at least 30 times greater than a commercial Pd-based membrane at 773 K. Permeation rates through these membranes were roughly in reverse proportion to the thickness, indicating that the rate determining step is involved in the bulk diffusion, even in such thin Pd film.

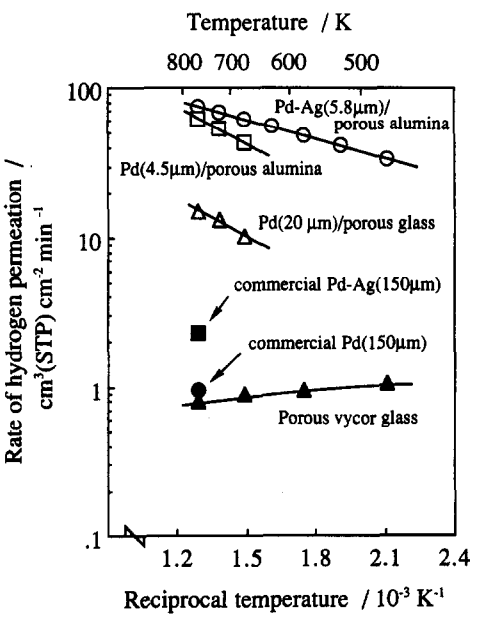

Fig. 1. Comparison of the rate of hydrogen permeation through various membranes [Pd or Pd–Ag (23 wt.-%)].

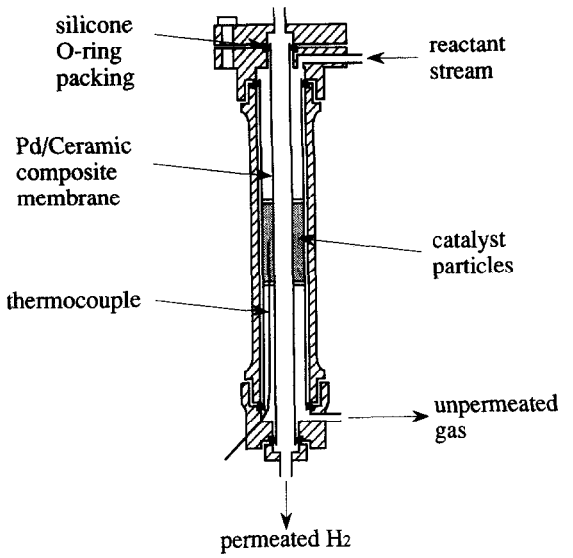

Fig. 2. Structure of the palladium membrane reactor.

3. Structure of the membrane reactor using a composite membrane

Fig. 2 shows the Pd membrane reactor used in our study. The reactor is a double tubular type, of which the inner tube (o.d. 10 mm diameter) is the composite membrane.

Catalyst particles are uniformly packed outside the membrane (the reaction side). Hydrogen permeation through the membrane is restricted only in the part of the catalyst bed. The area of membrane effective for hydrogen permeation is 12.6 cm^2. The permeated hydrogen can be swept off by inert purge gas or evacuated.

4. Characteristic features of heterogeneous catalysis in the membrane reactor

4.1. Steam reforming of methane

Hydrogen production through methane steam reforming prefers a high reaction temperature from a thermodynamic restriction. In this reaction system, the following two reactions take place and determine the thermodynamic composition of the reaction products.

$$CH_4 + H_2O = CO + 3H_2 \quad (2)$$

$$CO + H_2O = CO_2 + H_2 \quad (3)$$

If hydrogen is selectively removed from the reaction system, thermodynamic positions of these reactions are shifted to the product sides, and 100% conversion of methane to hydrogen and CO_2 can be attained even at low temperatures. The produced hydrogen is free of CO, so that it can be applied to a polymer electrolyte or a phosphoric acid-type fuel cell operating at low temperatures.

Fig. 3 shows the level of methane conversion as a function of the hydrogen permeability of the membrane employed. In these experiments, we used a Ni catalyst developed by Tokyo Gas Co. for low-temperature steam reforming to produce SNG. The catalytic activity was extremely high compared with the rate of hydrogen permeation, so that the level of methane conversion increased with the ability of the membrane to permeate hydrogen. The overall reaction is accompanied by volume expansion and lower reaction pressure is thermodynamically favored, while methane conversion was increased with increasing pressure which caused the increase in the rate of hydrogen permeation from the reaction side.

