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A novel tubular oxygen-permeable membrane reactor for partial oxidation of CH_4 in coke oven gas to syngas

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ABSTRACT

Dense $BaCo_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ (BCFNO) membrane tubes were prepared by slip casting and readily brazed to 310S stainless steel supports using a silver-based alloy. A novel tubular membrane reactor was constructed by placing a cylindrical Ni-based monolithic catalyst coaxially around the tubular membrane and a conventional Ni-based catalyst-bed apart from the membrane tube. The novel membrane reactor was successfully applied to partial oxidation of CH_4 in coke oven gas (COG). At 850 °C, 94% of CH_4 conversion, 93% of H_2 and as high as 11.3 $cm^3\ cm^{-2}\ min^{-1}$ of oxygen permeation flux were obtained. The experimental H_2 and CO selectivity and CH_4 conversion were close to the thermodynamically predicated ones. There was a good match in the coefficient of thermal expansion (CTE) among BCFNO membrane, Ag-based alloy and 310S metal support. Long-term operation test results indicate that the novel tubular BCFNO membrane reactor exhibited not only high activity but also good stability for the partial oxidation of CH_4 in COG to syngas.

1. Introduction

Coke oven gas (referred as COG), a by-product generated in the process of producing coke, is gaining increasing attention as one of the most attractive sources of syngas or hydrogen production [1–3]. The main components of COG are 54–59% H_2, 24–31% CH_4 and 5.5–7% CO [4]. As a potential source for syngas or hydrogen production from CH_4 by catalytic partial oxidation (CPO), COG can be as competitive as natural gas in the terms of energy consumption and amount of net carbon dioxide emission [5]. However, the partial oxidation of CH_4 in COG requires high-cost pure oxygen. Recently, our group has used mixed ionic-electronic conducting (MIEC) membrane reactor to produce syngas by reforming of CH_4 in COG [6–8]. The technologies based on MIEC membranes make it possible to integrate oxygen separation and catalytic partial oxidation in a single reactor and can significantly reduce the energy and cost for syngas production from methane [9,10]. The detailed performance and stability of the disc-shaped $BaCo_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ (BCFNO) membrane reactor under the condition of COG were investigated and the possible reaction pathways of partial oxidation of CH_4 in COG in the membrane reactor were deduced [11–13].

To develop a commercial process for syngas production from COG by a membrane reactor, high temperature and large area modules with gas-tight seals must be constructed. In all pervious studies, disc-shaped membranes with only a limited membranes area were employed for membrane reactors as they are easily fabricated [11–13]. Although the membrane area can be enlarged by employing a multiple planar stack, many problems such as sealing and pressure resistance have to be faced. In recent, tubular membranes have been

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developed to reduce the engineering difficulties, especially the problems associated with the high temperature seal [14–17].

In this article, the closed-one-ended BCFNO membrane tubes were fabricated and readily brazed to a stainless steel supports using a silver-based alloy. A novel tubular membrane reactor was constructed by placing a quartz tube coaxially around the membrane. The shell was filled with a cylindrical Ni-based monolithic catalyst and a conventional Ni-based catalyst-bed was packed apart from the membrane tube. The performance of the novel tubular BCFNO membrane reactor was evaluated under the condition of COG.

2. Experimental

2.1. Powder and membrane preparation

The BCFNO powder was prepared by solid state reaction. Details of the preparation procedure of the BCFNO powder has been given elsewhere [6]. The closed-one-ended membrane tubes were fabricated by slip casting [18]. Pouring aqueous slurry of ceramic powders into plaster mold could get closed-one-end tubular membranes. The green tubes were heated at a rate of 20 °C h^{-1} in the temperature range of 100–350 °C to facilitate the removal of the gaseous species formed during decomposition of the organic additives, then the tubes were sintered between 1000 and 1150 °C for 20 h. The final tubes had an outer diameter of about 16 mm and a wall thickness of 1 mm. In present study, a short membrane tube with a length of 110 mm was used.

