Application of a dense silica membrane reactor in the reactions of dry reforming and partial oxidation of methane

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The reactions of dry (CO_2) reforming and partial oxidation of methane have been investigated in a membrane reactor. The membrane is composed of a dense thin silica (SiO_2) film supported on porous Vycor tubes and was synthesized by chemical vapor deposition. The hydrogen permeance of the membrane was 0.2–0.3 $cm^3/(cm^2$ min atm) at 600°C combined with a H_2/N_2 selectivity of 200–300. Significant increases in methane conversion were attained in both reactions at 500–750°C, albeit at very low space velocities. The membrane permeance declined by ~50% after exposure to feeds containing H_2O, but otherwise exhibited excellent stability under reaction conditions.

Keywords: membrane reactors; methane reforming; methane oxidation

1. Introduction

The reaction of dry (CO_2) reforming of methane is an alternative route for the production of synthesis gas with a H_2/CO ratio close to unity. A foreseeable application of the CH_4/CO_2 reaction is in chemical energy transmission systems, which utilize solar or other renewable energy sources [1]. The reforming of CH_4 with CO_2 is a highly endothermic reaction,

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2, \quad \Delta H = +247 \text{ kJ/mol}, \quad (1)$$

and very high temperatures (> 800°C) are required for complete conversion of methane [2]. Simultaneous reforming of CH_4 with CO_2 and H_2O has often been applied in industrial practice in order to produce synthesis gas with a desirable H_2/CO ratio [2].

The partial oxidation of methane to synthesis gas has been attracting interest in recent years as an alternative to H_2O and CO_2 reforming:

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2, \quad \Delta H = -36 \text{ kJ/mol}. \quad (2)$$

The advantage of the partial oxidation route is that the heat required for the reforming steps (ii) and (iii) is supplied by initial combustion of part of methane, (i) [3]:

$$\begin{aligned} &\text{(i)} \quad CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \\ &\text{(ii)} \quad CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \\ &\text{(iii)} \quad CH_4 + H_2O \rightleftharpoons CO + 3H_2 \end{aligned} \quad (3)$$

Due to thermodynamic limitations, which also pertain in this case, reaction temperatures higher than 800°C are required for methane conversions exceeding 95% [4].

Employment of a membrane reactor, which selectively separates hydrogen from the reaction mixture along the reaction path can increase methane conversion and may permit operation of the reactor at lower temperatures. Reviews of the application of hydrogen-permeable inorganic membranes in equilibrium-limited reactions have appeared in the literature [5–7].

Steam reforming of methane in a membrane reactor has been studied by several investigators. Uemiya et al. [8] employed a composite membrane consisting of a thin palladium film deposited on a porous glass cylinder. A similar approach was followed by Shu et al. [9], who used a membrane consisting of a thin Pd or Pd–Ag film supported on a porous stainless steel tube. In both cases, methane conversions far exceeding equilibrium could be obtained at temperatures in the range of 300–500°C. A metal-impregnated porous alumina membrane was employed by Chai et al. [10]. Methane conversions twice as high as the equilibrium value were obtained in the temperature range of 300–500°C.

The catalytic partial oxidation of methane has also been studied in a membrane reactor [11]. The membrane consisted of a silica-modified porous alumina tube. The reaction was studied at temperatures in the neighborhood of 800°C and higher methane conversions were obtained in the membrane reactor.

A different type of a hydrogen-permselective membrane reactor has been applied in the present work, in the reactions of methane reforming with CO_2 and of partial oxidation of methane. This membrane reactor consists of a dense thin silica (SiO_2) film deposited on the inner surface of porous Vycor glass tubes. The advantages of silica membranes compared to membranes based on palladium are: stability at high temperatures (up to 850°C), chemical inertness (not susceptible to coking or poisoning) and lower cost. At this stage of development, though, the hydrogen permeance of silica

membranes is much lower compared to that of palladium membranes. Such a membrane type has already been applied in the reaction of isobutane dehydrogenation with considerable success [12].

2. Experimental

Dense silica membranes supported on porous Vycor tubes (5 mm i.d., 7 mm o.d., with 4 nm pore diameter, obtained from Corning, Inc.) were synthesized by chemical vapor deposition, using $SiCl_4$ and H_2O as precursors, at a deposition temperature of 700°C. The two reactants, diluted in nitrogen, were passed through the inner side of the tube, while vacuum was applied at the outer side of the tube. The methodology which was followed is essentially the same as the one described in detail in ref. [13], concerning the one-sided geometry of deposition.

