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A catalytic membrane reactor for water-gas shift reaction

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Abstract−We conducted the WGS reaction on a catalytic membrane reactor consisting of a WGS catalyst bed, Pt/CeO_2 and thin, defect-free, Pd-Cu alloy membranes. The presence of CO and other gases with H_2 reduced the H_2 permeation through the membrane by more than 50% and the effect of the other gases on the permeation reduction decreased in the following order: $CO>CO_2>N_2$. In a catalytic membrane reactor with helium sweep gas, the CO conversion was improved by about 65% compared with the catalyst without any membrane, and the CH_4 formed from an undesirable side reaction was significantly reduced. Although the H_2 permeation was severely reduced by surface phenomena such as blocking of available H_2 dissociation sites by CO, CO_2 and steam, the CO conversion was notably improved by the membrane presence. Moreover, the CO conversion was maintained at 98% even after 60 h of reaction and our Pd-Cu-Ni alloy membrane withstood the exposure of CO and the other gases. However, for separation of pure H_2, a newly designed, catalyst-membrane system is required with better sealing and the ability to withstand the high operating pressure that drives the H_2 permeation.

Key words: Water-gas Shift Reaction, Pd Membrane, Hydrogen, Catalytic Membrane Reactor, Permeation

INTRODUCTION

The water-gas shift (WGS) reaction ($CO+H_2O=CO_2+H_2$, $\Delta H=-41.1$ kJ/mol) is well established in industrial operations such as ammonia and hydrogen production plants. In recent years, the WGS reaction has been investigated widely in fuel cell technology and carbon capture and storage from coal gasification. However, the commercial, CuZnO-based catalysts used for the low-temperature shift step and the FeCr-based catalysts for the high-temperature WGS reaction step have strong drawbacks. The former require long-term activation procedures, are pyrophoric, and are intolerant of poisons, condensation and oxidation, while the latter have a very low catalytic activity [1]. Therefore, advanced catalysts, mainly platinum-group metals, base metals and gold on reducible oxide supports such as ceria, titania and zirconia, have been investigated to overcome the drawbacks [2-5].

More recently, an alternative approach, a catalyst-membrane system combining the reaction and H_2 separation by means of a selective membrane, has become possible and has been intensively investigated for the WGS reaction with the significant developments in membranes, especially metallic (Pd and Pd alloy) membranes [6-9]. Due to integrating reaction and separation in the same unit, the catalytic membrane reactor increases the CO conversion even at a higher temperature where the thermodynamic conversion is low. Consequently, the amount of catalyst necessary for a given conversion can be significantly reduced, thereby reducing the reaction volume required to achieve the same CO conversion. Barbieri et al. [6] have investigated an innovative configuration of a Pd-Ag membrane reactor for the WGS reaction. In their study, the volume of the typical Pd-alloy membrane reactor and their innovative membrane reactor was reduced by ca. 35% and 60% compared to that of the traditional catalyst reactor, respectively.

The representative catalytic membrane reactors [6-9] were a shell and tube type where the reactant gas flows into the catalyst bed in the shell and reacts with it and then produced H_2 is permeated through the membrane tube in the shell and finally separated. Iyoha [10] investigated the WGS reaction in a catalyst-free, Pd-Cu membrane reactor at 900 °C using a 1mm-thick, Pd-Cu dense film as the WGS catalyst and H_2 membrane. In his results, the CO conversion was enhanced beyond the equilibrium value of 54% at 900 °C in the absence of additional WGS catalysts.

As mentioned above, a catalytic membrane reactor is a promising device for the simultaneous reaction and separation. In the present work, we tested the WGS reaction with a catalytic membrane reactor consisting of a Pt/CeO_2 catalyst bed and a 4 μm-thick, defect-free, Pd-Cu alloy membrane. The surfaces of the catalyst bed and membrane were very closely contacted in the reactor due to their coin-shaped, plate structure. These shape and structure enabled many sheets of catalyst and membrane to be easily stacked for easier scale-up.

