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Promotion of Methane Steam Reforming Using Ruthenium-Dispersed Microporous Alumina Membrane Reactor

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A membrane reactor with the microporous ruthenium-dispersed alumina membrane is effective in promoting low temperature methane steam reforming. In the temperature range of 300-500 °C, the membrane reactor attained the methane conversion with a twice as large as the equilibrium value by the selective removal of hydrogen from the reaction system.

Methane steam reforming for hydrogen production requires high reaction temperature. One of possible way to liberate this reaction from equilibrium limitation and thus to attain high methane conversion at low temperatures is the use of membrane reactors. By employing hydrogen-permeable membranes, H_2 produced by steam reforming is removed from the reaction zone so that the chemical equilibrium shifts toward the completion of methane conversion. Based on this concept, some ceramic or metallic membranes have been examined for H_2 separation.[1-3] In particular, nonporous metallic membranes consisting of palladium or its alloy with selective H_2 permeability are believed as the candidate for the membrane reactor.[4-5] However, their brittleness in the H_2 atmosphere and/or low permeabilities remain as serious problems for the practical applications. It was also shown by Kameyama et al.[6] and Shinji et al.[7] that the equilibrium in decomposition of hydrogen sulfide and dehydrogenation of cyclohexane were shifted to the product side by removing H_2 with a use of porous glass membrane. In contrast to the nonporous metallic membrane, the low gas permselectivity of microporous membrane limits the equilibrium shift. In the previous study, we have proposed another type of membrane structure, i.e., microporous alumina containing highly dispersed metal particles. This membrane possesses high H_2 permselectivity which exceeds the value of Knudsen diffusion mechanism without deteriorating permeation rate. The H_2 permselectivity strongly depends on metals deposited in the micropores, being the highest by the use of Ru particles.[8-9] In this study, this high H_2 selective permeation of Ru-dispersed alumina membrane was used to the membrane reactor for apply to promote methane steam reforming at low temperatures (<600 °C).

Neat and Ru-dispersed alumina membranes were prepared by repeated dip-coating on a coarse porous tube (O.D. 10 mm, I.D. 8 mm, mean pore size 8 μm, supplied by TOTO) with the alkoxide-derived boehmite sol prepared by the reported procedure.[9] The dip-coating was repeated 40 times, until membranes with thickness of ca. 15 μm on the inside wall of the tube were obtained. The average pore diameter and pore volume of Ru-

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dispersed alumina membranes, are 3 - 3.5 nm and 0.13 - 0.20 cm^3/g, respectively. The reactor consists mainly of the membrane thus obtained and a catalyst bed of 1.33 wt% Ru/Al_2O_3(10-30 mesh) as shown in Fig. 1. A mixture of methane and steam (H_2O/CH_4 = 1.5-3.0) was continuously supplied to the catalyst bed at S.V.=750-1000 h^{-1} and at 115-120 kPa. The reaction was carried out at 300 - 600 °C. Argon gas was introduced to the permeation side to sweep the permeation gas. The gas compositions of permeated and unpermeated products were analyzed with on-line gas chromatographs. The overall conversion of methane was defined by the following equation,

$$X = \left(1 - \frac{FC_{CH_4} + fc_{CH_4}}{F(C_{CH_4}+C_{CO}+C_{CO_2}) + f(c_{CH_4}+c_{CO}+c_{CO_2})}\right) \times 100\ \%, \qquad (1)$$

where the F, C and f, c are flow rates and concentrations of the membrane reactor at the permeation side and unpermeation side, respectively.

Temperature dependences of methane conversion in the two types of membrane reactors are compared in Fig. 2, i.e., the reactors with the Ru dispersed alumina membrane and the neat alumina membrane. In comparison, the reaction was also carried out using the packed bed reactor supported by a nonporous ceramic tube. In the case of conventional packed bed reactor of a Ru/Al_2O_3, the methane conversion as well as other gas compositions agreed with the equilibrium compositions for the following two reactions:

$$CH_4 + H_2O \rightarrow CO + 3H_2, \qquad (2)$$
$$CO + H_2O \rightarrow CO_2 + H_2. \qquad (3)$$

