(12) STANDARD PATENT (11) Application No. **AU 2005287034 B2**
(19) AUSTRALIAN PATENT OFFICE

(54) Title
Membrane enhanced reactor

(51) International Patent Classification(s)
B01J 8/02 (2006.01) ***C01B 3/50*** (2006.01)
B01D 53/22 (2006.01)

(21) Application No: **2005287034** (22) Date of Filing: **2005.09.19**

(87) WIPO No: **WO06/034086**

(30) Priority Data

(31) Number	(32) Date	(33) Country
60/611,608	**2004.09.21**	**US**

(43) Publication Date: **2006.03.30**
(44) Accepted Journal Date: **2009.06.11**

(71) Applicant(s)
Worcester Polytechnic Institute

(72) Inventor(s)
Ma, Yi Hua;Matzakos, Andreas Nicholas;Engwall, Erik Edwin;Wellington, Scott Lee;Mardilovich, Ivan Petrovich

(74) Agent / Attorney
PIZZEYS, ANZ Centre Level 14 324 Queen Street, Brisbane, QLD, 4000

(56) Related Art
EDLUND D J et al: 'The relationship between inter-metallic diffusion and flux decline in composite-metal
membranes: implications for achieving long membrane lifetime', JOURNAL OF MEMBRANE SCIENCE, ELSEVIER
SCIENTIFIC PUBLICATIONS COMPANY.
US 5217506 A
WO 2004/022480 A
US 5498278 A
US 2002/141919 A1
WO 2004/098751 A
US 5393325 A
WO 2003/011433 A
SHU J et al: 'Structurally stable composite Pd-Ag alloy membranes: Introduction of a diffusion barrier'. THIN
SOLID FILMS, ELSEVIER-SEQUIOA S.A LAUSANNE, CH, vol. 286, no. 1, 30 September 1996, pages 72- 79,
XP004049419, ISSN: 0040-6090
WO 2002/066144 A
WO 1999/030806 A
US 2004/129135 A1

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
30 March 2006 (30.03.2006)

PCT

(10) International Publication Number
WO 2006/034086 A1

(51) International Patent Classification:
B01J 8/02 (2006.01) ***B01D 53/22*** (2006.01)
C01B 3/50 (2006.01)

(21) International Application Number: PCT/US2005/033267

(22) International Filing Date: 19 September 2005 (19.09.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/611,608 21 September 2004 (21.09.2004) US

(71) Applicants *(for all designated States except US)*: **SHELL OIL COMPANY** [US/US]; One Shell Plaza, P.O. Box 2463, Houston, TX 77252-2463 (US). **WORCESTER POLYTECHNIC INSTITUTE** [US/US]; 100 Institute Road, Worcester, MA 01609 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **WELLINGTON, Scott, Lee** [US/US]; 5109 Aspen Street, Bellaire, TX 77401 (US). **MATZAKOS, Andreas, Nicholas** [US/US]; 2115 Parkview Lane, Missouri City, TX 77459 (US). **MARDILOVICH, Ivan, Petrovich** [US/US]; 32A Boynton, Apt. 4, Worcester, MA 01609 (US). **MA, Yi, Hua** [US/US]; 50 Westwood Drive, Worcester, MA 01609 (US). **ENGWALL, Erik, Edwin** [US/US]; 24 Dean Street, Apt. 2A, Worcester, MA 01609 (US).

(74) Agent: TAYLOR, Richard, B.; Shell Oil Company, One Shell Plaza, P.O. Box 2463, Houston, TX 77252-2463 (US).

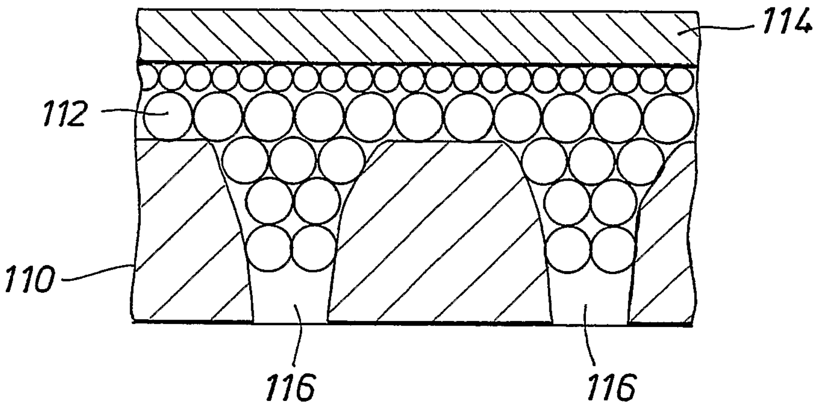
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: MEMBRANE ENHANCED REACTOR



(57) Abstract: A hydrogen producing reactor is disclosed. The hydrogen producing reactor has a reaction chamber containing a catalyst bed adapted to produce reaction products containing hydrogen from a hydrogen-producing feedstock. The reaction chamber also includes a hydrogen-selective, hydrogen-permeable gas separation module adapted to receive the reaction products from the catalyst bed and to separate a product stream containing hydrogen from the reaction products. The gas separation module comprises a porous substrate, an intermediate layer located at the porous substrate, and a hydrogen-selective membrane overlying the intermediate layer. The intermediate layer comprises particles and a binder metal, where the binder metal is distributed through out the intermediate layer. A steam reforming process is also disclosed using the disclosed reactor.

WO 2006/034086 A1

MEMBRANE ENHANCED REACTOR

Field of the Invention

This invention relates to reactor containing a high temperature gas separation membrane suitable for high temperature production and separation of product gases. The invention further relates to a process for producing a high purity gaseous product using said reactor.

Background of the Invention

Purified hydrogen is an important fuel source for many energy conversion devices. For example, fuel cells use highly purified hydrogen to produce electricity. Chemical processes, such as steam reforming, are usually operated at high temperature and produce hydrogen as well as certain by-products and impurities. Subsequent purification processes are required to remove the undesirable impurities to provide hydrogen sufficiently purified for certain applications, such as a fuel cell.

A majority of the hydrogen-producing chemical processes and subsequent processes of hydrogen purification occur in separate apparatus. It is advantageous to have a single, compact and more economical apparatus which combines a hydrogen-production reactor, such as a steam reformer, with a hydrogen separation and purification device which is operable at high temperature.

U.S. 5,997,594, issued December 7, 1999, discloses a steam reformer which contains a hydrogen purification palladium metal membrane module.

Typical hydrogen-selective metal membranes used in hydrogen gas separation modules must be free of defects and/or pinholes that breach the metal layer to prevent the migration of undesired gases through the metal membrane. Thick hydrogen-selective metal membranes, *e.g.*, palladium membranes, generally are very expensive. Porous substrates used in the fabrication of composite gas separation modules can have broad pore size distributions and/or rough surfaces such that thick gas-selective membranes can be needed to effectively separate gases. Generally, as the thickness of the gas-selective membrane increases, gas flux through the gas separation module decreases. However, in ordinary metal membranes operated at high temperature, intermetallic diffusion between the porous substrate and metal membrane will occur. This diffusion will cause deterioration of the hydrogen flux. Therefore, a need exists for a hydrogen gas separation module which is durable for a high temperature operation by preventing intermetallic diffusion while being thin enough to provide sufficiently high fluxes of hydrogen gas.

Typical reactors operated at high temperatures usually are made of metals which would withstand high temperature for producing hydrogen and high pressure and which are relatively expensive. It would be desirable if lower temperatures could be used so that lower-cost metallurgy can be utilized for the reactor. Therefore, there is a need for providing for the reactors with more uniform heating and having more control over temperatures at various points to avoid hot spots.

Furthermore, it would be desirable in the art to provide an integrated hydrogen-production and purification reactor design for producing high purity hydrogen having carbon and carbon oxides separated while having minimal production of NO_x within the integrated reactor. It would also be desirable to provide the modularity needed at bulk-hydrogen production scales so that a producer can match the desired capacity by installing multiple reactor units of the specific design. This is more cost-effective than either trying to scale up or down the existing large box furnace reactor designs or building several thousand single-tube reactors. It would also be desirable to employ less volume than conventional processes by intensifying the process and using less catalyst and smaller heater space. Furthermore, if the process produced CO_2 in higher concentrations and greater purity than other processes in the art, and the CO_2 could be sequestered for other uses, it would be extremely desirable. Such an integrated system would demonstrate far greater efficiency than any power generating system currently available.

Summary of the Invention

In one embodiment, the present invention is directed to a reactor, comprising:

a) a reaction chamber comprising:
   a catalyst bed adapted to produce reaction products comprising hydrogen gas from a hydrogen-producing feedstock; and
b) at least one hydrogen-selective, hydrogen-permeable gas separation module adapted to receive the reaction products from the catalyst bed and to separate the reaction products into (1) a product stream comprising hydrogen and (2) a byproduct stream, wherein the gas separation module comprises:
   (i) a porous substrate;
   (ii) an intermediate layer at the porous sub

strate that comprises particles and a binder metal, wherein the binder metal is distributed
throughout the intermediate layer; and
(iii) a hydrogen-selective membrane, wherein
the hydrogen-selective membrane overlies the
intermediate layer.

In another embodiment, the present invention is directed to a steam reforming process for the production of hydrogen, comprising:

(a) reacting steam with a hydrogen-producing feedstock at a temperature of from 200°C to 700°C and at a pressure of from 0.1MPa to about 20.0 MPa in a steam reforming reaction chamber containing a reforming catalyst to produce a mixture of primarily hydrogen and carbon dioxide, with a lesser amount of carbon monoxide; and

(b) separating hydrogen from the mixture produced by the reforming reaction with a hydrogen-selective, hydrogen-permeable gas separation module; wherein the gas separation module comprises:

(i) a porous substrate;
(ii) an intermediate layer at the porous substrate that comprises particles and a binder metal, wherein the binder metal is distributed throughout the intermediate layer; and
(iii) a hydrogen-selective membrane, wherein the hydrogen-selective membrane overlies the intermediate layer.

