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Triple-layer catalytic hollow fiber membrane reactor for hydrogen production

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ABSTRACT

Triple-layer hollow fiber catalytic membrane reactor (T-HFCMR) consisting of: (1) Ni-based catalyst (outer) layer; (2) porous inorganic support (middle) layer; and (3) ultrathin Pd-based membrane (inner) layer, has been successfully developed and used as a catalytic membrane reactor for hydrogen production. A 0.16 mol m^{-2} s^{-1} of H_2 gas can be produced from the T-HFCMR via catalytic decomposition of methane (as a model reaction) at 600 °C and 2 bar. Due to high H_2 permeability of the ultrathin (ca. 1.2 μm) Pd-based membrane, up to 84% of the total H_2 produced (H_2 recovery) can be extracted from the reaction side. Moreover, a constant permeation of H_2 from the reaction side also remarkably increases the reaction conversion. Furthermore, mechanical damages (e.g. scratching) of Pd–Ag membrane can also be prevented as the membrane is not exposed directly to the external surface, making it more flexible for practical applications.

1. Introduction

A diminishing of the worldwide petroleum reserves has shifted the focus of energy sources to other alternatives such as conversion of natural gas and biomass to H_2 [1]. Fuel cells that use H_2 as an energy source are environmentally friendly as compared to the traditional forms of combustion using fuels such as gasoline and diesel in the sense that the only one by-product from the H_2 fuel cells is water, thereby eliminating the emission of greenhouse gases [2,3]. Furthermore, the H_2 fuel cells also offer high energy conversion efficiency and a variety of possible uses in both mobile and stationary applications [4]. H_2 can be produced from many sources and by a variety of methods, such as electrolysis and photo-splitting of water, water-gas shift, reforming of hydrocarbons, alcohols and biomass [5–9].

Although the H_2 production from water is nearly carbon-free, the cost of water electrolysis is prohibitively high while the efficiency of photo-splitting of water is rather low for the large-scale production of H_2. Therefore, reforming reaction that is a primary conventional method for H_2 production remains the major method for a certain period. In order to improve the efficiency of H_2 production, reforming technology has been improved step by step. The replacement of conventional fixed-bed reactors with membrane reactors is believed to be one of the most important improvements on reforming technology. Recently, many attentions have been placed on the integration of separation (or purification) membrane and chemical reactor [10,11].

Catalytic membrane reactor (CMR), particularly Pd-based membrane reactor, which combines the Pd-based membrane as a part of separation unit and chemical reaction into one device is consequence of this integration. CMR is capable of promoting the reaction efficiency by selective removal of H_2 through the membrane from the chemical reaction, shifting the reaction equilibrium towards the product side [12,13]. As a result, the integration of these two units offers two prominent advantages [14–16]. Firstly, highly pure H_2 can be directly produced from the CMR without any requirement of further purification, hence reducing the cost of H_2 production. Secondly, the removal of H_2 from the reaction zone enhances the reaction efficiency by shifting the equilibrium forward, which is able to increase the reaction conversion as well as the H_2 selectivity and/or reduce the reaction temperature.

Table 1 summary the membrane type, operative condition and performances of the Pd-based membrane reactors and other types of CMRs which have been successfully used for H_2 production from hydrocarbons reforming and other reactions. Mostly, membrane reactors were made in the tubular structure which pure Pd or Pd-alloy membrane is deposited on the outer surface of the tubular porous support. Based on the configuration of catalyst bed, there are mainly two different types of the Pd-based membrane reactors, as schematically shown in Fig. 1. Firstly, the catalyst bed is packed inside the tubular porous support [19]; this configuration limits to the high pressure reactions. Alternatively, the catalyst bed is coaxially packed around the Pd-based membrane coated on the outer surface of the tubular porous support, enabling to avoid the

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Table 1
Operative conditions and performance of catalytic membrane reactors used to carry out hydrocarbons reforming and other reactions.

Reaction	Membrane	Type	Catalyst	Temperature (°C)	Pressure (bar)	H_2 recovery (%)	Conversion (%)	Ref
Methane steam reforming	Pd	Tubular	Pt_3Ni_{10}/CeO_2	525	10	> 80	> 90	[17]
	Pd-Ag	Tubular	Ni/ZrO	450	4.0	80	65	[18]
	Pd	Hollow fiber	$Ru/ZrO_2/La_2O_3$	525	1.0	30	45	[19]
Methane dry reforming	Pd-Ag	Tubular	$Ru/La_2O_2CO_3$	550	1.0	80	37.4	[20]
	Pd-Ag	Tubular	$Rh/CaO–SiO_2$	550	2.0	88	46	[21]
Propane steam reforming	Pd	Tubular	$Ni-Ag/CeO_2$	450	1.0		75	[23]
Ethanol steam reforming	Pd-Ag	Tubular	Ru/Al_2O_3	400	1.3		99	[24]
	Pd-Ru	Tubular	Pt-Ru/DND	450	1.0		99	[25]
	Pd-Ag	Tubular	Ru/Al_2O_3	450	4.0	97	> 98	[26]
Methanol steam reforming	Pd-Ag	Tubular		300	25	96		[27]
	Pd-Ag	Tubular	$Cu/ZnO/Al_2O_3$	250	1.3		80	[28]
	Pd-Ag	Tubular	Ru/Al_2O_3	350	1.3		30	[29]
	Pd-Ag	Hollow fiber	$Cu/Zn/GaO_X$	250	1.0	50	75	[38]
Acetic acid steam reforming	Pd-Ag	Tubular	Ni/Al_2O_3	400	4.0	70	92	[31]
Glycerol steam reforming	Pd-Ag	Tubular	Co/Al_2O_3	400	4.0	60	94	[31]
	Pd-Ag	Tubular	$Ni/CeO_2/Al_2O_3$	450	5.0		28	[32]
Water-gas shift	Pd	Tubular	Fe-Cr	400	2.0		59	[33]
	Pd-Ag	Hollow fiber	CuO/CeO_2	500	1.0	28	51	[34]
	Silica	Tubular	$Cu/ZnO/Al_2O_3$	300	1.0	40–80	80	[22]
	Cobalt-doped Silica	Tubular	Fe_3O_4/Cr_2O_3	450	15	95	93	[30]

