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Catalysis Today 25 (1995) 327–332

CATALYSIS TODAY

Asymmetric Pd–Ag/stainless steel catalytic membranes for methane steam reforming

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Abstract

Pd–Ag/porous stainless steel asymmetric membranes were prepared by successive palladium and silver platings in electroless hydrazine baths, followed by a thermal treatment in hydrogen of the as-deposited membranes above the Tamman temperatures for the alloy formation. The prepared membranes were permselective toward hydrogen separation. A membrane reactor made of stainless steel was designed to perform methane steam reforming. At mild reaction conditions, methane conversion is significantly enhanced by partial removal of hydrogen from the reaction location as a result of diffusion through the Pd-based membrane. These effects were examined under a variety of experimental conditions.

1. Introduction

Methane steam reforming (MSR) is one of the most important chemical processes for the production of hydrogen or synthesis gas [1]. The reforming reaction is strongly endothermic so that it is thermodynamically favored by high temperature. In the conventional technology, this reaction is conducted on supported Ni catalysts in multi-tubular reactors operated at temperatures up to 850°C, pressures ranging from 1.6 to 4.1 MPa and steam-to-methane ratios between 2–4. The endothermic reaction heat is supplied by burning fuel in a radiant furnace. Methane conversion is usually around 78%, limited by the thermodynamic equilibrium [2].

The development of Pd-based membrane separation processes [3–5] has opened up a new possibility to enhance the MSR conversion. With the continuous withdrawal of hydrogen by a Pd-based membrane from the reaction location, the equilibrium of the reforming reaction could be significantly shifted toward the right-hand side, resulting in an increase of methane conversion. In the meantime, high purity hydrogen could be obtained directly from the permeation side of the membrane reactor. Oertel et al. [6] performed a calculation for a modified MSR process with integrated hydrogen separation, and demonstrated that almost 90% of methane conversion could be achieved below 850°C by using a palladium membrane with a thickness of 50 μm. They also fitted a Pd membrane in a reformer to separate the produced hydrogen and obtained a methane conversion as high as 96%.

However, the high cost of palladium and the relatively low hydrogen permeation capacity do not allow massive palladium sheets to be commercially used on a large scale. An alternative choice is to develop composite thin palladium membranes. Kikuchi and coworkers [7–11] developed thin Pd and Pd–Ag membranes sup-

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0920-5861/95/$09.50
SSDI 0920-5861(95)00084-4

ported on either porous glass or porous Al_2O_3 ceramic substrates. These membranes showed much higher hydrogen permeability than commercial Pd-based sheets. Using these membranes combined with a low-temperature reforming Ni catalyst, these authors [8,9] showed that MSR can be promoted far beyond the equilibrium. The problem with these substrates is the mechanical and/or thermal properties. The present work deals with the preparation of thin Pd-based membranes supported on porous stainless steel (SS) substrate and their uses in performing MSR in a membrane reactor.

2. Experimental

2.1. Membrane preparation

A porous seamless 316L stainless steel (SS) tube having an outside diameter of 0.95 cm and a nominal particle retention size of 0.2 μm was purchased from Mott Metallurgical. The tube was cut into 3.6 cm long segments, welded to a dense SS tube, and cleaned in an ultrasonic bath of carbon tetrachloride. An asymmetric Pd–5.1% Ag membrane of about 10.3 μm thick was formed on the outer side of the porous tube by the electroless technique described previously [12–14]. The as-deposited Pd–Ag membrane was thermally treated above the Tamman temperatures of the components (550°C) for five hours in the presence of hydrogen for the formation of an impervious Pd–Ag alloy film. An Auger electron depth profiling analysis indicated that the Ag component diffused into the Pd layer to about 1.6 μm after a similar treatment at 500°C [15].

2.2. Reaction testing

Fig. 1 schematically shows the design of the membrane reactor. This reactor assembly could be easily configurated for the reaction test with or without a membrane by a simple replacement of the inner tube. The non-membrane reactor configuration could be made by using a dense stainless steel inner tube. The shell side of the reactor served as the reaction chamber and the tube side as the permeation chamber.