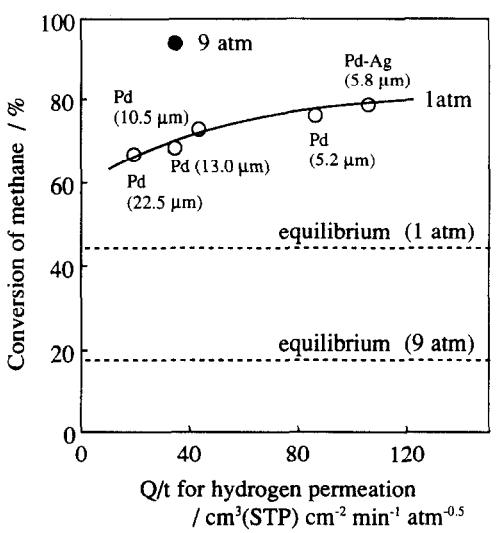

Fig. 3. Effect of permeation of hydrogen by the membrane on methane steam reforming at 773 K; W/F, 2000 g-cat min mol^{-1}. Rate of hydrogen permeation, $J = (Q/t) \times (p_1^{0.5} - p_2^{0.5})$.

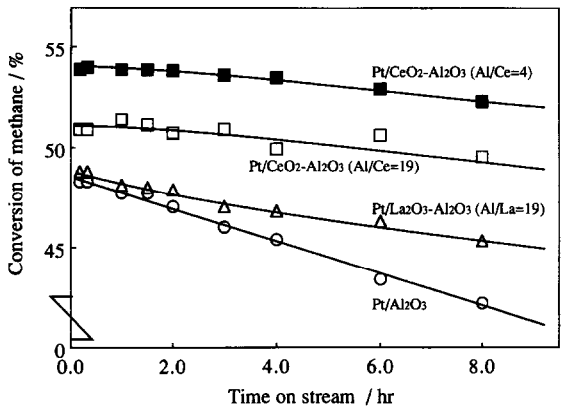

Fig. 4. CO_2 reforming of methane at 773 K in a membrane reactor. W/F, 4480 g-cat min mol^{-1}; molar $CH_4/CO_2 = 1$.

4.2. CO_2 reforming of methane

The stoichiometric equation of CH_4–CO_2 reaction is written as follows:

$$CH_4 + CO_2 = 2CO + 2H_2 \quad (4)$$

This is the algebraic sum of Eqs. (2) and (3), so that both steam and CO_2 reforming give similar products in the conventional reactor. In the membrane reactor, however, quite a different feature can be expected for these reforming reaction systems.

The selective removal of H_2 from the CH_4–CO_2 reaction system will yield a mixture of H_2 and CO, so called syngas, even at low reaction temperatures. The following side reactions are undesirable:

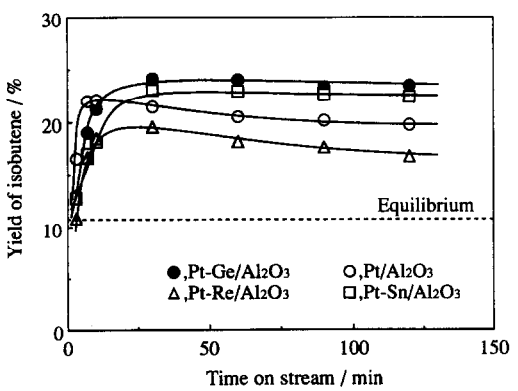

Fig. 5. Yield of isobutene with time-on-stream on various platinum catalysts in a membrane reactor. Reaction conditions: temperature 673 K; W/F, 8000 g-cat min mol^{-1}.

$$CO_2 + H_2 = CO + H_2O \quad (5)$$

$$2CO = C + CO_2 \quad (6)$$

Reaction (5) can be avoided if we use a membrane giving a higher rate of H_2 permeation than that of H_2 formation. As Ni catalysts are usually active for reaction (6), we must choose a suitable catalyst.

When Ni and some precious metal (Pd, Ru, Rh, Ir, and Pt) catalysts supported on Al_2O_3 were compared, Pt catalyst showed the least selectivity for coke formation with relatively high activity for the reforming reaction. Hydrogen formation on these catalysts was slower than hydrogen permeation, so that reaction (5) was not important in the membrane reactor. The activity of the Pt catalyst was stabilized by addition of basic compounds to the Al_2O_3 support, as typically shown in Fig. 4.

