Syngas Production

Conversion of Methane to Syngas by a Membrane-Based Oxidation–Reforming Process**

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Rational use of abundant natural gas is gaining importance as petroleum oil reserves are diminishing. Methane, the main component of natural gas, can be converted to liquid fuels, hydrogen, and other value-added chemicals through a syngas intermediate, a mixture of CO and H_2. Currently, syngas is produced by reacting methane with steam at high temperatures and pressures. This process is very energy- and capital-intensive, as the reaction is highly endothermic. An alternative process to produce syngas is the partial oxidation of methane (POM) with pure oxygen in the presence of a catalyst.[1,2] The exothermic nature of POM makes the process attractive in terms of energy consumption. The other advantage of POM over the steam-reforming process is that the H_2/CO ratio of ~2 of the as-produced syngas is highly suitable for subsequent conversion to environmentally friendly liquid fuels through a Fischer–Tropsch process. The main difficulty with POM lies in the consumption of large quantities of expensive pure oxygen that is produced by the cryogenic separation of air. A recent development in syngas production technology is the use of oxygen-permeable dense ceramic membranes[3,4] integrating the oxygen separation and POM processes in a single space.[5] The formidable problem for this approach is that the membrane must be chemically and mechanically stable at elevated temperatures in a large oxygen gradient with one side of the membrane exposed to oxidizing atmosphere (air) and the other side to the reducing atmosphere (the mixture of hydrogen and carbon monoxide). Herein we propose a two-stage membrane reactor, as depicted in Figure 1a, which may reduce the requirement on the stability of the membrane materials. In this reactor, part of the methane is converted into CO_2 and H_2O by reaction with oxygen permeated through the membrane from the air, and the resultant mixture is transferred to a catalyst bed where the remaining methane is reformed to syngas.

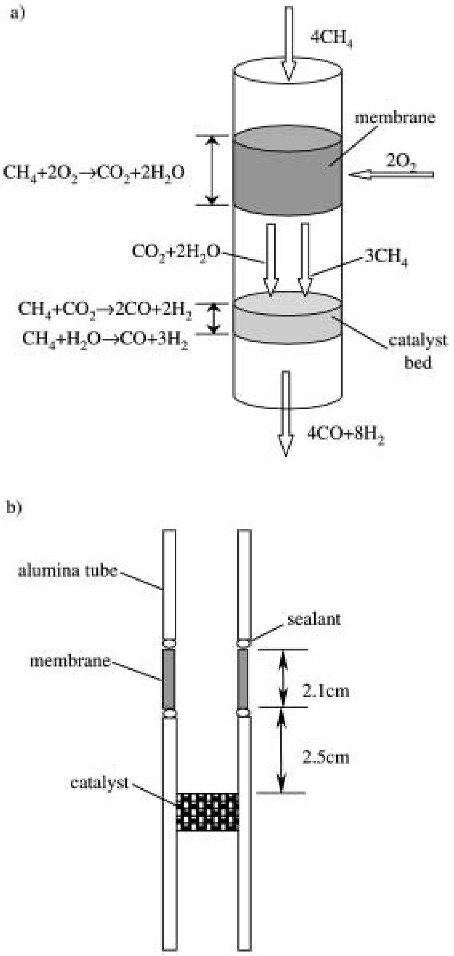

Figure 1. Schematic diagrams of two-stage oxygen-permeable membrane reactor for syngas production. a) The chemical conversions in different areas of the membrane reactor; b) the construction and dimensions of the reactor.

A ceramic composite of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (97.5 mol %) and Co_3O_4 (2.5 mol %) was used to construct a membrane reactor. The major phase of the composite was intended for separating oxygen from air[6] and the minor phase at the surface for catalyzing the reaction of methane with permeated oxygen;[7] in terms of mechanics, small cobalt oxide particles embedded in the bulk may also reinforce the major phase. The dense tubular membrane of the required phase composition was prepared by extrusion followed by sintering at 1100 °C for 10 h. A γ-Al_2O_3-supported catalyst was prepared with a nickel loading of 12.5 wt % and sieved to 40 ~ 60 mesh.[8] The reactor consisted of a membrane of length 2.14 cm, inner diameter 0.76 cm (membrane surface area 5.10 cm^2), and wall thickness 0.13 cm, and a catalyst bed containing 0.2 g Ni/γ-Al_2O_3; the membrane tube and the catalyst bed were separated by a distance of 2.5 cm (see Figure 1b). In order to improve the flow pattern in the reactor, an alumina cylinder was placed inside the reactor (not shown in Figure 1b for the sake of simplicity). The reactor was sealed with glass rings at 950 °C then cooled to 900 °C and maintained at that temperature. Pure methane was fed into the tubular reactor while air was simultaneously led

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over the shell side. The effluent was analyzed by on-line gas chromatography (Varian 3400), in which H_2, O_2, N_2, CH_4, and CO were separated by a 5-Å molecular sieve column and CO_2 by GDX-502 column, and H_2O was determined with a hydrogen atomic balance.

The performance of the reactor is shown in Figure 2. It can be seen that after a short activating period of about one hour, both the methane conversion and CO selectivity exceed 95 %.

