

Catalyst and Oxygen Permeable Membrane Synergy in Hydrocarbon Conversion Reactors

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Introduction

With the increasing global demand for cleaner energy, fuel cell hydrogen and ultraclean gas-to-liquid (GTL) fuels are receiving a great deal of attention as alternative energy sources. Synthesis gas, which serves as the intermediate between hydrocarbon feedstocks and both hydrogen and GTL fuels, can be produced by reforming reactions (steam, CO₂, and autothermal) or partial oxidation reactions. These reactions either require or can benefit from pure oxygen as a reactor feed. Because of the high economic, environmental, and safety costs associated with pure oxygen, oxygen-permeable ceramic membranes have been explored as an alternative oxygen source for hydrocarbon conversion reactors. In particular, non-porous, selective oxygen permeable ceramics with mixed ionic and electronic conductivity (MIECs) have received significant interest as a way to eliminate costly air separation steps and to achieve distributed addition of oxygen without the use of an external circuit to drive the ion transport. These non-porous ceramic materials conduct oxygen ions through the material lattice, resulting in 100% theoretical separation of oxygen.

Previous studies have shown that the currently obtainable fluxes in the MIEC's remain too low for widespread industrial-scale partial oxidation. In addition, ceramic compositions which exhibit high fluxes are often unstable in the highly reducing environment of the partial oxidation reaction. Some researchers have suggested adding small amounts of oxygen to make the reaction environment less reducing, but the addition of co-fed oxygen still requires an air separation step [1]. This work describes the use of a mixed conducting oxygen permeable SrFeCo_{0.5}O_x (SFC) membrane for the carbon dioxide reforming of methane. Specifically, the effect of membrane oxygen compared to co-fed molecular oxygen is investigated and the synergistic relationship between the catalysts and membrane is explored.

Materials and Methods

Flux and reaction experiments were conducted in a concentric quartz tube CSTR-type membrane reactor with disk-shaped SFC membranes. For the CO₂ reforming experiments, a traditional powder catalyst (0.5 wt% Pt/ZrO₂) was dispersed in a thin layer (~1 mm) across the membrane's permeate side to ensure good contact with the entire membrane surface. The Pt/ZrO₂ catalyst was chosen because it exhibits relatively rapid deactivation under the reaction conditions studied (800°C, 1:1 ratio of CH₄ and CO₂). The reactor feed contained 20% make-up argon to allow co-fed O₂ to be substituted for portions of the Ar during reactions without the membrane. The reactions without the membrane were performed over a stainless steel "blank" membrane coated with an inert BN₃ paint to prevent reaction on the blank. No catalyst reduction was performed prior to the membrane reactor tests.

Results and Discussion

Figure 1 shows the results for the CO₂ reforming reaction over the Pt/ZrO₂ catalyst on the stainless steel blank and on the SFC membrane. Incorporating the SFC membrane into the reactor resulted in a significant increase in the initial CH₄ conversion and the conversion after 14 hours when compared to the dry reforming reaction and the dry reforming reaction with 1% co-fed oxygen. Additional experiments were performed in which oxygen percentages of 0.2% and 2% were added. These values were chosen based on the estimates of membrane oxygen production under reaction conditions. In all of the co-fed oxygen cases, the CH₄ conversion was lower than the conversion observed on the SFC membrane. In addition, the rate of deactivation is greater in the presence of co-fed oxygen. It should be noted that CH₄ conversion on the membrane and the stainless steel blank without catalyst was less than 1% at all times. Thus, the combination of catalyst and SFC membrane is needed to produce the observed benefit from membrane oxygen; the SFC surface alone has minimal activity with the CO₂ reforming feed gases.

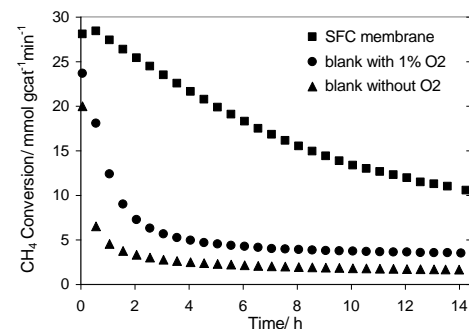


Figure 1. Membrane reactor test results for the SFC membrane and the stainless steel blank (with and without co-fed O₂). Reaction conditions: T = 800 °C, 1:1 ratio of CH₄ and CO₂, and a space velocity of 150 L/hr/g_{cat} with 0.5 wt% Pt/ZrO₂ catalyst.

Significance

The results of this work suggest that oxygen supplied via the oxygen permeable ceramic is more reactive than co-fed molecular oxygen and can significantly improve catalyst performance. In addition, these results demonstrate the potential application of MIEC membranes for reactions that can benefit from smaller amounts of distributed oxygen. This and other new applications, with less reducing environments, could increase the feasibility of membrane compositions previously determined to be unsuitable for the partial oxidation reaction.

References

1. Gu. X., Yang L., Jin W., Zhang L., and Xu N., *Industrial & Engineering Chemistry Research*, 42, 795 (2003).