Thermal Decomposition of Carbon Dioxide Coupled with POM in a Membrane Reactor

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In this study, we proposed coupling the thermal decomposition of carbon dioxide ($CO_2 \rightarrow CO + 1/2O_2$) with the partial oxidation of methane (POM) to syngas ($CH_4 + 1/2O_2 \rightarrow CO + 2H_2$) in a dense mixed-conducting membrane reactor, in which the reaction of CO_2 decomposition took place in one side of the membrane and the POM reaction occurred in the other side of the membrane simultaneously (or methane reacted with oxygen that was permeated through the membrane from the CO_2 decomposition, to produce H_2 and CO over supported transition metal catalysts). A perovskite-type oxygen-permeable membrane of $SrCo_{0.4}Fe_{0.5}Zr_{0.1}O_{3-\delta}$ (SCFZ) was used for the membrane reactor. The effects of temperature and the feed flow rates of CO_2 and CH_4 on the reaction performance of the SCFZ membrane reactor were investigated. It was found that the CO_2 conversion increased with increasing the temperature and decreased with increasing the feed flow rates of CO_2 or with decreasing the feed flow rates of CH_4. At 1173 K, the CO_2 conversion reached about 11.1%, and the CH_4 conversion, CO selectivity, and the ratio of H_2/CO were 84.5%, 93%, and 1.8, respectively. © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 2545–2550, 2006

Keywords: carbon dioxide, thermal decomposition, methane, syngas, membrane reactor

Introduction

Carbon dioxide (CO_2) is considered as the main contributor to the warming of the global atmosphere.[1] Many researchers have aimed at how to recover and sequestrate CO_2. One alternative process would be the thermal decomposition of carbon dioxide (TDCD) to CO and O_2 because CO can be utilized as a raw material in the synthesis of important basic chemical products and oxygen can be used for many cases. However, this reaction is a highly endothermic reaction ($2CO_2 \rightarrow 2CO + O_2$ $\Delta H^0_{298} = 552$ kJ/mol), takes place only at high temperature, and is limited by the thermodynamic equilibrium. Therefore, this reaction is not easy to be realized in conventional fixed-bed reactors. To date a few research groups have attempted to apply oxygen-permeable ceramic membrane reactors to realize this reaction.[2-4] The use of membranes in chemical reactors is motivated principally by the equilibrium shift, leading to a higher conversion or selectivity in a single pass. In 1986, Nigara et al.[2] first reported use of a ZrO_2-CaO membrane reactor for the TDCD at high temperature and observed that the conversion of CO_2 reached 21.5% at 1954 K (the corresponding thermodynamic equilibrium conversion of 1.2%) by using CO as a sweep gas in the permeation side. But it should be noted that the net conversion in the whole system was not changed as much because CO_2 was simultaneously produced by the reaction between the permeated O_2 and CO in the permeate side.

Subsequently, in 1993, Itoh et al.[3] studied the TDCD with a yttria-stabilized zirconia (YSZ) membrane in the temperature range of 1584-1782 K using argon as a sweep gas. Since argon cannot supply enough low oxygen partial pressure in the permeate side, the highest conversion of CO_2 obtained was about 0.6%. Recently, Fan et al.[4] investigated the TDCD in a mixed-conducting oxide ($SrFeCo_{0.5}O_x$) membrane reactor and found that the conversion of CO_2 was 10% at 1213 K when methane was used as a sweep gas in the permeate side. Although Fan et

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al.[4] made progress in the decrease of the reaction temperature, which was much lower than those reported previously in literature,[2,3] the combustion reaction of methane still occurred simultaneously in the permeate side and thereby CO_2 was produced at the same time.

As regards the partial oxidation of methane (POM) to syngas ($CH_4 + 1/2O_2 \rightarrow CO + 2H_2$ $\Delta H^0_{298} = -36$ kJ/mol), it has been extensively studied in mixed-conducting oxide (having both electronic and oxygen ionic conductivity at high temperature, typically above 973 K) dense membrane reactors (DMR) for over a decade,[5-11] since DMRs can offer several advantages as compared to conventional fixed-bed reactors. In the present-developed DMRs for POM reaction, air is used as the oxygen source. Herein we propose coupling the TDCD with the POM in a DMR, as illustrated in Figure 1, in which the TDCD takes place in one side of the membrane and the POM occurs simultaneously in the other side of the membrane (Figure 1a), or more clearly, methane reacts with oxygen, which is permeated through the membrane from the CO_2 decomposition, to produce H_2 and CO with a favorable ratio of 2:1 over supported transition metal catalysts (Figure 1b). For this process, on the one hand, CO_2 is used as the oxygen source for the POM reaction; on the other hand, the TDCD coupled with the POM could produce H_2 and more CO, which are important chemicals for the methanol synthesis, Fischer-Tropsch reactions, or fuels.

