353d Experimental Study and Thermodynamic Analysis of Steam Reforming of Methane with Membrane Reactor

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Steam reforming of methane by the membrane reactor is an attractive process for hydrogen production to fuel cell. The advantages of membrane reactor are to enable the reaction temperature lower and to make the reactor compact. We have already studied the membrane reactor for steam reforming of methane using dense Pd/Ag membrane with membrane thickness of a few microns. As a result, it was confirmed that the catalytic reaction was so fast that the hydrogen removal through membrane was the rate-determining step. Moreover, the mathematical simulation suggested that there was a room for improvement of methane conversion and hydrogen recovery by reducing the concentration polarization. In this study, we were focusing on two major subjects for steam reforming of methane with membrane reactor: improvement of performance and durability. In order to enhance methane conversion and hydrogen recovery, reduction of polarization effect was effective by optimizing the configuration of catalyst and membrane. This is because the decline in the hydrogen permeation through membrane by polarization inevitably caused the decline in hydrogen removal from reaction zone, thus leading to the decrease of methane conversion. As a result of experimental study, it was confirmed that narrowing the distance between the catalyst and the membrane from 15 mm to 3 mm decreased the polarization effect and increased methane conversion from 70% to 80%. Coke formation on the catalyst is one of the major concerns for long-term durability in membrane reactors. Thermodynamic analysis suggested that the coking occurred mainly by the dissociation of carbon monoxide ($2CO \rightarrow C+CO2$) under the reaction temperature of 823 K. It was also predicted that the possibility of the coking depended on hydrogen recovery. At hydrogen recovery of less than 80%, the degree of coking was estimated to become larger with the increase of hydrogen recovery. However, the coking was less likely to occur at hydrogen recovery of 80 % and above, because CO shift reaction was highly promoted and partial pressure of CO became quite low. In the presentation, the validity of thermodynamic analysis will be discussed by the experiments using commercial reforming catalysts. This work was performed as a part of the R&D project for High Efficiency Hydrogen Production/Separation System using Ceramic Membrane funded by New Energy and Industrial Technology Development Organization (NEDO).