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Decomposition of CO_2 coupled with POM in a thin tubular oxygen-permeable membrane reactor

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ABSTRACT

In this study, a SCFA (Al_2O_3 of 3 wt.% doped in $SC_{0.8}F_{0.2}O_{3-\delta}$) dense mixed-conducting thin tubular membrane was applied to a membrane reactor for coupling the thermal decomposition of carbon dioxide (TDCD) ($CO_2 \Leftrightarrow CO + 1/2O_2$) with the partial oxidation of methane (POM) to syngas, in which the reaction of CO_2 decomposition took place in the tube side of the membrane and the POM reaction occurred in the shell side of the membrane simultaneously. The reaction performance of the SCFA thin tubular membrane reactor was investigated as function of reaction temperature and the feed flow rates of CO_2 and CH_4. 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 the temperature of 900 °C, the CO_2 conversion reached about 12.4%, and the CH_4 conversion, CO selectivity and the ratio of H_2/CO were 86%, 93% and 1.8, respectively. Compared with the disc-shaped membrane, the CO_2 conversion in the thin tubular membrane is higher at the same operation temperature. The SCFA membrane reactor could be operated for about 62 h at the temperature of 900 °C.

1. Introduction

Recently, greater attention has been focused on global warming caused by increased emissions of greenhouse gases (mainly CO_2) into the atmosphere [1]. To minimize this undesirable climate change, many techniques have been proposed to recover and sequestrate CO_2 [2–5]. One potential route for the consumption of CO_2 is the thermal decomposition of carbon dioxide (TDCD) to CO and O_2 ($2CO_2 \rightarrow 2CO + O_2$, $\Delta H^0_{298K} = 552\,\mathrm{kJ/mol}$) 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 [6,7]. However, this reaction is a highly endothermic reaction, takes place only at high temperature, and is not easy to be realized in conventional fixed-bed reactors. Up to date, a few research groups have attempted to apply oxygen-permeable ceramic membrane reactors to realize this reaction [8–10]. The use of membranes in chemical reactors is motivated principally by equilibrium shift, leading to a higher conversion or selectivity in a single pass. In our previous work [11–13], we proposed a novel process of coupling the TDCD with the partial oxidation of methane (POM) to syngas in a dense $SrCo_{0.4}Fe_{0.5}Zr_{0.1}O_{3-\delta}$ (SCFZ) membrane reactor. In this coupling process, the TDCD reaction took place on one side of the membrane and the oxygen from the TDCD permeated through the oxygen-permeable membrane to react with CH_4 fed in other side of the membrane, which produced a mixture of H_2 and CO (syngas) over a supported Ni-based catalyst. For this process, on the one hand, CO_2 is used as the oxygen source for POM reaction; on the other hand, the TDCD coupled with the POM could produce H_2 and CO, which are the important chemicals for methanol synthesis, Fischer–Tropsch reactions or fuels. Moreover, we found that the oxygen permeation rate of the membrane affected the CO_2 conversion strongly [12]. In other words, the CO_2 conversion could be increased by increasing the oxygen permeation rate of the membrane.

In our previous work [13,14], a SCFA (Al_2O_3 of 3 wt.% doped in $SC_{0.8}F_{0.2}O_{3-\delta}$) thin tubular membrane with high mechanical strength has been successfully prepared by plastic extrusion. From the SEM micrographs of the membranes, it was found that the sintered thin tubular membrane had a symmetric and dense structure. Moreover, a high oxygen permeation flux was obtained in the oxygen separation and methane oxidative reaction. Compared with the conventional disc-shaped membrane, the oxygen permeation flux of the thin tubular membrane is much higher at the same operation condition. The increase of the oxygen permeation flux mainly results from the improved membrane design, i.e. reduced membrane thickness [14–17]. Herein, we

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attempt to perform the thermal decomposition of CO_2 coupling with the POM reaction in the SCFA thin tubular membrane reactor.

Therefore, this work continued our previous research on the reaction of TDCD in membrane reactor [11] and the main objective is to investigate the performance of the TDCD coupling with POM to syngas in the SCFA thin tubular dense mixed-conducting membrane reactor. Stable and high efficiency catalyst is one of the prerequisite for the stable operation of the membrane reactor for POM to syngas, besides the membrane material itself, especially for long-term run. According to the literatures [18–23], Ni/γ-Al_2O_3 is an excellent POM catalyst. Moreover, we have also successfully applied the Ni/γ-Al_2O_3 catalyst for the methane oxidation reaction at high space velocity in a thin tubular membrane reactor, during the 160 h run the catalyst performance was really stable [15]. So the Ni/γ-Al_2O_3 catalyst was selected as the POM catalyst in this work.

