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Steam reforming of methane in a membrane reactor

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Abstract

Methane reforming in a Pd/Ag membrane reactor was carried out. The operational limits for the steam-to-methane ratio are discussed. To avoid carbon formation, this ratio has to be higher in a Pd/Ag membrane reactor than in a conventional steam reforming tubular reactor.

1. Introduction

Steam reforming of methane is an endothermic process

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

$$(-\Delta H^0_{298} = -206.2\ \mathrm{kJ/mol})$$

$$K_1 = \frac{P(CO) \cdot P(H_2)^3}{P(CH_4) \cdot P(H_2O)}$$

$$CO + H_2O = CO_2 + H_2 \qquad (2)$$

$$(-\Delta H^0_{298} = 41.2\ \mathrm{kJ/mol})$$

The conversion of methane is limited by chemical equilibrium. It is enhanced by high temperature and low pressure and a high steam content (oxygen-to-carbon ratio). In the majority of industrial ammonia and hydrogen plants, a high pressure in the order of 3–4 MPa is to be preferred. Thus, temperatures around 1100 K are applied. These conditions are quite strenuous as regards construction material [1] and, therefore, expensive steel alloys are used.

From this point of view, there will be a considerable incitement to lower the reaction temperature. The equilibrium limitation then has to be overcome. Therefore, the reaction should be carried out either at a very low pressure or, alternatively, in a membrane reactor [2]. If a palladium membrane reactor is used it provides the additional advantage of delivering very pure hydrogen. This could be very important when a very pure hydrogen is needed, such as for certain types of fuel cells (PAFC, PEFC and AFC).

The advantage of using a membrane reactor is demonstrated by the above equilibrium constant where the hydrogen partial pressure enters the third power. The removal of hydrogen from the reaction zone increases the methane conversion [3–5]. The reaction may consequently be carried out at a lower temperature.

Besides an increased conversion of methane at lower temperatures, the removal of hydrogen from the reaction gas influences the potential for carbon formation via

$$CH_4 = C(s) + 2H_2 \qquad (3)$$

$$(-\Delta H^0_{298} = -75\ \mathrm{kJ/mol})$$

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$$2CO = C(s) + CO_2 \quad (-\Delta H^0_{298} = 173\ \text{kJ/mol}) \qquad (4)$$

A major drawback in the use of dense palladium membranes in large-scale reforming plants is the availability and the price of palladium. The hydrogen permeability of palladium (alloys) is low compared to the very high catalytic reaction rates and the high industrial space velocities. The development of membrane reactors with a high permeation rate is, therefore, very desirable.

The permeation of hydrogen through palladium alloy membranes is described by the following relation that is valid as long as the diffusion of hydrogen through the metal is considered the rate limiting step [6]:

$$F = \frac{D \cdot A}{l} \left(\sqrt{P_{H_{2,r}}} - \sqrt{P_{H_{2,s}}}\right) [\text{Nm}^3/\text{h}] \qquad (5)$$

D is the apparent diffusion coefficient ($m^2\ h^{-1} \sqrt{bar^{-1}}$), which is dependent on temperature and the nature of the Pd alloy present. A is the area of the membrane (m^2); l is the membrane thickness (m); $P_{H_{2,r}}$ and $P_{H_{2,s}}$ are the partial pressures of hydrogen (bar) on the reaction and separation side of the membrane.

The only way to drastically increase the permeation rate is to decrease the membrane thickness. Research in preparation of ultrathin supported Pd membranes has therefore been carried out [7,8]. Gains with respect to a higher diffusivity, improved mechanical properties and improved resistance to poisoning may be obtained by modifying the alloying composition [9,10].

Minor additional gains with respect to minimizing the needed palladium membrane area can be achieved by performing the reforming reaction at conditions with a high partial pressure of hydrogen.

In this study we have investigated the steam reforming of methane in a Pd/23% Ag membrane reactor at temperatures from 350 to 500°C and at pressures from 0.6 to 1 MPa. Conditions favouring a high partial pressure of hydrogen on the reaction side are being reviewed. We have further established criteria for carbon-free operation.

