

CATALYTIC HOLLOW FIBERS

BACKGROUND

Catalytic membrane reactors are useful for producing hydrogen gas, a green
5 energy source.

A conventional membrane reactor typically contains a catalyst bed, either
packed inside the tubular support of the reactor or arranged outside the tubular support,
and a palladium or palladium-alloy membrane coated on the outer surface of the tubular
support. The membrane reactor converts hydrocarbons to hydrogen gas by the
10 reforming reaction in the catalyst bed. The hydrogen gas thus generated is separated
from the reaction mixture through the palladium or palladium-alloy membrane. See
Amiridis et al., International Patent Application Publication WO 1999/043610 A1; and
Hattori et al., US Patent Application Publication US 2008/0241058 A1.

During the reforming reaction, residual carbonaceous materials, formed and
15 deposited in the catalyst bed, cause coke formation, which gradually deteriorates
catalyst efficiency and leads to a dangerous pressure build-up inside the membrane
reactor. Further, in a conventional membrane reactor, the palladium or palladium-alloy
membrane is subjected to cracking as it is on the outside surface of the tubular support
and exposes to catalyst particles and high temperature. Such reactors are therefore not
20 durable. See Nakamura et al., US Patent Application Publication 2008/0226544 A1.

There is a need to develop a safe and durable membrane reactor useful for
producing hydrogen gas.

SUMMARY

25 The catalytic hollow fiber of this invention exhibits, unexpectedly, both high
safety and great durability in producing hydrogen gas in a membrane reactor.

One aspect of this invention relates to a hollow fiber having an outer diameter
of 500 to 4000 μm (e.g., 1000 to 3000 μm) and an inner diameter of 100 to 2000 μm
(800 to 1600 μm). It contains three layers: (i) a porous support layer having an outer
30 surface and an inner surface, (ii) a catalyst layer coated on the outer surface, and (iii) a
selection layer coated on the inner surface.

The support layer has a thickness of 100 to 500 μm (e.g., 150 to 250 μm) and a
pore size of 50 to 400 nm (e.g., 100 to 300 nm). The catalyst layer has a thickness of

100 to 500 μm (e.g., 150 to 250 μm) and a pore size of 200 to 2000 nm (e.g. 400 to 1500 nm). It contains a catalyst, which causes or accelerates the production of hydrogen gas in a chemical reaction, e.g., a reforming reaction. Examples of the catalyst include a metal or metal oxide containing Fe, Ni, Co, Cu, Mo, Rh, Ru, Pd, La, or a combination thereof (e.g., LaNiO_3). The selection layer has a thickness of 0.3 to 10 μm (e.g., 0.3 to 2 μm and 0.3 to 0.8 μm). It contains a palladium or palladium-alloy film that selectively permeates hydrogen gas. A palladium alloy is an alloy of palladium and a metal such as Pt, Ni, Ag, Ta, V, Y, Nb, Ce, In, Ho, La, Au, and Ru (e.g., palladium-silver alloy, palladium-silver-copper alloy, palladium-silver-cobalt alloy, palladium-gold-cobalt alloy, palladium-gold-iridium alloy, and palladium-gold-rhodium alloy). More examples are described in Matzakos et al., US Patent 6,821,501 and Noda, US Patent Application Publication 2010/0092353. A preferred palladium-alloy film contains palladium-silver alloy that has 20-30 % silver by weight.

Another aspect of this invention relates to a method of preparing the hollow fiber described above. The method includes the steps of: (1) providing a porous hollow fiber support having an outer surface, an inner surface, an outer diameter of 200 to 3000 μm , and an inner diameter of 100 to 2000 μm ; (2) coating a catalyst layer on the outer surface; and (3) coating a selection layer on the inner surface, thereby forming the hollow fiber. Optionally, the method also includes, before step (3), forming a protection film covering the catalyst layer; and, after step (3), removing the protection film.

The details of one or more embodiments of the invention are set forth in the description and the drawings below. Other features, objects, and advantages of the invention will be apparent from the description, the drawings, and the claims.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a schematic diagram of a hollow fiber of this invention.

FIG. 2 is a schematic diagram of a method of preparing a hollow fiber of the invention.

FIG. 3 is a schematic cross-sectional view of a reactor containing a hollow fiber of this invention.

