

The Interaction Between SrFeCo_{0.5}O_x (SFC) Ceramic Membrane and the Catalyst Pt/CeZrO₂ for Syngas Production from Methane

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There is an increasing interest in the development of a process for producing syngas (CO+H₂) from methane using non-porous oxygen-conducting ceramic membranes with mixed ionic and electronic conductivity (MIECs) as an alternative to the conventional expensive process based on air separation plant [1, 2]. Our previous studies [2], which focused on the use of SrFeCo_{0.5}O_x (SFC) dense ceramic membranes for the Carbon dioxide reforming of methane at 800 °C, have shown that the presence of the catalyst Pt/CeZrO₂ on the surface of an SFC membrane can give higher methane conversion compared to the methane conversion in the presence of other catalysts like Pt/ZrO₂ [3]. However, the roles of ceramic membrane in the enhancement of this reaction and the interaction between SFC and the catalyst have not yet been investigated. This work presents the results from studies undertaken to clarify the role of SFC ceramic membrane in the enhancement of catalytic conversion of methane to syngas through a series of pulse studies over small particles of SFC (<250 μm) and Pt/CeZrO₂ at 800 °C. These pulse studies have been conducted in order to better understand the surface reactions happening during partial oxidation and carbon dioxide reforming of methane.

The SFC powder (from Praxair Specialty Ceramics) was passed through a 60-mesh sieve and coated with 1 wt% ethylcellulose binder prior to pressing. SFC powder was then pressed and sintered in flowing air for 10 hours and finally crushed and passed through a sieve. The catalyst Pt/CeZrO₂ was prepared by depositing Pt on commercially available CeZrO₂ support material (MEI CHEM) using the incipient wetness impregnation technique (0.5% wt Pt supported on CeZrO₂). The catalyst was characterized by conducting ICP and TEM studies.

For some of the reaction tests, a physical mixture of SFC and the unreduced Pt catalyst with a specific mass ratio was fed into the reactor tube, which was made of quartz. For other reaction tests, the catalyst and SFC were loaded into the reactor tube layer by layer. The total material loading was held constant for each experiment (20 mg). The reactor was heated to 800 °C in the presence of argon and then 50 μl pulses of methane or a 1:1 CH₄/CO₂ ratio was injected into the reactor until no changes were observed. The effluent gas was analyzed by mass spectrometer.

It was found out that mixing pattern of SFC and the catalyst and the mass ratio of SFC to the catalyst plays an important role in the methane conversions for both CH₄ injections and CH₄+CO₂ injections. Regardless of the type of reactant, the highest conversion was obtained at mass ratio of one and with the catalyst and SFC well-mixed in the reactor. Adding CO₂ to CH₄ in the inlet stream increased the amount of methane conversion for the case when the SFC and catalysts were well-mixed.

When the Pt/CeZrO₂ catalyst and SFC were well mixed, the hydrogen that formed during the decomposition of methane was able to interact with the oxygen in the SFC to form water. In addition, it is believed that the CO can adsorb on the SFC surface and, using oxygen from the SFC structure, react to form CO₂. The water and CO₂ formed can

then subsequently react with methane in the presence of the catalyst to form additional hydrogen and CO via steam and carbon dioxide reforming of methane. Since the SFC has a higher capacity to adsorb CO, the H₂/CO ratio for the case of the SFC and catalyst being well mixed is very high, as shown in Figure 1. When the SFC is located below the catalyst in a segregated layer, the CO and H₂ produced on the catalyst still interacts with the SFC to form water and CO₂. However, the water and CO₂ are swept out of the reactor without contacting the catalyst zone and no steam or carbon dioxide reforming occurs. This results in a H₂/CO ratio that is closer to what would be expected for partial oxidation. The final case, when SFC is located as a segregated layer above the catalyst zone results in minimal contact between the SFC and catalyst. The H₂ and CO formed during these studies is removed from the reactor without interacting with the SFC. This results in minimal water and CO₂ formation. In this case, the H₂/CO ratio is less than 1 because some of the hydrogen is consumed during the insitu reduction of the metal. The results of this study clearly demonstrate that a synergistic relationship exists between the catalyst and the membrane material.

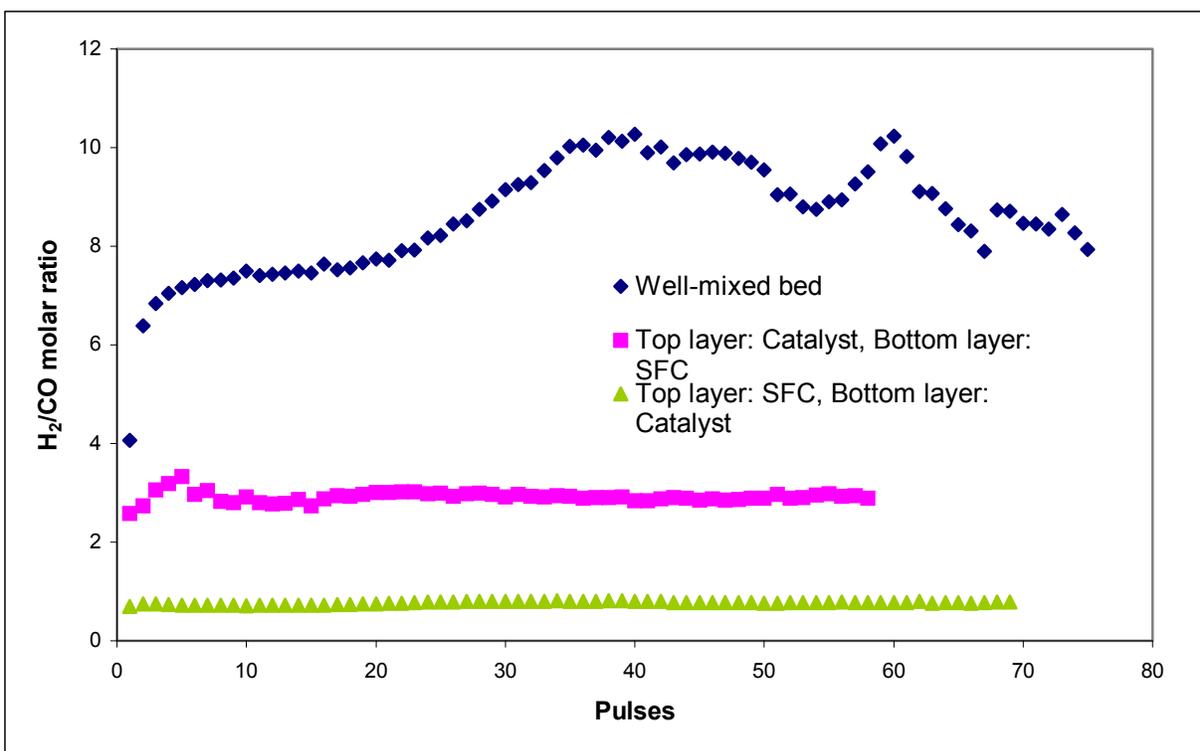


Figure 1: The H₂/CO molar ratio resulted from pulse injections of CH₄ at 800 °C where the mass ratio of SFC to the catalyst was equal to 1.

References:

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- [3] Q. Jiang, S. Faraji, D. A. Slade, K. J. Nordheden, and S. M. Stagg-Williams, "Performance analysis of mixed-conducting ceramic membranes for membrane reactor applications," *AIChE Annual Meeting*, Paper no. 509aO, Salt Lake City, 2007.