In our previous research, we developed a new series of perovskite-type mixed-conducting oxides of $SrCo_{0.4}Fe_{0.6-x}Zr_xO_{3-\delta}$ ($0 \leq x \leq 0.2$).[12] The incorporation of Zr and its effect on the crystal chemistry, oxygen permeation, and structural stability of $SrCo_{0.4}Fe_{0.6-x}Zr_xO_{3-\delta}$ were studied. It was found that substitutions of 10 mol % Zr were considered to be enough for the structural stability with higher oxygen permeability. Therefore, the perovskite-type oxide of $SrCo_{0.4}Fe_{0.5}Zr_{0.1}O_{3-\delta}$ (SCFZ) was applied to construct the membrane reactor.

Experimental Section

Membrane preparation

$SrCo_{0.4}Fe_{0.5}Zr_{0.1}O_{3-\delta}$ powders were synthesized by the solid-state reaction method. The required amounts of $SrCO_3$, Co_2O_3, Fe_2O_3, and monoclinic ZrO_2 were mixed and milled for 24 h, followed by calcinations in air at 1223 K for 4 h with heating and cooling rates of 2 K/min. The calcined powders were pressed into disks of 16 mm diameter with an oil pressure of 200MPa and then sintered in air at 1473K for 5 h to form dense membranes. The sintered membranes were polished before being used in experiments. The disk-shaped membranes with thickness of 1.50 mm were used for the POM study. Powder XRD data were collected on a Bruker D8 Advance diffractometer with Cu Kα radiation. The diffraction patterns were collected at room temperature by step scanning at an increment of 0.05°/s in the range of $20° \leq 2\theta \leq 80°$.

Catalyst preparation

The 4.77 wt% NiO/Al_2O_3 catalysts used in our experiments were prepared by the impregnation technique. An appropriate amount of γ-Al_2O_3 (20-40 mesh) was impregnated by an aqueous solution of $Ni(NO_3)_2 \bullet 6H_2O$ (the Second Chemical Industry of Shanghai; purity of 99.9%). After being dried at 333 K for 24 h, the catalytic precursors were calcined in air at 1023 K for 4 h. The color of the particles turned from green to dark blue after calcination. Finally, the catalyst particles were sieved to 60-80 mesh. The catalysts were pretreated in a 1:1 mixture of H_2 and He for 3 h at 973 K before use.