FIG. 4 shows the SEM images of hollow fiber 3, a hollow fiber of this invention, and comparative hollow fiber 3', which had a selection layer on its outer

surface. **FIG. 4 (a)** is the SEM image of comparative hollow fiber 3'; **FIG. 4(b)** is the SEM image of hollow fiber 3; and **FIG. 4(c)** is the SEM image of hollow fiber 3 at 100X magnification.

FIG. 5 is a schematic diagram showing (a) delaminating of the selection layer of a comparative hollow fiber having an outer selection layer and (b) penetration of the selection layer into the support layer in a hollow fiber of this invention.

FIG.6(a) shows H_2 and N_2 permeation flux and H_2 selectivity of comparative hollow fiber 3' during a stability test (5 cycles, 10 hours/cycle) at a temperature of 450 °C and a pressure difference of 100 kPa.

FIG.6(b) shows H_2 and N_2 permeation flux and H_2 selectivity of hollow fiber 3 during a stability test (5 cycles, 10 hours/cycle) at a temperature of 450 °C and a pressure difference of 100 kPa.

FIG. 7 shows the SEM images of hollow fiber 3, comparative hollow fiber 3', a small crack on the surface of comparative hollow fiber 3' after the third cycle of a stability test, and a larger crack after the fifth cycle.

FIG. 8 is a graph showing methane conversion rates as a function of reaction temperature during decomposition of methane in a conventional fixed-bed reactor and hollow fiber 2, a hollow fiber of this invention, at different reaction pressures, i.e., 1 bar, 1.5 bar, and 2 bar.

FIG. 9 is a graph showing H_2 permeation flux and hydrogen selectivity during decomposition of methane in hollow fiber 2, a hollow fiber of this invention, as a function of reaction temperature at different reaction pressures, i.e., 1 bar, 1.5 bar, and 2 bar.

FIG. 10 is a graph showing H_2 recovery rates during decomposition of methane in hollow fiber 2, a hollow fiber of this invention, as a function of reaction temperature at different reaction pressures, i.e., 1 bar, 1.5 bar, and 2 bar.

DETAILED DESCRIPTION

FIG. 1 schematically shows an embodiment of the hollow fiber of this invention, i.e., hollow fiber 4. It contains three layers: (i) porous support layer 2, (ii) catalyst layer 1 coated on the outer surface of support layer 2, and (iii) selection layer 3 coated on the inner surface of support layer 2. Also shown in this figure is reactor shell 6.

Support layer 2 is formed of porous materials, e.g., ceramic materials that have high mechanic strength, high thermal stability, and high chemical resistance. Examples include, but are not limited to, titania, silica, and alumina (e.g., α -Al₂O₃). Optionally, two or more ceramic materials are used to prepare the support layer. CeO₂, γ -Al₂O₃, or yttria-stabilized zirconia ("YSZ") can be used together with α -Al₂O₃ to form a porous support having a large surface area and small pores, e.g., a pore size of 10-100 nm. If YSZ is used with α -Al₂O₃, its preferred amount is 10-50 % (e.g., 20 %) by weight of α -Al₂O₃.

Referring back to FIG. 1, catalyst layer 1, containing a catalyst, is coated on the outer surface of support layer 2, in which reforming reactions take place. As shown in this figure, hydrocarbons, i.e., C_xH_y, upon contact with catalyst layer 1 on the retentate side (or shell side) of hollow fiber 4, is converted to H₂ and other gases such as CO₂, CO, H₂O, and C_xH_{y-2} at a high temperature (e.g., 450-600 °C). H₂ passes through selection layer 3, enters the permeate side (or core side) of hollow fiber 4, and is thus separated from the mixture on the retentate side.

Turning to selection layer 3, it is formed of palladium or a palladium alloy, e.g., a palladium-silver alloy. This layer, interlocked with support layer 2 on its inner surface, is an ultrathin and dense film free of any defects, which selectively permeates hydrogen gas. A thinner palladium or palladium alloy film is not only more cost effective but also provides higher permeability of hydrogen gas as compared to a thicker film. A thickness of 2 μ m or less is preferred. This film typically has a hydrogen permeation flux of 0.4-1.2 mol m⁻²s⁻¹ (e.g., 0.45-0.55 mol m⁻²s⁻¹) and a hydrogen selectivity (over nitrogen) of 500-1500 (e.g., 1000-1500).

