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1 Introduction

Demand of pure hydrogen for fuel will rapidly increase due to spread of fuel cell for vehicles, houses and power stations. One of the most promising pathways to produce and supply hydrogen in near to mid-term future is on-site production from natural gas, because of its high overall energy efficiency and substantial reduction of greenhouse gas emissions. On the other hand, some hydrogen production methods by using renewable energy such as solar energy are researched actively; however they are far from practical use level. A membrane reactor system is an efficient hydrogen production system. This is because in a membrane reactor steam reforming reaction of hydrocarbon fuels (natural gas, etc.) and hydrogen separate process proceed in a single reactor simultaneously. Tokyo Gas has developed and operated a 40 Nm³/h-H₂ class membrane reactor system, and demonstrated its high efficiency of 81.4 % (HHV) at a hydrogen refuelling station for fuel cell vehicles in Tokyo [1]. However, more compact and inexpensive MRF systems are required for commercialization. In these few years, we have successfully developed a new type of hydrogen production and separation module which we call MOC (Membrane On Catalyst) module [2-4]. It requires no separate catalyst parts, and can make a membrane reactor system more compact and inexpensive. More to say, MOC is designed to have a membrane of palladium-based alloy prepared on the surface of the tubular structured catalyst that has catalytic activity for steam reforming reaction, thermal expansion matching with the membrane material, proper porosity and so on. We also have reported some MOC properties [5-6]. For example, our electroless plating membrane of less than 10 μm thick showed hydrogen permeability of over 30 Ncc/min/cm² and conversion of methane was higher than the equilibrium conversion under the same temperature. In this work, duration properties of hydrogen permeation and hydrogen production were especially focused.

2 Configuration of the MOC Module

The structure of MOC is schematically shown in Figure 1 as compared with the conventional membrane reactor module. The conventional module consists of reforming catalyst and hydrogen separation membrane on a porous support as shown in Figure 1 (A). Hydrogen produced from reforming of methane and steam in the catalyst layer permeates the membrane and passes through the porous support. In contrast, the MOC module consists of hydrogen separation membrane on porous support which has catalytic activity and requires no separate catalyst layers as shown in Figure 1 (B). Feedstock gases, i.e. methane and steam, are reformed and converted to hydrogen, carbon monoxide and carbon dioxide in the

catalytic porous support and only hydrogen permeates the membrane to produce highly-pure product hydrogen. The MOC module has four favourable characteristics. Firstly, it is more compact than the conventional module because the porous support has catalytic activity and requires no separate catalysis layers. Secondly, it may be durable because no friction of membrane with catalyst will occur. Thirdly, it can offer higher hydrogen permeability because plating technology can be applied to prepare a thin film membrane on the porous support. Lastly, manufacturing cost may be significantly reduced because well-established mass production technology can be applied to produce the porous supports, and because the amount of expensive rare metals, i.e. palladium and silver, can be reduced by plating thin membranes.

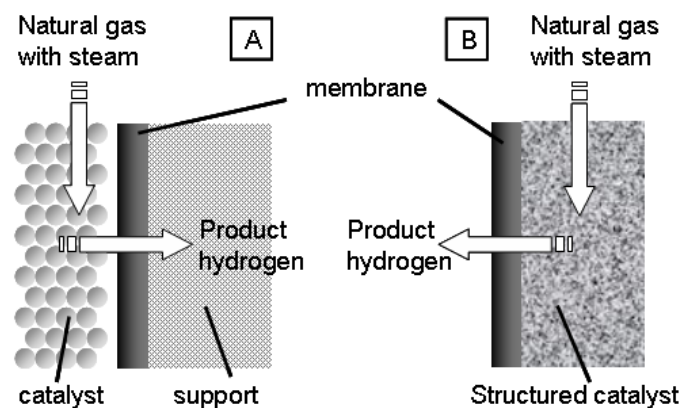


Figure 1: Structure of the conventional module and catalyst (A) and the MOC module (B).