Brief Description of the Drawings

Figure 1 is a schematic diagram of the novel hydrogen producing reactor with catalyst section, and a hydrogen gas separation tube placed in order from the outside in.

Figure 2 is a schematic diagram of one of the configurations of the hydrogen gas separation tubes useful for the present hydrogen-producing reactor and process.

Figure 3A, EB, 3C, 3D, and 3E are cross-section representations of various composite hydrogen gas separation modules in the present reactor.

Figure 4 is schematic diagram of a multi-tubular, distributed combustion heated, radial flow, membrane, steam reforming reactor in accordance with the invention. Some of the inlet and outlet streams of the membrane and distributed combustion tubes have been omitted for simplicity.

Figure 5 is a cross section of the shell of the multi-tubular, distributed combustion heated, radial flow, membrane reactor shown in Figure 4.

Figures 6A and 6B are schematic diagrams of a "closed ended" and of an "open ended" distributed combustion ("DC") tubular chamber used to drive the reforming reactions in the process and apparatus of the present invention.

Figure 7 is a schematic diagram of a multi-tubular, DC heated, axial flow, membrane steam reforming reactor in accordance with the invention.

Figures 8 is a cross section of the shell of the multi-tubular, distributed combustion heated, axial flow, membrane reactor shown in Figure 7.

Figures 9A & 9B and 9C & 9D are schematic diagrams of two baffle configurations which can be employed to increase the contact of the reactant gases with the catalyst in a multi-tubular, distributed combustion-heated, axial flow, membrane reactor in accordance with the invention.

Figures 10, 11, 12, and 13 are top cross section views of the shells of other embodiments of the multi-tubular, distributed combustion heated, axial flow, membrane, steam reforming reactors of the invention.

Figure 14 is a simplified flow diagram of the distributed combustion membrane steam reformer fuel hybrid power system.

Detailed Description of the Invention

The invention relates to a membrane-enhanced reactor which comprises a reaction chamber and a gas separation module. The present invention provides a new apparatus and process for producing high purity hydrogen from a hydrogen producing feedstock, said process being accomplished in one reactor, constantly removing pure hydrogen, and optionally using distributed combustion as a heat source which provides great improvements in heat exchange efficiency and load-following capabilities to drive the steam reforming reaction. The hydrogen-selective gas separation module has a thinner dense gas-selective membrane producing higher rates of gas flux, e.g. hydrogen flux, while durability (such as with reduced diffusion of substrate components), hydrogen permeation as well as selectivity are maintained or improved. In another embodiment, the invention is also a zero emission hybrid power system wherein the produced hydrogen is used to power a high-pressure internally or externally manifold fuel cell, such as a molten carbonate fuel cell. The design can be a membrane steam reforming reactor (MSR) fueled hybrid system that makes it possible to capture high concentrations of CO_2 for sequestration or use in other processes. Finally, the design of the system may be scaled down to a mobile, lightweight unit.

Moreover, at bulk-hydrogen production scales, a multi-tubular (multiple distributed combustion tubes and/or multiple hydrogen selective and permeable membrane tubes) containing reactor disclosed herein provides the modularity needed. A producer can match the desired capacity by installing multiple reactor units of the specific design or having multiple distributed combustion tubes and/or multiple hydrogen selective and permeable membrane units in a large steam reformer. This is more cost-effective than either trying to scale up or down the existing large box furnace reactor designs or building several thousand single-tube reactors.

The hydrogen-producing reactor of the present invention comprises a) reaction chamber comprising:(i) an inlet adapted to receive a hydrogen-producing feedstock, and (ii)a catalyst bed for producing reaction products comprising hydrogen gas from the hydrogen-producing feedstock; and b)at least one hydrogen selective, hydrogen permeable composite gas separation module adapted to receive the reaction products from the catalyst bed and to separate the reaction products into (1) a product stream comprising a major amount of hydrogen and (2) a by-product stream; wherein the composite gas separation module comprises: (i) a porous substrate, (ii) an intermediate layer at the porous substrate that comprises particles and a binder metal, wherein the binder metal is uniformly distributed throughout the intermediate layer; and (iii) a dense gas-selective membrane, wherein the dense gas-selective membrane overlies the intermediate layer. In one particular embodiment, the composite gas separation module is made by a process comprising the steps of: 1) depositing a preactivated powder over a porous substrate; 2) depositing a binder metal onto the preactivated powder; and 3) depositing a dense gas-selective membrane to overlie the preactivated powder and binder metal, thereby forming the composite gas separation module. In a particular embodiment, the intermediate layer comprises a gradient of particle size from a surface of the intermediate layer proximate to the porous substrate to a surface of the intermediate layer distal to the porous substrate.

Non-limiting illustrative examples of the hydrogen-producing feedstock include natural gas, methane, ethyl benzene, methanol, ethane, ethanol, propane, butane, light hydrocarbons having 1-4 carbon atoms in each molecule, light petroleum fractions including naphtha, diesel, kerosene, jet fuel or gas oil, and hydrogen, carbon monoxide and mixtures thereof.

In a particular embodiment, the catalyst bed contains baffles in a form selected from the group consisting of (i) washers and disks, and (ii) truncated disks.

In a particular embodiment, the reactor is suitable for a dehydrogenation reaction and has a dehydrogenation chamber containing a dehydrogenation catalyst bed with a dehydrogenation catalyst such as an iron-oxdide-containing catalyst. The invention also relates to a process for the dehydrogenation of ethylbenzene comprising the steps of feeding ethylbenzene into the reactor as described above to produce styrene and hydrogen.

The reactor can be a steam-reforming reactor wherein the reaction chamber is a steam reforming reaction chamber comprising a catalyst bed comprising a steam reforming catalyst. In another embodiment, the present invention also relates to a steam reforming process comprises the steps of reacting a hydrogen-producing feedstock and steam in a reactor as described above. The steam reforming process for the production of hydrogen can comprise the steps of a) reacting steam with a hydrogen-producing feedstock at a temperature of from about 200°C to about 700°C and at a pressure of from about 1 bara (absolute) to about 200 bara (absolute) in a steam reforming reaction chamber containing a reforming catalyst to produce a mixture of primarily hydrogen and carbon dioxide, with a lesser amount of carbon monoxide; and b) conducting said reaction in the vicinity of at least one hydrogen-permeable, hydrogen-selective membrane tube, whereby hydrogen formed in said reaction zone permeates through said hydrogen selective membrane tube and is separated from said carbon dioxide and carbon monoxide; wherein the hydrogen selective, hydrogen permeable membrane tube is made of a composite gas separation module as described herein. In a particular embodiment, the carbon dioxide produced from said steam reforming chamber may have a pressure of from about 0.1 to about 20 MPa, particularly from about 1 to about 5 MPa, and the carbon dioxide produced from the steam reforming chamber has a concentration of from about 80% to about 99% molar dry basis, or of from about 90% to about 95% molar dry basis. In a particular embodiment, the carbon dioxide produced from the steam reforming chamber is used at least in part for enhanced recovery of oil in oil wells or enhanced recovery of methane in coal bed methane formations.

In some embodiments, the afore-mentioned hydrogen-producing reactors, including the steam reformer and dehydrogenation reactor, further comprise at least one heater comprising a distributed combustion chamber in a heat transferring relationship with the catalyst bed. The distributed combustion chamber comprises an inlet and a flow path for an oxidant, an outlet for combustion gas, and a fuel conduit having an inlet for fuel and a plurality of fuel nozzles or openings which provide fluid communication from within the fuel conduit to the flow path of said oxidant. The plurality of fuel nozzles or openings are sized and spaced along the length of said fuel conduit to avoid hot spot formation when the fuel is mixed with said oxidant in said distributed combustion chamber. In one embodiment, the distributed combustion does not form any flame when the fuel is mixed with said oxidant in said distributed combustion chamber and during its heating operation. The distributed combustion heater(s) may also have a preheater capable of preheating the oxidant, such as air or oxygen, to a temperature that when said fuel and said oxidant are mixed in the distributed combustion chamber, the temperature of the resulting mixture of said oxidant and fuel exceeds the autoignition temperature of said mixture. In some other embodiments, the ratio of the surface area of said distributed combustion chambers to the surface area of said membrane tubes is from about 0.1 to about 20.0, particularly from about 0.2 to about 5.0, more particularly from about 0.5 to about 5.0, and still more particularly from about 0.3 to about 3.0 and even more particularly from about 1.0 to about 3.0. In still some other embodiments, the distributed combustion chamber may have an external tubular dimension such that the length to diameter ratio is higher than 4, or higher than 10.

As a particular embodiment, the hydrogen-selective, hydrogen-permeable composite gas separation module is connected to a section containing a metal hydride precursor, and the hydrogen formed in the reforming chamber permeates through the gas separation module to the section containing the metal hydride precursor which reacts with the permeated hydrogen to form hydride. This reaction reduces the effective partial pressure of hydrogen in the permeate stream and drives the equilibrium within the reaction chamber to produce more hydrogen from the feedstock.

In some embodiments, the reactor may contain multiple distributed combustion chambers and/or multiple hydrogen separation tubes. In some embodiments, the products produced are separated by hydrogen-selective, hydrogen-permeable hydrogen separation membrane tube(s) having a ratio of length to diameter of less than about 500, wherein gaps between the membrane tubes are from about ¼ inch (about 0.64 cm) to about 2 inches (about 5.08 cm), and gaps between the membrane and distributed combustion ("DC") tubes are from about ¼ inch (about 0.64 cm) to about 2 inches (about 5.08 cm); or the hydrogen-selective and hydrogen-permeable membrane tube(s) have a ratio of length to diameter of less than about 250, wherein gaps between the membrane tubes are from about ½ inch (about 1.27 cm) to about 1 inch (about 2.54 cm), and gap between the membrane and DC tubes is from about ½ inch (about 1.27 cm) to about 1 inch (about 2.54 cm).