Selection layer 3 (i.e., the inner layer) is separated from catalyst layer 1 (the outer layer) by support layer 2, providing protection for selection layer 3 from mechanical damages (e.g., scratching) and exposure to high temperature resulting from sudden combustion of hydrocarbons in the reforming reaction. Further, catalyst layer 1 is coated on the outer surface of support layer 2. Coke formation is avoided. Therefore, the hollow fiber of this invention is not only safe, it is also durable even at high temperature and high pressure.

Also within the scope of this invention is a method of preparing the above described catalytic hollow fibers. FIG. 2 illustrates an exemplary preparing process: (1) providing a porous hollow fiber support (e.g., containing α -Al₂O₃ and YSZ) having an

outer surface and an inner surface; (2) coating a catalyst layer on the outer surface, e.g., by a dip-coating method, and optionally sintering the support and the catalyst layer (e.g., at 20-1100 °C for 1-12 hours); (3) forming a protection film (e.g., by dip coating) to cover the catalyst layer; (4) coating a selection layer on the inner surface (e.g., by an electroless plating method); (5) removing the protection film; and (6) annealing the hollow fiber precursor thus obtained (e.g., at 60-480 °C for 1-10 hours), thereby forming the hollow fiber having catalyst layer 1, support layer 2 and selection layer 3.

Still within the scope of this invention is a reactor containing the hollow fiber described above, useful for producing hydrogen gas via the reforming reaction, e.g., catalytic decomposition of methane. FIG. 3 schematically shows a cross-sectional view of an exemplary reactor, which includes hollow fiber 4 containing catalyst layer 1, support layer 2, and selection layer 3. Both ends of the reactor are sealed using reactor shell 6, which can be formed of stainless steel, gas-tight material 5, and terminal closure member 7. Gas-tight material 5 can be an epoxy resin or a silicon rubber, preferably a silicon rubber having a temperature resistance of at least 450 °C. During operation of the reactor, the central portion of the reactor is heated, preferably using electrical heating wires 8 around reactor shell 6; the feed stream, i.e., hydrocarbons shown as C_xH_y in FIG. 1, enters the reactor via gas inlet 9; C_xH_y is converted to H_2 and other gases such as CO_2 , CO , H_2O , and C_xH_{y-2} ; H_2 passes through selection layer 3 and becomes permeate which is carried out of hollow fiber 4 by the sweep gas; and retentate including CO_2 , CO , H_2O , C_xH_{y-2} , unreacted C_xH_y , and remaining H_2 , exits the reactor via gas outlet 10.

The reactor described above is operated either in a concurrent or counter-current configuration. In a concurrent configuration, the sweep gas, e.g., N_2 and He , flows in the same direction as the feed stream, i.e., hydrocarbons. On the other hand, in the counter-current configuration, the sweep gas flows in the opposite direction as the feed stream. FIG. 3 shows that the reactor is operated in the counter-current configuration as an example.

The specific examples below are to be construed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever. Without further elaboration, it is believed that one skilled in the art can, based on the description herein, utilize the present invention to its fullest extent. All publications cited herein are incorporated by reference in their entirety.

EXAMPLE 1

An exemplary hollow fiber, i.e., hollow fiber 1, was prepared following the procedures described below.

Preparing a hollow fiber support

A porous hollow fiber support containing a ceramic material, i.e., α -Al₂O₃, was prepared by a phase-inversion method. More specifically, a mixture of 20 vol% *N*-methyl-2-pyrrolidone ("NMP") and 80 vol% water was used as both internal and external coagulants. A mixture of NMP (42 wt%) and polyethersulfone ("PESF"; 8 wt%) was used as a polymer solution. The ceramic material was slowly added to the polymer solution at room temperature under continuous stirring until a homogeneous ceramic-polymer dope was obtained, which was extruded under N₂ at 1.5 bar through a tube-in-orifice spinneret (tube/orifice diameter, 0.72/2.0 mm) at a controlled extrusion rate. The internal coagulant continuously flew through the inner tube of the spinneret during the extrusion. The thus-obtained nascent hollow fiber support passed through an air-gap of 1 cm before falling into the external coagulant. After the nascent hollow fiber support was completely solidified in the external coagulant during a period of 24 hours, it was cut into 25-cm segments, washed with water, and air-dried at room temperature. Finally, these segments were sintered at 500 °C at a heating rate of 1°C/minute for 2 hours to remove the polymer, followed by sintering at 1600 °C at a heating rate of 2°C/minute for 10 hours to yield a hollow fiber support.

