

論文の内容の要旨

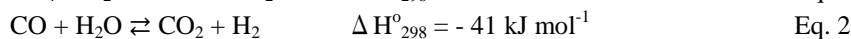
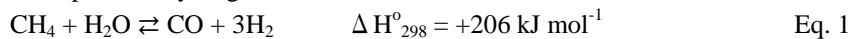
Abstract of the thesis

論文題目

Kinetic and Membrane Reactor Studies of Steam Methane Reforming on Ni-Based Catalysts
(ニッケル触媒を用いたメタン水蒸気改質の速度論解析と膜反応器に関する研究)

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Hydrogen is envisioned to be a significant energy carrier for a sustainable energy delivery system of the future. Presently, natural gas is one of the most important sources for hydrogen production because of its abundant supply and its relatively low cost. The steam reforming process is the most important commercial process for the production of hydrogen and synthesis gas (a mixture of H₂ and CO) from natural gas. It is used in conjunction with the water-gas shift reaction to produce hydrogen.



Many studies employ Ni as the principal component of the catalyst but use different supports like CaO-Ca₅Al₆O₁₄, γ -Al₂O₃, K₂Ti_xO_y-Al₂O₃, α -Al₂O₃, NiAl₂O₄, TiO₂, SiO₂, ZrO₂. In this study, a kinetic analysis of steam methane reforming (SMR) was carried out by the fitting of a kinetic model to experimental data. A simulation with the model was also developed. The operation of the SMR with a silica-alumina composite membrane was investigated and a semi-batch reactor was operated and analyzed with a simple model.

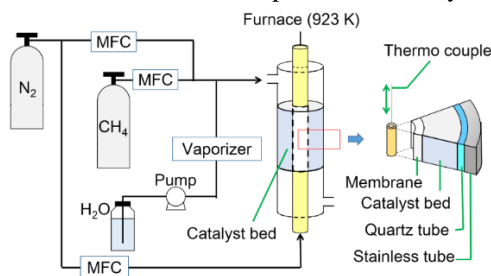


Fig. 1. Reactor for steam methane reforming

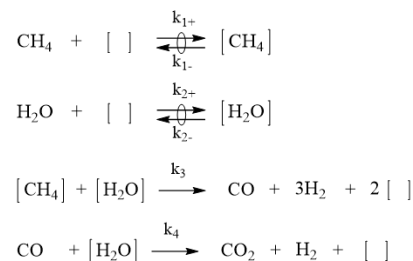


Fig. 2. Reaction model

A hydrogen perm-selective membrane or nonporous alumina tube was placed vertically in a reactor with a quartz sleeve and a stainless shell. The catalytic steam methane reforming was operated with the catalyst placed in the annular region between the sleeve and the membrane/dense tube (Fig. 1). The catalyst was a Ni/MgO-SiO₂ provided by JGC Catalysts and Chemicals Ltd.. The experiments were conducted at a temperature of 923 K, total pressure of 0.40 MPa, and WHSV of 48000 Ncm³ h⁻¹ g_{cat}⁻¹. The output gas was analyzed with a gas chromatograph equipped with a thermal conductivity detector (TCD). The H₂O component was fed as a liquid and was vaporized before mixing with the CH₄. Alumina silica composite membranes were synthesized by chemical vapor deposition (CVD) process.

In chapters 2 and 3, the experimental results were analyzed by different kinetic models. First, a simple model was used which incorporated Langmuir-Hinshelwood (L-H) and Eley-Rideal (E-R) steps, in order to have the smallest numbers of variables. This model assumes that the steam methane reforming takes place between adsorbed methane and water, and that the water gas shift occurs between adsorbed water and gaseous carbon monoxide (Fig. 2).