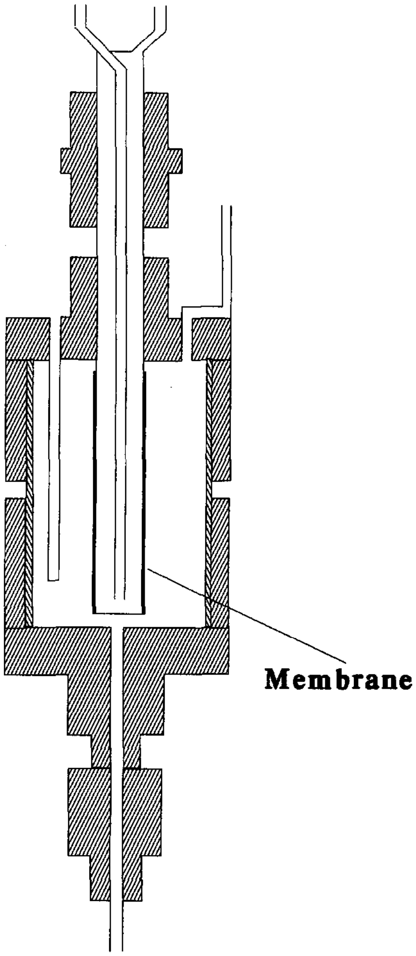

Fig. 1. Tubular membrane reactor design.

To enhance the reforming conversion, a commercial 12% Ni/Al_2O_3 catalyst was used. About 11 g of catalyst (18–30 mesh size) were packed inside the reaction chamber. An in-situ activation of the catalyst was done by first heating the catalyst bed to 300°C in a helium atmosphere to prevent the Pd-based membrane from developing cracks or pinholes, followed by introducing a hydrogen stream to the reactor at atmospheric pressure. Then the temperature was increased stepwise to 400°C and 550°C, each step lasted for one hour.

For MSR, the activated system was first heated to 300°C in a helium atmosphere. A preheated reactant mixture of steam and $CH_4 + 5\%$ He, in a steam/methane ratio of 3, was then fed into the catalytic bed. Inert helium gas of 40 SCCM passed through the permeation side in a cocurrent flow mode to purge the permeated hydrogen. The steam reforming was conducted in the temperature range of 300–550°C and a typical pressure of 136 kPa. A $CH_4 + 5\%$ He gas flow-rate of 42 SCCM was used corresponding to a gas hourly space velocity (GHSV) of about 1067 h^{-1}. After condensation of the unreacted steam, the effluent was analyzed using an on-line mass spectrometer.

3. Results and discussion

3.1. Temperature effect in membrane reactor

The major advantage of the membrane reactor is the conversion enhancement of an equilibrium-limited reversible reaction by selective hydrogen removal. Fig. 2 shows an equilibrium calculation of the MSR conversion as a function of hydrogen removal ratio. This was done by simply setting a residual hydrogen partial pressure in the equilibrium calculation for MSR.

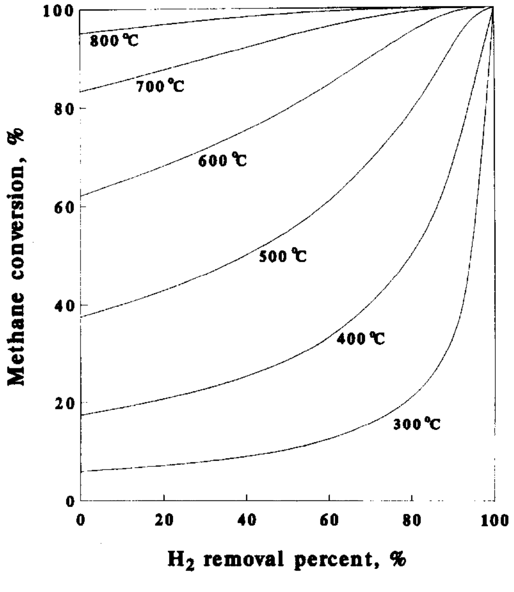

Fig. 2. Hydrogen removal on equilibrium MSR conversion.

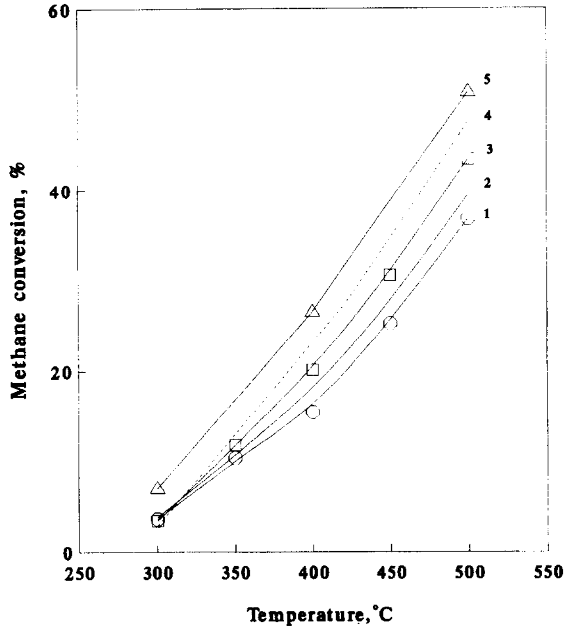

Fig. 3. Temperature effect: (1) non-membrane; (2) equilibrium; (3) Pd/SS; (4) by model; (5) Pd–Ag/SS. 136 kPa; $H_2O/CH_4 = 3$; GHSV = 1067 h^{-1}.