3 Experimental

The fabrication process of the MOC module is roughly divided into three steps; production of porous support, coating of barrier layer and plating of palladium alloy membrane. Figure 2 shows the cross-section of the MOC module.

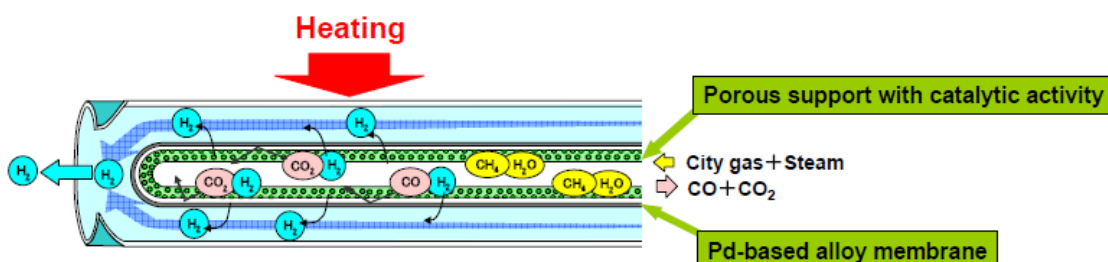


Figure 2: Cross-section of the MOC module and schematic flow of several gases.

NiO and 8YSZ (8 mol % Y₂O₃-ZrO₂) powders were blended at the weight ratio of 60:40 and formed into a tube by an extrusion molding method. The porous support was produced by sintering the tube in air at 1673 K. A slurry of 8YSZ was dip-coated on the outer surface of

the support and fired to form a barrier layer. The barrier layer is 20-60 μm in thickness and prevents interdiffusion of palladium and silver in the membrane and Ni in the catalytic support. The hydrogen permeation membrane was formed on the support coated with barrier layer by electroless plating of palladium and silver and subsequent heat treatment for alloying of them. The thickness of the membrane was 6-20 μm . The module was heat-treated in H_2 atmosphere at 873 K for three hours to reduce NiO in the support into Ni. The size of MOC module was 10 mm in outside diameter and 100 mm or 300 mm in length.

Hydrogen permeation and reforming tests were conducted with the 100 mm and 300 mm long MOC modules. The MOC module was kept at 823 K and inlet gases, i.e. pure hydrogen for permeation test and natural gas and steam for reforming tests, were introduced into the inside of the module (process side). The pressure of process side and permeation side were 0.1 MPaG and 0.0 MPaG in hydrogen permeation test, and 0.8 MPaG and -0.06 or 0.0 MPaG, in reforming tests, respectively. The schematic flow diagram of the experimental apparatus for hydrogen permeability and reforming tests for the MOC modules is shown in Figure 3. A flow of hydrogen or city gas and steam was controlled by mass flow controller and fed into the MOC module after heated in a pre-heater. The MOC module was placed in a chamber and heated to a given temperature. Test gases were introduced into inside of MOC module (process side) and hydrogen permeates through the membrane to the outside of MOC module (permeation side). The amount of permeated hydrogen flux was measured by a wet gas flow meter and the amount of off gas which was not-permeated hydrogen and residual gases from reforming reaction was also measured by a wet gas flow meter. The composition of off gas was measured by a gas chromatography. The gas pressure of the process side was regulated by a back pressure valve located after the MOC module and that of the permeation side was atmospheric pressure or under ambient pressure. The long-term hydrogen permeation test was conducted with pure hydrogen at 0.1 MPaG of process side pressure at 823 K. The reforming performance tests were carried out with natural gas and steam at 0.8 MPaG of process side pressure from 773 to 823 K, and the long-term reforming test at 823 K.