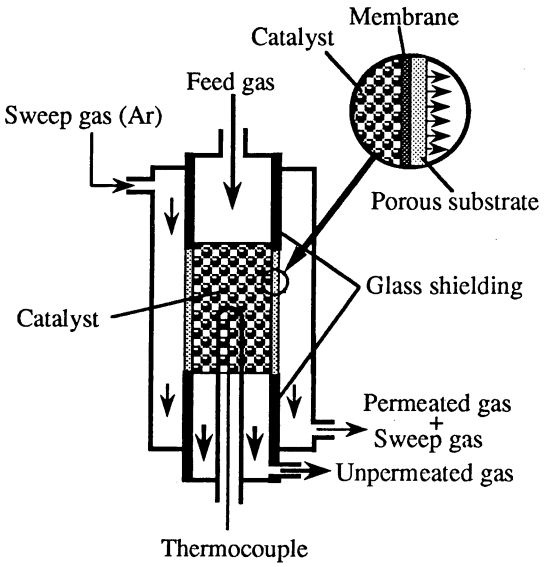

Fig.1. Schematic structure of the membrane reactor.

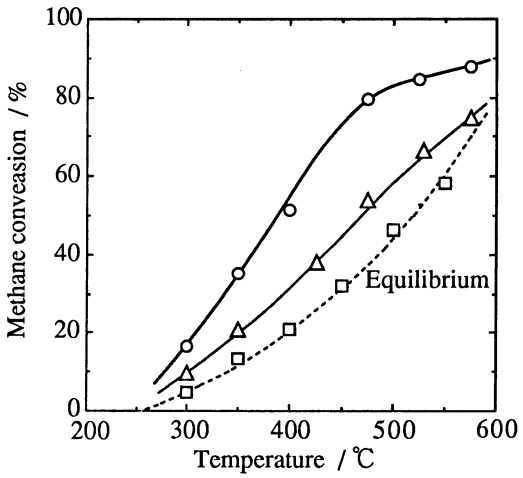

Fig. 2. Effect of temperature on the membrane reactor and packed bed reactor. ○, Ru-Al_2O_3 membrane, △, Al_2O_3 membrane, □, packed bed reactor. Reaction conditions: S.V.=750 h^{-1}, ΔP= 30 kPa, H_2O/CH_4=3.0, Flow rate of sweep gas = 75 cm^3 (STP)/min.

The use of neat and Ru-dispersed alumina membrane reactors was effective in enhancing the overall methane conversion to exceed the equilibrium conversion in the whole temperature range. In case of the neat alumina membrane, however, it seems difficult to further improve the methane conversion, because under Knudsen diffusion mechanism the ideal separation factor is determined by the ratio of the reciprocal square root of the molecular weights of the gaseous species. As reported previously,[9] hydrogen gas permeation through the microporous alumina membrane is strongly promoted in the presence of metal fine particles highly dispersed in the pores. The separation factor of Ru-dispersed membranes for the H_2/N_2 mixture, α= 4.5-6.0, was higher than that expected from ideal Knudsen mechanism (α=3.74). Thus, an additional separation mechanism should be taken into consideration. The promotion of hydrogen permselectivity was also observed for Rh-, Pd-, and Pt-dispersed alumina membranes. This is probably related to chemisorption of hydrogen on the Ru deposits and surface diffusion in the micropore. As a result of the high H_2 permselectivity, H_2 removal from the catalyst zone attained excellent promotion of the methane steam reforming in the whole temperature range (Fig. 2). Below 500 °C the methane conversion was twice as large as the equilibrium value for at least 50 h on stream(Fig. 3).

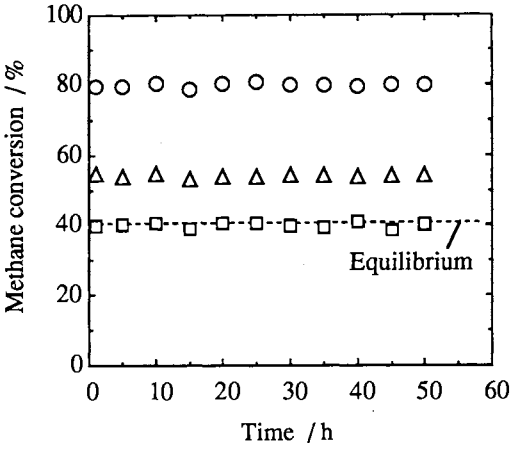

Fig. 3. Comparison of the methane conversion between the packed bed reactor and two types of membrane reactors. ○, Ru-Al_2O_3membrane, △, Al_2O_3 membrane, □, packed bed reactor. The reaction conditions is same as in Fig. 2.