2. Experimental studies

2.1. Powder and membrane preparation

The Al_2O_3-doped $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCFA) powders were synthesized by the conventional solid-state reaction method with appropriate amounts of $SrCO_3$, Co_2O_3, Al_2O_3 and Fe_2O_3 [23]. The plastic extrusion was used to prepare the green thin tubular membranes. The starting extrusion mixture was composed of 76 wt.% Al_2O_3-doped $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ powders, 10 wt.% PVA solution (10 wt.%), 10 wt.% dextrin and 4 wt.% tung oil. A die with an orifice diameter and inner diameter of 3.4 and 2.2 mm was applied to form the thin tubular membrane precursors. Then the precursors were sintered at the temperature of 1200 °C for 5 h to form the dense thin tubular membrane. The detailed procedure was described in our previous work [14].

2.2. Catalyst preparation

The Ni/Al_2O_3 catalysts used in our experiments were prepared by the impregnation techniques. An appropriate amount of γ-Al_2O_3 (20–40 mesh) was impregnated by an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ (the 2nd Chemical Industry of Shanghai; purity of 99.9%). After being dried at 60 °C for 24 h, the catalytic precursors were calcined in air at 750 °C 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 700 °C before use. The XRD analysis confirmed that the nickel in the fresh NiO/Al_2O_3 catalyst exists as the formation of NiO and $NiAl_2O_4$. After reducing at the H_2 atmosphere, the main formation of nickel in the NiO/Al_2O_3 catalyst is Ni^0. The membrane reaction was conducted in the presence of the reduced Ni/Al_2O_3 catalyst.

2.3. Membrane reactor set-up

The reaction of the thermal decomposition of carbon dioxide was conducted using only dense thin tubular membranes without defects, which were checked by home-made gastight measurements before assembly. The experimental apparatus and reactor module used in this study are shown in Fig. 1, to some extent, are

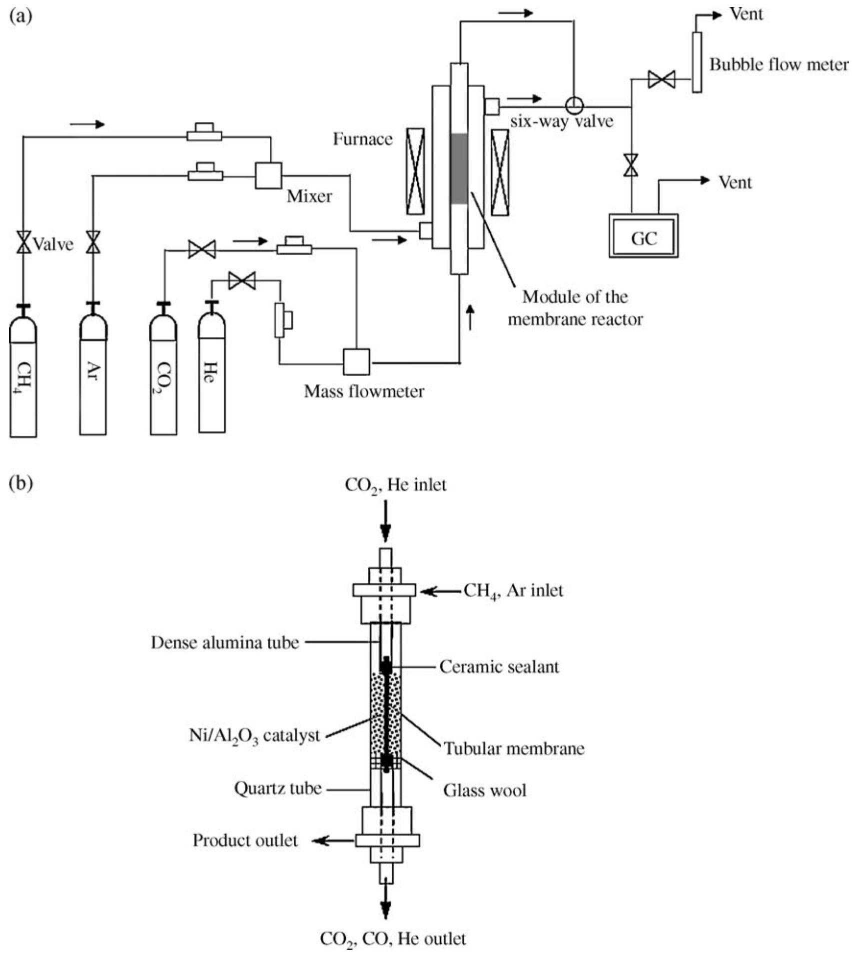

Fig. 1. Schematic diagrams of a membrane reactor for coupling thermal decomposition of CO_2 with partial oxidation of methane to syngas. (a) Schematic diagram of a complete reactor set-up. (b) Module of a thin tubular membrane reactor.