2.2. Membrane reactor set-up

A high temperature membrane reactor system for assessing oxygen permeation flux and the conversion of CH_4 in COG was used, schematically shown in Fig. 1. The closed-one-ended membrane tube was sealed on the stainless steel support by a silver-based RAB (reactive-air-brazing)-alloy [19]. Then the membrane tube on the steel support was placed inside a larger quartz tube. A cylindrical Ni-based monolithic catalyst (Catalyst A shown in Fig. 1) was placed in the annulus region. The catalyst LiLaNiO/γ-Al_2O_3 was prepared via the impregnation

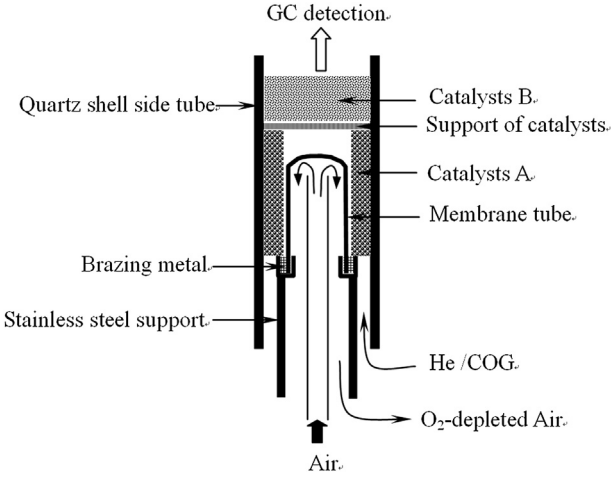

Fig. 1 – Diagram of tubular ceramic membrane reactor.

according to report [6] and used as the catalysts A. A porous cylindrical γ-Al_2O_3 was used as a catalyst support. The annulus distance between the membrane and the monolithic catalyst was about 1 mm. At the same time, a conventional Ni-based catalyst-bed (Catalyst B shown in Fig. 1) was packed a few centimeters apart from the membrane tube along the downstream. The catalysts B was a commercial Z111 series reforming catalyst supplied by the southwest research and design institute of chemical industry in China. Helium or COG was passed through the annulus between the larger quartz and membrane/stainless steel tube. The model COG was a typical mixture expected in a commercial recycle feed that contained 57.09%H_2, 28.18%CH_4, 7.06%CO, 3.16%CO_2 and 4.51%Ar. Membrane gas leak free conditions were ensured by monitoring nitrogen concentration on the permeation side. N_2 in the model COG was substituted with Ar in order to ensure the reliability of monitoring nitrogen concentration. In present experiments, no nitrogen leakage was detected. Inside the stainless steel support tube was a smaller tube through which air was introduced to the dead-end side of the membrane tube. The membrane module was heated by a temperature programmable tubular furnace. The temperature was measured by a K-type thermocouple encased near the membrane tube. The flow rates of the feed gas were controlled by mass flow controllers. On the outside of the membrane, the effluent compositions were measured by a gas chromatograph (VARIAN, CP3800) equipped with a thermal conductivity detector. When the model COG was fed, the oxygen permeation flux was determined from the content of CO and CO_2 in the reacted gas and the yield of H_2O evaluated from the balance of hydrogen before and after the reaction. The conversion of CH_4 in the model COG, the selectivities of CO and H_2 were defined as reference [11].

The phase and crystal structures of the sintered membranes and the samples after experiments were characterized with an X-ray diffractometer (XRD, Rigaku D-Max/RB). The surface morphology of the membranes was observed using a scanning electron microscope (SEM, JSM-6700F). Measurements of the coefficient of thermal expansion (CTE) as a function of temperature were conducted on 25 mm long × 3 mm diameter bars of BCFNO membrane, silver-based alloy and metal support using a Netzsch dilatometer DIL 402C.

3. Results and discussion

3.1. Morphology of the tubular membranes

The plasters mold and tubular membranes are shown in Fig. 2. The surfaces and cross-section of the fresh tubular BCFNO membrane were characterized by SEM and the results are presented in Fig. 3. As shown in Fig. 3(a) and (b), it can be seen that the ceramic grains exhibit clear grain boundaries with size of several microns. Fig. 3(c) shows that there exist some pores that are visible in the cross-section but do not communicate with either membrane surface. The nitrogen permeation measurements confirmed that the BCFNO tubular membrane is gastight and no open pores exists. The relative densities of the sintered tubular membranes determined by Archimedes method were higher than 93%, which showed that the tubular membranes were dense. A regular circular