

Application of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_x$ Asymmetric Oxygen Permeable Membranes for Hydrocarbon Conversion Reactions

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Introduction

Mixed oxygen ionic-electronic conductive (O-MIEC) perovskites have gained significant attention as desirable materials for catalytic reactors due to their infinite theoretical oxygen separation factor and ability to deliver staged addition of oxygen. Natural gas conversion by integrating oxygen separation and reaction into one single step is one of the most desirable applications. However, many perovskite or perovskite-like membranes being investigated, suffer from low oxygen flux. Thus, research efforts are focused on developing new high oxygen flux materials.

We have recently shown that dense $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_x$ (BSCF) membranes are bulk diffusion limited when the thickness of the membrane is near 2 mm [1]. Thus, decreasing the thickness of the membranes or adopting a bilayer fabrication method (coating the thin dense layer of perovskite material on the porous support) should enhance the oxygen permeation as long as the mechanical stability can be maintained. This study reports on the preparation of asymmetric BSCF membranes and the utilization of the high oxygen flux membrane in hydrocarbon conversion reactions.

Materials and Methods

BSCF powders were prepared by Citrate-EDTA method. The asymmetric BSCF membranes were prepared by the dry-pressing method [1]. Oxygen flux tests and the CO_2 reforming reaction were performed in a two-chambered concentric quartz tube reactor, which was heated using a tubular furnace. To avoid gas leakage from the ambient air atmosphere, the reactor was sealed at 1073K using gold ring gaskets between the outer quartz tubes and the membrane surfaces. Air was introduced into the oxygen supply side of reactor, at the same time, Ar or reactant gas (CO_2 and CH_4) was introduced to the permeate side of the membrane reactor. For the reforming reactions 10 mg of a 0.5wt% Pt/CeZrO₂ catalyst was loaded on the permeate side of the membrane reactor. Characterization was performed using scanning electron microscopy (SEM) and x-ray diffraction (XRD).

Results and Discussion

Figure 1 shows an SEM image of the asymmetric membrane with a thickness of the dense layer of approximately 300 microns. Elemental analysis and XRD performed on both the dense and the porous layer confirmed the composition and the perovskite structure of the BSCF membranes. Before exposure to reaction mixture or flux studies, the integrity of the membrane was assessed using He on the air side and monitoring for He on the permeate side using a mass spectrometer. No He was observed before the reaction, which indicates that no significant defects are formed in the dense layer during the asymmetric fabrication process. The oxygen flux for the BSCF

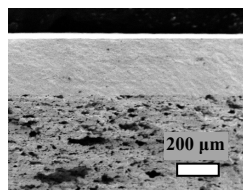


Figure.1 SEM micrograph of BSCF asymmetric membranes (cross-section)

asymmetric membrane measured in an Air:Ar gradient at 800°C is near $0.8 \text{ ml}\cdot\text{cm}^{-2}\cdot\text{min}^{-1}$. Figure 2 shows the methane conversion and oxygen permeation during the CO_2 reforming reaction at 800°C using a 0.5 wt% Pt/CeZrO₂ catalyst on the BSCF asymmetric membrane. For comparison, the methane conversion with the same catalyst using a low oxygen flux SrFeCo_{0.5}O_x membrane is also shown. The CH_4

conversion is approximately 50% higher for the BSCF membrane which is ascribed to the higher oxygen flux. In addition, the CH_4 conversion remains high for 30 hours of reaction, unlike when the low flux membrane is used and deactivation is observed. The oxygen flux observed increases during the reaction, with the flux after 30 hours being 5 times greater than the flux in the air:Ar gradient. The permeation tests were completed after reaction and no He was observed on the permeate side, demonstrating the mechanical stability of the BSCF asymmetric membranes in reducing environments.

Significance

The results of this work show that high oxygen flux asymmetric membranes can be prepared using a dry pressing method. The fluxes increase 5 fold under reaction conditions and are expected to increase even further in more reducing reaction environments. In addition, the oxygen added via the membrane reactor can be used to increase catalyst stability. The increased stability observed during reactions, in which a catalyst suffers from deactivation, may benefit from the addition of oxygen as a means of reducing catalyst deactivation. In addition, the oxygen species added using the membrane reactors behave differently than co-fed oxygen which could lead to benefits in selectivity and conversion.

References

1. Q. Jiang, K. J. Nordheden and S. M. Stagg-Williams, *AIChE Annual Meeting*, paper no.695e, Philadelphia, PA, 2008.

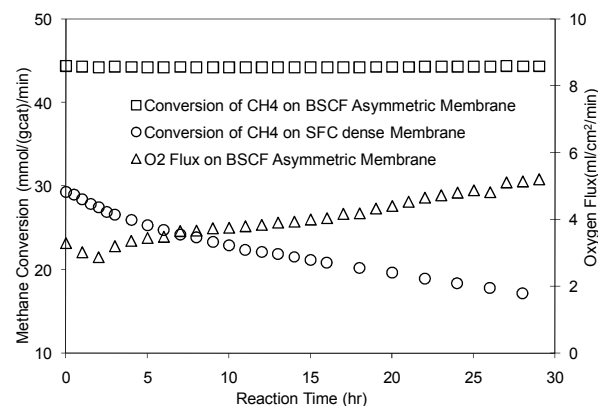


Figure. 2 CO_2 reforming reaction over Pt/CeZrO₂ catalyst with the SFC and BSCF membranes. $T = 800^\circ\text{C}$, 1:1 ratio of CH_4 and CO_2 , and a space velocity of $150 \text{ L}\cdot\text{h}\cdot\text{g}_{\text{cat}}^{-1}$