Coating a catalyst layer

A catalyst layer formed of LaNiO₃ perovskite was coated on the outer surface of the hollow fiber support by a dip-coating and phase-inversion method. More particularly, 30 wt% of LaNiO₃ perovskite, 20 wt% of α -Al₂O₃, and 50 wt% of the polymer solution were mixed under continuous stirring for 24 hours to obtain a catalyst-polymer dope solution. The hollow fiber support was dipped into the dope solution. The thickness of the catalyst layer was controlled (e.g., 50 to 300 μ m) in order to obtain a LaNiO₃ perovskite content of 50 to 250 mg. More specifically, a catalyst layer having a thickness of 200 μ m was obtained, containing 200 mg of LaNiO₃ perovskite. The hollow fiber support and the catalyst layer were sintered at 1100 °C at a heating rate of 1°C/min to obtain a double-layered hollow fiber support.

Coating a selection layer

A selection layer, i.e., a palladium-silver alloy film, was coated on the inner surface of the hollow fiber support by a sequence electroless plating method. First, the external surface of the doubled-layered hollow fiber support was coated with a protection film by applying a mixture of 42 wt% NMP and 8 wt% PESF to the hollow fiber support. The protection film prevented deposition of palladium and silver on the catalyst layer during the electroless plating. After the protection film was applied, the double-layered hollow fiber was dipped into a 1 mM HNO_3 aqueous solution for two hours to remove any contaminating substrate adherent to the inner surface. Prior to electroless plating of palladium and silver, the double-layered hollow fiber was sensitized using a SnCl_2 solution for pattern delineation and activated using a PdCl_2 solution to provide Pd nuclei pre-seeding. These two steps ensured more uniform deposition and also made the inner surface of the hollow fiber support more active for electroless deposition. More specifically, the cleaned double-layered hollow fiber support was immersed in a 5 mM SnCl_2 solution at 50 °C for 20 min and then rinsed with water. It was further immersed in a 5 mM PdCl_2 solution at 50 °C for 20 min and also rinsed with water. This immersing-rinsing procedure was repeated for five times to obtain a highly uniformed Pd nuclei seeding on the inner surface, which was used to initiate deposition of palladium and silver.

Two plating solutions, i.e., a Pd plating solution and an Ag plating solution, were prepared using the composition shown in Table 1 below. To obtain the Pd plating solution, PdCl_2 , Na_2EDTA , and NH_4OH were added to 50 ml of 0.1 M HCl aqueous solution under continuous stirring until a homogenous clear solution was obtained. Similarly, to obtain the Ag plating solution, AgNO_3 , Na_2EDTA , and NH_4OH were added to 50 ml of 0.1 M HNO_3 to obtain a homogenous clear solution. The pH of both plating solutions were adjusted to 8-9 using 20% NH_4OH solution. Finally, 0.3 ml of 1 M $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ was slowly added to the pH-adjusted plating solutions to start deposition of palladium and silver. Namely, the hollow fiber support was first immersed in the palladium plating solution and thoroughly washed with water. It was then immersed in the silver plating solution and also subsequently washed with water. After plating, the hollow fiber having a protection layer was air-dried at 60 °C. The thickness of

palladium-silver layer was controlled by the immersing time and measured by the weight difference between the initial and final membranes. The polymer protection layer on the outer catalyst layer was mechanically or chemically removed to obtain a hollow fiber precursor, which was annealed at 480°C for 10 hours under H₂ atmosphere to form a palladium-silver alloy with a dense structure.

Table 1. Composition and condition of the electroless plating baths of Pd and Ag

Pd plating solution		Ag plating solution	
Component	Quantity	Component	Quantity
PdCl ₂	0.38g	AgNO ₃	0.40g
Na ₂ EDTA	2g	Na ₂ EDTA	2g
NH ₄ OH (28%)	15g	NH ₄ OH (28%)	15g
HCl (0.1M)	50ml	HNO ₃ (0.1M)	50ml
N ₂ H ₄ ·H ₂ O (1M)	0.3ml	N ₂ H ₄ ·H ₂ O (1M)	0.3ml
Temperature (°C)	50	Temperature (°C)	60
pH	8-9	pH	8-9

The hollow fiber thus obtained, i.e., hollow fiber 1, had an outer diameter of 2000 μm, an inner diameter of 1200 μm, and a thickness of 400 to 500 μm including a support layer of about 200 to 250 μm, a catalyst layer of 200 μm, and an ultrathin selection layer of less than 2 μm.

