CFD-simulation of membrane reactor for methane steam reforming

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Abstract

A membrane reactor is a reaction system that provides higher productivity and lower separation cost in chemical reaction processes. In this paper, packed bed catalytic membrane reactor with palladium membrane for methane steam reforming was analyzed both experimentally and numerically.

The numerical model consists of a full set of partial differential equations derived from conservation of mass, momentum, heat and chemical species, respectively, with chemical kinetics and appropriate boundary conditions for the problem. The solution of this system was obtained by computational fluid dynamics (CFD). To perform CFD calculations, a commercial solver FLUENT^{TM} has been used and the selective permeation through the membrane has been modeled by user defined functions.

The CFD simulation resulted to exhibit the flow distribution in the reactor by inserting a membrane protection tube, in addition to the temperature and concentration distribution in the axial and radial directions in the reactor, as reported as membrane reactor numerical simulation. On the basis of the simulation results, effects of the flow distribution, concentration polarization and mass transfer in the packed bed will be shown in the presentation to design a membrane reactor system.

Introduction

A membrane reactor is a reaction system that provides higher productivity and lower separation cost in chemical reaction processes. The reactions of interest in the membrane reactor application are endothermic, such as steam reforming of methane, water gas shift reaction, and dehydrogenation of alkanes. Many researchers energetically studied on the development of high performance membranes and catalysts, and on the evaluation of the combined system characteristics for the process design.

Also, some efforts have been made the membrane reactor system analysis by a numerical simulation. Most of reports show analyses according to one-dimensional basic

equations with the concentration gradient respect of reactants and products, and temperature gradient in the reactor (Itoh, 1987). Recently, a two-dimensional analysis which considers the mass and heat transfer in the axial and radial directions was studied (Assabumrungrat, 2002; Fukuhara, 2003). Computational fluid dynamics (CFD) have exhibited new investigation possibilities in this field (Koukou, 1999; Staudacher, 2002).

Considering the advantage of CFD calculations for membrane reactor simulation, we performed a comprehensive study on a membrane reactor for methane steam reforming to evaluate the performance characteristics of the reactor.

Experimental

A cross-sectional view of the reaction cell, a main part of the reactor, is shown in Fig. 1. A thin layer of palladium was deposited on the surface of porous alumina tubing by electroless plating method, The inner tube which is perforated with circular holes protects the palladium membrane not to touch directly with the cylindrical Ru-catalyst pellets which contains 0.5% ruthenium supplied form N.E.Chem-Cat. Alumina pellets were packed in the annular region between outer and inner tubes to keep the Ru-pellets. Reaction experimental conditions are summarized in Table. 1.

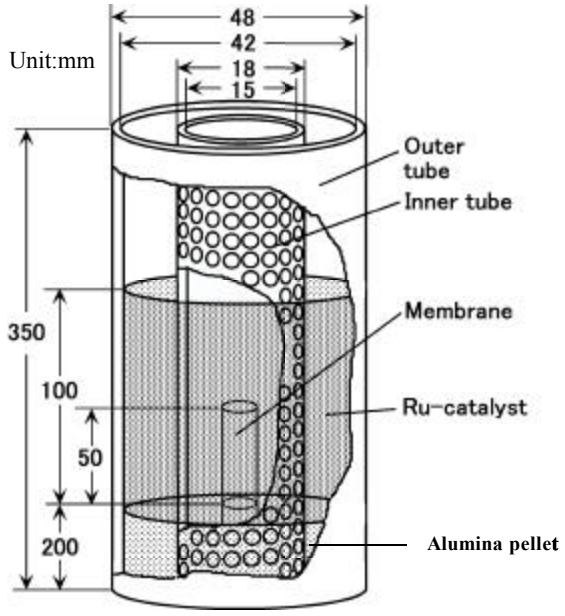

Fig. 1 reaction cell

Table 1 Experimental conditions

Temperature T [K]	623 - 773
Pressure P [MPa]	0.2
Superficial spacevelocity Sv [s-1]	0.031 - 0.16
Feed gas	CH_4:H_2O = 1 : 3
Sweep gas (Ar) [ml/min]	157
Permeance of H_2 P_{H2} [mol m^{-2} Pa^{-1} s^{-1}]	3×10^{-9}
Ru-Catalyst	
Diameter [mm]	3.2
Length [mm]	3.4
Bed porosity [-]	0.39

Simulation model

In this section, the simulation model used in this study is described briefly.

The model consists of theoretical equations to describe the transport phenomena of the mass, momentum, energy and chemical species, and the process of selective permeation through the membrane.

The discretized equations were coupled and solved using the SIMPLE algorithm on a CFD software package, FLUENT version 6.1. Fig. 2 shows a numerical grid of the membrane reactor. Physical properties of chemical species such as viscosity, heat capacity and thermal conductivity were taken from the literature and were expressed as functions of temperature. The properties of the mixed gas were estimated based on conventional methods. The molecular diffusivity of each component in the gas mixture was calculated by applying the Maxwell-Stefan equations.