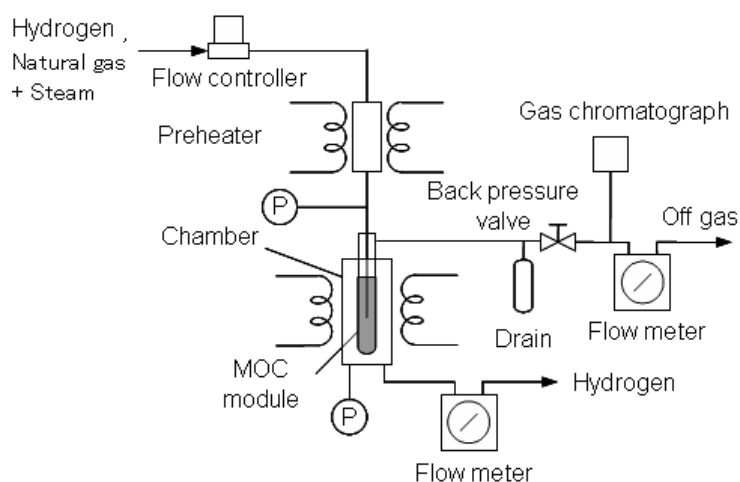


Figure 3: Schematic flow diagram of the reforming test apparatus.

4 Results and Discussions

4.1 Long-term hydrogen permeation test

Figure 4 shows permeated hydrogen flux or leakage of helium gas versus time. Quick increasing of permeated hydrogen flux occurred in the early several ten hours and hydrogen permeation increased up to 37 Ncc/min/cm² slowly until 1000 hour and maintained 37-38 Ncc/min/cm² through 3000 hour. This result indicated that hydrogen permeability for palladium alloy membrane (by electroless plating) has a long-term durability for at least 3000 hours. On the other hand, leakage increased gradually, because some pin-holes were formed by reaction between palladium and metal like particulates on the membrane. The particles should be removed in the gas flow system in the membrane reactor system to avoid formation of pinholes in long-time operation.

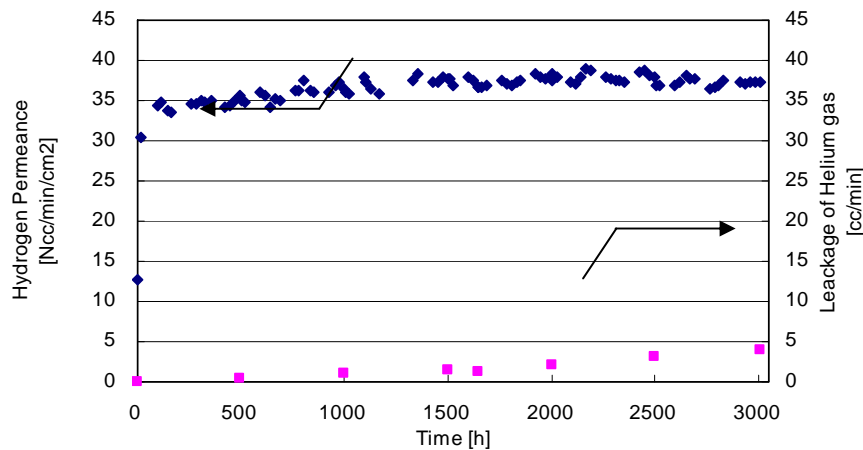


Figure 4: Hydrogen permeability of a 100 mm long MOC module at 823 K.

4.2 Reforming performance

Figure 5 shows the reforming temperature dependence of hydrogen product, conversion and hydrogen recovery at the pressure of process side, 0.8 MPaG. S/C (Steam/Carbon) was 3.0. Figure 4 (A) and (B) indicated the results at the pressure of the permeation side 0.0 MPaG and -0.06 MPaG, respectively. Hydrogen recovery was defined as the ratio of permeated hydrogen to all hydrogen generated by reforming reaction. It was found that the conversion was higher than equilibrium conversion in all temperature range and the effect was greater at elevated temperature. This is because the hydrogen permeation and the equilibrium conversion increased at elevated temperature in both test conditions. However, hydrogen recovery showed different behaviour. Only when the pressure of the permeation side was -0.06 MPaG, hydrogen recovery did not decrease at lower temperatures. Different rate limiting steps in both conditions were suggested. Figure 6 shows the result of long-term reforming test using another MOC module. Hydrogen product maintained constant (4.6 - 4.9 Ncc/min/cm²) up to near 750 hours as well as the conversion (50 -55 %). These indicated

that not only hydrogen permeation but also catalytic activity did not degrade for 750 hours at least.

