



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/hydro

Methane steam reforming using a membrane reactor equipped with a Pd-based composite membrane for effective hydrogen production

Chang-Hyun Kim^{a,c}, Jae-Yun Han^{a,c}, Hankwon Lim^{b,***},
Kwan-Young Lee^{c,**}, Shin-Kun Ryi^{a,*}

^a Advanced Materials and Devices Laboratory, Korea Institute of Energy Research (KIER), 152 Gajeong-ro, Yuseong-Gu, Daejeon, 305-343, South Korea

^b Department of Advanced Materials and Chemical Engineering, Catholic University of Daegu, 13-13 Hayang-yep, Gyeongsan, Gyeongbuk, 38430, South Korea

^c Department of Chemical and Biological Engineering, Korea University, 5-1, Anam-dong, Sungbuk-ku, Seoul, 136-701, Republic of Korea

ARTICLE INFO

Article history:

Received 18 August 2017

Received in revised form

25 September 2017

Accepted 10 October 2017

Available online xxx

Keywords:

Methane steam reforming

Membrane reactor

Pre-combustion

Pd-based membrane

Hydrogen

Long-term stability

ABSTRACT

Herein, a methane steam reforming (MSR) reaction was carried out using a Pd composite membrane reactor packed with a commercial Ru/Al₂O₃ catalyst under mild operating conditions, to produce hydrogen with CO₂ capture. The Pd composite membrane was fabricated on a tubular stainless steel support by the electroless plating (ELP) method. The membrane exhibited a hydrogen permeance of $2.26 \times 10^{-3} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-0.5}$, H₂/N₂ selectivity of 145 at 773 K, and pressure difference of 20.3 kPa. The MSR reaction, which was carried out at steam to carbon ratio (S/C) = 3.0, gas hourly space velocity (GHSV) = 1700 h⁻¹, and 773 K, showed that methane conversion increased with the pressure difference and reached 79.5% at $\Delta P = 506 \text{ kPa}$. This value was ~1.9 time higher than the equilibrium value at 773 K and 101 kPa. Comparing with the previous studies which introduced sweeping gas for low hydrogen partial pressure in the permeate stream, very high pressure difference (2500–2900 kPa) for increase of hydrogen recovery and very low GHSV (<150) for increase hydraulic retention time (HRT), our result was worthy of notice. The gas composition monitored during the long-term stability test showed that the permeate side was composed of 97.8 vol% H₂, and the retentate side contained 67.8 vol% CO₂ with 22.2 vol% CH₄. When energy was recovered by CH₄ combustion in the retentate streams, pre-combustion carbon capture was accomplished using the Pd-based composite membrane reactor.

© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

* Corresponding author.

** Corresponding author.

*** Corresponding author.

E-mail addresses: hklim@cu.ac.kr (H. Lim), kylee@korea.ac.kr (K.-Y. Lee), h2membrane@kier.re.kr, h2membrane@gmail.com (S.-K. Ryi).

<https://doi.org/10.1016/j.ijhydene.2017.10.054>

0360-3199/© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Hydrogen is heavily utilized for ammonia production, methanol production, in the cryogenic industry, and for refinery hydrogenation, as shown in Table 1 [1]. Recently, hydrogen has received much attention as a promising alternative fuel due to its high energy yield and eco-friendliness [2]. A large amount of hydrogen is derived by the conversion of natural gas into hydrogen using commercial processes for hydrogen generation, such as methane steam reforming (MSR), auto-thermal reforming (ATR), and partial oxidation (POx) [2,3]. Among them, MSR has been widely used industrially because it provides the highest hydrogen yield per methane feed [2,3]. In order to obtain high-yield and high-purity hydrogen, MSR requires three stages: the MSR reaction and two water gas shift (WGS) reactions (high temperature shift-HTS and low temperature shift-LTS), followed by purification to separate hydrogen from the reformed stream [4–6]. However, in terms of operating conditions, the MSR reaction requires a very high temperature (>1123 K) owing to its endothermic character [7]. Thus, a lot of research has focused on the development of advanced technologies for energy enhancement and cost saving [8–11].

