

## Chapter 6

### Conclusions

In this work, a highly hydrogen selective alumina-silica membrane was successfully prepared on a macroporous alumina support by chemical vapor deposition in an inert atmosphere at high temperature. Multiple graded layers of alumina were coated on the alumina support with a mean pore size of 100 nm by the sequential application of three boehmite sols with gradually decreasing sol particle sizes of 630, 200 and 40 nm, respectively. The SEM microphotograph of the fracture surface of the composite membrane indicated a thin silica-alumina layer with a thickness of 30-40 nm deposited on the multilayer alumina substrate. Significantly, the H<sub>2</sub> permeance through the composite membrane was decreased by less than half after exposure to 16 mol% water vapor at 873 K for 520 h. It was also found out that the silica densification process was slowed down by the addition of alumina in the ratios of Al:Si of 0.02 to 0.065.

In addition, the mechanism of gas transport through the silica membranes was studied by using a statistical thermodynamic approach and the unusual permeance order of He > H<sub>2</sub> > Ne was explained by using the experimental performance parameters. The transport of small gas molecules through the silica based membranes occurs by the molecular diffusion process, in which the molecules diffuse by jumping to adjacent solubility sites. The permeance of gases through the silica based membranes depended on mostly the number of solubility sites and the

activation energy for diffusion. Compared to pure silica membranes, a higher number of solubility sites and a higher activation energy of silica-alumina membranes implied that the composite membrane is more dense than the pure silica membranes.

A DFT method with a high level basis set was also used to optimize the equilibrium geometries of planar  $H_{2n}Si_nO_n$  ( $n = 4-8$ ) molecules. The experimental activation energies of diffusion of He and  $H_2$  fall between 6 and 7-membered siloxane rings which indicates that the structure of the silica membranes is more open than that of vitreous glass. An increase in Si-O-Si bond angles is observed as the size of the ring increases which directs the oxygen atoms towards to the center of the rings. It is observed that the distance of the diffusing species to the oxygen atoms increase with ring size and leads to an exponential decay in activation energy of diffusion of He and  $H_2$  molecules.

Finally, the methane steam reforming reaction was conducted experimentally in a packed-bed reactor (PBR) and a membrane reactor (MR) at various temperatures (773-923 K) and pressures (1-20 atm). The hydrothermally stable silica-alumina membrane mentioned earlier was used in the membrane reactor. A commercial Ni/MgAl<sub>2</sub>O<sub>4</sub> catalyst was used in both of the reaction systems. The steam reforming of methane is not favored at higher pressures because of the increase in moles in the reaction. However, permeance increases at higher pressures because of the increase in driving force. Significant enhancements in  $H_2$  yields were obtained with the MR over the PBR at higher pressures. The present work also proposes the one-dimensional and the two-dimensional modeling of the packed bed and the membrane reactor at the same

experimental conditions. Even though both models are equally capable of predicting the experimental values, the estimations obtained by using the two-dimensional model were much closer to the experimental values obtained in the membrane reactor. The declining radial profiles through the membrane obtained by the two-dimensional model at high pressures predicted lower hydrogen yields which will be important for the design of an industrial membrane reactor.