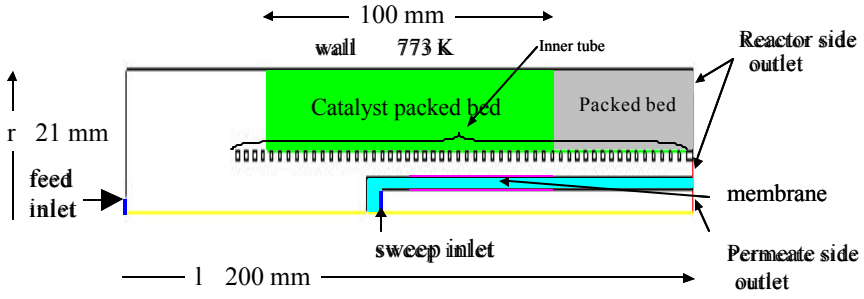

Fig. 2 numerical grid (100×50) used in simulation

For the packed bed region, the well-known Ergun equation was used to describe the momentum loss, in term of pressure gradient. In this study, the gas velocity through the packed bed was sufficiently small, and the effective heat and mass transfer coefficient in the packed bed was properly estimated to be independent of the gas velocity.

The hydrogen selective permeation through membrane was calculated as a function of permeance, absolute pressure, temperature and mass fraction of hydrogen in each cell of membrane surface according to Eq. (1).

$$J = P_{H2} \times \left(p_{H2,reac.} - p_{H2,sweep} \right) \quad (1)$$

where P_{H2} is hydrogen permeancem [mol m^{-2} Pa^{-1} s^{-1}], $p_{H2,reac.}$ and $p_{H2,sweep}$ is hydrogen partial pressure of reaction and sweep side, respectively.

The calculated permeation flux through the membrane was implemented as absorbed or desorbed flux to the both side of membrane surface for each cell as boundary condition using user defined function.

Results and discussion

Fig .3 shows the flow pattern in the reactor without membrane. The geometry of the reactor, containing a protection tube and packed bed, affects strongly the gas flow pattern in the reactor. Gas velocity in packed bed is sufficiently small, therefore the effective mass and heat transfer coefficients in the packed bed were assumed same as those without flow. The amount of the gas flowing the space between protection tube and the membrane tube was very high. Because the reaction occured in catalyst packed bed, gas flow field in the catalyst packed bed strongly affected the CH_4 conversion. Considering the flow distribution mentioned above, the reaction rate constants derived from reaction rate equation (2) (Lunde, 1973) were determined.

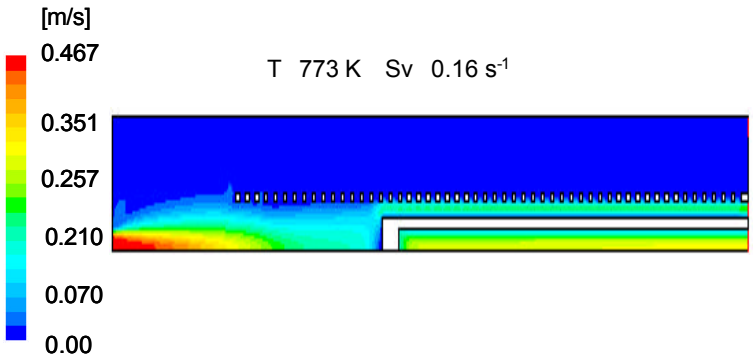

Fig. 3 Velocity field in the reactor

$$r_{CH4} = \frac{1}{RT} \cdot k \cdot \exp(-\frac{E_a}{RT}) \times \left\{ [p_{CH4}] \cdot [p_{H2O}]^2 - \frac{[p_{CO2}] \cdot [p_{H2}]^4}{K(T)} \right\} \quad (2)$$

where k is the constant rate of reaction rate constant [Pa^{-2}], Ea is the activation energy [J mol^{-1}] and K(T) is equilibrium constant [Pa^{-2}]. Results of the best fit results shown in Fig. 4 agree well with experimental results. The value of k was about five times larger than that determined from the one-dimensional model in which the flow distribution was ignored. This difference shows the importance of considering the flow distribution in the reactor. Traditionally one-dimensional model leads to an overestimation of gas flow through catalyst region followed by an overestimation of reactor conversion.

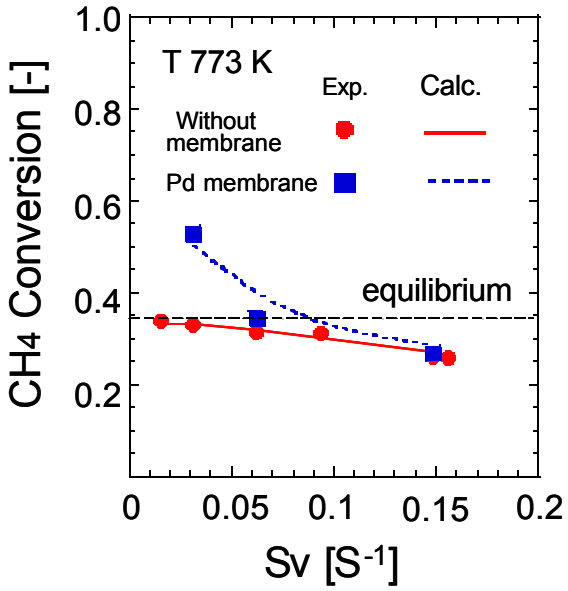

Fig. 4 Comparison of CH_4 conversion under various Sv with and without Pd membrane