4.3. Dehydrogenation of isobutane

Dehydrogenation of hydrocarbons is also an endothermic and thermodynamically limited reaction. As an industrial dehydrogenation process is usually performed at extremely high temperatures, the practical catalysts are designed to work stably under such conditions.

To carry out dehydrogenation at lower temperatures, we first investigated the activities and selectivities of supported precious metal catalysts, which are active for the reverse reaction (hydrogenation) at low temperatures. As previously shown [11], Pt supported on Al_2O_3 exhibited high catalytic activity compared with a commercial Cr_2O_3–Al_2O_3 catalyst. Use in the membrane reactor accelerated coke formation taking place initially on the Pt catalyst. As shown in Fig. 5, modification of the Pt catalyst with GeO_2 or SnO_2 enhanced and stabilized the activity and improved the durability.

Fig. 6 compares the product selectivities obtained in the membrane reactor with those in the conventional reactor, as a function of isobutane conversion. It is obvious that undesirable side

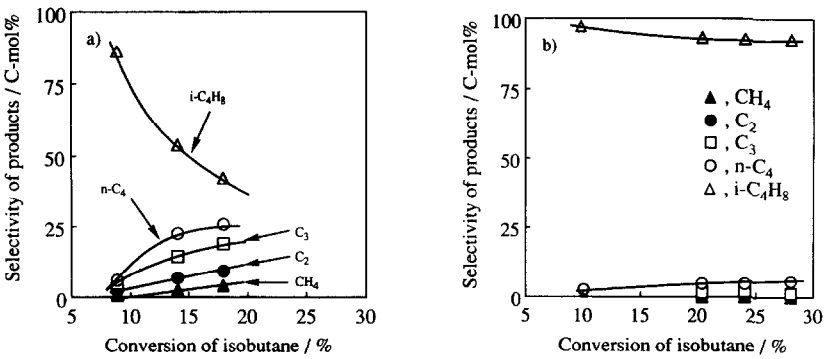

Fig. 6. Selectivity of products from isobutane dehydrogenation on Pt/Al_2O_3 at 673 K in: (a) conventional and (b) membrane reactors.

reactions caused by the action of hydrogen, such as hydroisomerization and hydrogenolysis, were suppressed in the membrane reactor, leading to high selectivity for isobutene.

5. Conclusion

The following conclusions can be drawn in the present paper:

(1) Efficient and selective hydrogen permeation is achieved by use of a composite membrane consisting of thin Pd or Pd–Ag film on the outer surface of an inorganic porous ceramic tube.

(2) The membrane reactor incorporated with this composite membrane effectively promotes catalytic reactions, by shifting thermodynamic equilibrium towards the product side, and/or by preventing side reactions.

(3) Some membrane catalysis requires its own catalyst which is not always the same as that for the conventional process.

Acknowledgements

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References

[1] J.N. Armor, CHEMTECH, 22 (1992) 557.
[2] G. Saracco and V. Specchia, Catal. Rev. Sci. Eng., 36 (1994) 305.
[3] S. Uemiya, Y. Kude, K. Sugino, N. Sato, T. Matsuda, and E. Kikuchi, Chem. Lett., (1988) 1687.
[4] S. Uemiya, N. Sato, H. Ando, Y. Kude, T. Matsuda and E. Kikuchi, J. Membrane Sci., 56 (1991) 303.
[5] S. Uemiya, T. Matsuda and E. Kikuchi, J. Membrane Sci., 56 (1991) 315.
[6] E. Kikuchi and S. Uemiya, Gas Separation and Purification, 5 (1991) 261.
[7] S. Uemiya, N. Sato, H. Ando, T. Matsuda and E. Kikuchi, Appl. Catal., 67 (1991) 223.
[8] E. Kikuchi, S. Uemiya and T. Matsuda, Stud. Surf. Sci. Catal., 61 (1991) 509.
[9] E. Kikuchi, S. Uemiya, N. Sato, H. Inoue, H. Ando and T. Matsuda, Chem. Lett., (1989) 489.
[10] S. Uemiya, N. Sato, H. Ando and E. Kikuchi, Ind. Eng. Chem. Res., 30 (1991) 585.
[11] T. Matsuda, I. Koike, N. Kubo and E. Kikuchi, Appl. Catal., A96 (1993) 3.
[12] S. Uemiya, I. Koike, and E. Kikuchi, Appl. Catal., 76 (1991) 171.