Hollow fiber 1, as well as hollow fiber 2 described in Example 2 below, was subjected to Energy-Dispersive X-ray spectrometry (EDX) to determine the composition of its palladium-silver selection layer. It was found that the average silver content, for both hollow fiber 1 and hollow fiber 2, was 21 wt%, in line with a preferred silver wt%, i.e., 20-30 wt%, in the selection layer. See Cheng et al., Journal of Membrane Science, 158, 127-41(1999).

Also measured were physical properties of hollow fiber 1, i.e., volumetric porosity, mechanical strength, internal pore size, and amount of pores. These data are shown in Table 2 below.

Note that the physical properties of hollow fiber 2 described below are also shown in Table 2. Comparison of hollow fibers 1 and 2 is discussed in Example 2 below.

5 Table 2. Summary of physical properties of porous hollow fiber membrane support

Hollow Fiber	YSZ: Al ₂ O ₃ (weight %)	Volumetric porosity (%)	Mechanical strength (MPa)	Internal diameter pore size (μm)		Amount of pores on surface	
				Maximum	Average	External	Internal
1	0 : 100	361.3	358.9	0.435	0.390	many	little
2	20 : 80	265.4	416.2	0.126	0.068	little	rare

EXAMPLE 2

Hollow fiber 2 was prepared following exactly the same procedure as described in Example 1 except that the ceramic used to prepare the hollow fiber support was α-Al₂O₃ and 20% YSZ (by weight of α-Al₂O₃) instead of α-Al₂O₃ solely.

Physical properties of hollow fiber 2 were measured and summarized in Table 2 above.

Hollow fiber 2, containing α-Al₂O₃ and YSZ, showed a smaller pore size and a higher mechanical strength than hollow fiber 1. These results suggest that smaller particles of YSZ helped minimize the amount and size of pores on the surface of the support layer.

A comparative conventional fixed-bed reactor was prepared, in which solid catalyst particles are packed in a tubular reactor.

The performance of hollow fiber 2 and the conventional fixed-bed reactor was tested as shown in Example 8 below. The results are shown in FIGs 8-10 and discussed in detail in Example 8.

EXAMPLE 3

Hollow fiber 3 was prepared following the same procedure as described in Example 2 except that no catalyst layer was coated onto the outer surface of the hollow fiber support and the thickness of the selection layer was 1.2 μm.

Comparative hollow fiber 3' was prepared in the same way as hollow fiber 3 except that the selection layer was coated on the outer surface of the hollow fiber support.

5 SEM images

Both hollow fiber 3 and comparative hollow fiber 3' were viewed under a scanning electron microscope (SEM). FIG. 4 shows the SEM images of the cross-sectional structure of hollow fiber 3, i.e., FIGs. 4(b) and (c), and that of the comparative hollow fiber 3', i.e., FIG. 4(a). Delamination, observed in comparative hollow fiber 3',
10 was identified as the primary reason for cracking of this hollow fiber at a high temperature, which in turn resulted in loss of H₂ selectivity as described below. Unexpectedly, hollow fiber 3, showing no delamination, exhibited a stronger adhesion between the selection layer and the support layer. Indeed, the palladium-silver alloy of the selection layer interlocked with (more specifically, penetrated and plugged into) the
15 pores of the selection layer, as shown in FIGs. 4(b) and (c).

Interlocking occurred at the annealing step of preparing the hollow fiber as the thermal-expansion coefficient of the palladium-silver alloy ($\sim 10^{-7} \text{ K}^{-1}$, indicating a higher thermal expansion) is different from that of the hollow fiber support ($\sim 10^{-6} \text{ K}^{-1}$, indicating a lower thermal expansion). FIG. 5 shows that during annealing of a hollow
20 fiber having an outer selection layer, e.g., comparative hollow fiber 3', its palladium-silver alloy moves away from the hollow fiber support, causing delamination as shown in FIG. 5(a); and, in a hollow fiber having an inner selection layer, e.g., hollow fiber 3, the palladium-silver alloy unexpectedly penetrates into the pores of the hollow fiber support, interlocking the selection layer and the support layer as shown in FIG. 5(b).