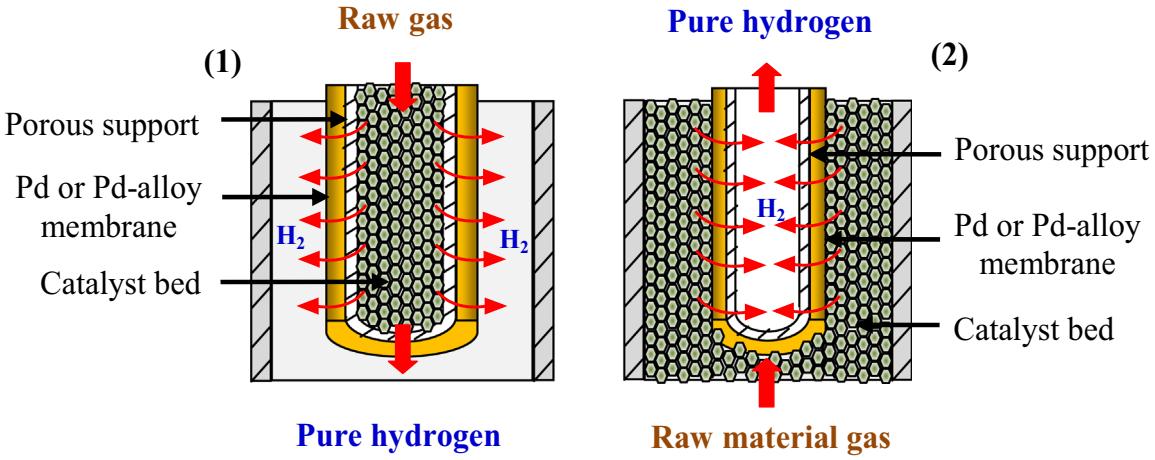

Fig. 1. Two main different types of palladium-based membrane reactors extraordinary.

problem of the first configuration [22–25]. These previous works show that the reaction conversion and the reaction efficiency can be greatly improved by replacing the conventional fixed-bed reactor with the catalytic membrane reactor. However, such previous works still have a number of drawbacks, especially the catalytic membrane reactors those the catalyst bed is arranged in the vicinity of the Pd-based membrane. In certain reactions such as auto-thermal reforming reaction, a sudden combustion reaction may takes place and generates heat to the portion of the catalyst layer. As a result, the Pd-based membrane can be exposed directly to high temperature, which may affect the durability of the membrane [35]. Furthermore, palladium can be reacted with the CO or CO_2 produced in the catalyst layer, forming the PdC_x-species on the surface of the Pd-based membrane which can significantly lower the separation efficiency of the Pd-based membrane [36].

Therefore, this work mainly concentrates on the above problems and develops the new triple-layer catalytic membrane reactor which consists of: (1) highly porous inorganic support (middle) layer; (2) catalyst (external) layer, capable of converting hydrocarbon to H_2; and (3) Pd-based membrane (internal) layer for H_2 separation. In other words, the Pd-based membrane will be not directly contacted with the catalyst layer by means of a porous support layer. Another task of this work is to further enhance efficiency of the catalytic membrane reactor by means of hollow fiber membrane which is capable of providing much larger surface area for gas permeation and chemical reaction as compared to the conventional tubular and dish-shaped membrane reactors with the same volume. More particularly, this work involves the development of triple-layer hollow fiber catalytic membrane reactor (T-HFCMR) which comprises:

(1) A highly porous α-Al_2O_3 hollow fiber membrane, which provides high mechanical strength, high thermal stability and high chemical resistance, is used as the support. However, the presence of large pores as a defect on the membrane surface is the main problem of the α-Al_2O_3 support. These defects make it difficult to form the thin and dense Pd-based membrane by using the method of electroless plating. Therefore, another ceramic material (i.e. YSZ) was added to fill up the large pores of the α-Al_2O_3 support.
(2) A catalyst layer, which is capable of converting hydrocarbons into hydrogen, is coated on the outer surface of the porous YSZ-doped α-Al_2O_3 hollow fiber membrane support wherein reforming reactions take place. The reforming catalyst used in this work is Ni-based catalyst which is well-known as the most effective, due to its high catalytic activity for reforming reactions and its low cost. In our previous works [37,38], Ni-based perovskite oxide have been successfully used as catalyst