EXPERIMENTAL

1. Catalyst Preparation

Pt/CeO_2 catalyst was prepared by incipient wetness impregnation method over the homemade CeO_2 support synthesized by the conventional precipitation procedure. The basic solution of NH_4OH was dropped in an aqueous solution of $Ce(NO_3)_3\cdot 6H_2O$ under vigorous mixing at room temperature until the pH reached 9. The resultant precipitate was filtered and dried at 110 °C overnight. The dried sample was calcined in air at 400 °C for 4 h to obtain a lemon yellow,

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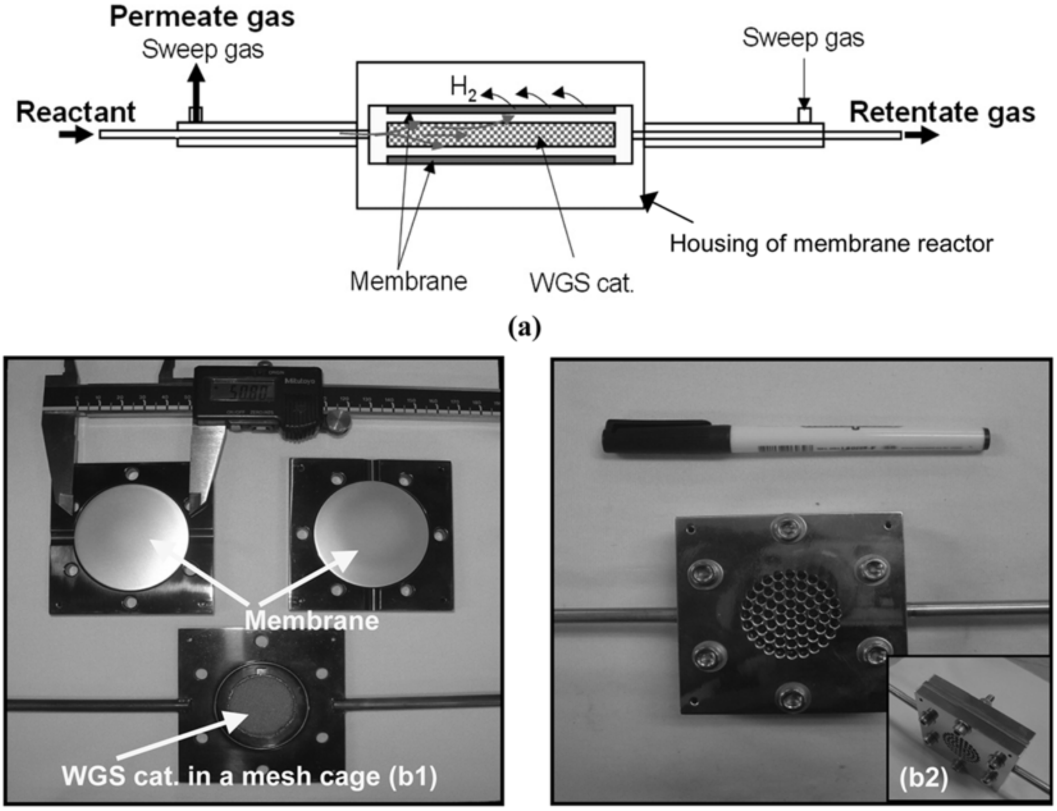
nano-crystalline, CeO_2 powder. 1 wt% Pt was impregnated over the synthesized support using an aqueous solution of $H_2PtCl_6 \cdot 6H_2O$, after which the catalyst was air dried, calcined at 400 °C for 4 h and characterized by BET-surface area (ASAP 2400), X-ray powder diffraction (XRD, D/MAX IIIC) and CO chemisorption (BEL-CAT, O_2-CO_2-H_2-CO pulse method suggested by Takeguchi et al. [11]) for Pt dispersion.

2. Membrane Preparation

For the Pd-Cu-Ni ternary alloy membrane, the porous nickel support and the supported defect-free membrane were fabricated by our own method [12-17] as follows. Nickel powder (mean diameter: 100 nm and purity: 99.9%) from Nano Technology Co was compressed without a binder in a cylindrical metal mold (diameter of 50 mm) using a homemade press, treated at 700 °C under H_2 for



(a)

(b)

Fig. 1. Configuration (a) and photographs (b) of the catalytic membrane reactor.

