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Syngas Production Using an Oxygen-Permeating Membrane Reactor with Cofeed of Methane and Carbon Dioxide

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Abstract: CH_4-CO_2-O_2 reforming to syngas in a novel $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ oxygen-permeable membrane reactor using LiLaNiO/γ-Al_2O_3 as catalyst was successfully reported. Excellent reaction performance was achieved with around 92% methane conversion efficiency, 95% CO_2 conversion rate, and nearly 8.5mL/min.cm^2 oxygen permeation flux. In contrast to the oxygen permeation model with the presence of large concentration of CO_2 (under such condition the oxygen permeation flux deteriorates with time), the oxygen permeation flux is really stable under the CH_4-CO_2-O_2 reforming condition.

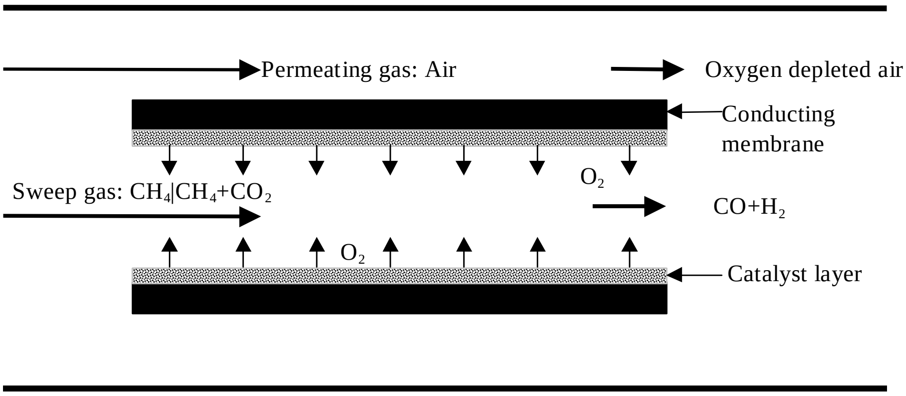
Keywords: Ceramic membrane reactor, oxygen permeation, methane, syngas.

Methane utilization has been drawing considerable attention recently due to the large amount of natural gas available to be upgraded and the worldwide demand for low-cost transportation fuels[1,2]. Among the many conversion routes, partial oxidation of methane (POM) to syngas proved a new way for the potential alternative to today's industrial steam reforming processes. However, although very active catalysts for the POM to syngas have been reported, large-scale plants have not yet been constructed. A large adiabatic temperature rise at the front of the co-bed easily causes reactor runaway. A second drawback is that pure oxygen must be used as the oxidant, so a costly oxygen production plant is needed.

Ceramic oxygen membrane reactors (COMR) make the POM and the oxygen separation into one operation, thus reduce the capital cost significantly. Also the hot spots in the catalyst bed can be effectively controlled due to the gradual oxygen supply through a membrane (as shown in **Figure 1**). Significant progress has been made in the development of COMR in the latest decade[3]. However, some problems also emerged. For examples, the membrane reactor would easily break into pieces in case of sudden sharp temperature change, the industrial scale of the membrane reactor system is mainly determined by its oxygen permeability, which usually is limited.

On the other hand, it is well known that CO_2 reforming is a light endothermal process. As to methane transformation using COMR, the advantages of mixed reforming (CH_4-CO_2-O_2) over traditional one (CH_4-O_2) include: i) moderating the temperature variation in the membrane reactor, so beneficial to the integrity of the membrane, ii) reducing the membrane scale for the reducing in O_2/CH_4 ratio. However, no reports in open literature were available about such research work due to the general belief that the membrane material is unstable in the presence of CO_2. In this letter, we initiate the report on the syngas production with an oxygen-permeating membrane reactor with the cofeed of methane and carbon dioxide.

Figure 1. Schematic diagram of a tube-shape dense membrane reactor



A novel mixed conducting material $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCFO) developed by our group was used for the construction of the membrane reactor[4]. Disk-shape membrane was used for the reaction test, detailed setup of the membrane reactor was reported elsewhere[5]. LiLaNiO/γ-Al_2O_3 was used as the catalyst, the preparation procedure has been described previously[6]. Products of the reaction were analyzed by gas chromatography with a TCD detector. The oxygen permeation flux was calculated according to carbon balance and oxygen balance. The membrane and catalyst was submitted to XRD, SEM, O_2-TPD, H_2-TPR characterization or oxygen permeation studies.

The XRD results show that BSCFO has a cubic perovskite structure with crystal parameter a=3.9795Å. Pure phase perovskite was sustained at 850°C under the oxygen partial pressure of $1\sim10^{-6}$atm, demonstrating the high phase stability of the materials.

