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Syngas production in a novel perovskite membrane reactor with co-feed of CO_2

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Abstract

Partial oxidation of methane (POM) co-fed with CO_2 to syngas in a novel catalytic $BaCo_{0.6}Fe_{0.2}Ta_{0.2}O_{3-\delta}$ oxygen permeable membrane reactor was successfully reported. Adding CO_2 to the partial oxidation of methane reaction not only alters the ratio of CO/H_2, but also increases the oxygen permeation flux and CH_4 conversion. Around 96% CH_4 conversion with more than 93% CO_2 conversion and 100% CO selectivity is achieved, which shows an excellent reaction performance. A steady oxygen permeation flux of 15 mL/(cm^2 min) is obtained during the 100-h operation, which shows good stability as well.

Keywords: POM; Oxygen separation; CO_2; Perovskite; Membrane reactor

Environmental concerns and the limited availability of world's crude oil reserves are the main driving forces for a future shift towards more sustainable feedstock for the chemical industry. Economical uses of natural gas have attracted extensive attention in the world [1]. In order to reduce the transportation cost of natural gas, gas-to-liquid (GTL) is a promising way. During GTL, natural gas is first converted to syngas *via* steam reforming of methane (SRM) or partial oxidation of methane (POM) or combination of them. It is well known that the SRM to syngas needs an extensive energy supply because it is a strong endothermic reaction. On the other side, POM is a weak exothermic reaction and the reaction rate is 1–2 orders of magnitude faster than the reforming reaction. Furthermore, the H_2/CO ratio is 2, which is suitable for Fisher–Tropsch process. Although POM with air as the oxygen source is a potential alternative to SRM, downstream process cannot tolerate nitrogen. Therefore, pure oxygen is required, and the most cost associated with conventional POM to syngas is that of the oxygen separation plant.

A mixed oxygen ion and electron conducting membrane (MIECM) reactor, in which oxygen is separated from air and simultaneously fed into the methane stream for the partial oxidation, offers a potential solution. Significant progresses have been made in the development of POM in the MIECM reactor [2–8]. However, there are also some problems. For example, POM reaction would easily cause runaway due to the hot spot formation, especially at high space velocity, which makes the process very difficult to control. One of the possible solutions to the hot spots is to couple POM with CO_2 reforming [9,10]. Compared to the conventional POM reaction, there are several advantages of POM co-fed with CO_2 in the membrane reactor: (1) moderating the temperature variation which is beneficial for the

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membrane reactor; (2) making the process most energy efficient, and also avoiding the hot spot formation; (3) using the C and O in CO_2 (a greenhouse gas) and thus reducing the membrane reactor scale due to the reducing the O_2/CH_4 ratio. However, only few researches are reported about POM in the MIECM reactor with co-feed of CO_2 because it is often believed that CO_2 would kill the membrane reactor.

$BaCo_{0.8-x}Fe_{0.2}Ta_xO_{3-\delta}$ ($0 < x < 0.4$) has been reported to be an excellent mixed conducting oxygen permeable material which shows an excellent oxygen permeable performance and chemical stability [11]. In this paper, a novel mixed conducting material of $BaCo_{0.6}Fe_{0.2}Ta_{0.2}O_{3-\delta}$ (abbreviated as BCFT) developed by our group was used for constructing the membrane reactor. The effect of CO_2 on the reaction performance of POM in BCFT oxygen permeable membrane reactor as well as the stability will be investigated.

1. Experimental

The BCFT powder was synthesized by a solid state reaction. The apparatus consisted of a gas supply system and gas mass flow controllers (MFC, Seven Star D08-4F/ZM), a home-made high-temperature cell with a furnace shown in Fig. 1 and online gas chromatography (GC, Agilent 7890A) with a TCD. A ceramic sealant was used as the binding agent to seal the polished BCFT disk membrane onto the middle tube. Air was fed through the shell side as oxygen feed, gas mixture of CH_4, CO_2 (reactant), He (balance gas) and Ar (inert standard gas) were fed as sweep gases on the core side. CH_4–CO_2–O_2 reforming took place on the Ni-based catalyst packed on the disk membrane and the product of reaction was analyzed by GC. The air flow rate was 200 mL/min, the total sweep flow rate was 50 mL/min and the catalyst amount was 300 mg in all the experiments. The oxygen permeation flux is calculated based on the oxygen balance, which is described as follows:

$$F_{H_2} = F_{total} - F_{N_2} - F_{O_2} - F_{CO} - F_{CO_2} - F_{CH_4} - F_{He} - F_{Ar} \text{ (total gas flow balance)} \quad (1)$$

$$F_{H_2O} = 2 \times (F^{in}_{CH_4} - F^{out}_{CH_4}) - F_{H_2} \text{ (hydrogen balance)} \quad (2)$$

$$F_{O_2} = 0.5 \times (F_{CO} + F_{H_2O}) + F^{out}_{CO_2} - F^{in}_{CO_2} \text{ (oxygen balance)} \quad (3)$$

$$J_{O_2} = \frac{F_{O_2}}{S} \quad (4)$$

$$X_{CO_2} = \frac{F^{in}_{CO_2} - F^{out}_{CO_2}}{F^{in}_{CO_2}} \quad (5)$$

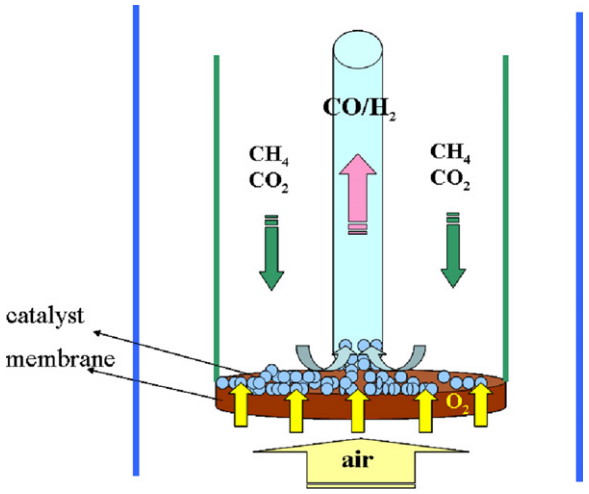

Fig. 1. Configuration of membrane reactor for the POM co-fed with CO_2.