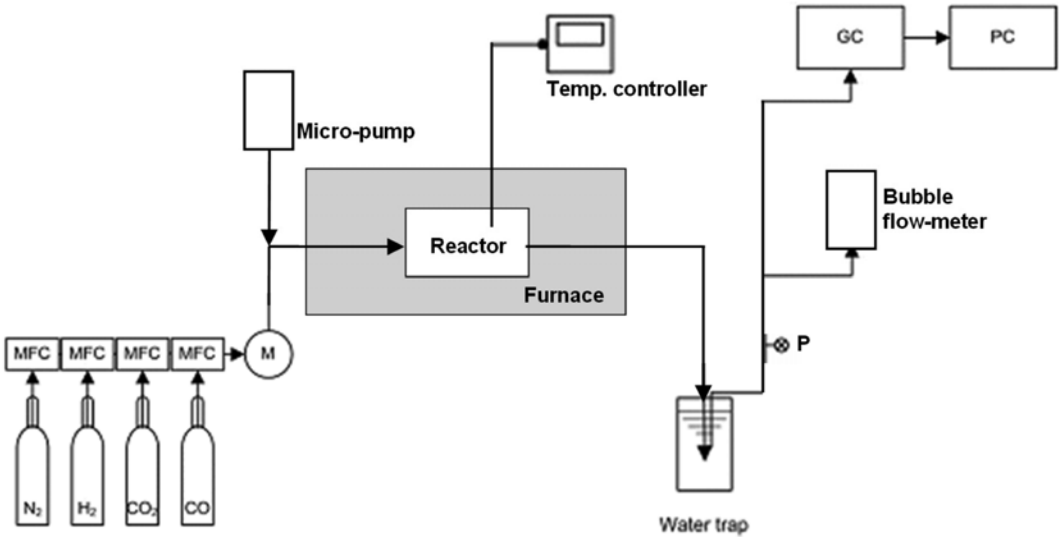
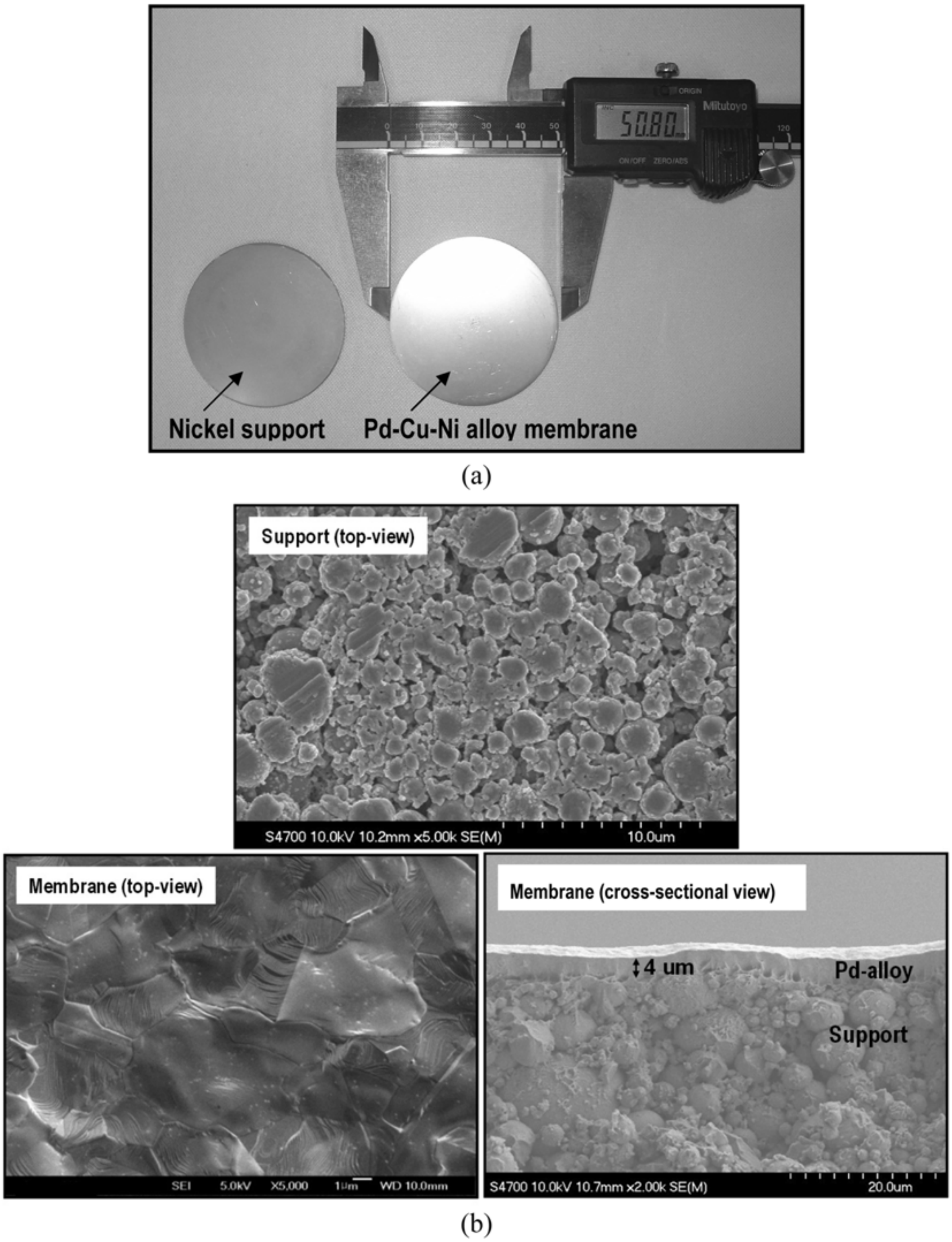