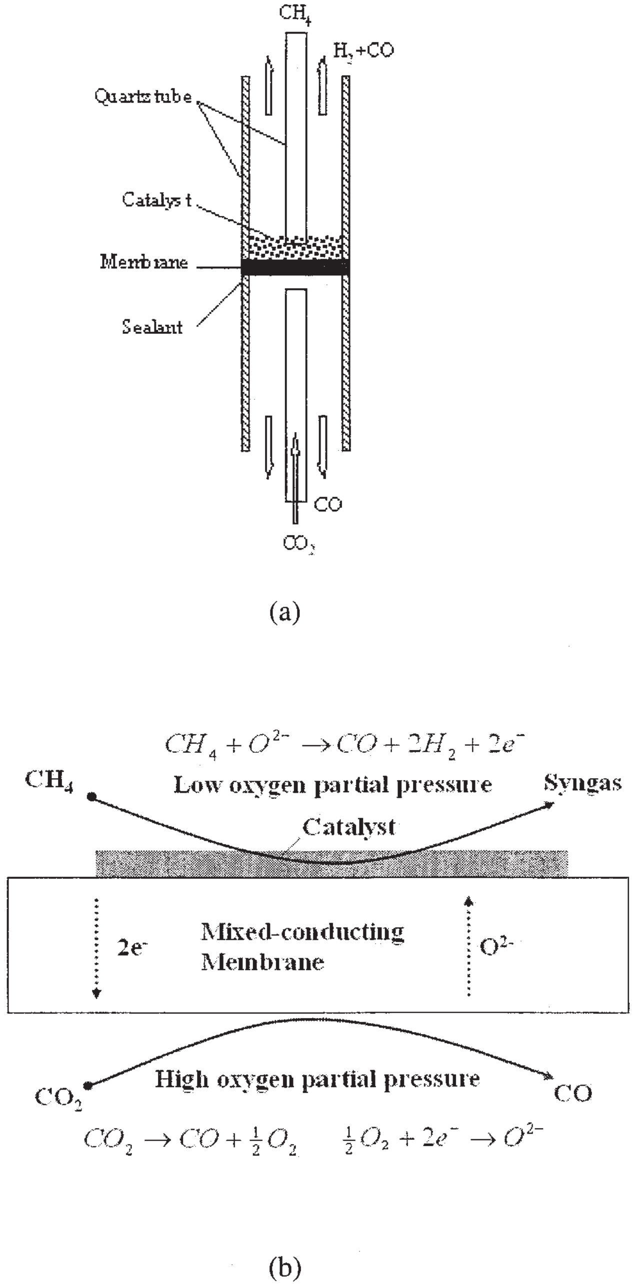

Figure 1. Membrane reactor for coupling thermal decomposition of CO_2 with partial oxidation of methane to syngas.

(a) Construct of the membrane reactor; (b) The mechanism of the membrane reactions.

Membrane reactor setup and experimental procedures

The reactor module (Figure 2a) and the experimental apparatus (Figure 2b) used in this study, to some extent, were similar to those reported previously by our lab.[10,13] A disk-shaped SCFZ membrane between two gold rings (0.05 mm thickness) was held in place by two quartz tubes (6 mm ID, 12 mm OD). The gold rings were the same dimensions as the quartz tubes, which left an effective area of about 0.283 cm^2 for oxygen permeation. An inner quartz tube (2.3 mm ID, 4.3 mm OD) was used to introduce a gas mixture of CO_2 and helium to the lower chamber, while the other quartz tube was used to introduce a gas mixture of CH_4 and Ar to the upper chamber. The clearance of the inner quartz tube and membrane surface was about 2~3 mm. The 4.77wt%Ni/γ-Al_2O_3 catalysts of 0.09g were packed on the surface of the membrane in the upper chamber. Before the experiments were performed, the temperature around the SCFZ membrane was held at 1313 K for 4 h to ensure the softening of the gold rings. Gas leakage, if present, could be detected by monitoring the argon concentration in the effluent from the underchamber. The inlet gas flow rates were controlled by mass flow controllers (Model D07–7A/ZM), which were calibrated by a bubble flowmeter. Both sides of the membrane were maintained at atmospheric pressure. A programmable temperature controller (Model AI-708PA) monitored the temperature around the membrane. The effluent streams were analyzed by two on-line gas chromatographs (Model Shimadzu GC-7A and Model SP-6800) with about 1 cm^3 sample loop. A 2-m 5A molecular sieve column was used for the separation of H_2, O_2, CH_4, and CO, and a 1-m TDX-01 column was used for the separation of CO_2. The chromatograph with the 5A molecular sieve column was operated under the current of 180 mA and the attenuation of 1, under which a trace amount of oxygen (>1 Pa) could be detected. The analysis was checked by the carbon balance, which was within 5% for all reaction experiments. The oxygen flux through the dense SCFZ membrane could be calculated by the mass balance on the basis of the components of CO, H_2, CH_4, CO_2, O_2, and H_2O in the exit stream from the upper chamber, which is as follows[10]:

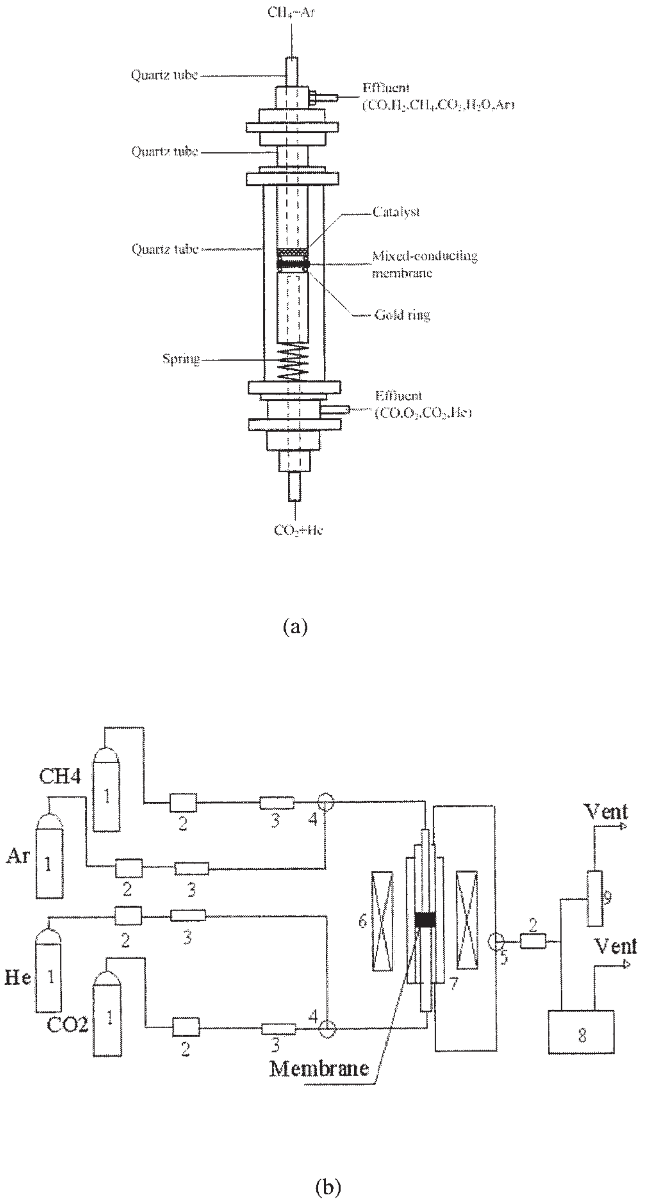

Figure 2. Reactor module and experimental apparatus.

(a) The reactor module; (b) The experimental apparatus (1: gas cylinder, 2: gas dryer, 3: mass-flow controller, 4: mixer, 5: six-way valve, 6: electric furnace, 7: membrane reactor, 8: chromatogram, 9: bubble flowmeter).

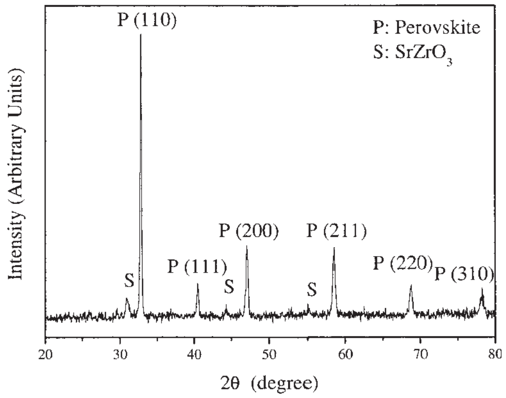

Figure 3. XRD pattern of SCFZ oxide powder calcined at 1223 K.

$$F_{O_2\text{inlet}} = F_{O_2\text{outlet}} + \frac{1}{2}F_{CO} + F_{CO_2} + F_{CH_4\text{inlet}} - F_{CH_4\text{outlet}} - \frac{1}{2}F_{H_2}$$

where F_i is the flow rate of species i, in mol/s.

Results and Discussion

Characterization of the membrane materials

The crystal phase of the SCFZ oxide observed by XRD was of a cubic perovskite structure along with a trace of the $SrZrO_3$ phase (Figure 3), which was attributed to a solid-state reaction between ZrO_2 and perovskite oxide at elevated temperature.[12] The relative densities of the sintered membranes determined by the Archimedes method exceeded 90% of the theoretical density.

Effect of temperature

We first investigated the performance of the membrane reactor in the temperature range of 1123-1223 K. CO_2 diluted

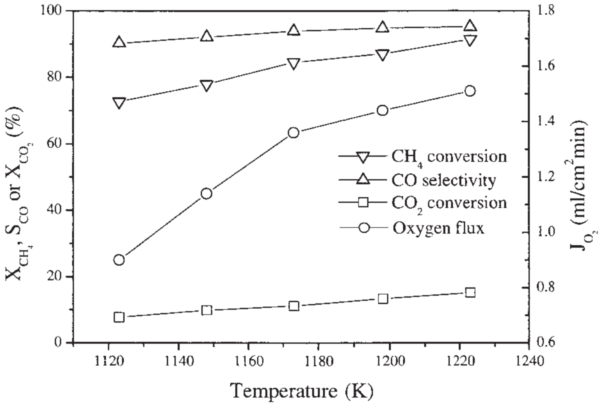

Figure 4. Temperature dependences of the conversion of CO_2 (X_{CO_2}), oxygen flux (J_{O_2}), the conversion of CH_4 (X_{CH_4}), and the selectivity of CO (S_{CO}).

