



Autothermal reforming of ethanol in dense oxygen permeation membrane reactor



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ABSTRACT

Perovskite-type $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) material was synthesized by the combined EDTA–citric acid complexing method and the disk-type BSCF dense membrane reactor (DMR) was constructed for H_2 production by ethanol oxidative steam reforming reaction. The autothermal reaction conditions in the DMR were obtained through optimizing the ethanol oxidative steam reforming reaction (EOSR). The results showed that the hydrogen yield decreases ($3.5\text{--}3.2\text{ mol/mol}_{\text{EtOH}}$) with the net heat of reaction Q decreases from 0 to $-257\text{ J/mol}_{\text{EtOH}}$ because the oxygen permeation flux for the membrane increases with temperature. The hydrogen production is $3.5\text{ mol/mol}_{\text{EtOH}}$ at autothermal temperature of $750\text{ }^\circ\text{C}$ and the oxygen permeation flux of the dense ceramic membrane reactor is $6.5\text{ ml(STP)/cm}^2\text{ min}$. The activation energy for oxygen permeation was 46.4 kJ/mol under the air/Ar gradient, as compared to about 20.1 kJ/mol under EOSR reaction, respectively. The BSCF DMR performed stably under the autothermal reaction condition was stable for at least 180 h. These results indicate the BSCF membrane holding the high oxygen permeation flux, the excellent phase reversibility and the good stability under the highly reducing atmosphere, shows great application potential for H_2 production via the autothermal reaction.

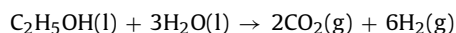
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1. Introduction

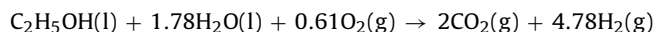
Hydrogen is one of the most promising energy carriers in the future and the production of hydrogen from alternative resources has attracted considerable interest [1]. Among the candidates for hydrogen production, ethanol produced by the fermentation of biomass offers some advantages over fossil fuels because it can be produced renewably from various biomass sources, agricultural waste materials, forestry residue materials, organic fraction of municipal solid waste [2,3]. Moreover, it is low toxicity, easy to transport and can be reformed in the presence of water to generate a hydrogen-rich mixture that is free from sulfur [4,5].

Hydrogen production from ethanol by steam reforming (ESR), partial oxidation (EPOX) and oxidative steam reforming (EOSR) has been the subject of several recent studies [1–11]. ESR (R1) is a strong endothermic process and a great amount of energy must be provided. Heat could be supplied externally or pure oxygen (or

air) could be fed to the reforming reactor to burn a portion of the ethanol. To achieve thermal neutrality, 0.61 mol of oxygen per mole of ethanol must be fed. This process is known as EOSR reaction (R2).



$$\Delta H_{298} = 347\text{ kJ/mol} \quad (\text{R1})$$



$$\Delta H_{298} = 0 \quad (\text{R2})$$

Extensive research efforts on EOSR in the past were directed toward mainly process concepts based on the fixed-bed reactors (FBR) by adding oxygen (or air) in reaction system [4,6,11]. Regarding the new type reactors, it must be pointed out the dense oxygen-permeable membrane reactors (DMR) allow a cost-effective use of air instead of oxygen and possibly higher productivity as flammability issues of the reactant mixture close to stoichiometry could be avoided. Moreover, the DMR has a significant advantage over the FBR since the oxygen concentration can be

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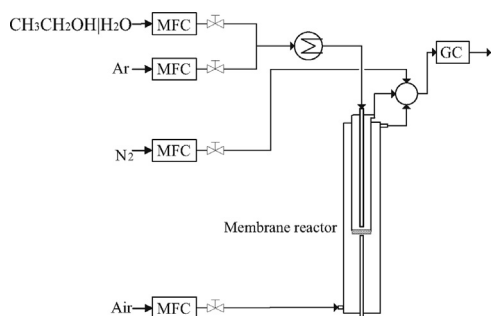


Fig. 1. Scheme of the membrane reactor setup.

controlled by adjusting the feed pressure of oxygen, and it is possible to maintain the oxygen concentration at a uniformly low value along the reactant flow direction [12–15].

The DMR allows gradual supply of oxygen to the reaction through a dense perovskite metal oxide layer that is a mixed electronic and oxygen ionic conductor with high oxygen permeability and permselectivity. Mixed conducting ceramic membranes have attracted much interest in the last two decades because the reactors couple air separation with the improved control of distribution of oxygen to avoid the hot spot in the reactors [12–14]. $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) dense membrane was widely studied for oxygen separation and as a DMR for the partial oxidation of methane to syngas, and for the selective oxidation of light hydrocarbons [14–16].

Up to date, however, essentially no experimental work was performed on the EOSR reaction in the DMR except for a sequential simulation of the DMR for the autothermal steam reforming of ethanol (AESR) [17]. In this study, we synthesized BSCF material powders by combined citrate–EDTA complexing method and prepared the disk-type DMR reactor. Meanwhile, we selected traditional $\text{Ni}/\alpha\text{-Al}_2\text{O}_3$ catalysts as the EOSR catalyst. The overall objective of this paper is to investigate the autothermal steam reforming of ethanol (AESR) in a BSCF disk-type DMR for the maximum hydrogen production and to obtain the best reaction condition. Moreover, special attention was paid to the oxygen-permeation properties of the membrane reactor under reaction condition and suitability of the $\text{Ni}/\alpha\text{-Al}_2\text{O}_3$ catalyst at high temperature for EOSR reaction.