similar to those reported by our lab [11]. To prepare a membrane module, a SCFA thin tubular membrane with the i.d./o.d. of 1.7/2.6 mm and the length of 10 mm was sealed with two dense Al_2O_3 ceramic tubes (i.d. = 3.5 mm, o.d. = 4.5 mm) at both the ends of the membrane. A quartz tube (i.d. = 5.5 mm) surrounding the two alumina tubes formed the shell side of the reactor. Basing on our previous study, the Ni/Al_2O_3 catalyst of 0.15 g was packed on the shell side of the thin tubular membrane [24]. The reactor module was surrounded by a tubular furnace and the temperature was measured by a type K thermocouple. A microprocessor temperature controller (model 708PA) was used to control the temperature to within ±1 K of the set points. The tube side of the membrane was exposed to the gas mixture of CO_2 and helium, while the shell side was exposed to a mixture of methane and argon. Both the shell side and tube side of the membrane were maintained at atmospheric pressure. The effluent streams were analyzed by two gas chromatographs (model Shimadzu GC-8A, Japan), which were connected online to the reactor. A 2 m 5 A 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 5 A molecular sieve 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.

$$X_{CO_2} = \frac{F_{CO,outlet}}{F_{CO_2,outlet} + F_{CO,outlet}}$$

The oxygen permeation flux through the dense 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 shell side of the membrane.

3. Results and discussion

3.1. Effect of temperature on membrane reaction

Fig. 2 shows the effect of the reaction temperature on the performance of the thin tubular membrane reactor in the temperature range of 850–950 °C. CO_2 diluted 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 tube side of the membrane 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 shell side of the tubular membrane. As shown, both conversions of CO_2 and CH_4 increase with increasing temperature. This can be attributed to the improvement of oxygen permeability of the SCFA thin tubular membrane. Generally, the rate at which oxygen permeates through a mixed-conducting dense membrane is essentially controlled by the rate of oxygen diffusion across the membrane bulk and interfacial oxygen exchange on either side of the membrane. On the one hand, the oxygen permeation rate through the SCFA membrane bulk increased with increasing temperature according to the Wagner equation [25]. On the other hand, because of the presence of CO_2 decomposition and the oxidation of methane respectively in either side of the SCFA membrane, the rate of interfacial oxygen exchange on either side of the SCFA membrane increased, or, the oxygen partial pressure gradient across the SCFA membrane was enhanced. Therefore, the overall rate of oxygen permeation through the SCFA membrane under the reaction atmosphere increased with increasing temperature. In terms of the thermodynamic equilibrium, the increase of the oxygen permeation rate is beneficial to CO_2 decomposition. From 850 to 950 °C, the CO_2 conversion is from 8.4% to 17.2% (Fig. 2), which is higher than the best values reported in literatures so far and our previous work [8–13], for example, at 900 °C, the conversions of CO_2 is 12.4% while the corresponding thermodynamic equilibrium conversion is only 0.00052%. Meanwhile, the CH_4 conversion in the shell side of the membrane increased from 74% to 93% and the CO selectivity decreased slightly. At the temperature of 900 °C, for example, the CH_4 conversion, CO selectivity and the ratio of H_2/CO are 86%, 93% and 1.8, respectively.

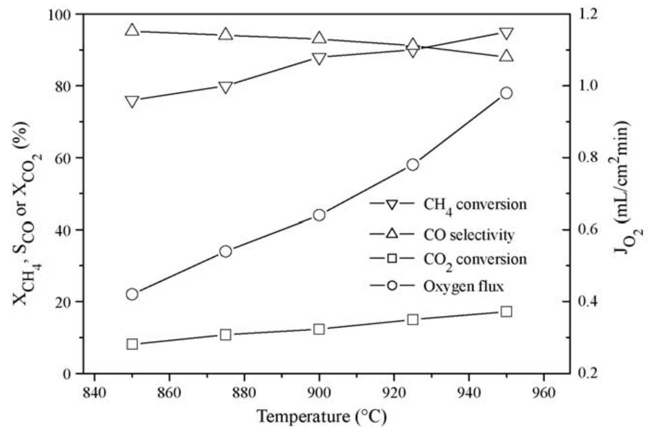

Fig. 2. Temperature dependence of CO_2 conversion (X_{CO_2}), oxygen flux (J_{O_2}), CH_4 conversion (X_{CH_4}) and CO selectivity (S_{CO}) (feeding conditions – in shell side: 6 cm^3 (STP) min^{-1} CO_2 and 24 cm^3 (STP) min^{-1} He; in tube side: 1 cm^3 (STP) min^{-1} CH_4 and 19 cm^3 (STP) min^{-1} Ar).