The Mears criterion and the Weisz-Prater criterion were calculated and it was verified that the reactions were not mass and heat transfer limited. Thus, it can be concluded that there were no internal nor external heat or mass transfer limitations in the present studies. Methane consumption in this model is described by the third reaction in Fig. 2 and the following rate expression can be obtained:

$$r_3 = k_3' \theta_{[CH_4]} \theta_{[H_2O]} = \frac{k_3' K_1 K_2 P_{CH_4} P_{H_2O}}{(1 + K_1 P_{CH_4} + K_2 P_{H_2O})^2}$$

where k_3' : reaction rate coefficient, K_1 and K_2 adsorption equilibrium constant for CH_4 and H_2O , respectively.

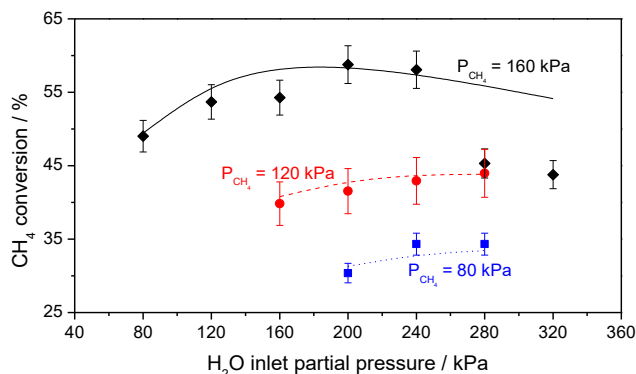


Fig. 3. Experimental result and fitting curve by hybrid model

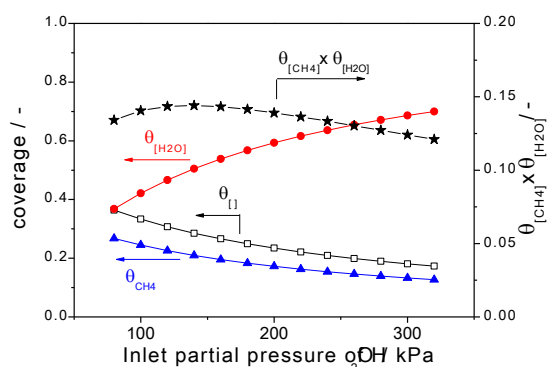


Fig. 4. Surface coverage calculated by hybrid model

Fig. 3 shows experimental results of CH_4 conversion versus inlet partial pressure of H_2O for three levels of inlet partial pressure of CH_4 . Generally, the CH_4 conversion increased with increase of inlet partial pressure of H_2O , but at high partial pressure of H_2O (around 160~240 kPa), the CH_4 conversion started to decline or level off. The simple model explained this behavior well, as due to competition of surface sites by H_2O . These results were confirmed by the calculation of the surface coverage of the catalyst (Fig. 4). This model explains the SMR behavior in the reactor well and the investigation of the model improvement of applying the product adsorption was found to be redundant. With this model, the simulation shown in Fig. 5 was obtained. In this simulation, the inlet gas composition was fixed at $H_2O: CH_4: N_2 = 2:1:2$, the total pressure of the reactant and WHSV were varied and the results were estimated by the kinetic model. In the high WHSV region, which is not close to the equilibrium state, the rate at higher pressure is higher, even though the reaction was favored at lower pressure from equilibrium. This result rationalizes why SMR is operated at high pressure commercially even though the reaction is not thermodynamically favorable at high pressure.

Fig. 6 summarizes recent reported data (since 2013) and displays the result of this work (X in the Fig 6). There is a cluster of points in the upper and lower regions, correspond to higher and lower H_2O/CH_4 ratios and are consistent with the obtained data. The most obvious difference in experimental conditions between them is the pressure, and when the simple hybrid model is adjusted for a pressure, there is very good agreement (the square in Fig. 6).