(Feeding conditions: in the lower chamber 6 cm^3 (STP) min^{-1} CO_2 and 24 cm^3 (STP) min^{-1} He; in the upper chamber 1 cm^3 (STP) min^{-1} CH_4 and 19 cm^3 (STP) min^{-1} Ar.)

with helium (He) (CO_2 of 6 cm^3 (STP) min^{-1} and He of 24 cm^3 (STP) min^{-1}) was fed into the lower chamber of the membrane reactor, while CH_4 diluted with argon (Ar) (CH_4 of 1 cm^3 (STP) min^{-1}and Ar of 19 cm^3 (STP) min^{-1}) went into the upper chamber. As shown in Figure 4, both conversions of CO_2 and CH_4 increase with increasing temperature. This is mainly attributed to the oxygen permeability of the SCFZ membrane. Generally, the rate at which oxygen permeates through a mixed-conducting dense membrane is essentially controlled by two factors: the rate of oxygen diffusion across the membrane bulk and the rate of interfacial oxygen exchange on either side of the membrane.[14] On the one hand, the rate of oxygen permeation through the bulk of the SCFZ membrane increased with increasing temperature according to the Wagner equation.[15] On the other hand, because of the presence of CO_2 decomposition and the oxidation of methane, respectively, in either side of the SCFZ membrane, the rate of interfacial oxygen exchange on either side of the SCFZ membrane increased, or the oxygen partial pressure gradient across the SCFZ membrane was enhanced. Therefore, the overall rate of oxygen permeation through the SCFZ membrane under the reaction atmosphere increased with increasing temperature, as shown in Figure 4.

In terms of the thermodynamic equilibrium, the increase of the oxygen permeation rate is beneficial to both CO_2 decomposition and POM reactions (Figure 1b). Thus, high conversion of CO_2 can be obtained. From 1123 K to 1223 K, the conversion of CO_2 was from 7.7% to 15.1% (Figure 4), which were higher than the best values reported in the literature so far.[4] Meanwhile, the conversion of CH_4 increased from 72.7% to 91.4%; the CO selectivity increased slightly and exceeded 90% (Figure 4). The effluent gases of the upper chamber consisted of CO, H_2, unreacted CH_4, and a small amount of CO_2 and H_2O. For example, at 1173 K, the CH_4 conversion, CO selectivity, and ratio of H_2/CO were 84.5%, 93%, and 1.8, respectively, and the composition of the effluent was CO of 29.2%, H_2 of 52.6%, CO_2 of 2.2%, H_2O of 10.2%, and unreacted CH_4 of 5.7% (not including the diluting argon gas).

Effect of CH_4 feed rate

The effect of the CH_4 feed rate on the membrane reaction performance at 1173 K is shown in Figure 5. The CH_4 feed rate was changed from 1 to 3 cm^3 (STP) min^{-1} in the upper chamber (total CH_4 and Ar feed rate was kept at 20 cm^3 (STP) min^{-1}), while the CO_2 feed rate was kept constant (CO_2 of 6 cm^3 (STP) min^{-1} and He of 24 cm^3 (STP) min^{-1}) in the lower chamber. The CH_4 conversion decreased with increase in the CH_4 feed rate; on the contrary, CO selectivity, oxygen flux, and CO_2 conversion increased with increasing the CH_4 feed rate. This phenomenon suggests that the POM reaction in the membrane reactor follows the combustion and reforming mechanism.[16] That is to say, all permeated oxygen is reacted with methane to form carbon dioxide and steam first, and then residual methane is reformed by steam and carbon dioxide to form syngas. When the methane feed increased, the increased methane reacted with CO_2 and H_2O to form syngas, which would result in the increase of CO selectivity. At the same time, the oxygen permeation flux increased due to the decrease in partial oxygen pressure near the surface of the membrane, which would lead to the increase in the CO_2 conversion.