25 Durability

Both hollow fiber 3 and comparative hollow fiber 3' were subjected to hydrogen permeation tests following the procedure described in Example 7 below. Five cycles were performed. Each cycle lasted for 10 hours. The results are shown in FIGs. 6(a) and (b).

30 As shown in FIG. 6(a), comparative hollow fiber 3' demonstrated constant H₂ and N₂ permeation flux and H₂ selectivity in the first two cycles. Significant N₂ leakage and dramatic decrease of H₂ selectivity was observed after the third cycle, indicating cracking of the selection layer. The SEM images shown in FIG. 7 confirmed

formation of small cracks after the third cycle and large cracks after the fifth cycle. By contrast, hollow fiber 3 exhibited constant N₂ permeation flux and H₂ selectivity during all the five cycles. See FIG. 6(b).

Referring to FIG. 7, it shows a SEM image of (1) hollow fiber 3 (top left in the figure) having the selection layer interlocked with the support layer, (2) comparative hollow fiber 3' (bottom left) having the selection layer delaminated from the support layer, (3) a small crack on the selection layer contained in comparative hollow fiber 3' after the third cycle (a, top right), and (4) a large crack growing from the small crack after the fifth cycle (b, bottom right).

The tests unexpectedly showed that hollow fiber 3 was more durable than comparative hollow fiber 3'.

EXAMPLES 4-6

Hollow fibers 4, 5, and 6 were prepared following exactly the same procedure described in Example 2 except that the selection layers were 0.4 μm , 0.8 μm , and 1.2 μm , respectively.

These three hollow fibers were viewed under a scanning electron microscope (SEM), showing free of defects in their selection layers.

The hollow fibers were also tested for pressure-hold capacity at room temperature using hydrogen gas. They exhibited nearly identical pressure-hold capabilities at 300 kPa, demonstrating high safety.

The hollow fibers were also tested for hydrogen-permeable performance, following the procedure described in Example 7 below. The results are shown in Table 3 below.

According to Table 3, hollow fiber 5, containing the thinnest selection layer among the three hollow fibers, showed the highest H₂ reflux and the lowest H₂ selectivity; on the other hand, hollow fiber 7, containing the thickest selection layer, showed the lowest H₂ reflux and the highest H₂ selectivity; further, hollow fiber 6, containing the selection layer of an intermediate thickness, showed H₂ permeation flux similar to that of hollow fiber 5 and H₂ selectivity similar to that of hollow fiber 7. In sum, a hollow fiber containing a thinner selection layer had higher H₂ permeation flux and a hollow fiber containing a thicker selection layer had a higher H₂ selectivity.

Table 3. Hydrogen-permeable performance of hollow fibers 4, 5, and 6

	Pd-Ag Membrane thickness	H ₂ flux (mol m ⁻² s ⁻¹)	N ₂ flux (mol m ⁻² s ⁻¹)	H ₂ selectivity [§] (H ₂ /N ₂)
Hollow fiber 4	0.4 μm	0.87	0.00209	416
Hollow fiber 5	0.8 μm	0.80	0.00066	1212
Hollow fiber 6	1.2 μm	0.57	0.00036	1583

Note: [§] H₂ selectivity = H₂ permeance/N₂ permeance

EXAMPLE 7

Hollow fibers 3-6 described above were tested for hydrogen-permeable performance, using both H₂ gas and a H₂/N₂ mixture at 450 °C. The gas permeation tests were carried out on a reactor as shown in FIG. 3, which contained a 15-cm long hollow fiber. Both open ends of hollow fiber 4 were placed in stainless steel reactor shell 6. A feed stream, i.e., H₂/N₂, was pressurized and fed into the reactor via inlet 9 on stainless steel reactor shell 6. The pressure difference, controlled by a back-pressure regulator, was 100 kPa across the hollow fibers during the test. Helium, a sweep gas, was fed into hollow fiber 4 from one end at a flow rate of 20 ml/min. The permeated gas left hollow fiber 4 from the other end and was continuously analyzed by online gas chromatography having a thermal conductivity detector.

The results are shown in Table 3 above.

