

Chapter 6

Conclusions

The presented work studied hydrogen separation silica membranes and the catalytic reforming of CH₄ with CO₂ in a membrane reactor at high pressures. The silica membranes were prepared by chemical vapor deposition (CVD) of a thin silica layer on porous supports, leached Vycor and porous alumina. The deposition process was accomplished by high temperature thermal decomposition of TEOS at inert atmospheric pressure. The membranes obtained displayed high hydrogen permeability (in the order of magnitude from 10⁻⁷ to 10⁻⁸ mol m⁻² s⁻¹ Pa⁻¹ at 873 K) and practically 100 % selectivity for H₂ over other gases (CH₄, CO, CO₂). The permeability and selectivity results along with Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) images of the membranes indicated that the method used for membrane preparation in this work is excellent in controlling uniformity and thickness of the silica perm-selective layer.

The mechanism of gas transport through the membranes was studied using a statistical thermodynamic approach, and the results gave explanations for the permeability and selectivity characteristics of the membranes. Basically, the transport of the small gas molecules (He, Ne, and H₂) through the silica membranes occurs by the molecular diffusion process, in which the molecules adsorbed on solubility sites in the silica structure diffuse by jumping to adjacent solubility sites. The size of solubility sites in the silica structure is approximately 3 nm in diameter, and this provides the selective permeation for only the small gas molecules while excluding transport of larger gas molecules by size differentiation. The study showed that permeability of the silica membranes largely depends on the number of solubility sites in the silica structure available for adsorption of gas molecules. This implies that modification of the silica matrix structure providing increased number of solubility sites or changing size of solubility sites could result in an enhanced permeability and selectivity in favor of gas species of interest. This may be viable by incorporating heterogeneous oxides such as alumina, titania, or zirconia, in the silica matrix structure.

The catalytic reforming of CH₄ with CO₂ was studied in a hydrogen separation membrane reactor (MR) at various pressures (1-20 atm) and temperatures (873 K and 923 K), and the results were compared to those obtained in a packed-bed reactor (PBR) of the same geometry. It was found that the concurrent and selective removal of hydrogen from the reaction in the MR gave rise to significant improvements in the yields and selectivity for H₂ and CO in the reaction products. However, as pressure was increased the enhancement in H₂ and CO yields in the MR went through a maximum and then declined. This occurred because the conversions of the reactants decreased with increasing pressure, while the rate of hydrogen separation increased with increasing pressure. Thus, the maximum was due to a tradeoff between a thermodynamic quantity (hydrogen production) and a transport property (hydrogen separation), which had opposing pressure dependencies. It was also found that the reverse water-gas shift (RWGS) reaction ($\text{H}_2 + \text{CO}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$) occurred simultaneously with the reforming reaction, and at high pressures significantly reduced the amount of hydrogen production in favor of water. This makes the dry-reforming reaction impractical for commercial hydrogen generation regardless of the type of reactor used.