Effect of CO_2 feed rate

The effect of the CO_2 feed rate on the performance of the membrane reactor was observed at 1173 K. The CO_2 feed rate was changed from 6 to 15cm^3 (STP) min^{-1} in the lower chamber (total CO_2 and He feed rate was kept at 30 cm^3 (STP) min^{-1}), while the CH_4 feed rate was kept constant (CH_4 of 1 cm^3 (STP) min^{-1} and Ar of 19 cm^3 (STP) min^{-1}) in the upper chamber. With increasing the CO_2 feed rate, the CO_2 conversion decreased, while the CH_4 conversion first increased slightly and then approached to a constant, which was about 92% (Figure 6). For a mixed-conducting membrane, if it is operated at a given temperature and a constant sweep-gas rate in the permeation side, the oxygen permeation flux is finite.[17] As shown in Figure 6, the oxygen permeation flux increases rapidly with increasing the CO_2 feed rate from 6 to 12 cm^3 (STP) min^{-1}, but with further increasing the CO_2 feed rate it levels off to a constant value of 1.5 cm^3 (STP) cm^{-2} min^{-1}.

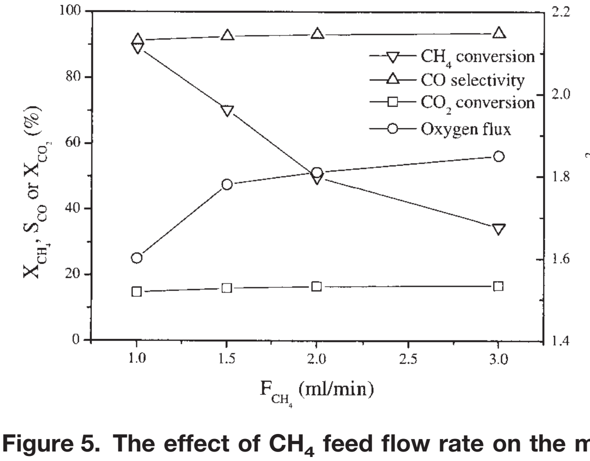

Figure 5. The effect of CH_4 feed flow rate on the membrane reaction performance.

(Feeding conditions: in the upper chamber 20 cm^3 (STP) min^{-1} (CH_4 + Ar); in the underchamber 6 cm^3 (STP) min^{-1} CO_2 and 24cm^3 (STP) min^{-1} He, T = 1173 K.)

Although more oxygen could be produced from the CO_2 decomposition with increasing the CO_2 feed rate in the lower chamber, not all of the produced oxygen could permeate through the membrane to the upper chamber due to both the oxygen permeation capability of the membrane and the constant CH_4 feed rate in the upper chamber; thus, the excess oxygen could react with CO produced from the CO_2 decomposition to recreate the CO_2. Therefore, the CO_2 conversion decreased with increasing the CO_2 feed rate.

This suggests that the operation of the membrane reactor should be at a low CO_2 feed rate to avoid the low CO_2 conversion. From the viewpoint of kinetics, the production rate of oxygen from the CO_2 decomposition, the oxygen permeation rate through the membrane, and the consumption rate of the permeated oxygen should match each other under a given operation condition. Otherwise, the slowest of these three steps limits the overall performance of the membrane reactor. The related theoretical and experimental studies are underway in our lab.

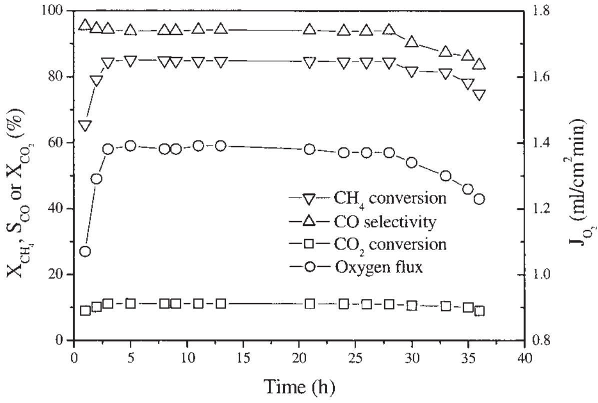

Figure 7. Stability of the membrane reactor.

(Feeding conditions: in the lower chamber 6 cm^3 (STP) min^{-1} CO_2 and 24 cm^3 (STP) min^{-1} He; in the upper chamber: 1 cm^3 (STP) min^{-1} CH_4 and 19 cm^3 (STP) min^{-1} Ar, T = 1173 K.)

Long-time stability of the membrane reactor

Figure 7 shows the stability of the SCFZ membrane reactor at 1173 K. At the initial stage (first 3 h), the CH_4 conversion increased sharply, along with increases in the CO_2 conversion and the oxygen flux. This could be attributed to the POM reaction reaching its equilibrium state. From 3 to 28 h, the conversion of CH_4 (84%) and the selectivity of CO (93%) leveled off, together with the conversion of CO_2 (11%) and the oxygen flux (1.36 ml cm^{-2} min^{-1}). But after 28 h, the variables observed in Figure 7 decreased slightly until the membrane significantly broke at about 33 h (a great amount of argon was detected in the effluent stream from the lower chamber by gas chromatograph at this time).