In some embodiments, a sweep gas is used to promote the diffusion of hydrogen through the hydrogen separation module. The sweep gas can be, but is not limited to, steam, carbon dioxide, nitrogen and condensable hydrocarbon.

In some embodiments, the hydrogen-selective membrane is palladium or an alloy thereof and the porous substrate is a porous metal substrate or a porous ceramic substrate. Non-limiting illustrative examples of the palladium alloy include alloys of palladium with least one of the metals selected from the group consisting of copper, silver, gold, platinum, ruthenium, rhodium, yttrium, cerium and indium. Illustrative non-limiting examples of the porous metal substrate include (i) stainless steel, (ii) an alloy comprising chromium and nickel, (iii) a nickel-based alloy, (iv) an alloy comprising chromium, nickel and molybdenum, (v) porous Hastelloy®, and (vi) porous Inconel.

In a particular embodiment, the composite gas separation module is made by a process further comprising the step of treating the composite gas separation module with hydrogen gas at a temperature of up to about 250°C.

In another particular embodiment, the particles or the preactivated powder have an average diameter ranging from about 0.01 to about 5 micrometers. As used herein, the term micron(s) means micrometer(s).

In some embodiments, the binder metal is a hydrogen selective metal or an alloy thereof. In some embodiments, the particles are selected from the group consisting of metal particles, metal oxide particles, ceramic particles, zeolite particles, and combinations thereof; and the preactivated powder is selected from the group consisting of preactivated metal powders, preactivated metal oxide powders, preactivated ceramic powders, preactivated zeolite powders, and combinations thereof. In a particular embodiment, the particles comprise aluminum oxide particles and the preactivated powders comprise preactivated aluminum oxide particles. In certain embodiments, the intermediate layer has an average thickness of at least about 0.01 micrometers or from about 1 to about 3 micrometers. In a particular embodiment, the composite gas separation module is made by a process further comprising the step of: a) depositing an additional preactivated powder over the deposited preactivated powder and binder metal; and b) depositing an additional binder metal onto the additional preactivated powder; wherein the dense gas-selective membrane is deposited to overlie the additional preactivated powder and the additional binder metal. In a particular embodiment, the additional preactivated powder has an average particle size that is smaller than the average particle size of the preactivated powder. In some embodiments, the preactivated powder has an average particle diameter ranging from about 0.3 to about 3 micrometers, and the additional preactivated powder has an average particle diameter ranging from about 0.01 to about 1 micrometer. In a particular embodiment, the powder is surface activated by seeding the powder with nuclei of a hydrogen-selective metal to form the preactivated powder.

In some embodiments, the composite gas separation module is made by a process further comprising the step of (i) oxidizing the surface of the porous metal substrate prior to depositing the preactivated powder, (ii) depositing a powder over the porous substrate prior to depositing the preactivated powder, (iii) exposing porous substrate anchoring sites following deposition of the preactivated powder over the porous substrate, (iv) exposing porous substrate anchoring sites prior to applying the dense gas-selective membrane, (v) surface activating the deposited preactivated powder and binder metal prior to depositing the dense gas-selective membrane, or (iii) the combination thereof. In a particular embodiment, the gas separation module or membrane tube further comprises a layer of particles underlying the intermediate layer wherein a binder metal is not uniformly distributed.

In some embodiments, the hydrogen flux through the module is at least about 4 Nm^3/m^2-hr, particularly at least about 10 Nm^3/m^2-hr, and more particularly at least about 28 Nm^3/m^2-hr at about 350°C and with a hydrogen partial pressure difference of about 1 bara (absolute)(0.1 MPa (absolute)) in the permeate side and 2 bara (absolute) (0.2 MPa (absolute)) in the process side.

In one embodiment, the present invention relates to a distributed combustion heated, membrane, dehydrogenation reactor comprising:

a) a dehydrogenation chamber containing a catalyst bed, said dehydrogenation chamber having an inlet for vaporizable hydrocarbon, a flow path for hydrogen and product gases resulting from the dehydrogenation reactions taking place in said dehydrogenation chamber and an outlet for said product gases,

b) at least one distributed combustion chamber in a heat transferring relationship with said catalyst bed whereby a distributed, controlled heat flux is provided by said distributed combustion chamber to said catalyst bed, said distributed combustion chamber comprising an inlet and a flow path for an oxidant, an outlet for combustion gas and further comprising a fuel conduit having an inlet for fuel and a plurality of fuel nozzles which provide fluid communication from within the fuel conduit to the flow path of said oxidant, said plurality of fuel nozzles being sized and spaced along the length of said fuel conduit so that no flame results when said fuel is mixed with said oxidant in said distributed combustion chamber;

c) a preheater capable of preheating said oxidant to a temperature that when said fuel and said oxidant are mixed in said distributed combustion chamber, the temperature of the resulting mixture of said oxidant and fuel exceeds the autoignition temperature of said mixture; and

d) at least one hydrogen-selective, hydrogen-permeable, membrane tube in contact with said catalyst bed, said membrane tube having an outlet whereby hydrogen formed in the dehydrogenation chamber permeates into said membrane tube and passes through said outlet.

In the present invention, heat transfer limitations are overcome by the innovative use of distributed combustion (distributed combustion) as the primary heat source. Distributed combustion is used to distribute heat throughout the reactor at high heat fluxes without high temperature flames and with low NO_x production. This is achieved by injecting small quantities of fuel into a preheated air stream and reaching autoignition conditions. Fuel quantity is controlled by nozzle size, the temperature rise is very small, and there is much reduced or substantially no hot spots such as flame associated with the combustion (combustion is kinetically limited, rather than mass-transfer limited).

Distributed combustion is disclosed in U.S. 5,255,742, U.S. 5,862,858, U.S. 5,899,269, U.S. 6,019,172, and EP 1 021 682 B1.

An important feature of the distributed combustion is that heat is removed along the length of the combustion chamber so that a temperature is maintained that is significantly below what an adiabatic combustion temperature would be. This almost eliminates formation of NO_x, and also significantly reduces metallurgical requirements, thus permitting the use of less expensive materials in construction of equipment.

Generally, distributed combustion involves employing a fuel conduit having an inlet for fuel and a plurality of fuel nozzles or openings which provide fluid communication from within the fuel conduit to the flow path of said oxidant. The plurality of fuel nozzles or openings are sized and spaced along the length of said fuel conduit to avoid hot spot formation when the fuel is mixed with said oxidant in said distributed combustion chamber. It also involves preheating combustion air and fuel gas (e.g., methane, methanol, hydrogen and the like) sufficiently such that when the two streams are combined the temperature of the mixture exceeds the autoignition temperature of the mixture, but to a temperature less than that which would result in the oxidation upon mixing, being limited by the rate of mixing. Preheating of the combustion air and fuel streams to a temperature between about 1500°F (about 815°C) and about 2300°F (about 1260°C) and then mixing the streams in relatively small increments will result in distributed combustion to avoid hot spots, such as flames. For some fuels such as methanol, preheating to a temperature above about 1000°F about (about 537°C) is sufficient. The increments in which the fuel gas is mixed with the combustion gas stream preferably result in about a 20 (about 11°C) to about 200°F (about 111°C) temperature rise in the combustion gas stream due to the combustion of the fuel.

With most hydrogen-producing, such as steam methane reforming, controlling the temperature in the catalyst bed is a problem. The advantages of the distributed combustion as a heat source in the present process and apparatus can be summarized as follows:

- DC helps maintain a more uniform temperature, but simultaneously controls heat flux to match the local heat needed for the material left to be reacted. At the highest heat flux there is as much heat present as can be accommodated by the reaction and as the process progresses less and less heat is required to drive the reaction.
- DC has a lower maximum-temperature combustion gas.
- DC does not have hot spots which might damage the hydrogen-selective, hydrogen-permeable membrane.
- DC has a negligible NO_x production.
- DC makes it easier to tailor axial heat flux distribution to minimize entropy production or energy loss and, thus, making it more efficient.
- DC permits a more compact reactor design that is less expensive to build.
- DC permits a modular reactor design, at a wide range of sizes and heat duties.
- DC provides a tapered heat flux profile.

Thus, the distributed combustion (DC) used to drive the steam reforming reactions in the present invention can be described as comprising:

a) preheating either a fuel gas or oxidant or both to a temperature that exceeds the autoignition temperature of the mixture of the fuel gas and oxidant when they are mixed;

b) passing said fuel gas and oxidant in into a heating zone which is in heat transferring contact along a substantial portion of the reaction zone (i.e., the zone in which said reforming reactions take place); and

c) mixing the fuel gas and oxidant in said heating zone in a manner that autoignition occurs, resulting in combustion without high temperature hot spots such as flames, thereby providing uniform, controllable heat to said reaction zone.

In the practice of the invention, some degree of sulfur removal will probably be necessary to protect the palladium material making up the hydrogen-permeable separation membrane and the Ni reforming catalyst. Sulfur is a temporary poison to such catalysts, but the catalyst activity can be regenerated by removing the source of sulfur. The sulfur tolerance of commercial reforming catalysts is dependent upon process conditions. On average, sulfur must be reduced to below 10 ppb to allow the catalyst to function properly.

Feed clean up with ZnO beds or by other means known in the art may be used to remove impurities such as H_2S and other sulfur containing compounds in the feed that could contribute to membrane degradation. For heavier hydrocarbons, like naphtha, some hydrotreating may be necessary to convert organic sulfur to H_2S, as known in the art. Heavy oil, solids carried by liquid water, oxygen, amines, halides, and ammonia are also known poisons for palladium membranes. Carbon monoxide competes with hydrogen for active surface sites, thus reducing the hydrogen permeability by 10% at 3-5 Bar (0.3-0.5 MPa). Thus, the partial pressure needs to stay low for best performance, as is the case in our preferred design.

