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CO_2-stable $Ce_{0.9}Gd_{0.1}O_{2-\delta}$-perovskite dual phase oxygen separation membranes and the application in partial oxidation of methane to syngas

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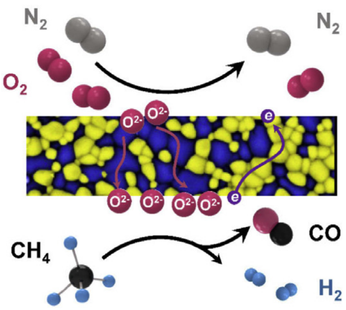
HIGHLIGHTS

- Universal stability in CO_2 of CGO-perovskite dual phase membranes was demonstrated.
- Good performance of partial oxidation of methane was achieved in a membrane reactor.
- No performance degradation was observed with pure CH_4 as reactant in long-term test.

GRAPHICAL ABSTRACT

Three type CGO-perovskite dual phase membranes were prepared to demonstrated their universal stability in CO_2. Then one model material ($Ce_{0.9}Gd_{0.1}O_{2-\delta}$-$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$) was chosen as a dual phase membrane reactor to be applied in partial oxidation of methane (POM) to syngas. At 900 °C, the oxygen permeation flux of 14 mL/min cm^2, CH_4 conversion of 96% and CO selectivity of 97% were achieved. And no performance degradation of the membrane reactor was observed during continuously 230 h operation by using pure CH_4 for POM at 900 °C, which indicates that the CGO-perovskite dual phase membranes can be steadily operated in POM process with good performance.



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ABSTRACT

To improve the chemical stability of perovskite materials (alkaline earth metal containing) in CO_2-containing atmosphere, based on the dual phase structure membranes, we prepared three CO_2-stable CGO ($Ce_{0.9}Gd_{0.1}O_{2-\delta}$)-perovskite dual phase membranes, which takes the perovskite oxides as the electrons conducting phase and the fluorite CGO oxide (possesses inherently high chemical stability against CO_2) as the oxygen ionic conductor. During the oxygen separation tests, all the membranes exhibit good reversibility when periodically changing the sweep gases from CO_2 to Helium and good long-term stability in CO_2, which demonstrate these CGO-perovskite dual phase membranes possess universal stability in CO_2. Then one of these dual phase membranes ($Ce_{0.9}Gd_{0.1}O_{2-\delta}$-$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (CGO-BSCF)) was chosen as a model material to be applied in partial oxidation of methane (POM) to syngas. At 900 °C, the oxygen permeation flux of 14 mL/min cm^2, CH_4 conversion of 96% and CO selectivity of 97%, and the H_2/CO of 2 were achieved. And no performance degradation of the membrane reactor was observed during continuously 230 h operation by using pure CH_4 for POM at 900 °C. Due to the good CO_2 stability and good performance in POM, the CGO-perovskite dual phase membranes could potentially stimulate their applications in industrial applications.

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1. Introduction

Economical and efficient uses of natural gas have attracted extensive attention all over the world. However, a major fraction of the natural gas is located in remote or stranded areas so that the transport cost of natural gas rapidly rises with increasing distance. As methane is the main component of the nature gas, enormous efforts are currently being undertaken to develop the gas-to-liquid (GTL) technologies that can convert methane into easily transportable liquids [1-3]. Conversion of methane to syngas ($CO + H_2$) is an important intermediate process for the gas-to-liquid process via existing processes, such as Fischer-Tropsch (F-T) synthesis and methanol synthesis [4-6]. Up to now, the commercial production of syngas is based on steam reforming of methane (SR) ($CH_4 + H_2O \rightarrow CO + 3H_2$, ΔH (25 °C) = 206.16 kJ/mol). However, the SR process is highly energy intensive and the high H_2/CO production ratio is unsuitable for the F-T synthesis [7-10]. A promising alternative for the syngas production is the partial oxidation of methane (POM) process ($CH_4 + 1/2O_2 \rightarrow CO + 2H_2$, ΔH (25 °C) = −36 kJ/mol), as it is mildly exothermic and can produce syngas with a H_2/CO molar ratio of 2/1, which can be directly used as the feed for methanol synthesis or F-T reaction [7,11,12]. However, F-T synthesis cannot tolerate nitrogen, as downstream processing requires the product stream to be free of nitrogen, therefore, pure oxygen is required. Dense ceramic oxygen permeable membranes are promising oxygen supplier for POM process. The oxygen permeable membranes are mixed oxygen ionic and electronic conducting materials (MIECMs) which separation oxygen through oxygen ions with 100% selectivity [13,14]. In the oxygen permeable membrane reactors, oxygen separation process can be combined with POM reaction so that the high purity oxygen can be in-situ supplied [15-17].