The permeance of the membranes was measured with the following methodology: pure hydrogen was passed through the bore and pure nitrogen through the annulus side of the membrane at a flow rate of 100–300 cm^3/min and atmospheric pressure. The effluents of both sides were analyzed by a gas chromatograph equipped with a thermal conductivity detector in order to determine the concentration of permeated hydrogen or nitrogen. The permeance of the membrane for a specific gas was then determined by the equation: $Q = Fx/(A\Delta P)$, where: Q is the permeance ($cm^3/(cm^2\ min\ atm)$), F the gas flow rate (cm^3/min), x the molar fraction of permeated gas (kept below 10%), A the geometric area of the membrane (cm^2) and ΔP the partial pressure difference (being approximately equal to 1 atm).

The Vycor tube, which was welded to quartz tubes (6 mm o.d.) on both sides, was placed concentrically within a wider quartz tube (12 mm o.d.). The catalyst bed was located at the inner side of the Vycor tube. A 0.1% Rh/SiO_2 catalyst was employed for all the experimental runs, based on the fact that rhodium is a very active and stable catalyst for both reactions [2,14,15]. The catalyst bed occupied the entire volume of the tube where the membrane was located. In the case of MR1, part of the catalyst was also contained in a section of the tube before the membrane. This section acted as a pre-reactor in order to bring the reaction mixture close to equilibrium. The feed to the reactor consisted of either an equimolar undiluted mixture of CH_4 and CO_2 or of an undiluted mixture of CH_4 and O_2 with a 2 : 1 ratio. Nitrogen, at a flow rate of 150 cm^3/min, was used as a purge gas to remove hydrogen which permeated through the membrane. The reactions were studied in the temperature range of 500–750°C.

3. Results and discussion

3.1. Membrane characterization

The properties of the two membranes (named MR1 and MR2), which were synthesized by the aforementioned technique and were used in the experiments, are given in table 1. The hydrogen permeance of the membranes was found to be approximately half of the permeance of the untreated Vycor tube (without membrane). This is due to the added resistance of the dense silica layer. The separation selectivity between hydrogen and nitrogen, however, was significantly increased from the value of 3.7 for the Vycor tube (corresponding to a Knudsen diffusion mechanism of separation) to 200–300. MR2 has a hydrogen permeance, Q_{H_2}, 1.5 times larger than MR1. The activation energy for hydrogen permeation of both membranes before use was found to be 16–17 kJ/mol. After exposure of MR2 to a water containing mixture for several days the activation energy for hydrogen permeation increased to 24 kJ/mol, while the hydrogen permeance decreased by approximately 50%. This phenomenon is discussed in a later section.

3.2. Reforming of methane with CO_2

The membranes were found to retain their permeance and selectivity characteristics for several days of operation under conditions of methane reforming with CO_2. No coking was observed to take place on the membrane itself. The maximum methane conversion obtained in the MR1 and MR2 (see table 1) as a function of temperature employing a feed of undiluted equimolar mixture of CH_4 and CO_2 is compared to the equilibrium conversion in fig. 1. These results correspond to the lowest space velocity employed in each case, which was 15 h^{-1} for MR1 and 5 h^{-1} for MR2. The space velocity has

Table 1
Characteristics of the membrane reactors

Reactor	Length (cm)	Q_{H_2} [a] ($cm^3/(cm^2\ min\ atm)$)	Selectivity [a] H_2/N_2	E_{act} (kJ/mol)
MR1	10.5	0.22	300	17
MR2	25.0	0.32 (0.15) [b]	200	16 (24) [b]

[a] $T = 600$°C.
[b] After exposure to water containing atmosphere for 10 days at 700°C.