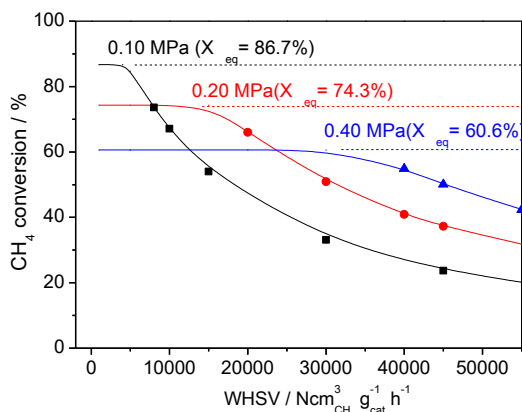


Fig. 5. Calculated CH_4 conversion change varying CH_4 WHSV and total pressure

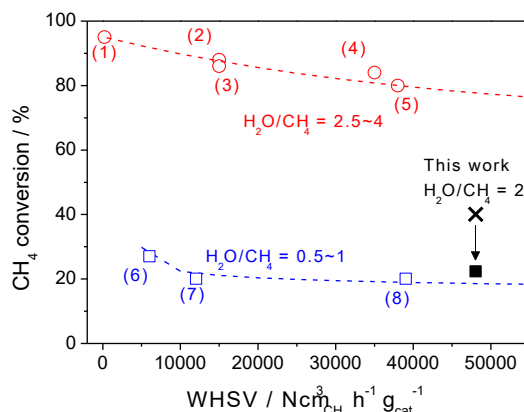


Fig. 6. The comparison between recent report and this work

In chapter 4 membrane reactor operation was studied. Membrane reactors are attractive because they combine reaction and separation steps in a single unit. In addition, the continuous removal of hydrogen from the system shifts the equilibrium of the reforming reaction to side of the products and enhances yields (Fig. 7 gives a schematic representation of the membrane reactor. However, their application is limited by high material costs and problems of catalyst coking and poisoning by contaminants such as sulfur or chlorine and even carbon monoxide. Previous studies have reported the use of alumina membranes and microporous silica membranes for the steam reforming of methane. Although these types of membranes are very sensitive to water vapor, successful results have been obtained in several cases. In this project use is made of silica-alumina membrane with good water vapor tolerance prepared by chemical vapor deposition (CVD) of tetraethylorthosilicate and aluminum tri-sec-butoxide.

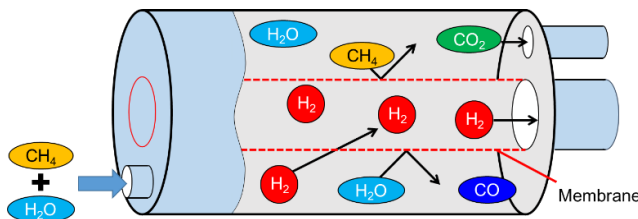


Fig. 7 Illustration of membrane steam methane reformer

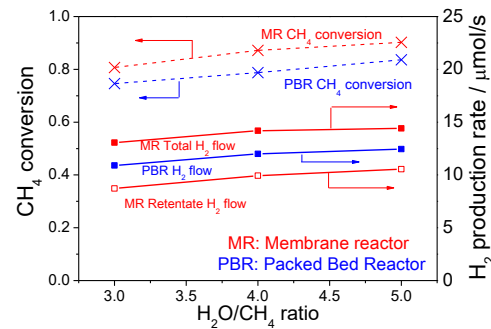


Fig. 8. H₂ production rate and CH₄ conversion in membrane reactor and packed bed reactor

Before the CVD process, a γ -alumina intermediate layer was placed on the porous alumina support by dip-coating and calcination of a boehmite sol. With the progress of CVD, a thin amorphous silica-alumina layer was gradually formed and the permeance decreased gradually. When the thin layer almost completely covered the whole surface of the intermediate layer, the permeance of nitrogen showed a significant decrease while the permeance of hydrogen was not greatly reduced. Then the H₂/N₂ selectivity increased to as high as 500. This membrane was set at the center of the reactor, which was then operated as a membrane reactor. A flow of a sweep gas was passed on the inner side of the membrane to remove the permeated gas from the reactor, avoiding reverse diffusion. Thus if this sweep flow was stopped and the exit of the inside of the membrane was closed, the permeation through the membrane gradually decreased and finally stopped, so this state could be taken as the condition of a traditional packed-bed reactor. Fig. 8 compares the results of the SMR operated in a membrane reactor and packed-bed reactor with varying inlet H₂O/CH₄ ratio. In the membrane reactor, a part of the produced hydrogen permeated through the membrane, so that the total H₂ flow comprised the sum of the H₂ flow on both sides of the membrane. At all conditions, the membrane reactor operation achieved higher H₂ production and CH₄ conversion.

