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The thesis written by Kageyama Naoki concerns the subject of hydrogen selective silica-based membranes applied for use in a membrane reactor for the steam methane reforming.

First, the effect of various reaction conditions on a Ni steam methane reforming catalyst was investigated in a conventional packed-bed reactor (PBR).　Second, for a membrane reactor (MR) applications, hydrothermally stable silica-based membranes were developed by modifying precursors and permeance mechanisms of small and large gases through the membranes were studied with experimental and simulated data.　Third, a study was carried out in which the membrane reactor was used in batch mode to utilize the natural pressure rise due to the increase in the number of moles in the reaction.

Chapter 1 introduces the background of the study referring to previous reports on hydrogen production and its separations especially hydrogen selective membranes.

Chapter 2 deals with the steam methane reforming (SMR) reaction studied on a Ni/ MgO-SiO$_2$ catalyst at 923 K (650 °C) and 0.40 MPa in a tubular packed-bed reactor. Experimentally, the CH$_4$ conversion increased with the inlet partial pressure of H$_2$O and decreased with the inlet partial pressure of CH$_4$. However, at low CH$_4$ inlet partial pressures, i.e., at 40 and 60 kPa, the conversion passed through a maximum. Rate expressions were derived based on a simple two-step sequence. A statistical analysis led to adequate in a certain degree, as indicated by a low F value of model adequacy which is very close to tabulated value. The model was able to correctly describe the experimentally observed maximum in the methane conversion and allowed relating this behavior to CH$_4$ and H$_2$O surface coverages. The effect of changing the total pressure and H$_2$O/CH$_4$ ratio on the CH$_4$ conversion as a function of the space velocity was simulated and corresponded to both the experimental and literature data. A major finding of the modeling was that as flow rate was increased there was a crossover in the order of conversion with pressure due to a transition from　thermodynamic to kinetic control.

Chapter 3 concerns a detailed kinetic analysis of SMR on Ni catalyst. The optimization and full understanding of chemical reactions aids the construction of an adequate kinetic model. Steam methane reforming on the Ni/MgO-SiO$_2$ case study is used for this purpose, that is, the construction of a kinetic model that embeds a maximum amount of information contained in the dataset. The kinetic model is expanded stepwise from a power law model over a model with reactant　adsorption　toward　a　Langmuir–Hinshelwood–　Hougen–Watson　model.　The

performance of the initially underparameterized model improved significantly by adding reactant adsorption, yet including product adsorption led to overparameterization rather than enhanced model performance.

Chapter 4 describes hydrothermally stable silica-alumina composite membranes synthesized through chemical vapor deposition of tetraethylorthosilicate and aluminium tri-sec-butoxide precursor at 923 K on porous alumina supports. The membranes showed high hydrogen permselectivity comparable to that of pure silica membrane but with superior hydrothermal stability, and were used in a membrane reactor. The permeation of small gas species (H_2, He, Ne) was well explained by a solid-state diffusion mechanism, involving jumps of the permeating species between solubility sites. The permeation mechanism of large gas molecules (CH_4, CO_2, N_2) was explained by the gas translation mechanism involving large pore defects. SMR on a Ni/MgO-SiO_2 catalyst was carried out at 923 K in the membrane reactor mode and in a packed-bed reactor mode. The membrane contributed to an increase in the hydrogen production rate by the selective extraction of hydrogen from the reaction zone.

Chapter 5 describes the studies conducted in a packed-bed membrane reactor operated as a semi-batch membrane reactor (SBMR) to capture the pressure generating potential of the reaction. The actual system investigated is the steam methane reforming, a reaction in which the number of moles doubles on a Ni/$MgAl_2O_4$ catalyst. A silica-alumina membrane prepared in the same manner as chapter 4 was used in the membrane reactor. The hydrogen productivities obtained in the SBMR were compared with the productivities obtained in a membrane reactor operated at the same conditions. At low pressures (~1.0 MPa) the hydrogen productivities of the SBMR were comparable to those obtained with the continuous membrane reactor, but at high pressure (1.5 MPa) the SBMR showed superior performance. One-dimensional modeling studies gave good agreement between simulated and experimental results obtained from both reactor types.

Chapter 6 describes the general conclusion of the study and future visions of the contributions of membranes in hydrogen production.

The collection of work meets the requirements for the doctoral degree in engineering and can be judged to contribute to the development of chemical systems engineering.