2. Experimental set-up

The reactor was installed in a furnace and consists of a Pd–23 wt.-.% Ag tube (0.1 mm thick, 380 mm long, outer diameter 1.55 mm) centred within an outer reactor tube (inner diameter 4.47 mm) made of stainless steel. The applied catalyst was a commercially available (Haldor Topsøe A/S) steam reforming catalyst. The catalyst was based on Ni and MgO and had a high activity at low temperatures. 4.65 g of the catalyst was crushed and packed uniformly in the reaction zone between the two tubes. The length of the catalyst bed was 320 mm. This means that the hydrogen diffusion is not solely restricted to the catalyst zone. About 30 mm of space was available for hydrogen diffusion before the inlet and after the exit of the catalyst bed.

A feed gas of 99.99% CH_4 was supplied from a bottle and was led over a Cu/ZnO catalyst at 275°C for final purification. The gas flow of CH_4 was controlled by a mass flow-meter. The water was purified by ion exchangers, supplied by a pump and evaporated at 200°C.

The reaction gas was mixed to a steam-to-methane ratio of 2.9 and preheated before entering the reactor. The space velocity was 0.5 Nl CH_4/g catalyst/h. The sweep gas (10 Nl/h of N_2) flowed countercurrently to the reaction gas.

At the exit of the reaction side of the membrane the unreacted water was condensed and measured. The hydrocarbon containing dry gas was analysed on a gas chromatograph. The dry exit gas flows were measured by use of mass flow-meters.

The temperature used is the oven temperature and the system pressure was measured at the reactor system exit. The reforming experiments were performed at temperatures between 350–500°C. The pressure on the reaction side was in the range of 6.1–10 bar g. The pressure on the sweep side was 0.5 bar g.

The conversion of methane was calculated as:

$$\text{Conversion of CH}_4 = \frac{Y_{CO_2} + Y_{CO}}{Y_{CH_4} + Y_{CO} + Y_{CO_2}} \qquad (6)$$

where Y is the mole fraction in the exit gas from the reaction side.

The hydrogen-to-carbon ratio (H/C) of the exit gas from the reaction side was calculated as:

$$H/C = \frac{2 \cdot Y_{H_2} + 2 \cdot Y_{H_2O} + 4 \cdot Y_{CH_4}}{Y_{CH_4} + Y_{CO} + Y_{CO_2}} \qquad (7)$$

3. Results and discussion

3.1. Experimental results

The measured conversion of methane in the membrane reactor as a function of temperature is summarized in Fig. 1. As expected it is verified that the conversion of methane increases when H_2 is removed from the reaction system.

At 500°C and 6 bar g the conversion of methane was measured without gas flow on the sweep-side. The measured conversion corresponds very well with the expected equilibrium conversion of 21% at these conditions.

At 500°C, 6 bar g and with a gas flow on the sweep-side, 51% of the methane is converted. A 51% conversion corresponds to an equilibrium temperature of 639°C calculated from the inlet gas (1). At 500°C and 10 bar g the conversion is increased to 61% corresponding to an equilibrium temperature of 707°C. The highest conversion of methane is obtained at the highest temperature and pressure level.

The reaction gas from the catalyst bed exit is in chemical equilibrium. Fig. 2 shows the conversion of methane as a function of the H/C ratio of the process gas. The fully drawn line is calculated from an equilibrated gas. The measured points are generally placed a little to the left of the calculated equilibrium curve because the exit gas looses some hydrogen to the sweep side before entering the measuring system.

Fig. 3 shows the calculated equilibrium partial pressure of hydrogen at the experimental condi-

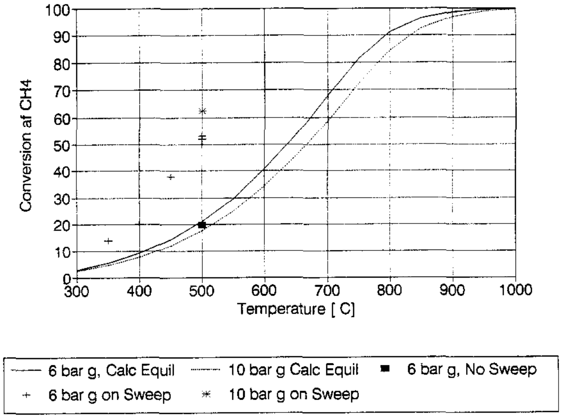

Fig. 1. Plots of measured conversion of methane as a function of temperature. The fully drawn lines are the calculated equilibrium curves. Steam-to-carbon ratio is 2.9.