As can be seen from Fig. 2, when the temperature is below 400°C, the reforming reaction could not reach a satisfactory conversion level until a high hydrogen separation efficiency, say 90%. Over 700°C, the hydrogen removal through the membrane can only slightly shift the reforming equilibrium due to the intrinsically favorable temperature effect. At a moderate temperature of 500–600°C, membrane separation can result in a great improvement on the MSR equilibrium.

The temperature effect of membrane separation on MSR was examined using Pd/SS and Pd–Ag/SS membranes. Fig. 3 illustrates the total methane conversion against the reaction temperature. Curve 3 corresponds to the Pd/SS membrane having a Pd thickness of 19.8 μm. In comparison with the methane conversion in the non-membrane system (Curve 1), the membrane effect is clear in the Pd/SS membrane case. This conversion curve is also beyond the calculated equilibrium methane conversion (Curve 2). No deactivation evidence of the membrane was observed after about 47 hours of reaction tests. Curve 5 is the methane conversion performed in the Pd–Ag/SS membrane reactor. Evidently, MSR was greatly enhanced by using this Pd–Ag membrane. For example, at a total pressure of 136 kPa, a reaction temperature of 500°C, and a molar steam-to-methane ratio of 3, a methane conversion of 50.9% was achieved, much higher than that in the non-membrane system (36.7%). The methane conversion was reproducible after a series of reaction tests. In comparison with the result obtained with the Pd membrane, the enhanced methane conversion in the case of Pd–Ag/SS membrane should be attributed to the combination of the use of a thinner film and a possibly higher hydrogen permeability through the Pd–Ag membrane.

The temperature effect was also calculated using a kinetic permeation model for the Pd/SS membrane [16]. Under the above mentioned reaction conditions, methane conversions at various temperatures were predicted, as shown in Fig. 3 (Curve 4). Comparing the calculated data with Curve 3, it can be seen that the two lines fit essentially at temperatures below 350°C. With raising reaction temperature, the measured conversions become lower than the predicted ones. This deviation is attributed to the temperature gradient inside the membrane reactor. Both the endothermal behavior of the steam reforming and the cooling effect of the sweep gas yield temperature decreasing toward the inner tube.

3.2. *Influence of the H_2O/CH_4 ratio*

MSR usually proceeds in the presence of an excess of steam to prevent the carbon deposition over the catalyst surface and to enhance the steam reforming. The effect of molar steam-to-methane (S/C) ratio on methane conversion was examined by varying the ratio from 2 to 4. The results obtained at 500°C are drawn in Fig. 4. Curve 1 is the experimental data obtained from the non-membrane system. Curve 2 is the calculated equilibrium conversion, exhibiting monotonic increase with the S/C ratio. It can be seen that these points are slightly lower than the equilibrium conversion, showing the same trend as in Fig. 3. In the case of the Pd/SS membrane, an enhancement of the membrane separation efficiency was practised by continually pumping the permeation side (tube side) with a rotary vacuum pump. The pumping kept the permeation side under a low pressure, resulting in a relatively high driving force of hydrogen permeation through the Pd membrane. The measured methane conversion against the S/C ratio is shown as Curve 4 in Fig. 4. It is clear that the methane conversion was greatly enhanced in this manner. For the Pd–Ag/SS membrane, the effect of S/C is shown in Curve 3. In this case, helium passed through the permeation side at a flow-rate of 40 SCCM. The promotion of the reforming conversion is clearly exhibited. It should be noticed that the lower conversion obtained with the Pd–Ag/SS membrane is due to the fact that in this experiment a smaller difference in hydrogen partial pressure in the two compartments was implemented which induced a lower H_2 permeation flux.