In another embodiment of the present invention the pure hydrogen generated by the present reactor and process is used in an integrated design to power a fuel cell such as high pressure molten carbonate fuel cell, PEM (proton exchange membrane) fuel cells or SOFC (solid oxide fuel cells) and the like. This embodiment of the present invention has the potential for about 71% or greater efficiency in the generation of electricity from starting fuel. In addition, due to the unique integration of the system, CO_2 is produced in high concentrations from about 80% to about 95% molar dry basis, and high pressure of from about 0.1 to about 20 MPa, particularly from about 1 to about 5 MPa, and is easier to separate from nitrogen, which makes the system even more efficient.

Referring now to Figure 14, a hydrogen-producing feedstock such as vaporizable hydrocarbon and steam **5** are fed into the catalyst section **4** of a DC-membrane reactor of the type described in Figure 1, while preheated air **7** and fuel **14** are fed into the DC heating section **2** of the reactor containing fuel tubes **10**. A sweep gas (in this case steam) is fed into the DC-membrane reactor at **6**. The produced high purity hydrogen stream **12**, is directed to the anode compartment of the molten carbonate fuel cell, **20**, operating at about 650 °C and 5 Bar (0.5 MPa). The reactor effluent **13** containing the unreacted steam, CO_2 and low quantities of methane, hydrogen and CO, and the flue gas **11** from the DC heater and air, **16** are fed to the cathode compartment of the same fuel cell, **17**. The CO_2 reacts with the O_2 to form $CO_3^=$ anions that transport through the molten carbonate membrane.

The $CO_3^=$ anions are constantly renewed. The reactions with indicated transport are described as follows:

$$CO_{2\,cathode} + 1/2\ O_{2\,cathode} + 2e^-_{cathode} \rightarrow CO_3^={}_{cathode} \qquad R. 1$$

$$CO_3^={}_{cathode} \rightarrow CO_3^={}_{anode} \qquad R. 2$$

$$CO_3^={}_{anode} \rightarrow CO_2 + 1/2\ O_{2\,anode} + 2e^-_{anode} \qquad R. 3$$

$$H_{2\,anode} + 1/2\ O_{2\,anode} \rightarrow H_2O_{anode}\ -242\ kJ/gmol\text{-}H_2 \qquad R. 4$$

Net: $H_{2\,anode} + 1/2\ O_{2\,cathode} + CO_{2\,cathode} + 2e^-_{cathode} \rightarrow$

$$H_2O_{anode} + CO_{2\,anode} + 2e^-_{anode}\ -242\ kJ/gmol\text{-}H_2 \quad R. 5$$

Electricity generated by the fuel cell is shown as electrical output **21**. The stream from the anode, **22**, now contains the permeated CO_2 and steam but no hydrogen, nitrogen, methane or oxygen, if hydrogen and oxygen are fed in exactly 2:1 stoichiometry. A portion of stream **22** may recycled to the cathode compartment **17** of the fuel cell. The CO_2 recycle stream is shown as **23** on Figure 6. A portion of streams **22** and/or **13** also may be put through a turbine expander to generate electrical or mechanical work **30** and **24,** respectively. In the present invention CO_2 is separated from nitrogen essentially for free while electricity is simultaneously generated. Furthermore the CO_2 capture leverage is high. As shown above, each mole of methane is converted to 4 moles of H_2. Therefore 4 moles of CO_2 per mole of converted methane are required to transport the oxygen in the fuel cell and are therefore separated from the nitrogen. Thus, this process can also be used to separate CO_2 from an external CO_2 containing stream. The high concentration CO_2 stream, **29**, is now a prime candidate for sequestration after the steam is condensed. The CO_2 can be used for oil recovery, or injected into subterranean formations, or converted to a thermodynamically stable solid. Also, since the present process can be operated to produce high purity hydrogen and nitrogen as well as concentrated CO_2, it can be used to facilitate the production of chemicals such as urea, which can be made from these three raw materials. Other chemicals which can be manufactured using the products and by-products of the present process include ammonia and ammonium sulfate. Other uses for the concentrated stream of CO_2 and the high purity hydrogen and nitrogen streams will be apparent to those skilled in the art.

The stream from the cathode, stream **18**, contains all the nitrogen, unreacted oxygen, a little unpermeated CO_2, and trace amounts of the methane, hydrogen and CO from the MSR effluent. All or part of this stream can be put through a turbine expander (not shown) to generate work (electrical or mechanical), **19**. The trace components of stream **18** may be oxidized in a catalytic converter, **26**, and emitted in the atmosphere as a low CO_2 concentration containing stream, **27**, containing less than 10% CO_2, preferably less than 1% CO_2. The trace components may also be oxidized inside the fuel cell if the appropriate catalyst is placed in the cathode compartment. A stream, **28**, containing water and steam exits condenser **25** and is recycled to the DC-MSR reactor, and reheated to between about 250 to 500°C.

The zero emission hybrid system of the present invention is extremely efficient. Byproduct compounds are separated, the steam and hydrogen are reheated efficiently, and electricity is produced. Furthermore, water is separated from purified CO_2 which is produced in concentrations large enough to be easily sequestered. Advantages include using waste heat to raise steam and using water collected for recycling to support additional steam reforming or other beneficial uses. The system is a totally integrated, extremely efficient design having the potential for greater than 71% generation efficiency as mentioned above. The 71% is approximately a 20% fractional improvement over the best results we are aware of in the art, the 60% figure mentioned above that is possible under laboratory conditions. In addition to the great improvement in efficiency, the integrated design provides a concentrated source of CO_2 for capture and sequestration as well.

Fuel cells which would be suitable for use in the present invention are those that could function in a highly pressurized system. Most fuel cells run at atmospheric conditions. For this reason, a high pressure molten carbonate fuel cell is preferred. However, other types of fuel cells, such as PEM fuel cells and SOFC, can also be effectively combined with the DC-MSR reactor of the present invention.

Another very attractive feature is that the DC powered MSR hydrogen generator produces very low NO_x, especially compared with the combined processes known in the art. Due to the use of distributed combustion very little NO_x is generated in this system. Furthermore, other steam reforming reactors used to generate hydrogen known in the art could not feed to the MCFC the flue gas from the furnace as in the present design, because they produce high NO_x, which would poison the molten carbonate membrane.

In a particular embodiment of the invention, the aforesaid distributed combustion heated, membrane hydrogen-producing reactor such as a steam reforming reactor contains multiple distributed combustion chambers (preferably, but not necessarily, in the form of tubes) and multiple hydrogen-selective, hydrogen-permeable membrane tubes disposed in, or otherwise in contact with, the reforming catalyst bed in the reforming chamber. Examples of multi-tubular reactors in accordance with the invention are shown in Figures 4-5, 7-8 and 10-13.

The multi-tubular, distributed combustion heated, membrane hydrogen-producing reactor such as steam reforming reactor in accordance with the invention may be either of the radial flow type as shown in Figures 4 and 5, or may be of the axial flow type as shown in Figures 7-8 and 12-13. In a radial flow reactor the gases generally flow through the reforming catalyst bed radically from outside to inside (or from inside to outside), while in an axial flow reactor the gases generally flow through the reforming catalyst bed in the same direction as the axis of the reactor. In the case of a vertical reactor, the flow would be from the top of the reactor to the bottom, or the bottom of the reactor to the top.

The multi-tubular, distributed combustion heated, membrane reactor such as a steam reforming reactor in accordance with the present invention may contain from as few as 2 distributed combustion tubes up to 100 or more, particularly 3 to 19, depending the size of the distributed combustion tubes, the size of the catalyst bed and the level of heat flux desired in the catalyst bed. The size of the distributed combustion tube can vary from about 1 inch outer diameter up to about 40 inches or more outer diameter. The number of hydrogen-selective membrane tubes may also vary from as few as 2 up to 400 or more, particularly 3 to 90. The outer diameter size of the membrane tubes may vary from about 1 inch up to about 10 inches or more. In general, the ratio of distributed combustion tube surface area to membrane tube surface area will be in the range of about 0.1 to about 20.0, particularly from about 0.2 to about 5.0, more particularly from about 0.5 to about 5.0, still more particularly from about 0.3 to about 3.0 and even more particularly from about 1.0 to about 3.0. The term "surface area" when used in reference to the above ratios, means the external (circumferential) area of the distributed combustion tubes and the membrane tubes. For instance, a 1 inch outer diameter tube of 12 inches length would have an external surface area of 37.6 square inches.

Each distributed combustion tube or chamber will have at least one fuel conduit disposed therein. Large distributed combustion chambers generally will have multiple fuel conduits. The distributed combustion chambers or tubes employed in the multi-tubular reactors of the invention may be "open ended" or "closed ended" as discussed below in connection with Figures 6A and 6B.

A sweep gas may be used to promote the diffusion of hydrogen through the hydrogen-selective, hydrogen-permeable membrane. In case a sweep gas is employed, the membrane tube may contain an inlet and flow path for sweep gas feed and a flow path and outlet for the return of sweep gas and permeated hydrogen.

Baffles and/or screens may also be employed in the multi-tubular reactors of the present invention to improve contact of the reactive gases with the catalyst and to improve flow distribution. The distributed combustion tubes and/or membrane tubes may also be surrounded by cylindrical screens to protect the tubes from direct contact with the catalyst.

In a further embodiment of the invention the reforming chamber of a reactor in accordance with the invention is in communication with a high pressure molten carbonate fuel cell, wherein the outlet for hydrogen from the reformer is in communication with the anode of said fuel cell and the outlet for by-product compounds is in communication with the cathode of said fuel cell.

In one embodiment, the present reactor is an integrated distributed combustion-steam reformer, and the present process or apparatus of is capable of producing high purity hydrogen with minimal production of CO, particularly less than about 5 molar%, more particularly less than 3 molar %, and still more particularly less than 2 molar% on a molar dry basis of the total products, and with less than 1000 ppm of CO and particularly less than 10 ppm of CO on a dry basis, more particularly virtually no CO in the hydrogen stream produced. By practice of the present invention it is possible to produce high purity hydrogen e.g., hydrogen having a purity on a dry basis of greater than 95%. The present invention can be used to produce hydrogen having purities as high as 97%, 99%, or under optimum conditions 99+%. The effluent (by product) stream from the MSR reactor will typically contain more than 80% CO_2 on a dry basis, e.g., 90% CO_2, 95% CO_2 or 99% CO_2, and less than about 10% CO on a dry basis, e.g., less than about 5% CO, preferably less than 1% CO.