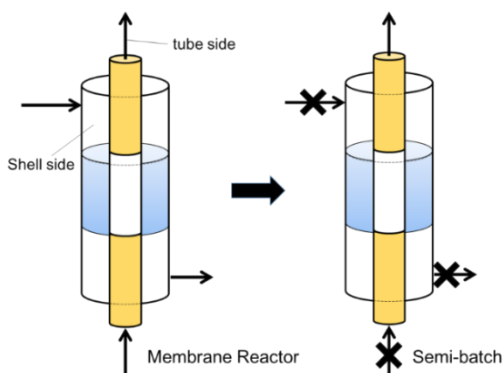


Fig. 9. Switching to semi-batch mode

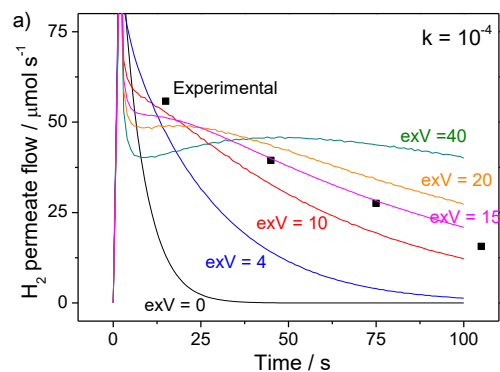


Fig. 10. Model fitting to the experimental data

In chapter 5, the semi-batch operation of membrane reactors was studied. The objective of this study was to explore a means of alleviating the requirement of the pressure gradient in membrane reactors for a certain class of chemical reactions. The class of reactions that will be considered in the separator mode will be that in which there is a net increase in the number of moles. This is a common situation, as exemplified for technologically important hydrogen-producing reactions. The increase in moles offers the potential of utilizing the reaction itself to overcome pressure drop losses through the membrane. In this study the throttling process, where the flow is restricted, was applied

at the limit of zero flow for demonstration of the concept. In this case the membrane reactor is operated as a semi-batch reactor. During the membrane reactor operation, the entrance and exit of the feed gas (shell side) and the entrance of sweep gas was closed at the same time (Fig. 9). Then the hydrogen would permeate through the membrane and slowly come out from the inside of the reactor (tube side).

The simulation was carried out with one-dimensional equations that were solved by using the ordinary differential equation solver in the program Polymath and the flow of the reactants and products were obtained. The total H₂ amount was obtained by integrating the hydrogen flow curves.

In the calculation a total volume (V_{total}) was considered which included the volume of the catalyst bed (V_{cat}) and extra volume (other parts of the reactor including the valves). To make the calculation, a constant k was defined to describe the mass transfer between the catalyst bed and the additional volume. (F_i : mole flow of i [mol/s], ΔP_i : partial pressure difference of i)

$$F_i = kD_{self,i}\Delta P_i$$

The constant exV was defined as

$$exV = \frac{V_{total} - V_{cat}}{V_{cat}}$$

To optimize the two constants, k and exV, a calculation based on the Xu and Froment kinetic model was used. In Fig. 10, exV was varied from 0 to 40 while k was varied at the value of 10^{-4} . When exV = 15, the curve showed an excellent fit to the experimental value, showing the same long tail in the H₂ permeation curve. In total it showed higher yield of hydrogen thus it could be applied to novel hydrogen production process.

Conclusions

Steam methane reforming was operated and analyzed by Langmuir-Hinshelwood and Eley-Rideal Hybrid models. The models explained the characteristic behavior of the experimental result by the use of calculated surface coverages. The membrane reactor was operated and the membrane contribution to the hydrogen production was demonstrated. The membrane reactor was also operated in semi-batch mode and was shown to have higher productivity than a continuous membrane reactor. The results showed the various possible applications of hydrogen permselective membranes.