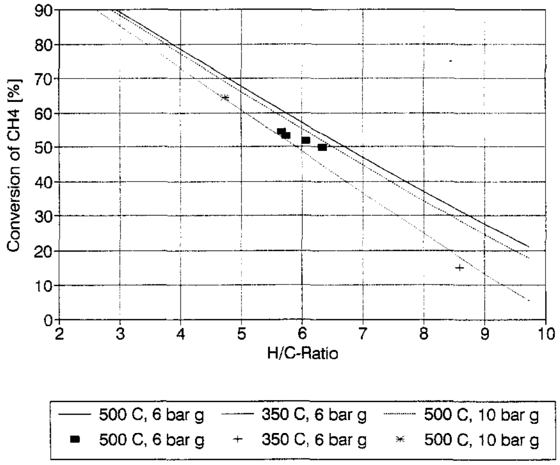

Fig. 2. Plots of measured conversion of methane as a function of the hydrogen-to-carbon ratio of the exit gas from the reaction side. The fully drawn lines are the calculated equilibrium curves.

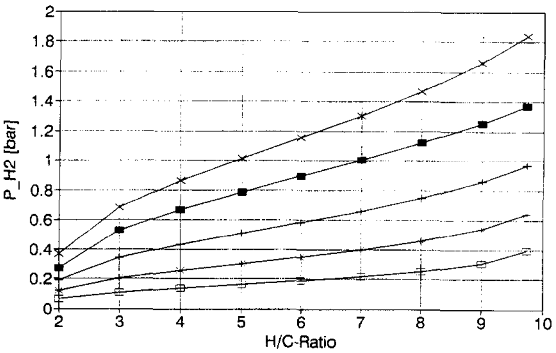

Fig. 3. Calculated equilibrium partial pressure of hydrogen for a gas with a constant oxygen-to-carbon ratio of 2.9 as a function of the hydrogen-to-carbon ratio of the gas. (×) 500°C, 10 bar g; (■) 500°C, 6 bar g; (+) 450°C, 6 bar g; (second line from bottom) 400°C, 6 bar g; (□) 350°C, 6 bar g.

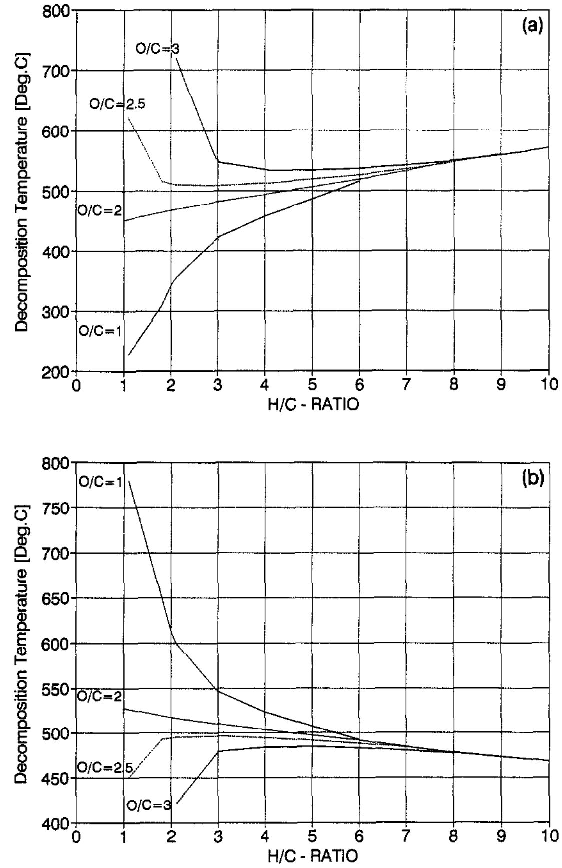

Fig. 4. (a) Upper carbon limit temperatures (T_M) based on graphite data. $T = 500°C$. $P = 6$ bar g. (b) Lower carbon limit temperature (T_B) based on graphite data. $T = 500°C$. $P = 6$ bar g.

tions of temperature, pressure and steam-to-carbon ratio as a function of the H/C ratio of the process gas. Maximum partial pressure of hydrogen is reached at high temperature and pressure.

As the catalyst is considered active enough to establish equilibrium at the actual process conditions the effect of increasing the pressure from 6 to 10 bar g on the reaction side (Fig. 1) is easily understood. An increase of the total pressure results in an increase of the partial pressure of hydrogen, thereby helping the membrane to remove hydrogen down to a lower H/C ratio of the process gas, which results in a higher methane conversion.