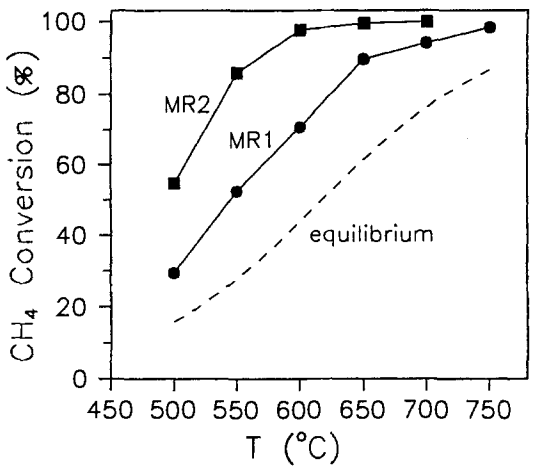

Fig. 1. Methane conversion as a function of temperature obtained in membrane reactors MR1 and MR2 under CH_4/CO_2 reaction conditions.

been calculated based on the volume of the membrane section of the reactor. It can be seen that methane conversion is considerably enhanced when the reaction is carried out in the membrane reactors. As expected, higher methane conversions were obtained in MR2, because the amount of permeating hydrogen is larger in this case due to the higher permeability of the membrane and the lower space velocity. In the case of MR1, 90% methane conversion was obtained at the temperature of 650°C,which is 130–150°C lower than the temperature required to achieve the same conversion at equilibrium conditions. In the case of MR2, methane conversions higher than 95% were already obtained at 600°C.

The use of the membrane reactors was also found to have a beneficial effect on H_2 selectivity, as can be seen in fig. 2. Hydrogen selectivities higher than 95% were obtained in MR1 at temperatures higher than 500°C, while for MR2, hydrogen selectivity was higher than 99% at temperatures higher than 550°C. In a conventional reactor, selectivities higher than 95% can only be achieved at aproximately 750°C. The enhancement of H_2 selectivity can be explained by considering the water–gas shift reaction:

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \quad (4)$$

Removal of hydrogen from the reaction mixture through the membrane shifts the equilibrium towards the left side, thus enhancing the H_2 selectivity of the reforming reaction.

It has to be noted that the aforementioned results were obtained at rather low space velocities, of the order of 5–15 h^{-1}. Hydrogen permeation through the membrane is the slow step of the entire process. The specific membrane reactors which were used could transport approximately 4–12 cm^3 H_2/min for a partial pressure difference, ΔP_{H_2}, of 1 atm. However, the values of ΔP_{H_2} under reaction conditions are lower than 0.4 atm, thus the highest diffusion rate of hydrogen through the specific membranes is of the order of 1–4 cm^3 H_2/min or 60–240 cm^3/h. Dividing by the membrane reactor volumes, which are 2 and 5 cm^3 respectively, space velocity values in the range of 30–50 h^{-1} are obtained, which shows that only at space velocities of this order of magnitude and lower, the membrane reactor can exert significant effects on conversion and selectivity. This is illustrated in fig. 3, in which the methane conversion obtained at 650°C in the two membrane reactors is plotted as a function of space velocity. The equilibrium methane conversion at this temperature is also shown as an horizontal dashed line. At space velocities higher than 300 h^{-1} the effect of the membrane on methane conversion is small, while at space velocities smaller than 50 h^{-1} the enhancement of methane conversion becomes significant. It is also obvious that a larger price (with respect to space velocity) has to be paid in order to increase the conversion above 90%. At high space velocities, MR2 was found to be less efficient than MR1. This, in most prob-

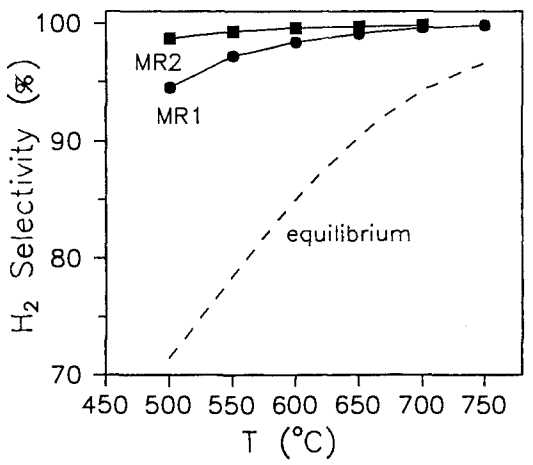

Fig. 2. Hydrogen selectivity as a function of temperature obtained in membrane reactors MR1 and MR2 under CH_4/CO_2 reaction conditions.