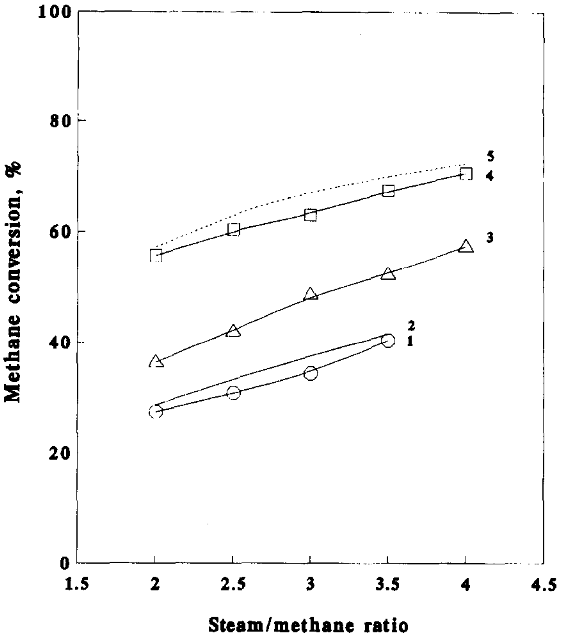

Fig. 4. S/C effect: (1) non-membrane; (2) equilibrium; (3) Pd–Ag/SS; (4) Pd/SS with pumping; (5) by model. 500°C; 136 kPa; GHSV = 1067 h^{-1}.

3.3. Pressure effect in the membrane reactor

In a conventional reactor, the increase of pressure results in a decrease of the methane conversion. However, the incorporation of a hydrogen permeable membrane would change this general trend. Although a high reaction pressure depletes the steam reforming equilibrium conversion, the increase of hydrogen partial pressure in the reaction side would increase the driving force for hydrogen permeation, resulting in an enhancement of the methane conversion under certain conditions.

The effect of pressure on MSR conversion was examined in the present study. As expected, in the case of the non-membrane system, the methane conversion decreased with raising total reaction pressure, in agreement with the equilibrium calculation. However, in the case of the Pd–Ag/SS membrane a decreasing variation in the methane conversion with the increase of pressure was also observed. This seems to indicate a low membrane separation efficiency.

Uemiya et al. [9] noticed a conversion increase with increasing reaction pressure. The sweep gas they used was an argon stream in a flow-rate of 400 SCCM, ten times higher than in our case. We calculated the dependence of methane conversion on the total pressure in various purging conditions for a Pd membrane of 20 μm thick. It was found that the increasing tendency exists in the case where hydrogen separation is efficient. If the separation is relatively weak, for example with a mild purging effect in the permeation side, the decreasing methane conversion upon pressure is maintained in the low pressure region. Thus in our case, the use of a mild purge flow-rate (40 SCCM) and a low reaction pressure yielded a decreasing conversion dependence upon the pressure.

3.4. Purge effect

Purging the permeation side is important in maintaining a high hydrogen partial pressure difference between the two sides of the membrane and moving out hydrogen product from the reaction system. As discussed above, the increase of the purge gas flow-rate is expected to enhance the methane conversion owing to the decrease of the hydrogen partial pressure in the permeation side. This effect was examined in the Pd-based/SS membrane system. The methane conversion was found slightly increased with raising the purge gas flow-rate from 40 to 180 SCCM.

The computer model analysis for the Pd membrane predicts a stronger sweeping flow-rate effect on the methane conversion than the one determined in our experiment. The higher the flow-rate of the purge gas, the more the measured methane conversion deviated from the predicted value. This was quite possibly caused by the cooling effect of the purge gas stream. In general, increasing the purge gas flow-rate enhances the hydrogen separation efficiency. However, the economy in a large scale industrial application may not permit the use of large amounts of inert gas. Instead, in the case of MSR, steam may be used as the purge gas. This would also make the subsequent separation of hydrogen from the purge stream much easier since steam can be easily condensed from the mixture. Another choice to increase the hydrogen permeation driving force is the vacuum operation in the permeation side, as already demonstrated in this study. It seems that operation under rough vacuum ranging from 101 kPa to ca. 100 Pa is industrially acceptable from economic considerations.

4. Conclusions

Electrolessly prepared Pd/SS and Pd–Ag/SS composite membranes were used to perform MSR in the presence of a Ni/Al_2O_3 catalyst. The methane conversion was significantly enhanced as a result of hydrogen permeation through the Pd-based membrane. For example, at a total pressure of 136 kPa, a temperature of 500°C and a molar steam-to-methane ratio of 3, a methane conversion 1.4 times higher than that in the non-membrane system was reached using the Pd–Ag/SS membrane. Membrane effects were examined under a variety of experimental conditions and predicted using a computer model.

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