Fig. 2. Schematic diagram for the WGS membrane reactor test.

2 h to improve its mechanical strength, and polished to reduce its surface roughness. The Pd alloy membrane was prepared by magnetron sputtering Pd and Cu on the polished nickel support by 60 and 16 min, respectively, followed by Cu-reflow. After the Pd-Cu deposition, the Cu-reflow and Pd-Cu-Ni alloy were performed at 700 °C for 1h. The detailed fabrication conditions of the Pd-Cu-Ni alloy membrane have been described previously [12-17]. The permeation measurements were performed in pure hydrogen and/or mixture (H_2 and the other gases as an inhibitor) at 390 °C and 152 kPa with no sweep gas. The permeation area for one membrane was 11.94 cm^2. The porosity and pore size distribution of the support and the surface image of the support and membrane were characterized by Mercury Porosimeter (Autopore IV9500) and FE-SEM (HITACHI S-7400).

3. Catalyst-membrane System and Reaction Test

Fig. 1 shows the configuration (a) and photographs (b) of the catalyst-membrane system. It consists of a catalyst bed and 2 plate-type membrane disks where each membrane placed just on and under the catalyst bed in order to effectively separate the produced H_2. The WGS catalyst was palletized, crushed into 40-60 mesh and in-



(a)

(b)

Fig. 3. Photographs and SEM images of the porous nickel support and Pd-alloy membrane.

serted into the small, coin-shaped, mesh cage (b1 in Fig. 1(b)) with a diameter of 29 mm. The sweep gas was blown against the reactant gas at the outer of the membrane reactor to expel the separated H_2. The photographs of the assembly (b2) are shown in Fig. 1(b).

The WGS reaction test was performed under the real reformate gas comprised of 7.0 vol% CO, 8.5 vol% CO_2, 22.0 vol% H_2O, 37 vol% H_2 and 25.5 vol% N_2. The apparatus for the WGS membrane reactor test is schematically shown in Fig. 2. The total flow rate of the dry reactant gas was fixed at 100 ml/min (gas-hourly-space-velocity, GHSV=3,000 h^{-1}). Prior to the reaction test, the catalyst was reduced by 10% H_2/N_2 at 350 °C for 1 h. Helium was used as the sweep gas and the ratio of reactant and sweeping gases was denoted as "I". The feed and converted mixture gases were analyzed by an on-line gas chromatograph (GC6890, Agilent) equipped with two TCD detectors.

RESULTS AND DISCUSSION

1. Characterization of Catalyst and Membrane

The prepared Pt/CeO_2 catalyst had a surface area of 44 m^2/g and the CeO_2 crystalline size, estimated by Scherrer's equation from the XRD data (not shown here), was about 15 nm. The dispersion and cluster size of Pt were 84% and 1.3 nm, respectively.

The photographs (a) and SEM images (b) of the porous nickel support and membrane are shown in Fig. 3. Contrary to the porous surface of the nickel support, the membrane surface was dense and defect free and the deposited Pd alloy on the support was about 4 μm thick. The pore size distribution of the fabricated nickel support is presented in Fig. 4. The porosity was 35.7% and average pore diameter was 440 nm.