EXAMPLE 8

The performance of hollow fiber 2 was studied in carrying out catalytic decomposition of methane to produce H₂ at different temperatures (i.e., 450 °C, 500 °C, 550 °C, and 600 °C) and at difference pressures (i.e., 1 bar, 1.5 bar, and 2 bar). Helium was used as the sweep gas in the counter-current configuration. The results are shown in FIGs 8, 9, and 10 below.

FIG. 8 shows methane conversion rates as a function of reaction temperature during decomposition of methane in the conventional fixed-bed reactor described above in Example 2 (shown in FIG. 8 as O) and in hollow fiber 2 at a constant space velocity of 6,000 cm³ g⁻¹ h⁻¹. The reactions were carried out at 1 bar (shown in FIG. 8 as ♦), 1.5 bar (shown in FIG. 8 as ●), and 2 bar (shown in FIG. 8 as ▲). Unexpectedly, hollow fiber 2 showed a 10% increase in the methane conversion rate as compared to the conventional fixed-bed reactor. Hollow fiber 2 achieved a methane conversion rate of 55% at 600 °C and 2 bar.

FIG. 9 shows H₂ permeation flux and H₂ selectivity as a function of reaction temperature during decomposition of methane in hollow fiber 2. The reactions were carried out at 1 bar (shown in FIG. 9 as ♦), 1.5 bar (shown in FIG. 9 as ●), and 2 bar (shown in FIG. 9 as ▲). This figure shows that both H₂ permeation flux and H₂ selectivity increased as the reaction temperature or the reaction pressure increased. Hollow fiber 2 unexpectedly achieved H₂ permeation flux of 0.16 mol m⁻² s⁻¹ and H₂ selectivity of 98% at 600 °C and 2 bar.

FIG. 10 shows H₂ recovery as a function of reaction temperature during decomposition of methane in hollow fiber 2. The reactions were carried out at 1 bar (shown in FIG. 10 as ♦), 1.5 bar (shown in FIG. 10 as ●), and 2 bar (shown in FIG. 10 as ▲). As shown in FIG. 10, hollow fiber 2 unexpectedly achieved H₂ recovery of 84% at 600 °C and 2 bar.

WHAT IS CLAIMED IS:

1. A hollow fiber for use in production of hydrogen gas, the hollow fiber comprising a porous support layer having an outer surface and an inner surface, a
5 catalyst layer coated on the outer surface, and a selection layer coated on the inner surface, wherein the hollow fiber has an outer diameter of 500 to 4000 μm and an inner diameter of 100 to 2000 μm ; the support layer has a thickness of 100 to 500 μm and a pore size of 50 to 400 nm; the catalyst layer contains a catalyst, has a thickness of 100 to 500 μm , and has a pore size of 200 to 2000 nm; and the selection layer contains a
10 palladium or palladium-alloy film and has a thickness of 0.3 to 10 μm .
2. The hollow fiber of claim 1, wherein the hollow fiber has an outer diameter of 1000 to 3000 μm and an inner diameter of 800 to 1600 μm , the support layer has a thickness of 150 to 250 μm , the catalyst layer has a thickness of 150 to 250 μm , and the
15 selection layer has a thickness of 0.3 to 2 μm .
3. The hollow fiber of claim 2, wherein the catalyst is a metal or metal oxide containing Fe, Ni, Co, Cu, Mo, Rh, Ru, Pd, La, or a combination thereof; and the palladium or palladium alloy film is a film containing palladium, palladium-silver
20 alloy, palladium-silver-copper alloy, palladium-silver-cobalt alloy, palladium-gold-cobalt alloy, palladium-gold-iridium alloy, palladium-gold-rhodium alloy, or a combination thereof.
4. The hollow fiber of claim 3, wherein the catalyst is LaNiO_3 and the
25 palladium or palladium alloy film is a film containing palladium-silver alloy.
5. The hollow fiber of claim 1, wherein the catalyst is a metal or metal oxide containing Fe, Ni, Co, Cu, Mo, Rh, Ru, Pd, La, or a combination thereof.
- 30 6. The hollow fiber of claim 5, wherein the catalyst is LaNiO_3 .

7. The hollow fiber of claim 6, wherein the palladium or palladium alloy film is a film containing palladium, palladium-silver alloy, palladium-silver-copper alloy, palladium-silver-cobalt alloy, palladium-gold-cobalt alloy, palladium-gold-iridium alloy, palladium-gold-rhodium alloy, or a combination thereof.