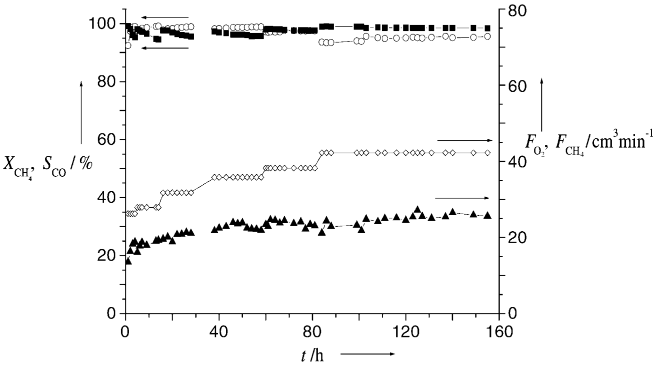

Figure 2. Methane conversion (X_{CH_4}, ○) and CO selectivity (S_{CO}, ■), and methane feeding rate (F_{CH_4}, ◇) and O_2 permeation rate (F_{O_4}, ▲) in a membrane reactor. Conditions: $T = 900\,°C$; $p = 1$ atm; membrane surface area $= 5.1$ cm^2.

The CO selectivity does not change very much with variation of the methane feeding rate. The throughput conversion of methane decreases slightly with increasing methane feeding rate. When methane was fed at a rate of ~38 cm^{3}min^{-1}, the reactor attained a desirable state: syngas production rate ~20 cm^{3}cm^{-2} membrane surface min^{-1}, equivalent O_2 permeation flux ~4.6 cm^{3}cm^{-2}min, H_2/CO ~1.8, CO selectivity ~98 %, methane throughput conversion ~97 %. After the reactor had been operated at 900 °C for ~400 h, the experiment was voluntarily terminated, and the membrane remained almost intact.

In order to establish the reaction pathways we performed experiments with blank tubular reactors in which the Ni/γ-Al_2O_3 catalyst was either simply left out or replaced with γ-Al_2O_3 powder. For the former configuration comprising a tubular membrane with an inner surface area of 4.32 cm^2, when methane was fed into the reactor at a rate of 19.4 cm^{3}min^{-1} at 900 °C, the effluent was found to contain a large quantity of CO_2 (15.3 %), H_2O (35.1 %), and unreacted CH_4 (52.9 %) as well as small amounts of CO (1.2 %), H_2 (1.8 %),C_2H_4 (1.8 %), C_2H_6 (0.4 %), O_2 (0.03 %), and N_2 (0.2 %). For the latter configuration comprising a tubular membrane with a surface area of 4.58 cm^2, the dominant components in the effluent remained to be CO_2 (14.6 %), H_2O (34.0 %), and CH_4 (45.3 %). Similar results were reported by Balachandran et al. who found that in an $SrFeCo_{0.5}O_x$ tubular membrane reactor (membrane surface area 8 cm^2) in the absence of a reforming catalyst, the permeated oxygen reacted with methane, yielding CO_2 and H_2O.[5] The presence of CO_2, H_2O, CH_4, and O_2 were also reported by Tsai et al. in the effluent of an $La_{0.2}Ba_{0.8}Fe_{0.8}Co_{0.2}O_{3-\delta}$ disk-shaped membrane reactor (membrane surface area 0.28 cm^2) without a catalyst.[9] All these observations combined allow us to establish the reaction pathways for syngas formation in the two-stage reactor. At one side of the membrane, which is in contact with air, oxygen molecules are incorporated as oxide ions into the bulk of the membrane. At the other side of the membrane, methane molecules adsorb and partly react with the permeated oxide ions to yield CO_2 and H_2O, a reaction catalyzed by the Co_3O_4 embedded in the membrane. The mixture of unreacted methane, CO_2, and H_2O is then transferred to the Ni/γ-Al_2O_3 catalyst bed and converted into syngas.

The membrane-based two-stage reactor has a number of important features. The two-stage configuration poses less stringent limitations on membrane materials than the reactor in which the catalyst is located inside the membrane.[5] In the former case, where the membrane is exposed to the mixture of CO_2, H_2O, and CH_4, the oxygen partial pressure p_{O_2} is calculated to be 10^{-13}–10^{-14} bar based on the thermodynamic data for the reaction $CO + \frac{1}{2}O_2 \Leftrightarrow CO_2$.[10] In the real situation, the oxygen partial pressure is higher and a small amount of oxygen is present in the effluent, indicating that the reaction does not attain the equilibrium state. In the latter case, where the catalyst is within the membrane and the membrane is in contact with H_2 and CO, the p_{O_2} is around 10^{-19} bar.[11] The formation of coke on the catalyst in the two-stage reactor is also much less severe than that in the single-stage reactor in which the reforming catalyst is in intimate contact with the membrane. In terms of the strategy of developing and operating the membrane reactor, the two-stage configuration allows us to distribute the overall risk among the two separate components. Such a configuration is also ideal in terms of energy consumption, for the heat released by the deep oxidation of part of the methane at the membrane stage of reactor is supplied to the catalyst bed where endothermic reforming reactions take place. The as-produced syngas is desirable for applications, because it contains no nitrogen and has a lower H_2/CO ratio than that obtained by the regular steam reforming. The emission of NO_x is eliminated due to the use of an oxygen-permeable membrane that is impervious to nitrogen. Although the membrane-based two-stage reactor shows promise for applications, technical challenges remain in identification of membrane materials with long-term mechanical and chemical stabilities, development of reactor fabrication techniques, and scale-up of the reactors to industrial modules.

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