Fig. 5 presents the H_2 permeability for pure H_2 and the mixed (H_2 and inhibitor) gases. The permeability for H_2 alone was 11.8 $ml/min/cm^2/atm^{0.5}$. When another gas (N_2, CO or CO_2) was introduced with H_2 as a permeation inhibitor, the permeability decreased to less than half of that of H_2 alone and the reduction of H_2 permeance exhibited in the following order: $CO>CO_2>N_2$. Typically, this reduction has been attributed to (1) the blocking of available H_2 dissociation sites by the adsorption of CO on the membrane surface and the reduction of the active area available for H_2 permeation and (2) the interference of bulk diffusion through the membrane [10,18-22]. Iyoha [10] reported a similar observation relating to H_2 permeation using a 1 mm Pd-Cu membrane at 465 °C and about 1.5 Mpa. He observed a 5-7% reduction in H_2 permeation under the equimolar H_2-CO feed mixture. However, in the present study, although the ratio of inhibitor to H_2 was below 0.5, the H_2 permeation was seriously affected by the inhibitors. We attributed this difference to the membrane thickness. Namely, because H_2 permeation for a thinner (4 μm) membrane, compared with a thick membrane, is more strongly influenced by surface effects (gas adsorption or blocking of sites) than by bulk diffusion through the membrane, we believed that the inhibitor effects observed through the thinner membrane in this study were more notable.

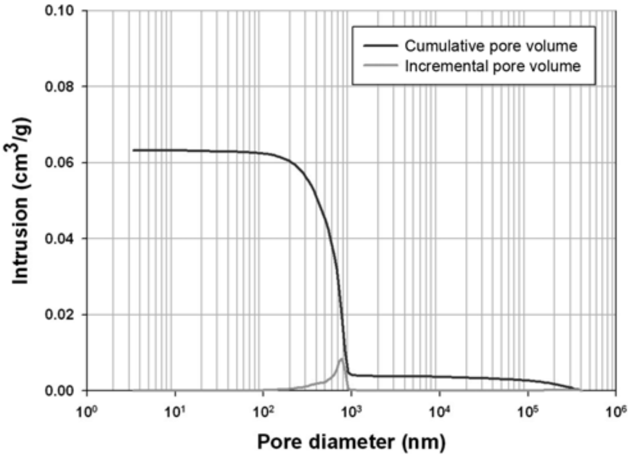
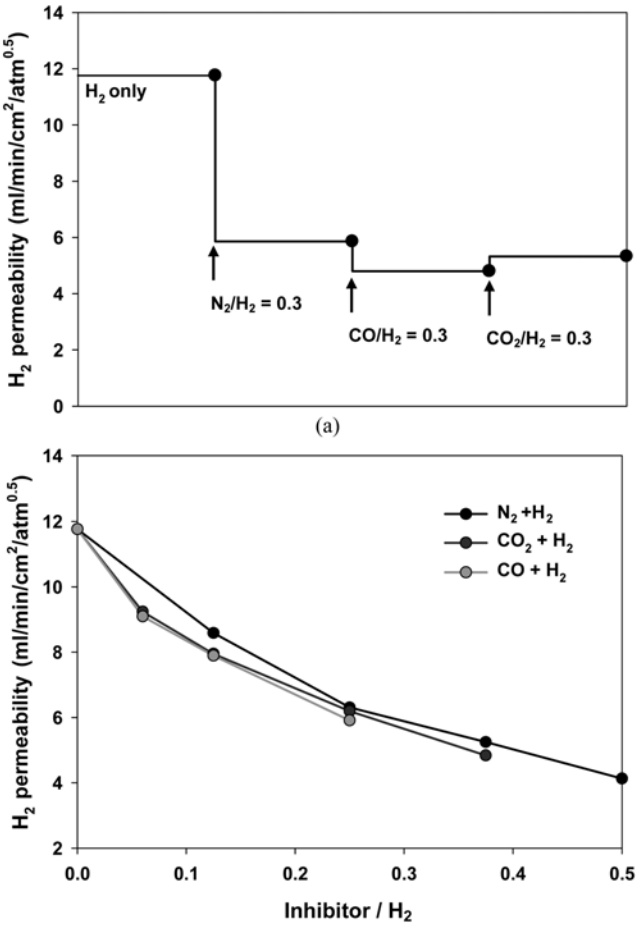


Fig. 4. Pore size distribution of the porous nickel support.