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8. The hollow fiber of claim 7, wherein the palladium or palladium alloy film is a film containing palladium-silver alloy.

9. The hollow fiber of claim 5, wherein the palladium or palladium alloy film is a film containing palladium, palladium-silver alloy, palladium-silver-copper alloy, palladium-silver-cobalt alloy, palladium-gold-cobalt alloy, palladium-gold-iridium alloy, palladium-gold-rhodium alloy, or a combination thereof.

10. The hollow fiber of claim 9, wherein the palladium or palladium alloy film is a film containing palladium-silver alloy.

11. The hollow fiber of claim 1, wherein the palladium or palladium alloy film is a film containing palladium, palladium-silver alloy, palladium-silver-copper alloy, palladium-silver-cobalt alloy, palladium-gold-cobalt alloy, palladium-gold-iridium alloy, palladium-gold-rhodium alloy, or a combination thereof.

12. The hollow fiber of claim 11, wherein the palladium or palladium alloy film is a film containing palladium-silver alloy.

13. The hollow fiber of claim 12, wherein the selection layer has a thickness of 0.3 to 2 μm .

14. The hollow fiber of claim 13, wherein the selection layer has a thickness of 0.3 to 0.8 μm .

15. The hollow fiber of claim 11, wherein the selection layer has a thickness of 0.3 to 2 μm .

16. The hollow fiber of claim 15, wherein the selection layer has a thickness of 0.3 to 0.8 μm .

17. The hollow fiber of claim 1, wherein the selection layer has a thickness of 0.3 to 2 μm .

18. The hollow fiber of claim 17, wherein the selection layer has a thickness of 0.3 to 0.8 μm .

19. The hollow fiber of claim 18, wherein the hollow fiber has an outer diameter of 1000 to 3000 μm and an inner diameter of 800 to 1600 μm , the support layer has a thickness of 150 to 250 μm , the catalyst layer has a thickness of 150 to 250 μm , and the selection layer has a thickness of 0.3 to 2 μm , the catalyst being a metal or metal oxide containing Fe, Ni, Co, Cu, Mo, Rh, Ru, Pd, La, or a combination thereof, and the palladium or palladium alloy film being a film containing palladium, palladium-silver alloy, palladium-silver-copper alloy, palladium-silver-cobalt alloy, palladium-gold-cobalt alloy, palladium-gold-iridium alloy, palladium-gold-rhodium alloy, or a combination thereof.

20. The hollow fiber of claim 19, wherein the catalyst is LaNiO_3 and the palladium or palladium alloy film is a film containing palladium-silver alloy.

21. The hollow fiber of claim 17, wherein the hollow fiber has an outer diameter of 1000 to 3000 μm and an inner diameter of 800 to 1600 μm , the support layer has a thickness of 150 to 250 μm , the catalyst layer has a thickness of 150 to 250 μm , and the selection layer has a thickness of 0.3 to 2 μm , the catalyst being a metal or metal oxide containing Fe, Ni, Co, Cu, Mo, Rh, Ru, Pd, La, or a combination thereof, and the palladium or palladium alloy film being a film containing palladium, palladium-silver alloy, palladium-silver-copper alloy, palladium-silver-cobalt alloy, palladium-gold-cobalt alloy, palladium-gold-iridium alloy, palladium-gold-rhodium alloy, or a combination thereof.

22. The hollow fiber of claim 21, wherein the catalyst is LaNiO_3 and the palladium or palladium alloy film is a film containing palladium-silver alloy.

23. A method of preparing a hollow fiber, the method comprising:

5 providing a porous hollow fiber support having an outer surface and an inner surface;

coating a catalyst layer on the outer surface; and

coating a selection layer on the inner surface, thereby forming the hollow fiber, wherein the porous hollow fiber support has an outer diameter of 200 to 3000 μm , an

10 inner diameter of 100 to 2000 μm , and a pore size of 50 to 400 nm; the catalyst layer contains a catalyst, has a thickness of 100 to 500 μm , and has a pore size of 200 to 2000 nm; and the selection layer contains a palladium or palladium-alloy film and has a thickness of 0.3 to 10 μm .

15 24. The method of claim 23, further comprising:

forming a protection film covering the catalyst layer before coating the selection layer; and

removing the protection film after coating the selection layer.

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