Le Chatelier's principle states that hydrogen removal from the products shifts the thermodynamic equilibrium restrictions toward the product with a consequential conversion enhancement [10]. In terms of cost effectiveness and process efficiency, membrane reactors (MRs) allow for a reduction in the reaction temperature and high-grade hydrogen collection in the permeate side of the membrane reactor. In MRs, hydrogen permeates through the membrane by the solution and diffusion mechanisms, and the hydrogen permeation flux is proportional to the square root of the transmembrane pressure difference, assuming that the hydrogen atom diffusion through the dense metal layer is rate-limiting, as in Sieverts' law [12]. Therefore, many previous studies have shown (Table 2) that a high transmembrane pressure difference or a sweeping gas is required to obtain sufficient methane conversion with the appropriate amount of hydrogen removal from the reformed gas, in order to overcome the thermodynamic disadvantage of the MSR reaction [13–21]. In a previous study [21], it was shown that using a highly permeable and moderately-selective membrane in the membrane reactor led to the improvement of methane conversion under a rather low operating pressure (250 kPa), which promoted the reaction

due to the equilibrium shift. This result is in good agreement with the results of Oyama and Lim [22], who showed that the hydrogen permeation rate was much more effective than selectivity (H_2/CH_4) regarding the methane conversion and hydrogen yield. Thus, hydrogen selectivity according to the ratio of single-gas permeance had a substantial influence on conversion and hydrogen yield enhancements in a membrane reactor, and a selectivity of 10 was enough to achieve sufficient conversion enhancement.

On the other hand, pre-combustion carbon capture has been established by separating CO_2 from the synthesis gas, i.e., a mixture of H_2 , CO , CO_2 , and CH_4 [23]. Studies have shown that Pd-based membranes enriched CO_2 by separating H_2 from WGS driven mixtures [24–26]; others have shown that a WGS reactor equipped with a Pd-based membrane produced H_2 with CO_2 capture [27–29]. Spallina et al. [30] reported that the cost of H_2 production with CO_2 capture was 21% lower than the conventional fired tubular reforming process.

The objective of this study is to propose an economic hydrogen production and carbon capture technique based on an MSR route using a Pd-based composite membrane reactor. In order to sufficiently recover H_2 and enrich CO_2 , a highly permeable and moderately-selective membrane was used. The MSR reaction was conducted in a membrane reactor equipped with commercial Ru/Al_2O_3 catalysts and a tubular Pd-based composite membrane at a temperature of 773 K and pressure difference range of 203–507 kPa. A Pd-based composite membrane was prepared by electroless plating (ELP) on a tubular porous stainless steel support (PSS) modified with a yttrium-stabilized zirconia (YSZ) inter-metallic barrier. The MSR reaction was monitored during the long-term stability test (~145 h), and the gas compositions on the permeate and retentate sides were analyzed by gas chromatography.

Experimental

Membrane preparation

The Pd-based composite membrane was prepared on tubular (diameter: 12.7 mm, length: 250 mm) porous stainless steel (PSS; Mott, 0.5 mm grade) by the blowing-coating and electroless plating method [31]. The tubular PSS was modified by YSZ powder filling and blowing-coating with YSZ paste, which decreased the surface roughness and entrance pore size. The diffusion barrier was deposited between the PSS and Pd layers.

Table 1 – Industries that utilize hydrogen [1].

Hydrogen usage category	Usage by industry (%)	Comments
Ammonia synthesis	37	An ammonia plant is typically a hydrogen plant with a second converter for the reaction of hydrogen with nitrogen
Merchant	3	This includes all bottled users, liquid hydrogen supplied in tank trucks, and gaseous hydrogen in short pipe lines (not including the over-the-fence hydrogen suppliers)
Methanol	10	
Refinery hydrogenation	19	Hydrocracking and hydrotreating
Cryogenics	17	
Refinery fuel gas	14	Last resort

Download English Version:

<https://daneshyari.com/en/article/7707156>

Download Persian Version:

<https://daneshyari.com/article/7707156>

[Daneshyari.com](https://daneshyari.com)