(a)

(b)

Fig. 5. H_2 permeability for single gas (H_2) and mixture (H_2 and inhibitor).

2. WGS Reaction Test in the Catalyst-membrane System

The reaction tests were carried out on a catalytic membrane reactor with or without membranes and their results are shown in Fig. 6. In the absence of the Pd membrane, the CO conversion and the amount of methane produced by the side reaction were 59.9% and 4.3%, respectively. Here, the methanation reaction is an undesirable side reaction because it consumes hydrogen. As expected, in the presence of the membrane, the CO conversion was increased to 98.2%. Furthermore, the amount of methane produced decreased to 1.1% compared with the absence of the membrane because of the rapid

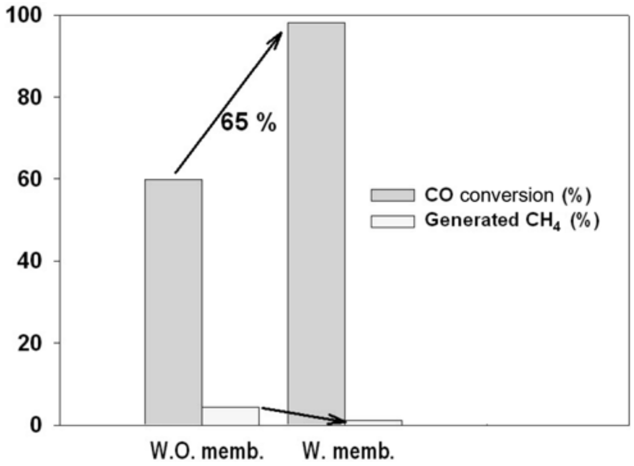


Fig. 6. Comparison of CO conversion/CH_4 formation with/without membranes in the catalytic membrane reactor.

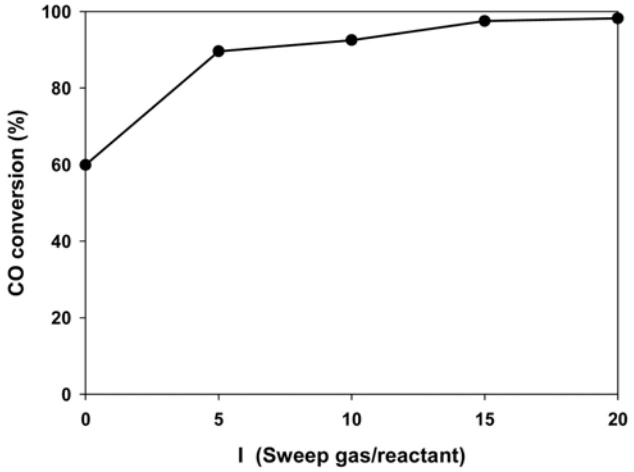


Fig. 7. The sweep gas effect on CO conversion in the catalytic membrane reactor.

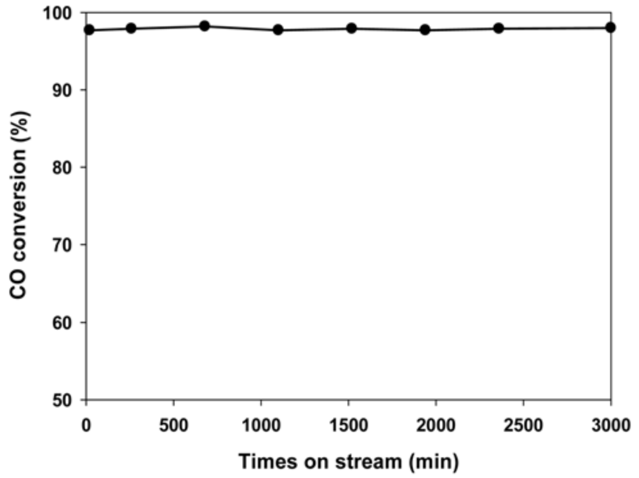


Fig. 8. Long-run WGS reaction results in the catalytic membrane reactor.

H_2 removal from the catalytic reaction zone through the membranes in spite of the reduced H_2 permeability in the presence of inhibited gases.