Total heat management and turbines may be included in the system to increase the efficiency and produce additional electricity or to do useful work such as compress gases or vapors.

One aspect of the present invention is a distributed combustion heated membrane steam reformer hydrogen generator. In the design of the invention there are disclosed distinct improvements in overall efficiency, particularly size, scalability and heat exchange. The present invention typically employs only one reactor to produce the hydrogen versus typically four reactors used in conventional processes, and part of the heat load is supplied by the water-gas-shift reaction. The design of the invention captures essentially all of the heat in the reaction chamber since heat exchange occurs on a molecular level, which reduces the overall energy requirements.

Chemical equilibrium and heat transfer limitations are the two factors that govern the production of hydrogen from hydrogen-producing feedstock in conventional reactors. These factors lead to the construction of large reactors fabricated from expensive high temperature tolerant materials. They are enclosed in high temperature furnaces that are needed to supply the high heat fluxes.

In the present invention the two major limitations of chemical equilibrium and heat transfer are overcome by the innovative combination of an in-situ membrane separation of hydrogen in combination with a heat source comprising distributed combustion ("DC") that makes it possible to more efficiently use all the energy in the system, as well as provide load following capabilities.

The reformer of the present invention reduces the operating temperature of the steam reforming reactor close to the lower temperature used in a shift reactor. With the temperatures for the steam reforming and shift closer, both operations are combined into one reactor. With both reactions occurring in the same reactor the exothermic heat of reaction of the shift reaction is completely captured to drive the endothermic steam reforming reaction. This reduces the total energy input for the sum of the reactions by 20%. The lower temperature reduces stress and corrosion and allows the reactor to be constructed from much less expensive materials. Combining the operations also reduces the capital and operating cost since only one reactor, instead of two or three, are required. Moreover, the reaction is not kinetics-limited even at the lower temperature, thus, the same or even less catalyst can be used.

The general description for steam reformers, including but not limited to the reactions, enthalpies, values of equilibrium constants, advantages of integrated distributed combustion-SMR reactor, as well as the advantages of the use of the membrane in the reactor can be found in US 2003/0068269.

The in-situ membrane separation of hydrogen employs a membrane fabricated, particularly from an appropriate metal or metal alloy, on a porous ceramic or porous metal support, as described below, to drive the equilibrium to high conversions. With constant removal of the hydrogen through the membrane, the reactor can be run at much lower than the commercially practiced temperatures of 700-900+°C. A temperature of 500°C is sufficient to drive the kinetics to high conversions when the equilibrium is shifted using the hydrogen separation membrane. At this temperature the selectivity to CO_2 is almost 100%, while higher temperatures favor the formation of CO as a major product.

The term “reforming catalyst” as used herein means any catalyst suitable for catalyzing a steam reforming reaction, which includes any steam reforming catalyst known to one skilled in the art, as well as any “pre-reforming catalyst” which is suitable for catalyzing steam reforming reactions in addition to being suitable for processing heavier hydrocarbons prior to a steam reforming reaction.

Figure 1 shows a schematic diagram of a hydrogen-producing reactor with catalyst section, and permeate section. The reactor **1** shown in Figure 1 consists of two concentric sections. The inner concentric section **3** is the permeate section. The annulus, **4**, in between is the catalyst section. A hydrogen-producing catalyst, such as a reforming catalyst, is loaded into the annulus section **4** wherein the above-described reactions take place. (section **4** is also variously referred as the catalyst section, the reaction section or the reaction zone). The membrane, **8**, is represented on the inside of the small section, **3**, (the permeate section) in Figure 1.

The feed stream containing hydrogen-producing feedstock, such as a mixture of vaporizable hydrocarbon-containing compounds (e.g. naphtha, methane or methanol) and H_2O with a minimum overall O: C ratio of 2:1 when a steam reforming reaction is carried out, enters catalyst section **4** at **5.** If used, sweep gas for promoting the diffusion of hydrogen through the membrane enters the top of the permeate section **3** at **6.** Alternatively, sweep gas can be introduced into the permeate section by means of a stinger pipe fitted to bottom of the permeate section. In case of this alternative, hydrogen in sweep gas would exit the permeate zone at the bottom of the permeate section. Optionally, the stinger pipe to introduce the sweep gas may be connected at the top of the permeate section in which case the hydrogen and sweep gas would exit at the top of this section. Hydrogen (pure or in sweep gas) exits at **12.** Unreacted products and by-products (e.g., CO_2, H_2O, H_2, CH_4, and CO) exit catalyst section **4** at **13.** It is also possible to remove the produced hydrogen using a vacuum instead of a sweep gas.

The catalyst beds, **4,** can be heated by any suitable heating method known to one skilled in the art, such as a by a traditional burner, an electric heating means, a microwave heating means, etc.

Any hydrogen-producing, particularly vaporizable, feedstock such as an (optionally oxygenated) hydrocarbon-containing compound(s) can be used in the present process and apparatus, including, but not limited to, methane, methanol, ethane, ethanol, propane, butane, light hydrocarbons having 1-4 carbon atoms in each molecule, and light petroleum fractions like naphtha at boiling point range of 120-400°F, which is a typical feed for commercial steam reformers. Petroleum fractions heavier than naphtha can also be employed like diesel or kerosene or jet fuel at boiling point range of 350-500°F (about 177-253°C) or gas oil at boiling point range of 450-800°F. Hydrogen, carbon monoxide and mixtures thereof, e.g., syngas, may also be used in the process and apparatus of the present invention, and are included in the definition of "hydrogen-producing feedstock" or “vaporizable hydrocarbon". Methane was used in the examples to demonstrate the process. The catalyst bed can be heated **107** by any suitable means **107**, such as electric heating, microwave, conventional combustion, distributed combustion, etc.

In some embodiments, with the distributed combustion-steam reforming process and apparatus of the present invention it is possible to use O: C ratios as low as 2.8, down to 2.6, without coking problems, with the minimum O: C ratio being about 2:1. This results lower energy costs if methane is used as the feed in the present invention, since lower steam to methane ratios can be used thus requiring less energy to vaporize water. Because of the ability to operate at lower O:C ratios, it is also possible to use heavier, less expensive feeds in the distributed combustion-MSR reactor of the present invention than can be used in conventional steam methane reformers.

In another embodiment of the invention, the integrated hydrogen-producing process and apparatus of the invention can be used to perform water-gas-shift reactions on syngas mixtures (i.e., mixtures of hydrogen and carbon monoxide) produced from conventional processes like Catalytic Partial Oxidation (CPO), Steam Methane Reforming (SMR) and Autothermal Reforming (ATR). The integrated distributed combustion-MSR reactor is well suited for this since it produces high purity hydrogen and converts carbon monoxide to carbon dioxide and more hydrogen. Thus, the versatile hydrogen-producing reactor of the invention is capable of replacing high temperature shift, low temperature shift and methanation reactors and a hydrogen purification section. A mixture of syngas and vaporizable hydrocarbon can also be used to yield a net reaction which may be either endothermic, thermally neutral or slightly exothermic.

The reactor annulus is packed with steam reforming catalyst and equipped with a perm-selective (i.e., hydrogen selective) membrane that separates hydrogen from the remaining gases as they pass through the catalyst bed. The steam reforming catalyst can be any known in the art. Typically steam reforming catalysts which can be used include, but are not limited to, Group VIII transition metals, particularly nickel. It is often desirable to support the reforming catalysts on a refractory substrate (or support). The support is preferably an inert compound. Suitable compounds contain elements of Group III and IV of the Periodic Table, such as, for example the oxides or carbides of Al, Si, Ti, Mg, Ce and Zr. The preferred support composition for the reforming catalyst is alumina.

The catalyst used in the examples to demonstrate the present invention was nickel on porous alumina. As the hydrogen is formed in the catalyst bed, it is transported out through the hydrogen-permeable separation membrane filter. Advantages of this technology include the capacity to separate essentially pure hydrogen from any poisons that may also be present, including CO and H_2S, and from other fuel diluents. The poisons do not pass through the separation membrane, which is fabricated from one of a variety of hydrogen-permeable and hydrogen–selective materials including ceramics.

Illustrative, but non-limiting examples of materials suitable for use as a support for the membranes which may be used in the apparatus and process of the present invention include an inorganic porous material such as palladium, platinum, palladium alloys, porous stainless steel, porous silver, porous copper, porous nickel, porous Ni-based alloys, metal mesh, sintered metal powder, refractory metals, metal oxides, ceramics, porous refractory solids, honeycomb alumina, aluminate, silica, porous plates, zirconia, cordierite, mullite, magnesia, silica matrix, silica alumina, porous Vycar, carbon, glasses, and the like.

The composite gas separation modules described herein include a dense gas-selective membrane such as, for example, a dense hydrogen-selective membrane. The dense hydrogen-selective membrane can include, for example, palladium or an alloy thereof. A "dense gas-selective membrane," as that term is used herein, refers to a component of a composite gas separation module that has one or more layers of a gas-selective material, *i.e.*, a material that is selectively permeable to a gas, and that is not materially breached by regions or points which impair the separation of the gas by allowing the passage of an undesired gas. For instance, in one embodiment, the dense gas-selective membrane is not materially breached by regions or points which do not have the desired gas selectivity properties of the gas-selective material. An example of a dense gas-selective membrane is a dense hydrogen-selective membrane that is substantially free of defects such as open pores, holes, cracks and other physical conditions that impair the gas-selectivity of the composite gas separation module by allowing the passage of an undesired gas.