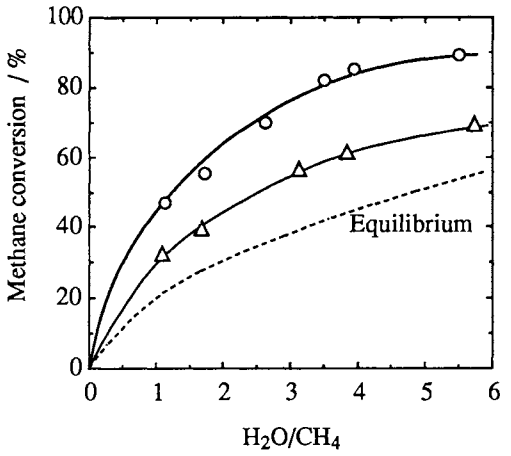

Fig. 4. Effect of the H_2O/CH_4 mol ratio on the membrane reactor. Membrane: ○, Ru-Al_2O_3, △, Al_2O_3. Reaction conditions: 475 ℃, S.V.= 750 h^{-1}, ΔP=30 kPa, Flow rate of sweep gas = 75 cm^3 (STP)/min.

In methane steam reforming, the equilibrium conversion unvaryingly increases with an increase of H_2O/CH_4 ratio in the feed gas as shown in Fig. 4. Therefore, the reaction with higher water vapor pressures is preferable to accelerate CH_4 conversion at low temperatures. The promotion effect of the membrane reactor can be observed in the whole H_2O/CH_4 range examined in this study. This result suggests that H_2 permselectivity is not deteriorated in the presence of water vaper. The methane

conversion increased with an increase of sweep gas rate in the permeation side(Fig. 5). The high sweep gas rate keeps the large concentration gradient of H_2 through the membrane, providing higher H_2 permeabilities. However, this effect is rather small for the neat alumina membrane reactor, because the H_2 separation should be governed by the Knudsen diffusion mechanism. On the other hand, the more remarkable effect was observed for Ru-dispersed membrane reactor with higher H_2 permselectivity because of the coupling of the Knudsen diffusion and surface diffusion of hydrogen. The use of steam as a sweep gas may be most interesting due to not only its ease in separation from H_2 by condensation but also the possibity of reactant supply from the sweep gas side to the membrane.

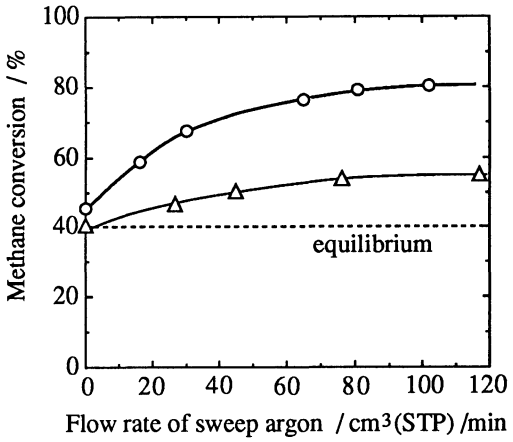

Fig. 5. Effect of the flow-rate of sweep gas on the membrane reactors. Membrane: ○, Ru-Al_2O_3, △, Al_2O_3. Reaction conditions: 475 ℃, S.V. = 750 h^{-1}, ΔP=30 kPa, H_2O/CH_4=3.0

Promotion of steam reforming beyond equilibrium limitation was also reported for the membrane reactor with a nonporous Pd film. Although the porous membranes could attain less selective hydrogen permeation than the Pd film, the high permeation rate for the Ru dispersed membrane is attracting for the application to a practical reactor system. The new material design for gas separation membrane, i.e., metal-dispersed porous membrane, will make the membrane reactor an attractive alternative in many industrial application.

References

1) H.P.Hsieh, Catal. Rev. -Sci. Eng., 33, 1-2, 1(1991).
2) J.N.Armor, Appl. Catal., 49, 1(1989).
3) H.P.Hsieh, P.R.Bhave, and H.L.Fleming, J. Membrane Sci., 39, 221(1988).
4) S.Uemiya, N.Sato, H.Ando, T.Matsuda, and E.Kikuchi, Appl. Catal., 67, 223(1991).
5) N.Itoh, AICHE J., 33, 1576(1987).
6) T.Kameyama, M.Dokiya, M.Fujishige, H.Yokokawa, and K.Fukuda, Int. J. Hydrogen Energy, 8, 5(1983).
7) O.Shinji, M.Misono, and Y.Yoneda, Bull. Chem. Soc. Jpn., 55, 2760(1982).
8) M.Chai, M.Machida, K.Eguchi, and H.Arai, Nihon Seramikkusu Kyokai Gakujutu Ronbunshi, 99, 530(1991).
9) M.Chai, M.Machida, K.Eguchi, and H.Arai, Chem. Lett., 1992, 979.

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