

**Studies on Hydrogen Selective Silica Membranes and  
the Catalytic Reforming of CH<sub>4</sub> with CO<sub>2</sub> in a Membrane Reactor**

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# Studies on Hydrogen Selective Silica Membranes and the Catalytic Reforming of CH<sub>4</sub> with CO<sub>2</sub> in a Membrane Reactor

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## Abstract

In this work the synthesis, characterization, and gas transport properties of hydrogen selective silica membranes were studied along with the catalytic reforming of CH<sub>4</sub> with CO<sub>2</sub> (CH<sub>4</sub> + CO<sub>2</sub> ⇌ 2 CO + 2 H<sub>2</sub>) in a hydrogen separation membrane reactor. The silica membranes were prepared by chemical vapor deposition (CVD) of a thin SiO<sub>2</sub> layer on porous supports (Vycor glass and alumina) using thermal decomposition of tetraethylorthosilicate (TEOS) in an inert atmosphere. These membranes displayed high hydrogen permeances (10<sup>-8</sup> – 10<sup>-7</sup> mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup>) and excellent H<sub>2</sub> selectivities (above 99.9 %) over other gases (CH<sub>4</sub>, CO, and CO<sub>2</sub>). The membranes were characterized using Scanning Electron Microscopy and Atomic Force Microscopy, and the mechanism of gas transport was studied applying existing theories with a newly developed treatment.

The catalytic reforming of CH<sub>4</sub> with CO<sub>2</sub> was carried out in a membrane reactor installed with a hydrogen separation ceramic membrane. The reaction was conducted at various pressures (1 – 20 atm) and temperatures (873 K and 923 K) at non-equilibrium conditions, and the results were compared with those obtained in a packed bed reactor in order to evaluate performance of the membrane reactor for the reaction. It was found that concurrent and selective removal of hydrogen from the reaction in the membrane reactor resulted in considerable enhancements in the yields of the reaction products, H<sub>2</sub> and CO. The enhancements in the product yields in the membrane reactor increased with pressure showing a maximum at 5 atm, and then decreased at higher pressures. This was due to a trade-off between a thermodynamic quantity (hydrogen production by the reaction) and transport property (hydrogen separation through the membrane). It was also found that the reverse water-gas shift (RWGS) reaction occurred simultaneously with the reforming reaction giving the detrimental effect on the reaction system by reducing the amount of hydrogen production in favor of water. This was particularly significant at high pressures.

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