The term "support," as used herein, includes a substrate, a surface treated substrate, a substrate upon which a material (*e.g.*, a gas-selective material) has been deposited, a substrate with an intermediate layer, or a subsequently plated substrate upon which a dense gas-selective membrane has been or will be formed. Serving as a support structure, the substrate can enhance the durability and strength of the composite gas separation module.

"Gas-selective material," as used herein, refers to those materials which, when formed into dense gas-selective membranes, allow the passage of a select gas, or select gases, through the dense gas-selective membrane. Suitable gas-selective materials include metals, ceramics (*e.g.*, perovskite and perovskite-like materials) and zeolites (*e.g.*, MFI and Zeolites A, X, etc.). In one embodiment, the gas-selective material is a hydrogen-selective metal such as palladium or an alloy thereof. Examples of suitable palladium alloys include palladium alloyed with at least one of the metals selected from the group consisting of copper, silver, gold, platinum, ruthenium, rhodium, yttrium, cerium and indium. For example, palladium/silver and palladium/copper alloys can be used to form dense hydrogen-selective membranes. In one embodiment, the gas-selective material is a ceramic such as oxygen gas-selective perovskite.

The side of the support upon which the dense gas-selective membrane is formed is referred to herein as the "outside" or "membrane-side" and the opposite side of the support is called the "inside" or "substrate-side" surface. However, it should be noted that the dense gas-selective membrane can be formed on the exterior surface and/or the interior surface of the substrate. For example, the dense gas-selective membrane can be formed on either or both surfaces of a planar substrate or can be formed on the exterior and/or interior surfaces of a substrate tube. Preferably, the dense gas-selective membrane is formed on only one surface of the substrate, for example, on either the exterior or the interior surface of a substrate tube.

In one embodiment, the gas-selective material can include a combination of substances, for example, a combination of a hydrogen-selective metal and a zeolite. In one embodiment, the zeolite used in a combination of substances is gas-selective. In an alternative embodiment, the zeolite used in a combination of substances is not gas-selective, for example, the zeolite used in a combination of substances is not hydrogen-selective.

The composite gas separation module includes an intermediate layer at a porous substrate. In one embodiment, for example, the intermediate layer has a top side and a bottom side and the intermediate layer is adjacent to the porous substrate on the bottom side and is adjacent to the dense gas-selective membrane on the top side. The intermediate layer can be a continuous or a discontinuous layer. In one embodiment, at least part of the intermediate layer is in pores of the porous substrate and/or covers pores of the porous substrate. In some embodiments, the intermediate layer is a discontinuous layer in the pores of the porous substrate, covering the pores of the substrate, and/or proximate to the pores of the substrate. Alternatively, the intermediate layer is a continuous layer that overlies the surface of the porous substrate including portions of the surface that do not contain pores.

The intermediate layer includes particles and a binder metal. The binder metal is uniformly distributed throughout the intermediate layer. The term "uniformly distributed," as used herein, refers to a uniform distribution of binder metal across the surface area of the particles of the intermediate layer. In one embodiment, the binder metal is a hydrogen-selective metal or an alloy thereof. "Hydrogen-selective metals" include, but are not limited to, niobium (Nb), tantalum (Ta), vanadium (V), palladium (Pd), platinum (Pt), zirconium (Zr) and hydrogen-selective alloys thereof. Palladium and alloys of palladium are preferred.

In some embodiments, the intermediate layer includes particles substantially uniform in size, *e.g.*, of substantially uniform diameter. Alternatively, the intermediate layer can include particles of varying sizes and/or size distributions. The intermediate layer can include blends and/or layering of different particles including particles of differing sizes. The intermediate layer can include a gradient of particle size from a surface of the intermediate layer proximate to the porous substrate to a surface of the intermediate layer distal to the porous substrate. In one embodiment, particles having a smaller average size overlie particles having a larger average size. For example, particles having a larger average size are located proximate to the porous substrate (*e.g.*, inside the pores of the porous substrate) and particles having a smaller average size are located distal to the porous substrate (*e.g.*, inside the pores of the porous substrate but closer to the membrane-side surface of the porous substrate).

In one embodiment, the particles can have an average particle diameter of at least about 0.01 micron such as at least about 0.1, 0.5, 1, or at least about 5 microns. The particles can include particles capable of fitting into pores of the porous substrate. In some embodiments, the particles can have an average particle diameter of less than 5 microns such as less than 1, 0.5, 0.1, or less than 0.01 microns. In one embodiment, the particles have an average diameter ranging from about 0.01 to about 5 microns. For example, the particles can have an average diameter ranging from about 0.01 to about 3 microns or about 0.3 to about 1 micron. As used herein, micron or microns mean micrometer or micrometers.

In one embodiment, the intermediate layer includes sublayers of particles and binder metal, *e.g.*, at least two sublayers of particles and binder metal. For example, the sublayers of particles and binder metal can include a first sublayer of a first population of particles and a first binder metal and a second sublayer of a second population of particles and a second binder metal, wherein the first population of particles has a larger average diameter than the average diameter of the second population of particles and wherein the second sublayer overlies the first sublayer. Thus, in one embodiment, the intermediate layer includes a sublayer of particles having a larger average diameter and an overlying sublayer of particles having a smaller average diameter. For example, the intermediate layer can include a sublayer of particles having an average diameter of about 0.3 to about 3 microns and an overlying sublayer of particles having an average diameter of about 0.1 to about 1 micron. Sublayers of particles and binder metal are not necessarily distinct sublayers. For example, the intermediate layer can include a gradient of particle sizes in a binder metal. In one embodiment, the intermediate layer includes a gradient of particle sizes ranging from generally larger particles at a point proximate to the porous substrate to generally smaller particles at a point distal to the porous substrate.

The particles of the intermediate layer can include metal particles, metal oxide particles, ceramic particles, zeolite particles, and combinations thereof, among others. For example, the particles can include such materials as tungsten, silver, copper oxide, aluminum oxide, zirconia, titania, silicon carbide, chromium oxide, and combinations thereof. Suitable metal oxide particles include, but are not limited to, aluminum oxide, titanium oxide, yttrium oxide, and chromium oxide. In some embodiments, the particles include aluminum oxide particles, *e.g.*, alpha-alumina particles and/or gamma-alumina particles. The particles can include a blend or a layering of different particles including particles of differing compositions and/or sizes. The particles of the intermediate layer can have various morphologies and shapes. For example, the particles can be ordered or amorphous (*e.g.*, crystalline). In one embodiment, the particles include spherical or mostly spherical particles.

In some embodiments, the particles can have a melting point temperature higher than the melting point temperature of the porous substrate, *e.g.*, a porous metal substrate. The intermediate layer can include particles having a melting point temperature higher than the melting point temperature of the dense gas-selective membrane. For example, in one embodiment, the intermediate layer includes particles having a melting point temperature higher than both the melting point temperature of the porous metal substrate and the melting point temperature of the dense gas-selective membrane.

In one embodiment, the intermediate layer is at least about 0.01, 0.1, 1, 2, 3, 4, or at least about 5 microns thick. For example, the intermediate layer can range from about 0.01 to about 5 microns thick, such as from about 0.1 to about 3 or from about 1 to about 3 microns thick. In one embodiment, the intermediate layer is not significantly less porous to helium gas flux than the porous substrate. The intermediate layer can have an average pore size that is less than the average pore size of the porous substrate. In one embodiment, the largest pore of the intermediate layer is smaller than the largest pore of the porous substrate. Maximum (largest) pore size can be measured by a typical "Bubble Point" test such as per ISO standard 4003 or per ASTM E-128

In another embodiment, the composite gas separation module can further include a layer of particles underlying the intermediate layer. In one particular embodiment, the composite gas separation module includes a layer of particles underlying the intermediate layer wherein a binder metal is not uniformly distributed throughout the layer of particles underlying the intermediate layer. For example, the binder material is not uniformly distributed across the surface area of this layer of particles underlying the intermediate layer. The layer of particles underlying the intermediate layer can include any of the particles described herein, *e.g.*, aluminum oxide particles.

The composite gas separation module used herein includes a porous metal substrate. The porous metal substrate can be formed from any of a variety of components known to those of ordinary skill in the art. Examples of suitable substrate components include, but are not limited to, iron, nickel, palladium, platinum, titanium, chromium, porous silver, porous copper, aluminum, and alloys thereof, *e.g.*, steel, stainless steel, porous stainless steel, HASTELLOY® alloys (*e.g.*, HASTELLOY® C-22®) (trademarks of Haynes International, Inc., Kokomo, IN) and INCONEL® alloys (*e.g.*, INCONEL® alloy 625) (INCONEL is a trademark of Huntington Alloys Corp., Huntington WV). In one embodiment, the porous metal substrate is an alloy containing chromium and nickel (*e.g.*, INCONEL® alloy 625). In an additional embodiment, the alloy contains chromium, nickel and molybdenum such as, for example, HASTELLOY® C-22® or INCONEL® alloy 625. The porous metal substrate can be porous stainless steel. Cylinders of porous stainless steel that are suitable for use as substrates are available from Mott Metallurgical Corporation (Farmington, CT) and from Pall Corporation (East Hills, NY), for example. The substrate can also be metal mesh, sintered metal powder, refractory metals, metal oxides, ceramics, porous refractory solids, honeycomb alumina, aluminate, silica, porous plates, zirconia, cordierite, mullite, magnesia, silica matrix, silica alumina, porous Vycar, carbon, glasses, and the like.

One of ordinary skill in the art can select substrate thickness, porosity, and pore size distribution using techniques known in the art. Desired substrate thickness, porosity and pore size distribution can be selected based on, among other factors, the operating conditions of the final composite gas separation module such as operating pressure. Substrates having generally higher porosities and generally smaller pore sizes are particularly suited for producing composite gas separation modules. In some embodiments, the substrate can have a porosity in a range of about 5 to about 75% or about 15 to about 50%. While the pore size distribution of a substrate can vary, the substrate can have pore diameters that range from about 0.1 microns or less to about 15 microns or more. Generally, smaller pore sizes are preferred. However, in some embodiments, a substrate having larger pores is used and an intermediate layer having generally smaller pore sizes is formed at the porous substrate (*e.g.*, a graded support is formed).