The effect of helium sweep gas on CO conversion is presented in Fig. 7. The CO conversion exceeded 90% when the ratio of sweep gas to reactant gas was above 5. In the present study, we had to use the sweep gas to increase the driving force instead of increasing the partial pressure of H_2 due to the operating pressure limitation of the present system. However, a newly designed, catalyst-membrane system with better sealing to withstand the high operating pressure is required to separate the pure H_2. Anyway, Fig. 7 shows the improvement in the CO conversion gained by using the sweep gas.

Fig. 8 presents the CO conversion on the stream according to the reaction time on the catalytic membrane reactor and Fig. 9 shows SEM images of the membrane surface before and after the WGS reaction. No notable surface modification of the membrane was observed after exposure to the WGS reactant at 400 ºC for 60 h. Iyoha [10] reported a small amount of carbon deposited on the Pd-Cu membrane surface (1 mm) after exposure of 50% H_2-CO feed stream at 600 ºC for 24 h and severe roughening of the membrane with increasing exposure temperature. Tosti et al. [23] reported that a 50 µm-wall Pd-Ag film supported commercial alumina tube suf-

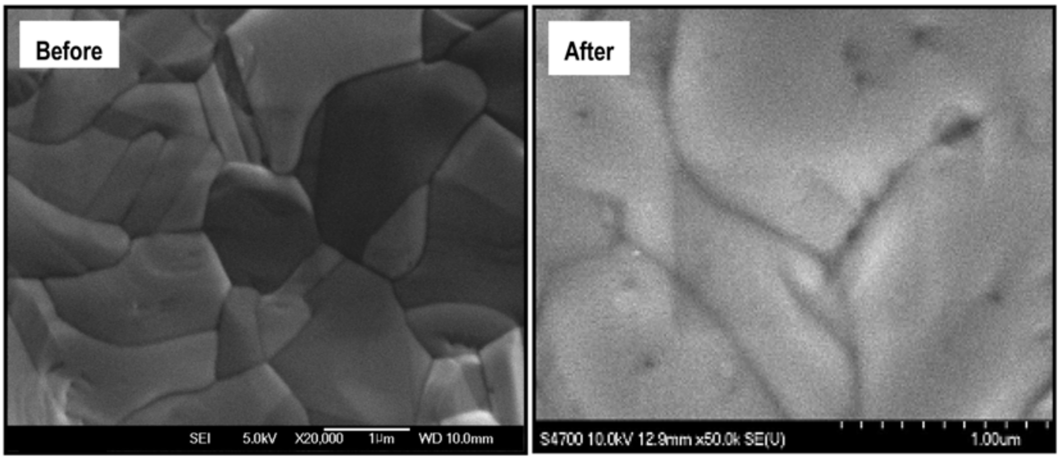


Fig. 9. SEM images of the membrane surface before/after the long-run WGS reaction.

fered from increased grain size or defect formation on the membrane surface during thermal and hydrogenation-dehydrogenation cycling. Compared with the thicker Pd-alloy membrane, the thinner, 4 μm-thick membrane fabricated in this study resulted in neither membrane defect (pinhole) nor carbon deposit on the membrane surface, even though it was exposed to the lower temperature and milder conditions (7% CO mixture) in this study.

CONCLUSIONS

We conducted the WGS reaction on a catalytic membrane reactor consisting of a WGS catalyst bed, Pt/CeO_2 and thin, defect-free, Pd-Cu alloy membranes. The presence of CO and other gases with H_2 reduced the H_2 permeation through the membrane by more than 50% and the effect of the other gases on the permeation reduction decreased in the following order: $CO>CO_2>N_2$. In a catalytic membrane reactor with helium sweep gas, the CO conversion was improved by about 65% compared with the catalyst without any membrane, and the CH_4 formed from an undesirable side reaction was significantly reduced. Although the H_2 permeation was severely reduced by surface phenomena such as blocking of available H_2 dissociation sites by CO, CO_2 and steam, the CO conversion was notably improved by the membrane presence. Moreover, the CO conversion was maintained at 98% even after 60 h of reaction and our Pd-Cu-Ni alloy membrane withstood the exposure of CO and the other gases. However, for separation of pure H_2, a newly designed, catalyst-membrane system is required with better sealing and the ability to withstand the high operating pressure that drives the H_2 permeation.

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