Fig. 5 and Fig.6 show the temperature and hydrogen concentration in the membrane reactor, respectively. In the reactor, gases were

fed at 423 K and heated by heat conduction from the wall. In order to assure a rapid reaction, the temperature at catalyst packed bed should be close to the wall. In lower SV case, the catalyst packed bed temperature was close to wall temperature, i.e. heat conducted in the catalyst packed bed to feed gas was sufficiently large. In higher SV case, i.e. a large amount of feed gas supplied, large temperature distribution was observed in the reactor as reported elsewhere. The amount of hydrogen produced and the heat absorbed by endothermic reaction in the reactor increased with the increase of the feed gas supply. This increase of heat absorption leads to the decrease of temperature in catalyst packed bed and the increase of the temperature distribution in the reactor.

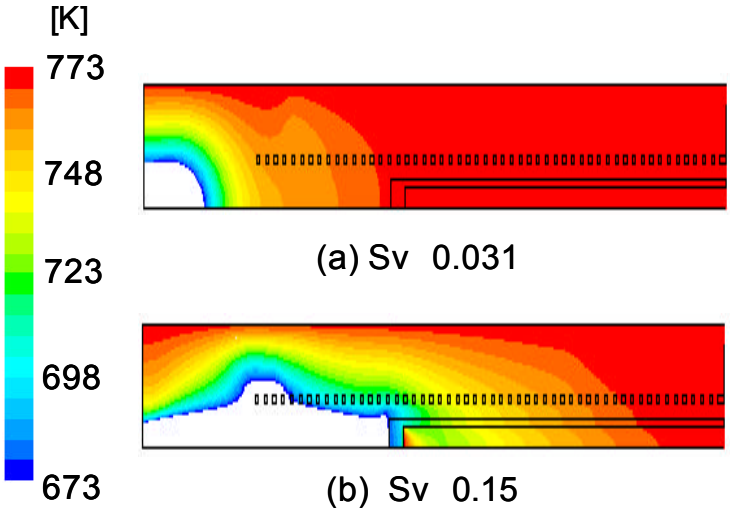

Fig. 5 Contour profile of temperature in the membrane reactor (reac temp 773 K)

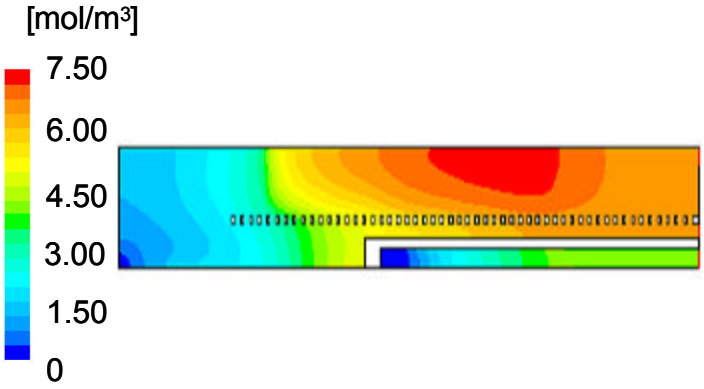

Fig. 6 Contour profile of hydrogen concentration in the membrane reactor (reac. temp 773 K Sv 0.15 s^{-1})

The increase of hydrogen concentration produced in the catalyst packed bed, the decrease of hydrogen concentration at the feed side membrane surface by selective hydrogen permeation through the membrane, i.e., concentration polarization and the increase of hydrogen concentration at the inside of membrane tube by permeation through the membrane were observed. Considering the effects of flow, temperature and concentration distributions mentioned above, CH_4 conversion was determined. As shown in Fig. 4, CFD calculations were good agreement both without and with membrane case. A comprehensive analysis, including momentum, heat and mass transfer, by CFD was shown and the possibility of CFD to membrane reactor design was suggested.

SUMMARY

In this study, a packed bed catalytic membrane reactor with palladium membrane for methane steam reforming was analyzed both experimentally and numerically. The numerical model consisted of the full set of partial differential equations described the conservation of mass, momentum, heat and chemical species with chemical kinetics and appropriate boundary conditions for the problem. The solution of this system was obtained by a computational fluid dynamics (CFD). For CFD calculations, the commercial solver FLUENT^{TM} has been used and the selective permeation through the membrane has been modelled by user defined functions.

The CFD simulation results exhibited the flow distribution in the reactor by an inserted membrane protection tube, in addition with the temperature and concentration distributions in the axial and radial directions in the reactor, as reported for such membrane reactor numerical simulation. The CFD calculations were in good agreement both with and without membrane case. The advantage of the comprehensive analysis, including momentum, heat and mass transfer, by CFD and possibility of membrane reactor design was suggested.

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