3.2. Effect of feed concentration on membrane reaction

We first investigated the influence of the CH_4 feed rate on CO_2 conversion, oxygen permeation flux and POM performance. Fig. 3 shows the influence of the CH_4 feed rate on the membrane reaction performance at the temperature of 900 °C. The CH_4 feed rate was changed from 1 to 3 cm^3 (STP) min^{-1} in the shell side of the membrane, 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 tube side of the membrane. On the tube side, as shown in Fig. 3, the CO_2 conversion increased with increasing the methane feed rate. For the POM reaction on the shell side, on the contrary, the CH_4 conversion decreased with increasing the CH_4 feed rate. And the CO selectivity, oxygen permeation flux increased with increasing CH_4 feed rate. Depending on above phenomena, the methane conversion mechanism in the thin tubular membrane reactor packed with Ni-based catalyst is most likely the combustion reform reaction (CRR) mechanism. In this process, that is to say, all the oxygen permeated from the membrane is firstly used up for the complete combustion of a part of the methane to CO_2 and steam ($CH_4 + O_2 = CO_2 + H_2O$); subsequently the residual methane reforms with steam and CO_2 to form CO and H_2 ($CH_4 + CO_2 = 2CO_2 + H_2$, $CH_4 + H_2O = CO + 3H_2O$). When the methane feed rate 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, oxygen permeation flux increased due to the decrease in partial oxygen pressure near the surface of the membrane, which would lead to the increase of CO_2 conversion.

Subsequently, we investigated the influence of the CO_2 feed rate on the performance of the membrane reactor at the temperature of 900 °C. The CO_2 feed rate was changed from 6 to 15 cm^3 (STP) min^{-1} in the tube side (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 shell side of the membrane. With increasing the CO_2 feed rate, as shown in Fig. 4, the CO_2 conversion decreased while the CH_4 conversion first increased slightly and then approached to a constant, which was about 96%. 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

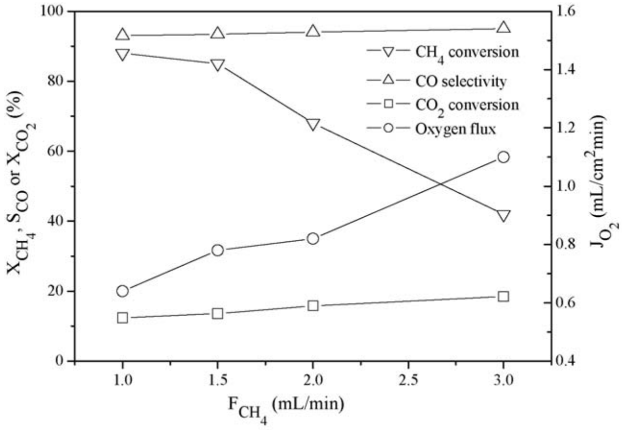

Fig. 3. Effect of CH_4 feed flow rate on membrane reaction performance (feeding conditions – in shell side: 20 cm^3 (STP) min^{-1} (CH_4 + Ar); in tube side: 6 cm^3 (STP) min^{-1} CO_2 and 24 cm^3 (STP) min^{-1} He, T = 900 °C).

is nearly finite. In other words, the oxygen produced from the CO_2 decomposition could not permeated through the membrane simultaneously with increasing the CO_2 feed rate, which lead to the decrease of CO_2 conversion. Therefore, the CO_2 conversion decreased with increasing 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.