2. Experimental

2.1. BSCF membrane preparation

The material powders of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) were synthesized by a combined citrate–EDTA complexing method [18–20]. The green powder was pressed into disks in a stainless steel mould (22 mm in diameter) under 250 MPa for 6 min. The disk-shaped membrane was then sintered in air at 1373 K for 5 h with a ramping and cooling rate of 2 K/min in a muffle furnace. Only those membranes with relative densities higher than 90% were used for permeation studies.

2.2. Membrane reactor configurations and operation

The experimental setup is schematically shown in Fig. 1. The diameters of the quartz reactor tube were 11 mm ID and 16 mm OD. The diameter of membrane was more than 16 mm and thickness was 1.324 mm. The membrane disk was sealed with high temperature ceramic sealants HBC-1096 (Guangzhou Pankie Environment Protection Chemical Co., Ltd., China) in between two quartz tubes.

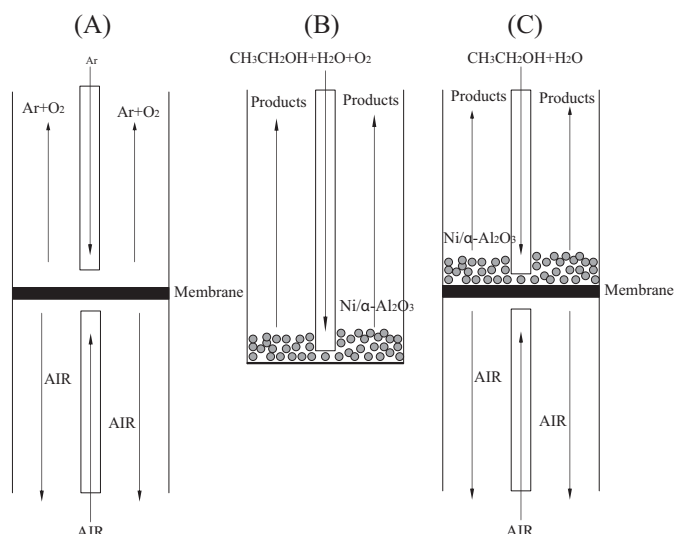


Fig. 2. Different operation configurations employed in this work: (A) membrane separation under air/Ar gradient, (B) fixed-bed reactor (FBR) and (C) membrane reactor (DMR).

The effective area of the membrane disk exposed to EOSR reaction side was 0.95 cm^2 .

The feed and products of reaction were analyzed on-line using a PerkinElmer Clarus 500 GC equipped with TCD and FID detectors, and a column of 5A molecular sieve packing material. High-purity nitrogen (36 ml/min) was added as an internal standard to aid in analysis of the product composition.

Fig. 2 illustrates three reactor configurations studied in this work. The experimental configuration for measurement of BSCF membrane oxygen permeability in air/Ar gradient is depicted in Fig. 2A, with highly pure Ar flowing on the permeate side at a flow rate of 40 ml/min and the other side was exposed to air at flow rate of 400 ml/min. Fig. 2B shows that selectivity and stability of $\text{Ni}/\alpha\text{-Al}_2\text{O}_3$ catalyst were tested for EOSR reaction in FBR, the feed was the mixed gas (preheated at 120°C) of ethanol, H_2O and O_2 . EOSR reaction in DMR experiments are illustrated in Fig. 2C, the mixture (preheated at 120°C) of ethanol and H_2O vapor was fed to the reaction side with catalyst, and air was fed to the other side of membrane at 400 ml/min. Similarly, the FBR and DMR were loaded with 300 mg of unreduced catalyst particles (20 wt% $\text{Ni}/\alpha\text{-Al}_2\text{O}_3$) (Qilu Research Institute of Petro Chemical Co., China). Experiments were conducted in $750\text{--}900^\circ\text{C}$ and at the atmospheric pressure. One of the thermocouples was inserted into a thermal well at the center of the catalyst bed.

2.3. Experiments on reactor performance

Prior to catalytic reaction testing, the catalyst was reduced in 30 ml/min reducing gas (5% $\text{H}_2\text{-Ar}$) at 900°C for 6 h with a heating rate of $2^\circ\text{C}/\text{min}$. After reduction, the catalyst was cooled down to reaction temperature at argon atmosphere. On the other hand, for DMR experiments, the catalysts were packed directly on the top of the membrane and the total flow rate of feed was 40 ml/min with $\text{H}_2\text{O}/\text{EtOH}$ molar ratio was 3:1. For the reaction experimental results, the oxygen leakage flux, which accounted for 0–2% of the total oxygen flux, was subtracted from the total oxygen flux. Ethanol conversion (X_{EtOH}), oxygen permeation flux (J_{O_2}) and the selectivity of H_2 (S_{H_2}), CO (S_{CO}), CO_2 (S_{CO_2}) and CH_4 (S_{CH_4}) were defined as follows:

$$X_{\text{EtOH}} = \frac{F_{X_{\text{EtOH}}} - V_{Y_{\text{EtOH}}}}{F_{X_{\text{EtOH}}}} \times 100\% \quad (1)$$

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