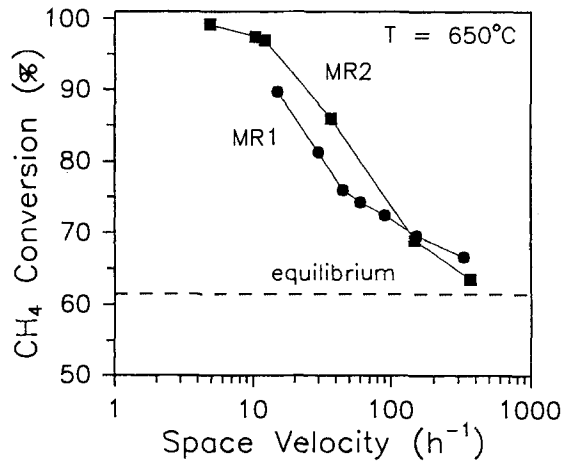

Fig. 3. Effect of space velocity on methane conversion obtained in membrane reactors MR1 and MR2 at 650°C under CH_4/CO_2 reaction conditions.

ability, must be attributed to the absence of a pre-reactor section in the case of MR2. Similar results concerning the effect of space velocity were obtained at the other reaction temperatures which were examined.

Because of the high separation selectivity of the membranes employed in the present study, essentially only hydrogen was found to permeate through the membrane. It was found that the quantities of CH_4 and CO_2 which permeate through the membrane at 650°C (and, as a consequence are not available for reaction) are less than 0.1% of the feed, even at the lowest space velocity employed. The composition of the reactor effluent stream at 650°C is shown as a function of space velocity in fig. 4. At space velocities higher than 300 h^{-1}, the gas phase composition closely approaches the thermodynamically predicted values. As the space velocity decreases, the concentration of CO increases up to about 90%, while the concentration of the other reacting components decreases. The increase in nitrogen concentration is largely due to permeation from the purge side to the reaction side (a small part is due to minor leaks and to nitrogen impurities in the feed). It can be seen that the carbon dioxide concentration does not decrease as rapidly as methane concentration does, with decreasing space velocity. In addition, carbon monoxide concentration tends to level off or to decrease slightly at very low space velocities. This implies that under these conditions, where the gas phase consists essentially of CO, the Boudouard reaction ($2CO \rightleftharpoons C + CO_2$) might become significant. It was found, by optical observation of the catalyst bed at the end of this reaction run, that the catalyst had turned black, especially towards the end of the bed. This is in accordance with the discussion above, because the reaction mixture is enriched in CO as it moves towards the end of the bed.

3.3. Partial oxidation reaction

The membrane reactor MR2 was used for the study of the partial oxidation of methane. Prior to the reaction experiments, the membrane was exposed to a $CH_4/CO_2/H_2O$ mixture (50/17/33) at 700°C for 10 days in order to examine the effect of water vapor on membrane properties. After this treatment, the hydrogen permeance declined from 0.32 to 0.15 $cm^3/(cm^2$ min atm) at 600°C and from 0.36 to 0.21 $cm^3/(cm^2$ min atm) at 700°C. This phenomenon is due to densification of the SiO_2 film in the presence of water vapor [16] and is accompanied by an increase in the activation energy of hydrogen permeation (table 1) reflecting the increased difficulty of hydrogen diffusion through a denser solid matrix. The permeance, however, did not decline further during the experiments with the CH_4/O_2 feed.

The reaction was studied in the temperature range of 550–700°C at space velocities in the range of 5–450 h^{-1}. The methane conversion obtained in the membrane reactor at the lowest space velocity used (5 h^{-1}) is presented as a function of reaction temperature in fig. 5. The equilibrium conversion is also included in the same figure for comparison. It is obvious that the methane conversion is significantly enhanced in the membrane reactor. At 600°C, the conversion was found to be greater than 86%, compared to the equilibrium value of 43%. At 700°C, the corresponding values were 97 and 75%, respectively. Hydrogen diffusion through the membrane is the slow step determining the performance of the membrane reactor. Therefore, very small space velocities had to be employed in order to observe significant enhancement in methane conversion. The effect of space velocity on methane conversion at a reaction temperature of 600°C is presented in fig. 6. It can be seen that at space velocities higher than 100 h^{-1}, the methane conversion is very close to the equilibrium value. This is due to the fact that the amount of hydrogen permeating through the membrane is only a small fraction of the hydrogen produced via the reaction, and, as a consequence, the shift of equilibrium is negligible. At lower space velocities, the

