

Oxygen permeable ceramic membranes for hydrocarbon conversion reactors

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Because of their various potential applications, non-porous, selective oxygen permeable ceramic membranes with mixed ionic and electronic conductivity (MIECs) have received significant interest over the past decade [1-8]. In particular, the incorporation of these materials into catalytic reactors for the oxidation of hydrocarbons is being investigated as a way to eliminate costly air separation steps and to achieve staged addition of oxygen [1-7]. Previous studies have typically focused on the use of ceramic MIEC membranes for the partial oxidation of methane and have shown that the presence of a catalyst near the permeate surface of a membrane can increase oxygen flux up to ten times by reducing the permeate side oxygen partial pressure [1,2]. However, currently attainable oxygen fluxes remain insufficient for widespread industrial-scale partial oxidation applications. This work describes the novel use of a mixed conducting oxygen permeable $\text{SrFeCo}_{0.5}\text{O}_x$ (SFC) membrane for the CO_2 reforming of CH_4 and demonstrates that oxygen evolved from a membrane in direct contact with a reforming catalyst can significantly enhance catalyst performance.

Flux and reaction experiments were conducted in a concentric quartz tube CSTR-type membrane reactor with disk-shaped SFC membranes. For the CO_2 reforming experiments, a traditional powder catalyst (0.5 wt% Pt/ ZrO_2) was dispersed in a thin layer (~1 mm) across the membrane's permeate side to ensure good contact with the entire membrane surface. The baseline reaction set includes tests with small amounts of co-fed oxygen to examine the effect of the mode of oxygen introduction on catalyst activity. These baseline reactions were performed over a stainless steel "blank" membrane coated with an inert BN_3 paint to prevent reaction on the blank. No catalyst reduction was performed prior to any of the membrane reactor tests.

The powder Pt/ ZrO_2 catalyst was chosen for the CO_2 reforming studies because it exhibits relatively rapid deactivation under the reaction conditions studied (800°C, 1:1 ratio of CH_4 and CO_2). The feed contained 20% make-up argon to allow co-fed O_2 to be substituted for portions of the Ar during experiments with the stainless steel blank. Blank tests were conducted with 1% co-fed O_2 and no co-fed O_2 (i.e., true CO_2 reforming), while membrane tests used only the oxygen produced by the SFC membrane. Similar tests were conducted in a conventional quartz tube packed-bed PFR reactor to assess pre-treatment effects and provide benchmarks for the membrane reactor tests.

As expected, the Pt/ ZrO_2 catalyst lost most of its activity within 2 hours of operation on the stainless steel blank (see Figure 1), which was consistent with this catalyst's performance in the packed-bed reactor configuration. Although co-fed oxygen produces slightly higher steady state CH_4 conversions than the no oxygen case, the CH_4 conversion trends for all cases tested with the blank are very similar, indicating a similar rate and extent of catalyst deactivation with and without co-fed oxygen. However, replacing the stainless steel blank with an SFC membrane dramatically reduces both the rate and extent of catalyst deactivation in addition to producing higher initial activity than with 1% co-fed oxygen. Furthermore, the oxygen flux through the membrane was estimated from material balances to have stabilized at the equivalent of 0.1% co-fed O_2 after approximately 6 hours of reaction time. These observations indicate that co-fed oxygen does not significantly retard the deactivation of this

Pt/ZrO₂ catalyst and suggest that oxygen added to the catalyst bed via the membrane is more beneficial than oxygen added to the reactor feed stream.