Large amounts of alkaline salt metal ions Sr^2+ and Ba^{2+} were present in BSCFO. Ba and Sr elements can easily combine with CO_2 to form carbonates. Since the carbonates are oxygen impermeable, it is generally believed that CO_2 in the permeating or sweeping gas is fatal to the oxygen permeation of the material. For BSCFO membrane, it was found that the oxygen permeation flux changed little in the presence of minor amount of CO_2 (less than 1%) in the air (permeating gas) at a temperature higher than 850°C. Temperature dependence of oxygen permeation flux (J_{O2}) of BSCFO in the presence of large amount of CO_2 (30%) in the sweeping gas [J_{O2}(air/He+CO_2)] is shown in **Figure 2**, the permeation flux without CO_2 in the sweeping gas [J_{O2}(air/He)] is also given out for comparison. At 1000°C, J_{O2} (air/He+CO_2) was only slight lower than J_{O2}(air/He), but with the decrease of temperature, J_{O2}(air/CO_2+He) decreased much more sharply than J_{O2}(air/He). Almost no oxygen flux was detected at 850°C for BSCFO membrane with CO_2 in the sweeping gas. Although, at 900°C J_{O2}(air/He+CO_2) still reached about 0.65mL/cm^2 initially, the permeation flux deteriorated with time until no oxygen permeation flux was detected.

Figure 2. Influence of CO_2 on oxygen permeation flux, air as feed gas at 150mL/min, sweep gas, a: He at 50mL/min, b: 30% CO_2 at 50mL/min

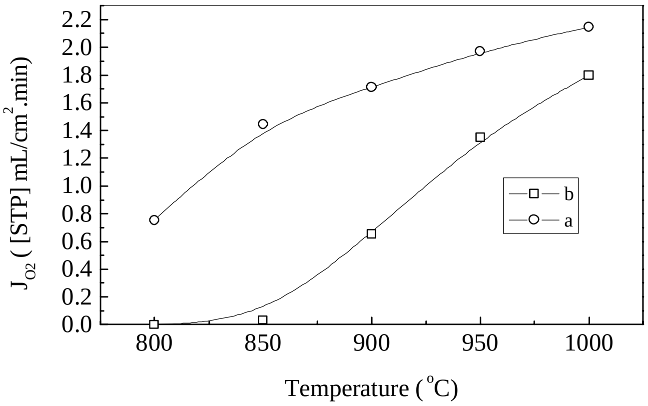
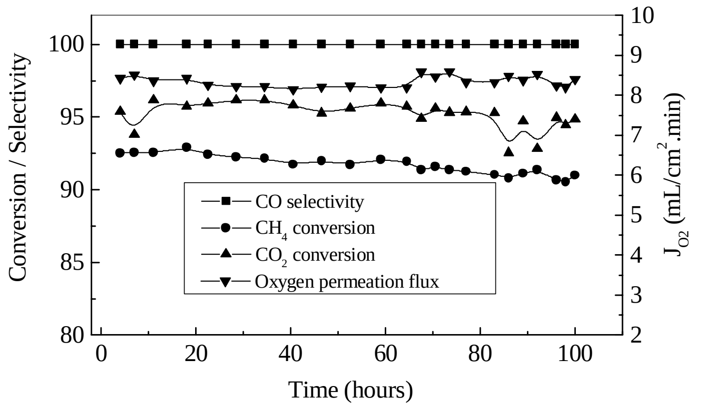


Figure 3. Methane and CO_2 conversion, CO selectivity and O_2 permeation flux in the membrane reactor at 900°C in CH_4-CO_2-O_2 reforming model



For the test of CH_4-CO_2-O_2 reforming into syngas in the membrane reactor, 300mg LiLaNiO/γ-Al_2O_3 attached to the inner surface (1cm^2) of the membrane reactor, was used as the catalyst. CH_4-CO_2-O_2 reforming was conducted at 900°C with the flow rate of diluted methane (50%He-50%CH_4) at 53mL/min and CO_2 at 8.8mL/min (serve as sweeping gas). The results are shown in **Figure 3**. Methane conversion efficiency was around 92%, and CO_2 conversion rate reached about 95%. During the 100h's operation, relatively stable methane conversion efficiency was achieved, and the methane conversion rate dropped only about 1.5 percent. H_2 to CO ratio was found around 1.46. The results demonstrated the feasibility of methane conversion to syngas in the novel membrane reactor at the presence of CO_2.

The measured oxygen permeation flux was around 8.5mL/min. Under the partial oxidation condition (CH_4+O_2) at 900°C, the oxygen permeation flux reached about $10 mL/cm^2$. It demonstrated that, under reaction condition with the presence of catalyst, the influence of high concentration of CO_2 in the sweeping gas was little on the oxygen permeation flux. The reason why CO_2 had a significant effect on the oxygen permeability and stability under the oxygen measurement model (without the existence of reforming catalyst), but negligible effect under CH_4-CO_2-O_2 reforming condition (with reforming catalyst) is still not clear. One possible explanation is that, under CH_4-CO_2-O_2 reforming condition, due to the increase in the oxygen partial pressure gradient across the membrane (air/syngas oxygen partial pressure gradient), the oxygen flux increased sharply, thus reducing the probability of CO_2 reaching the membrane surface where the carbonate formation took place. Further investigation to testify such assumption is just underway.

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