Uemiya et al. [11] have earlier demonstrated the benefit of performing the steam reforming reaction in a palladium membrane reactor. At 500°C and 10 bar g at the reaction side Uemiya et al. obtained about 80% methane conversion. The membrane thickness in Uemiya's experiments is only 20 micron which is a possible explanation for Uemiya's higher conversion. Uemiya also observed an increase in the methane conversion with an increase of the pressure on the reaction side.

3.2. *Criteria for carbon-free operation*

In addition to the reforming and shift reactions (1) and (2), carbon formation can take place by the endothermic decomposition of methane (3) or by the exothermic decomposition of carbon monoxide, i.e. the Boudouard reaction (4).

In a catalytic system the risk of carbon formation is normally evaluated by means of the so-called 'Principle of Equilibrated Gas' stating that carbon formation is to be expected if the gas shows affinity for carbon formation after the establishment of the reforming (1) and shift equilibria (2) [1].

The principle is developed in the light of the fact that the reforming and water-gas shift reaction is very fast. This means that the feed gas rapidly reaches equilibrium in the catalyst bed.

As the removal of hydrogen through a dense Pd/Ag membrane is slow compared to the catalytic reaction rate the gas composition near the membrane equals the gas composition in the catalytic bed. On the assumption that the effect of film diffusion is negligible the gas near the membrane surface is thus in chemical equilibrium and the principle can be extended to be valid for the membrane as well as the catalyst.

Calculations of the lower carbon temperature limit for the methane decomposition (T_M) and the upper temperature limit for the Boudouard reaction (T_B) are carried out as follows:

For a given feed gas composition, temperature and pressure, the gas composition after the establishment of the reforming and shift equilibria was calculated.

Then the reaction coefficient for the methane decomposition is calculated as:

$$K,ac,3=\frac{(Y_{H_2})^2\cdot P}{Y_{CH_4}} \tag{8}$$

and the reaction coefficient for the carbon monoxide decomposition is calculated as

$$K,ac,4=\frac{Y_{CO_2}}{(Y_{CO})^2\cdot P} \tag{9}$$

The calculated reaction coefficients are compared to the equilibrium constants obtained from literature data based on carbon as graphite [1] and the corresponding temperatures (T_M and T_B) above or below which there will be affinity for carbon formation is found.

Fig. 4 shows the upper temperature limit of the exothermic methane decomposition reaction (3) and the lower temperature limit of the exothermic carbon monoxide decomposition reaction (4) at various steam-to-carbon ratios of 500°C and 6 bar g, as a function of the H/C ratio of the process gas.

An ordinary, low-temperature steam reformer is operated at a constant steam-to-carbon ratio and at a constant hydrogen-to-carbon ratio. A relatively low steam-to-carbon of about 1 and a corresponding hydrogen-to-carbon ratio of 6 is thus sufficient to avoid carbon forming conditions.

When the reforming reaction is performed in a Pd/Ag membrane reactor hydrogen is selectively removed from the reaction gas, which results in a decline of the H/C ratio of the process gas. The oxygen-to-carbon ratio remains, however, constant.

Fig. 4 illustrates the approached temperature limits of carbon formation with the decline of the H/C ratio.

If a gas with a steam-to-carbon ratio of 1 is reformed in a membrane reactor the temperature limits of carbon formation are exceeded at an H/C ratio of 5.5. Recovery of further hydrogen from the gas results in operation at possible carbon forming conditions.

By keeping the steam-to-carbon ratio higher than about 2.5, it is possible entirely to avoid the theoretical temperature range of carbon formation, even if hydrogen is removed down to the least possible value of the H/C ratio.

4. Conclusion

As the catalytic reaction rate of the reforming reaction is fast compared to the rate of hydrogen removal through a dense palladium membrane the gas in the membrane reformer is very near chemical equilibrium.

As the equilibrium partial pressure of hydrogen increases with temperature and pressure, the obtained recovery of hydrogen through the membrane and the obtained conversion of CH_4 increase with increasing temperature and pressure

Due to the decline in the H/C ratio of the process gas the membrane reformer has to be operated at a higher steam-to-carbon ratio compared to an ordinary, low-temperature steam reformer.

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