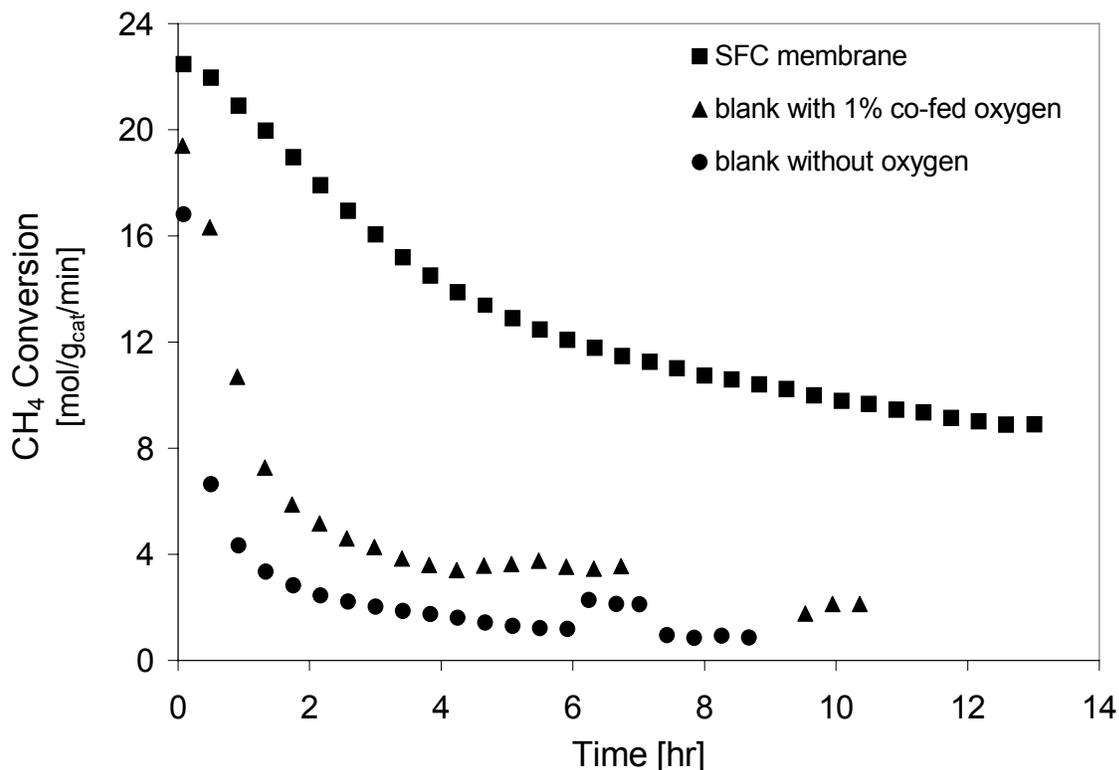


Figure 1: CH₄ Conversion in Membrane Reactor with 0.5 wt% Pr/ZrO₂ Catalyst at 800 °C. 1:1 ratio of CH₄ and CO₂. Space velocity = 150 L/hr/g_{cat}.

Catalyst deactivation for this type of catalyst typically results either from loss of metal surface area via platinum particle sintering or from carbon deposition and/or adsorption of other species. After six hours of reaction over the blank membrane without co-fed oxygen (the true CO₂ reforming case), 1% O₂ was temporarily added to the reactor feed. During this period, CH₄ conversion increased to a higher yet still steady value that was close to the conversion observed during the continuous 1% co-fed oxygen test at the corresponding reaction time. This reinforces the conclusion that the catalyst exhibits similar deactivation behavior with and without co-fed oxygen. Several hours after catalyst activity in the 1% oxygen test had stabilized, the CO₂:CH₄ feed was stopped and 1% O₂ in Ar was fed to the reactor for 2 hours in an attempt to remove any carbon deposits that might have formed on the catalyst. After switching back to CO₂ reforming with 1% co-fed oxygen, CH₄ conversion was actually lower than before the O₂/Ar feed period, indicating negligible catalyst deactivation from carbon deposition had occurred and implicating Pt particle sintering as the more significant contributor to catalyst deactivation.

This conclusion is supported by similar results from the packed-bed reactor tests, which included post-run temperature-programmed oxidations (TPOs) that indicated negligible carbon deposition on the unreduced Pt/ZrO₂ catalyst. In addition, preliminary transmission electron microscopy studies of post-reaction membrane reactor catalyst samples have shown

comparable platinum particle sintering with both the blank and the SFC membrane. The available evidence appears to confirm the conclusion that oxygen generated by the SFC membrane is more beneficial to catalyst activity than co-fed O₂.

Explanations for the apparent higher activity of membrane oxygen are currently being investigated. The most plausible do not involve gas phase reaction (i.e., the re-association and evolution of membrane oxygen) but rather the reaction of oxygen ions at the membrane surface. It is possible that the catalyst could experience more *in situ* reduction on the SFC membrane because of certain surface reactions. Also, the Pt/ZrO₂ catalyst could be promoted directly by the oxygen ions, excess electrons, or both at the membrane's anodic surface. Other ongoing work involves modifying membrane surfaces to increase oxygen flux [9] and determining the effects of increased flux on catalyst activity in the membrane reactor.

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