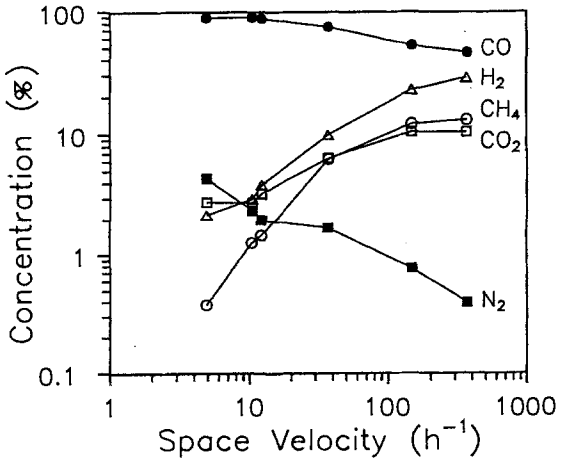

Fig. 4. Effect of space velocity on gas phase composition of the reactor MR2 effluent under CH_4/CO_2 reaction conditions. (Reaction temperature 650°C.)

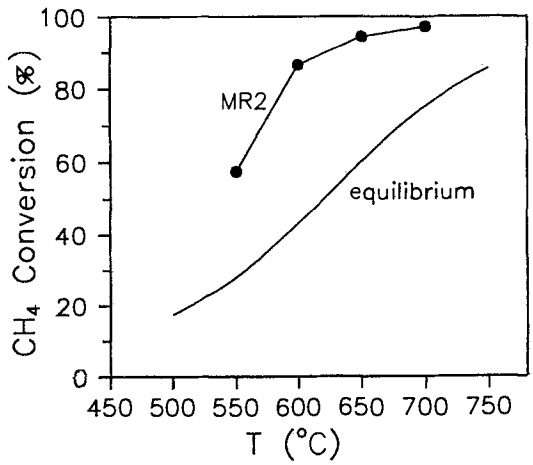

Fig. 5. Methane conversion as a function of temperature obtained in reactor MR2 under CH_4/O_2 reaction conditions.

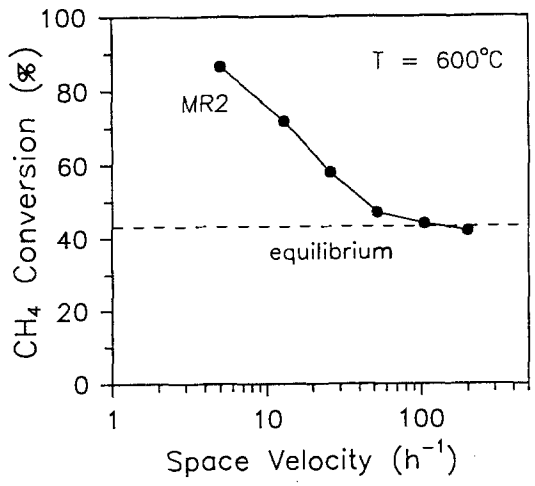

Fig. 6. Effect of space velocity on methane conversion obtained in reactor MR2 under CH_4/O_2 reaction conditions. (Reaction temperature 600°C.)

methane conversion increases beyond the equilibrium value.

Another interesting observation concerning the operation of the membrane reactor was that the carbon dioxide conversion did not increase monotonically with decreasing space velocity, as methane conversion did. In fact, the CO_2 conversion decreased initially to a value lower than the equilibrium conversion and only at sufficiently low space velocities did it increase to values higher than equilibrium. This is believed to be due to the effect of the water–gas shift reaction [4], whereas removal of hydrogen shifts equilibrium to the left.

The methane conversion obtained in the membrane reactor in the CH_4/O_2 reaction was lower compared to that in the CH_4/CO_2 reaction. This was expected since the hydrogen permeance of the membrane was decreased to about 50% of its original value because of the densification phenomenon.

4. Conclusions

The main conclusions of the present study of dry reforming and partial oxidation of methane in a membrane reactor are the following:

– SiO_2 membranes exhibit satisfactory stability and permselectivity under conditions of methane reforming employing CH_4/O_2 and CH_4/CO_2 feeds.

– After exposure to water vapor contained in the feed or produced during reaction, the permeance of SiO_2 membranes stabilizes to a lower value, which is approximately 50% of the initial permeance.

– SiO_2 membranes on Vycor tubes have very low hydrogen permeance, which makes them the slow step determining the performance of the membrane reactor. Therefore, significant improvement in methane conversion can be achieved only at sufficiently low space velocities.

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