In a membrane configuration, the stability of a mixed-conducting membrane is not only influenced by temperature and oxygen pressure but also by atmospheres in both sides of the membrane. Material degradation can occur either by reduction (phase decomposition) under reducing atmosphere (lower oxygen partial pressure) or by phase segregation under oxygen partial pressure gradient.[5-11,18-20] Due to the presence of TCDC and POM reactions, respectively, in either side of the SCFZ membrane, both surfaces of the membrane were exposed to the reducing atmospheres (one side is CO, the other side CO and H_2); besides, a larger oxygen partial pressure gradient existed. After the SCFZ membrane underwent a 25-h stability operation in reactive atmosphere, severe degradation of the SCFZ material occurred and finally the membrane cracked.

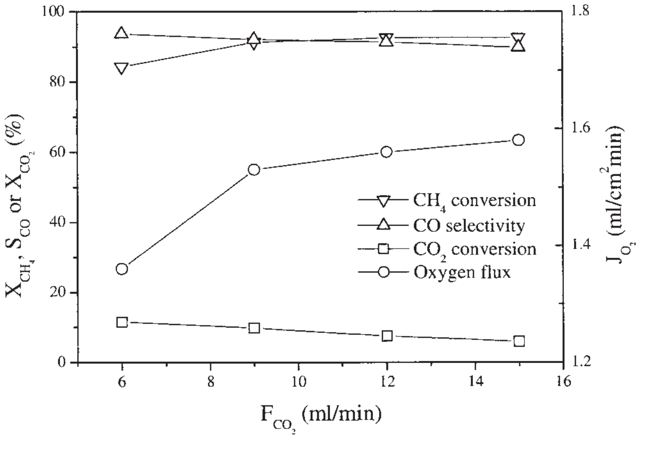

Figure 6. Influences of CO_2 feed rate on the CO_2 conversion (X_{CO_2}), oxygen flux (J_{O_2}), CH_4 conversion (X_{CH_4}), and CO selectivity (S_{CO}).

(Feeding conditions: in the underchamber 30 cm^3 (STP) min^{-1} (CO_2 + He); in the upper chamber: 1 cm^3 (STP) min^{-1} CH_4 and 19cm^3 (STP) min^{-1} Ar, T = 1173 K.)

Future work will undoubtedly, therefore, involve improving the stability of the membrane, which may be carried out by the following two routes. One is to coat a porous mixed-conducting oxide layer on the membrane surface. If a porous mixed-conducting oxide layer is coated on the CO_2 side of the membrane, the reaction of TDCD may occur mainly on the inner surface of the porous layer, instead of the membrane surface. The porous layer can reduce effectively the erosion of the atmosphere to the membrane surface, and the membrane stability could be expected to be improved. The other solution is to develop new membrane materials that can be stable in the reducing atmosphere for a long-term run, just as the previous works[21,22] for the POM reaction in the mixed-conducting membrane reactors.

Conclusions

Our preliminary experiments demonstrate that it is feasible to couple the thermal decomposition of CO_2 with the partial oxidation of methane to syngas in a mixed-conducting membrane reactor. From the viewpoint of the strategy of environmental protection as well as energy saving, the proposed process offers several advantages. The main advantage is utilizing CO_2 reasonably as the oxygen source, which reduces the discharge of CO_2 into atmosphere. Moreover, the process is avoiding the need to separate the nitrogen from air and eliminates the emission of NO_x because of not using air for the POM reaction. The proposed conception may be extended to the oxidation reactions of other hydrocarbons. The process optimization and technical solutions, such as formulating new materials with long-term chemical and mechanical stabilities, need to be carried out through further study.