In some embodiments, the mean or median pore size of the substrate can range from about 0.1 to about 15 microns, *e.g.*, from about 0.1 micron to about 1, 3, 5, 7 or about 10 microns. For example, the substrate can be an about 0.1 micron grade substrate to an about 0.5 micron grade substrate, *e.g.*, 0.1 micron, 0.2 micron, and 0.5 micron grades of stainless steel substrates can be used. In one embodiment, the substrate is 0.1 micron grade HASTELLOY® alloy.

The composite gas separation module can further include a substrate surface treatment. For example, a layer of a ceramic can be bonded to a porous metal substrate. The ceramic can include oxides, nitrides, and/or carbides, for example, iron oxide, iron nitride, iron carbide and/or aluminum oxide.

The composite gas separation module can also further comprise a layer of a metal selected from the group consisting of palladium, gold and platinum, wherein the layer of metal overlies the porous substrate and/or a substrate surface treatment.

The composite gas separation module includes a dense gas-selective membrane, wherein the dense gas-selective membrane overlies the intermediate layer. In one embodiment, the dense gas-selective membrane is selectively permeable to hydrogen, *e.g.*, the dense gas-selective membrane is a dense hydrogen-selective membrane and can include one or more hydrogen-selective metals or alloys thereof. As described above, hydrogen-selective metals include, but are not limited to, niobium (Nb), tantalum (Ta), vanadium (V), palladium (Pd), platinum (Pt), zirconium (Zr) and hydrogen-selective alloys thereof. Palladium and alloys of palladium are preferred. For example, palladium can be alloyed with at least one of the metals selected from the group consisting of copper, silver, gold, platinum, ruthenium, rhodium, yttrium, cerium and indium.

Where the gas separation module is to be used at temperatures below about 300°C, the dense gas-selective membrane can be formed of a palladium alloy such as, for example, an alloy of about 75 to about 77 weight percent palladium and about 25 to about 23 weight percent silver. An alloy is typically preferred at low temperatures because pure palladium can undergo a phase change in the presence of hydrogen at or below about 300°C and this phase change can lead to embrittlement and cracking of the membrane after repeated cycling in the presence of hydrogen.

In one embodiment, the dense gas-separation membrane can include one or more non-metallic components. In an additional embodiment, the dense gas-separation membrane can include one or more components that are not gas-selective materials, *e.g.*, components that are not hydrogen-selective materials.

In one embodiment, the thickness of the dense gas-selective membrane is less than about 3 times the diameter of the largest pore of the porous substrate. For example, the thickness of the dense gas-selective membrane can be less than about 2.5, 2, or less than about 1.5 times the diameter of the largest pore of the porous substrate. While the thickness of the dense gas-selective membrane can depend, among other factors, on the size of the largest pores in the porous substrate, in some embodiments the dense gas-selective membrane is less than about 25, 20, 15, 12 or less than about 10 microns in thickness. For example, in one embodiment, the thickness of the dense gas-selective membrane is less than about 14 microns such as about 3 to 14 microns. In one particular embodiment, the dense gas-selective membrane is of substantially uniform thickness.

In one aspect, performance of the composite gas separation modules described herein can be assessed by measuring hydrogen flux through the module during operation. For example, hydrogen flux through the composite gas separation modules, in some embodiments, is at least about 4, 10, 20, or at least about 30 $(m^3/m^2\text{-hr})_{STP}$ at about 350°C and with a hydrogen partial pressure difference of about 1 bar (O.1 MPa). In at least one embodiment, hydrogen flux through the composite gas separation module is at least about 33.6 $(m^3/m^2\text{-hr})_{STP}$ at about 350°C and with a hydrogen partial pressure difference of about 1 bar (0.1 MPa).

As an illustration of one embodiment of the present invention, FIG. 3A shows a partial cross-section of a composite gas separation module. Porous substrate **110** can include, for example, a porous metal substrate such as porous stainless steel. Intermediate layer **112** includes particles and a binder metal. Intermediate layer 112 is shown in FIG. 3A as a continuous layer at porous substrate **110**. The are two sublayers of particles. The first layer has a larger average diameter than the average diameter of the second layer. The second sublayer overlies the first sublayer. Dense gas-selective membrane **114** overlies the intermediate layer.

FIG. 3B shows a partial cross-section of a composite gas separation module. Porous substrate **110** can include, for example, a porous metal substrate such as porous stainless steel. Intermediate layer **112** includes particles and a binder metal, wherein the binder metal is uniformly distributed throughout the intermediate layer. Intermediate layer **112** is shown in FIG. 3B as a continuous layer at porous substrate. Dense gas-selective membrane **114** overlies the intermediate layer.

FIG. 3C shows a magnified partial cross-section of one embodiment of a composite gas separation module described by the present invention. Porous substrate 110 includes pores **116**. Intermediate layer **112** includes particles and a binder metal, wherein the binder metal is uniformly distributed throughout the intermediate layer. Intermediate layer **112** is shown in FIG. 3C as a discontinuous layer at porous substrate **110** wherein intermediate layer is contained within pores **116**. Dense gas-selective membrane **114** overlies intermediate layer **112**.

FIG. 3D shows a magnified partial cross-section of one embodiment of a composite gas separation module described by the present invention. Porous substrate 110 includes pores **116**. Intermediate layer **112** includes particles and a binder metal, wherein the binder metal is uniformly distributed throughout the intermediate layer. Intermediate layer **112** is shown in FIG. 3D as a discontinuous layer at porous substrate **110** wherein the intermediate layer is both within and covering pores **116**. In some embodiments, the intermediate layer only covers the pores of the porous substrate. Dense gas-selective membrane **114** overlies intermediate layer **112**.

FIG. 3E shows a magnified partial cross-section of one embodiment of a composite gas separation module described by the present invention. Porous substrate 110 includes pores **116**. Intermediate layer **112** includes particles and a binder metal, wherein the binder metal is uniformly distributed throughout the intermediate layer. Intermediate layer **112** is shown in FIG. 3E as a continuous layer at porous substrate **110** but in other embodiments the intermediate layer is a discontinuous layer. Dense gas-selective membrane 14 overlies the intermediate layer.

While FIGS. 3A to 3E illustrate planar cross-sections of composite gas separation modules, composite gas separation modules of the present invention can include planar and cylindrical composite gas separation modules such as those having flat porous substrates and tubular porous substrates. In addition, the composite gas separation modules illustrated in FIGS. 3A to 3E can also include a layer of particles (not illustrated) underlying intermediate layer **112** wherein a binder metal is not uniformly distributed throughout the layer of particles underlying the intermediate layer.

In one aspect, the invention includes a method for fabricating a composite gas separation module, comprising the steps of: (a) depositing a preactivated powder over a porous substrate; (b) depositing a binder metal onto the preactivated powder; and (c) depositing a dense gas-selective membrane to overlie the preactivated powder and binder metal, thereby forming the composite gas separation module. Suitable porous substrates, binder metals, and dense gas-selective membranes are described above.

In a particular fabrication method, any contaminants are initially cleaned from the substrate, for example, by treating the substrate with an alkaline solution such as by soaking the substrate in an approximately 60°C ultrasonic bath for about half an hour. Cleaning is typically followed by rinsing such as, for example, wherein the substrate is sequentially rinsed with tap water, deionized water and isopropanol or wherein the substrate is sequentially washed with deionized water and acetone. Preparation of the porous substrate can also include surface treatment; formation of an intermetallic diffusion barrier such as by oxidizing the substrate; surface activation, described *infra*; and/or deposition of a metal such as palladium, gold or platinum, described *infra*, prior to depositing the preactivated powder over the porous substrate.

An intermediate layer is generally formed at the porous substrate prior to deposition of a dense gas-selective membrane (*e.g.*, a hydrogen selective membrane). Generally, forming the herein-described intermediate layer includes depositing a preactivated powder over a porous substrate and depositing a binder metal onto the preactivated powder. An intermediate layer can be formed by depositing one or more sublayers that include powder and binder metal wherein at least one sublayer contains a preactivated powder. In some embodiments, one or more non-surface activated powders may be deposited over the porous substrate, over deposited preactivated powder, or over deposited preactivated powder and binder metal.

"Preactivated powder," as used herein, refers to a powder that has been surface activated by depositing metal nuclei on the surface of the powder. In one embodiment, the metal nuclei are nuclei of hydrogen-selective metals, *e.g.*, palladium nuclei.

The method for fabricating a composite gas separation module includes the step of depositing a preactivated powder over a porous substrate. In one embodiment, depositing the preactivated powder over the porous substrate includes depositing the preactivated powder into the pores of the porous substrate. The preactivated powder can include preactivated metal powder, preactivated metal oxide powder, preactivated ceramic powder, preactivated zeolite powder, and combinations thereof, among others. For example, the preactivated powder can include preactivated tungsten, silver, copper oxide, aluminum oxide, zirconia, titania, silicon carbide, chromium oxide, and combinations thereof. Suitable preactivated metal oxide particles include, but are not limited to, preactivated aluminum oxide, preactivated titanium oxide, preactivated yttrium oxide, and preactivated chromium oxide. In some embodiments, the preactivated powder includes preactivated aluminum oxide particles, *e.g.*, preactivated alpha-alumina powder and/or preactivated gamma-alumina powder. The deposited powder can include a blend or a layering of different powders including powders of differing compositions and/or sizes. The powder can include particles of various morphologies and shapes. For example, the particles can be ordered (*e.g.*, crystalline) or amorphous. In one embodiment, the powders include spherical or mostly spherical particles. In some embodiments, the powder can have a melting point temperature higher than the melting point temperature of the porous substrate, *e.g.*, a porous metal substrate, and/or higher than the melting point temperature of the dense gas-selective membrane.