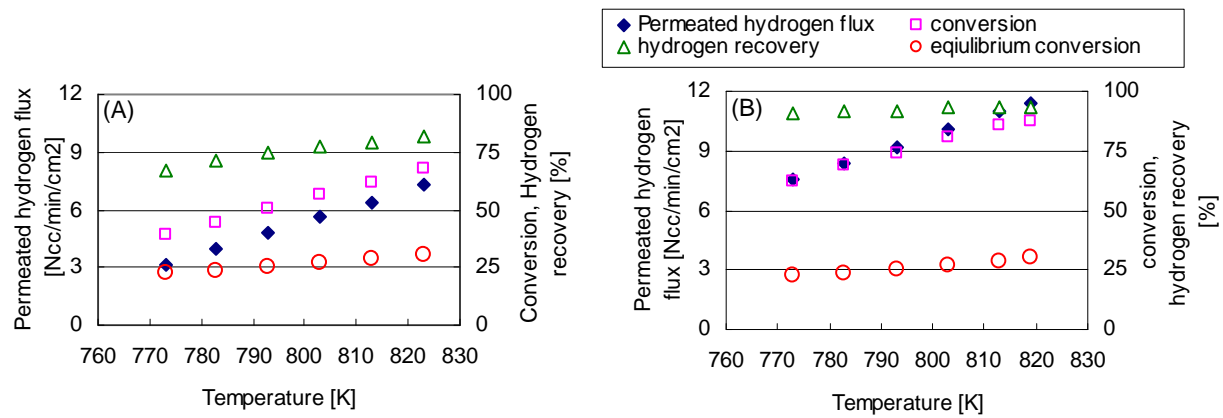


Figure 5: Reforming temperature dependence of permeated hydrogen flux, conversion and hydrogen recovery at the permeation side pressure of 0.0 MPaG (A) and of -0.06 MPaG (B).

5 Conclusions

We conducted hydrogen permeation or reforming tests using MOC modules at 823 K. Hydrogen permeability of membrane and catalytic activity were both demonstrated to have a long-term stability. However, pin-holes were formed and some leakages were observed. We will solve this problem and aim to have more durability for 8000 hours.

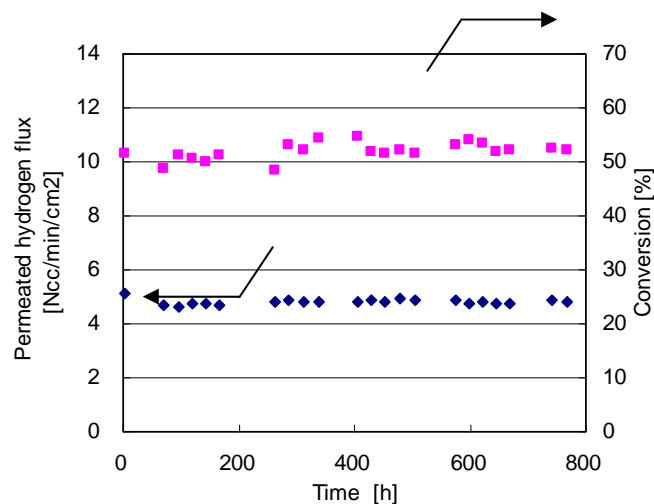


Figure 6: Long-term reforming test of a 100 mm long MOC module at 823 K.

Acknowledgements

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