For practical applications in POM, the oxygen-permeable membranes must possess sufficiently high oxygen permeability and good structural stability not only in syngas atmosphere but also in carbon dioxide, as methane is first oxidized to CO_2 and H_2O, after which these products are reduced by unreacted methane to CO and H_2 during POM process [1,18]. At present, the extensive investigated MIECMs are perovskite oxides due to their high oxygen permeability [19,20]. However, Arnold et al. observed an immediate stop of the oxygen permeation flux through the perovskite $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) membrane when pure CO_2 was used as sweep gas at 875 °C [21]. Martynczuk et al. reported that the formation of a small amount of carbonate on the surface of a perovskite $Ba_{0.5}Sr_{0.5}Fe_{0.8}Zn_{0.2}O_{3-\delta}$ (BSFZ) membrane is sufficient to result in rapid breakdown of the oxygen permeability at 750 °C under CO_2 atmosphere [22]. Yi et al. reported that the oxygen permeation flux through the perovskite $BaCo_{0.4}Fe_{0.4}Nb_{0.2}O_{3-\delta}$ (BCFN) membranes significantly decreased when CO_2 was introduced into the sweep gas [23]. The breakdown of the oxygen permeability of these perovskite-type membranes are due to the alkaline earth metal ions in the A site tend to react with CO_2 and form carbonates which result in the destruction of the perovskite structure. The poor stability in CO_2-containing atmosphere of perovskite membranes limits their industrial applications in POM reaction.

Based on the dual phase membranes concept, in our previous work, fluorite oxide $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (CGO) was introduced as the oxygen ionic conductor and the perovskite oxide act as the electronic conducting phase to prepare CO_2-stable dual phase oxygen separation membrane [24,25]. In CO_2, the alkaline earth metal (Sr, Ba) in the A site tend to form carbonates which destroy the structure of perovskite oxides, while their electronic conductivity contributor of continuous equipotential passages -O-B-O-B-O-chains might be still maintained because the B site ions (Co, Fe) formed cobalt oxides or ferric oxides, which are still good electronic conductors, so that the network of the electron transmissions could be reserved. Based on abovementioned concept, we have developed the CO_2-stable $Ce_{0.9}Gd_{0.1}O_{2-\delta}$-$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (CGO-BSCF) dual phase membrane [24]. Herein, to demonstrate the CGO-perovskite dual phase membranes possess universal stability in CO_2, we prepared the other two CGO-perovskite dual phase membranes with the composition of 60 wt% $Ce_{0.9}Gd_{0.1}O_{2-\delta}$-40 wt% $Ba_{0.5}Sr_{0.5}Fe_{0.8}Zn_{0.2}O_{3-\delta}$ (CGO-BSFZ) and 60 wt% $Ce_{0.9}Gd_{0.1}O_{2-\delta}$-40 wt% $BaCo_{0.4}Fe_{0.4}Nb_{0.2}O_{3-\delta}$ (CGO-BCFN), and investigated their oxygen separation performance in CO_2. Then, the CGO-BSCF membrane was chosen as a model membrane reactor for POM. The POM performance in such CGO-BSCF membrane reactor with Ni-based catalyst was investigated in detailed in this paper.

2. Materials and methods

2.1. Preparation of powder and membrane

The BSCF, BSFZ, BCFN powders were prepared by a combined citrate and ethylenediaminetetraacetic acid complexing method which was described in our previous work [24,25]. Commercial CGO powder (Yitong New Material Co. Ltd., Weifang, China) was used as starting material. The as-obtained CGO and BSCF, BSFZ, BCFN powders were mixed in a mortar at a weight ratio of 60:40 and carefully grounded. The as-prepared powders were then uniaxially pressed at 20 MPa to get green pellet membranes followed a sintering process of 1100 °C for 10 h. The sintered pellets had a diameter of approximately 12.5 mm. Densities of the sintered membranes were determined to be higher than 95% of the theoretical density using the Archimedes method in ethanol. Only those membranes that have the relative densities higher than 95% were used for oxygen permeation studies.

2.2. Characterizations by XRD, SEM, EDXS

The phase structures of the powders and the sintered disks were characterized by X-ray diffraction (XRD, Bruker-D8 ADVANCE, Cu Kα radiation). The spend membrane was studied by scanning electron microscopy (SEM) using a JEOL JSM-6700F at an excitation voltage of 2 kV. The elemental compositions of the membrane were determined by energy dispersive X-ray spectroscopy (EDXS), Oxford Instruments INCA-300 EDX spectrometer with an ultrathin window at an excitation voltage of 20 kV.

2.3. Measurements of membrane reactor for the POM

The oxygen permeability was studied in a home-made high-temperature oxygen permeation apparatus which was described in our previous work [26]. The membrane was sealed in a corundum tube by a commercial ceramic sealant (HT767, Huitian, Hubei, China). The Ni based catalyst was directly packed onto the top of membrane disc. Gases were delivered to the permeation cell by mass flow controllers (MFC, Seven star D08-4F/ZM) calibrated by a soap bubble flow meter. Air was fed to the feed side of the membrane and He/CH_4 was fed to the sweep side. The flow rates of the effluents were also measured by the soap bubble flow meter. A gas chromatograph (GC, Agilent Technologies, 7890A) connected to the permeation apparatus detected the composition of the effluents online. The leakage of oxygen due to the imperfect sealing was subtracted in calculation of the oxygen flux. The contribution of leakage to the apparent oxygen flux was below 0.5% in all cases. Assuming that leakage of nitrogen and oxygen is in accordance with Knudsen diffusion, the fluxes of leaked N_2 and O_2 are related by $J_{N_2}^{Leak} : J_{O_2}^{Leak} = \sqrt{\frac{32}{28}} \times \frac{0.79}{0.21} = 4.02$, and the CH_4 conversion (X_{CH_4}), CO selectivity (S_{CO}) and the oxygen permeation flux (J_{O_2}) can be