Acknowledgments

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Literature Cited

1. Johnson J. Putting a lid on carbon dioxide. *Chem & Eng News.* 2004;82(51):36-39.
2. Nigara Y, Cales B. Production of CO by direct thermal splitting of CO_2 at high temperature. *Bull Chem Soc Jpn.* 1986;59:1997-2002.
3. Itoh N, Sanchez MA, Xu W, Haraya K, Hongo M. Application of membrane reactor system to thermal decomposition of CO_2. *J Membr Sci.* 1993;77:245-253.
4. Fan Y, Ren JY, Onstot W, Pasale J, Tsotsis TT, Egolfopoulos FN. Reactor and technical feasibility aspects of a CO_2 decomposition-based power generation cycle, utilizing a high-temperature membrane reactor. *Ind Eng Chem Res.* 2003;42:2618-2626.
5. Balachandran U, Dusek JT, Mieville RL, Poeppel RB, Kleefisch MS, Pei S, Kobylinski TP, Udovich CA, Bose AC. Dense ceramic membranes for partial oxidation of methane to syngas. *Appl Catal A: General.* 1995;133:19-29.
6. Tsai CY, Dixon AG, Moser WR, Ma YH. Dense perovskite membrane reactors for the partial oxidation of methane to syngas. *AIChE J.* 1997;43:2741-2750.
7. Jin W, Gu X, Li S, Huang P, Xu N, Shi J. Experimental and simulation study on a catalyst packed tubular dense membrane reactor for partial oxidation of methane to syngas. *Chem Eng Sci.* 2000;55:2617-2625.
8. Ritchie JT, Richardson JT, Luss D. Ceramic membrane reactor for synthesis gas production. *AIChE J.* 2001;47:2092-2101.
9. Shao ZP, Dong H, Xiong GX, Gong Y, Yang WS. Performance of a mixed-conducting ceramic membrane reactor with high oxygen permeability for methane conversion. *J Membr Sci.* 2001;183:181-192.
10. Gu X, Jin W, Chen C, Xu N, Shi J, Ma YH. YSZ-$SrCo_{0.4}Fe_{0.6}O_{3-\delta}$ membranes for the partial oxidation of methane to syngas. *AIChE J.* 2002;48:2051-2060.
11. Chen CS, Feng S, Ran S, Zhu D, Bouwmeester HJM. Conversion of methane to syngas by a membrane-based oxidation-reforming process. *Angew Chem Int Ed.* 2003;42:5196-5198.
12. Yang L, Tan L, Gu X, Jin W, Zhang L, Xu N. A new series of $Sr(Co,Fe,Zr)O_{3-\delta}$ perovskite-type oxides for oxygen permeation. *Ind Eng Chem Res.* 2003;42:2299-2305.
13. Li S, Jin W, Huang P, Xu N, Shi J, Hu MZC, Payzant EA, Ma YH. Perovskite-related ZrO_2-doped $SrCo_{0.4}Fe_{0.6}O_{3-\delta}$ membrane for oxygen permeation. *AIChE J.* 1999;45:276-284.
14. Bouwmeester HJM, Burggraaf AJ. *Fundamentals of Inorganic Membrane Science and Technology.* Amsterdam: Elsevier; 1996:435-528.
15. Wagner C. Equations for transport in solid oxides and sulfides of transition metals. *Prog Solid State Chem.* 1975;10(1):3-16.
16. Zhang P, Chang X, Wu Z, Jin W, Xu N. Effect of packing amount of catalysts on POM reaction in a dense oxygen-permeable membrane reactor. *Ind & Eng Chem Res.* 2005;44(6):1954-1959.
17. Xu N, Li S, Jin W, Shi J. Experimental and modeling study on tubular dense membranes for oxygen permeation. *AIChE J.* 1999;45(12):2519-2526.
18. Pei S, Kleefisch MS, Kobylinski TP, Faber J, Udovich CA, McCoy VZ, Dabrowski B, Balachandran U, Mieville RL, Poeppel RB. Failure mechanisms of ceramic membrane reactors in partial oxidation of membrane to synthesis gas. *Catal Lett.* 1995;30:201-212.
19. Xu SJ, Thomson WJ. Stability of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ perovskite membranes in reducing and nonreducing environments. *Ind & Eng Chem Res.* 1998;37:1290-1299.
20. Elshof JE-ten, Bouwmeester HJM, Verweij H. Oxidative coupling of methane in a mixed-conducting perovskite membrane reactor. *Appl Catal A: General.* 1995;130:195-212.
21. Anthony F Sammells, Michael Schwartz, Richard A Mackay, Thomas F Barton, David R Peterson. Catalytic membrane reactors for spontaneous synthesis gas production. *Catalysis Today.* 2000;56:325-328.
22. Wang HH, Cong Y, Yang WS. Oxygen permeation study in a tubular $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ oxygen permeable membrane. *J Membr Sci.* 2002;210:259-271.

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