3.3. Long-time stability of membrane reactor

A long-term TDCD reaction in the thin tubular SCFA membrane reactor was performed at the temperature of 900 °C. The time dependence of the CO_2 and methane conversions, CO selectivity and oxygen permeation flux is presented in Fig. 5. At the initial stage (first 4 h), as can be seen, CO_2 and CH_4 conversion increased sharply, along with the increase of oxygen flux. This could be attributed to the POM reaction reaching to its equilibrium state. From 4 to 62 h, the CH_4 conversion (86%) and CO selectivity (93%) leveled off together with the CO_2 conversion (12.4%). However, we found that the membrane broke after 62 h continuous operation, which is nearly one times longer than the $SrCo_{0.4}Fe_{0.5}Zr_{0.1}O_{3-\delta}$ membrane used in our previous study [11]. In a membrane configuration, the stability of a mixed-conducting membrane is not only influenced by temperature and oxygen pressure but also influenced by atmospheres in both sides of membrane. Material degradation can occur either by reduction (phase decomposition) under reducing atmosphere or by phases segregation under oxygen partial pressure gradient. In our previous study [11,12], we found that CO_2 could interact with perovskite oxide to form carbonate (such as $SrCO_3$) on the side exposed to CO_2. Moreover, reducing gas (such as CH_4, CO and H_2) could erode the membrane material at high temperature. Due to the presence of CO, CO_2, CH_4 and H_2 respectively in either side of the SCFA membrane, both surfaces of the membrane were exposed to the corrosive atmospheres; besides, a larger oxygen partial pressure gradient existed. In this study, thus, the SCFA thin tubular membrane cracked after underwent a 62-h operation in reactive atmosphere.

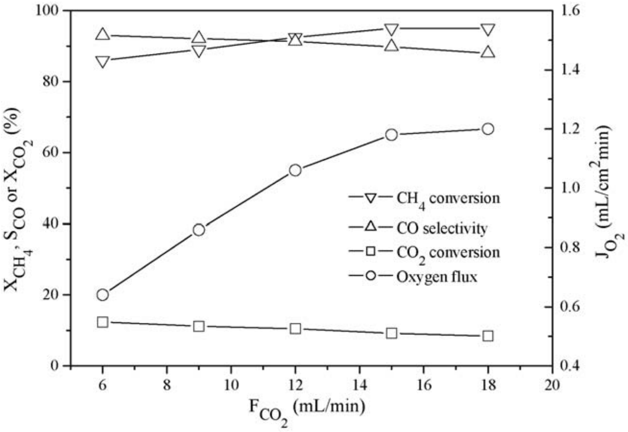

Fig. 4. Influences of CO_2 feed rate on the CO_2 conversion (X_{CO_2}), oxygen flux (J_{O_2}), CH_4 conversion (X_{CH_4}) and CO selectivity (S_{CO}) (feeding conditions – in shell side: 30 cm^3 (STP) min^{-1} (CO_2 + He); in tube side: 1 cm^3 (STP) min^{-1} CH_4 and 19 cm^3 (STP) min^{-1} Ar, T = 900 °C).

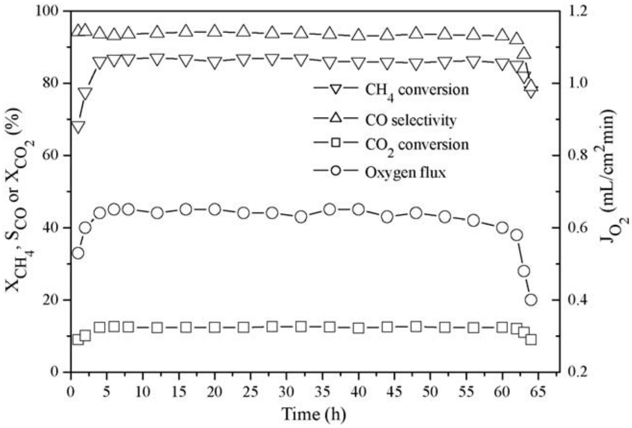

Fig. 5. Stability of the membrane reactor (feeding conditions – in tube side: 6 cm^3 (STP) min^{-1} CO_2 and 24 cm^3 (STP) min^{-1} He; in shell side: 1 cm^3 (STP) min^{-1} CH_4 and 19 cm^3 (STP) min^{-1} Ar, T = 900 °C).

4. Conclusions

In this work, we coupled the thermal decomposition of CO_2 with the partial oxidation of methane to syngas in the SCFA thin tubular mixed-conducting membrane reactor packed with a reduced Ni/Al_2O_3 catalyst. In this couple process, the reaction temperature, CO_2 and CH_4 feed rate had considerable influence CO_2 and CH_4 conversion, CO selectivity and oxygen permeation flux. At the temperature of 900 °C, the high CO_2 conversion of 12.4% was obtained in the thin tubular membrane. Compared with the SCFA disc-shaped membrane, the CO_2 conversion in the thin tubular membrane is higher at the same operation temperature. The increase of the CO_2 conversion, in this work, mainly results from the increasing the oxygen permeation rate by reducing membrane thickness. Furthermore, the SCFA thin tubular membrane could be operated for about 62 h.

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