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 (CO2) reforming and partial oxidation of methane have been investigated in a membrane reactor. The membrane is composed of a dense thin silica (SiO2) film supported on porous Vycor tubes and was synthesized by chemical vapor deposition. The hydrogen permeance of the membrane was 0.2-0.3 cm3/(cm2 min atm) at 600°C combined with a H2/N2 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 H2O, but otherwise exhibited excellent stability under reaction conditions.

Keywords: membrane reactors; methane reforming; methane oxidation

1. Introduction

The reaction of dry (CO2) reforming of methane is an alternative route for the production of synthesis gas with a H2/CO ratio close to unity. A foreseeable application of the CH4/CO2 reaction is in chemical energy transmission systems, which utilize solar or other renewable energy sources [1]. The reforming of CH4 with CO2 is a highly endothermic reaction,

\[ \text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2, \quad \Delta H = +247 \text{ kJ/mol}, \]  

and very high temperatures (> 800°C) are required for complete conversion of methane [2]. Simultaneous reforming of CH4 with CO2 and H2O has often been applied in industrial practice in order to produce synthesis gas with a desirable H2/CO ratio [2].

The partial oxidation of methane to synthesis gas has been attracting interest in recent years as an alternative to H2O and CO2 reforming:

\[ \text{CH}_4 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{CO} + 2\text{H}_2, \quad \Delta H = -36 \text{ kJ/mol}. \]  

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]:

(i) \( \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \)
(ii) \( \text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2 \)
(iii) \( \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \)  

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 CO2 and of partial oxidation of methane. This membrane reactor consists of a dense thin silica (SiO2) 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 SiCl4 and H2O 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 cm³/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:

\[ Q = \frac{Fx}{(A \Delta P)} \]

where: \( Q \) is the permeance (cm³/(cm² min atm)), \( F \) the gas flow rate (cm³/min), \( x \) the molar fraction of permeated gas (kept below 10%), \( A \) the geometric area of the membrane (cm²) and \( \Delta P \) 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/SiO₂ 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.

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, \( Q_{H2} \), 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 CO₂

The membranes were found to retain their permeance and selectivity characteristics for several days of operation under conditions of methane reforming with CO₂. 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 CH₄ and CO₂ 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>
<thead>
<tr>
<th>Reactor</th>
<th>Length (cm)</th>
<th>( Q_{H2} ) (cm³/(cm² min atm))</th>
<th>Selectivity* ( \frac{H2}{N2} )</th>
<th>( E_{act} ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MR1</td>
<td>10.5</td>
<td>0.22</td>
<td>300</td>
<td>17</td>
</tr>
<tr>
<td>MR2</td>
<td>25.0</td>
<td>0.32 (0.15)</td>
<td>200</td>
<td>16 (24)</td>
</tr>
</tbody>
</table>

* \( T = 600°C \).

* After exposure to water containing atmosphere for 10 days at 700°C.