In one embodiment, the preactivated powder can have an average particle diameter of at least about 0.01 micron such as at least about 0.1, 0.5, 1, or at least about 5 microns. The preactivated powder can include particles capable of fitting into pores of the porous substrate. In some embodiments, the preactivated powder can have an average particle diameter of less than 5 microns such as less than 1, 0.5, 0.1, or less than 0.01 microns. In one embodiment, the preactivated powder has an average diameter ranging from about 0.01 to about 5 microns. For example, the particles can have an average diameter ranging from about 0.01 to about 3 microns or about 0.3 to about 1 micron.

In one embodiment, the present invention includes the further step of surface activating a powder to thereby form the preactivated powder. For example, surface activating the powder to form the preactivated powder can include seeding the powder with nuclei of a hydrogen-selective metal, *e.g.*, palladium nuclei. In one embodiment, the powder is seeded with nuclei of a hydrogen-selective metal using an aqueous activation solution.

One technique for surface activating a powder to thereby form the preactivated powder includes placing the powder in an aqueous stannous chloride ($SnCl_2$) solution (*e.g.*, 1 g/L, pH=2) for sensitization and filtering the powder from the solution shortly after. Then, the filter cake can be placed in an aqueous palladium chloride ($PdCl_2$) (*e.g.*, 0.1g/L, pH=2) activation solution. Shortly after, the resulting mixture can be filtered and washed to recover the preactivated powder.

Another technique for surface activating a powder to thereby form the preactivated powder includes placing the powder in an aqueous $SnCl_2$ solution (*e.g.*, 1 g/L, pH=2). Shortly after, aqueous $PdCl_2$ solution (*e.g.*, 0.1 g/L, pH=2) can be added. The resulting mixture can be filtered and washed to recover the preactivated powder.

The preactivated powder can be deposited using any of a number of techniques for applying a powder to a porous surface. For example, the preactivated powder can be deposited after transport to the support by a gas (*e.g.*, a gas stream). In other embodiments, the powder particles are pressed and/or rubbed onto the support. In one embodiment, the preactivated powder is deposited from a slurry or suspension. For example, in one embodiment, the preactivated powder can be deposited from a liquid-based (*e.g.*, water-based) slurry or suspension. In some embodiments, the preactivated powder can be deposited from a composition of several powders of varying compositions and/or particle size, *e.g.*, from a slurry or suspension containing several different materials. For example, in one embodiment, a water-based slurry is prepared by mixing water with a preactivated powder selected from the group consisting of preactivated metal powders, preactivated metal oxide powders, preactivated ceramic powders, preactivated zeolite powders, and combinations thereof.

The slurry can contain, *e.g.*, about 0.1 to about 30 g/L preactivated powder. For example, the slurry can contain about 0.1 to about 20, about 1 to about 15, about 1 to about 10, about 1 to about 5, or about 1 to about 3 g/L preactivated powder. For example, in one embodiment, the slurry can contain about 0.1 to about 10 g/L preactivated alumina powder such as about 1 to about 3 g/L preactivated alumina powder.

The preactivated powder can be deposited from a slurry or suspension by filtering the slurry or suspension through a porous support. For example, in one embodiment, the preactivated powder is deposited on a porous support as a filter cake after a slurry is filtered through the porous support. In some embodiments, a vacuum is applied to one side of a porous support and a slurry is applied to the opposite side of the porous support. Thus, a filter cake can accumulate on the side of the support to which the slurry is applied and filtrate can be collected on the side of the support to which the vacuum is applied. In one embodiment, a vacuum is applied to the tube side of a tubular support and a slurry is applied to the membrane side of the tubular support.

In some embodiments, the preactivated powder is deposited using a liquid-based composition such as a water-based slurry. Following deposition of the preactivated powder, the liquid-wetted preactivated powder can be dried. In other embodiments, the preactivated powder can be kept wet.

In one embodiment, the method further includes the step of exposing porous substrate anchoring sites following deposition of the preactivated powder over the porous substrate. Porous substrate anchoring sites include, for example, the tips of porous substrate constituent particles. Porous substrate anchoring sites can be exposed, for example, by mechanically treating the surface of the support. In one embodiment, porous substrate anchoring sites are exposed by brushing or abrading the surface following deposition of the preactivated powder over the porous substrate.

The method for fabricating a composite gas separation module includes the step of depositing a binder metal onto the preactivated powder. The binder metal can be deposited onto the preactivated powder, for example, by electrolessly plating the binder metal onto the preactivated powder. Without wishing to be held to any particular theory, it is believed that by depositing a binder metal (*e.g.*, a hydrogen-selective metal or alloy thereof) onto the preactivated powder, the preactivated powder can be mechanically stabilized. It is thought that by depositing a binder metal onto a preactivated powder, a more uniform binder metal distribution results as compared to when a powder layer is applied to a support, the powder layer is surface activated, and then metal is deposited over the powder layer.

In one embodiment, the method for fabricating a composite gas separation module includes the further steps of: (a) depositing an additional preactivated powder over the deposited preactivated powder and binder metal; and (b) depositing an additional binder metal onto the additional preactivated powder; wherein the dense gas-selective membrane is deposited to overlie the additional preactivated powder and the additional binder metal.

In one embodiment, the additional preactivated powder has an average particle size that is smaller than the average particle size of the preactivated powder (*i.e.*, a prior deposited preactivated powder). For example, the preactivated powder can have an average particle diameter ranging, *e.g.*, from about 0.3 to about 3 microns and the additional preactivated powder can have an average particle diameter ranging, *e.g.*, from about 0.01 to about 1 micron. In some embodiments, the inventive method can include depositing multiple successive layers of powder and binder metal over the porous substrate wherein at least one of the successive layers contains a preactivated powder.

The present inventive method can also further include the step of depositing a powder over the porous substrate prior to depositing the preactivated powder. The powder deposited over the porous substrate can be preactivated or not preactivated. In one embodiment, this powder has an average particle size ranging from about 1 to about 5 microns. The powder can include any of the powders described herein, for example, aluminum oxide particles. This powder can be deposited using any of the techniques described herein for depositing a powder on a porous support, *e.g.*, the powder can be deposited from a slurry.

After deposition of a preactivated powder over a porous substrate and deposition of a binder metal onto the preactivated powder, a dense gas-selective membrane is deposited to overlie the preactivated powder and binder metal. For example, a dense gas-selective membrane can be deposited by depositing a gas-selective metal, *e.g.*, a hydrogen-selective metal, to overlie the preactivated powder and binder metal. In one embodiment, the method further includes the step of exposing porous substrate anchoring sites prior to applying the dense gas-selective membrane. Porous substrate anchoring sites include, for example, the tips of porous substrate constituent particles. Porous substrate anchoring sites can be exposed, for example, by mechanically treating the surface of the support. In one embodiment, porous substrate anchoring sites are exposed by brushing or abrading the surface of the support prior to depositing a dense gas-selective membrane.

In one embodiment, palladium or an alloy thereof is deposited, *e.g.*, electrolessly plated, to overlie the preactivated powder and binder metal, thereby forming a dense gas-selective membrane. Application of the dense gas-selective membrane can include surface activating the preactivated powder and binder metal prior to depositing dense gas-selective membrane components. In some embodiments, a vacuum is applied to one side of a porous support and an activation composition is applied to the opposite side of the porous support. In one embodiment, a vacuum is applied to the tube side of a tubular support and an activation composition is applied to the membrane side of the tubular support.

Components of the dense gas-selective membrane, *e.g.*, a hydrogen-selective metal or an alloy thereof, can be deposited to overlie the preactivated powder and binder metal using any of the techniques known in the art for depositing such materials on a support. For example, a component of the dense gas-selective membrane can be deposited on the support using electroless plating, thermal deposition, chemical vapor deposition, electroplating, spray deposition, sputter coating, e-beam evaporation, ion beam evaporation or spray pyrolysis. In some embodiments, a vacuum is applied to one side of a porous support and an plating composition, such as an electroless plating solution, is applied to the opposite side of the porous support. In one embodiment, a vacuum is applied to the tube side of a tubular support and a plating composition is applied to the membrane side of the tubular support.

An alloy of a gas-selective metal can be deposited over the deposited preactivated powder and binder metal as a component of the dense gas-selective membrane. In one embodiment, a palladium/silver alloy is formed by first depositing palladium onto the support by electroless deposition and then depositing silver, also by electroless deposition, onto the support. An alloy membrane layer can then be formed by heating the silver and palladium layers, for example, to about 500°C to about 1000°C in an inert or hydrogen atmosphere. In one embodiment, metal components can be co-deposited onto the support to form a layer of a finely divided mixture of small regions of the pure metal components. In another embodiment, a technique such as sputtering or chemical vapor deposition is used to simultaneously deposit two or more metals to form an alloy layer on the support.

In one embodiment, the present inventive method can further include the step of depositing a gas-selective material to overlie the preactivated powder and binder metal, thereby forming a coated substrate and abrading the surface of the coated substrate, thereby forming a polished substrate, prior to formation of the dense gas-selective membrane (*e.g.*, a dense hydrogen-selective membrane) over the intermediate layer.

The composite gas-separation module can be treated with hydrogen gas at a temperature of up to about 250°C. In one embodiment, the pressure of the hydrogen gas can range up to about 8 bar (0.8 MPa). Typically, the treatment with hydrogen gas lasts for at least about 1 hour, for example, about 1 hour to about 4 hours or about 3 to about 4 hours. Without wishing to be held to any particular theory, it is believed that by exposing newly formed palladium-containing membranes to hydrogen at a low temperature (*e.g.*, up to about 250°C such as about 200°C to about 250°C) and at a low pressure (*e.g.*, up to about 8 bar (0.8 MPa) such as up to about 2 or 3 bar (0.2 to 0.3 MPa)), palladium grain growth is slowed and membrane cracking is slowed or prevented. It is believed that suitable hydrogen temperatures and pressures for this treatment are those that lie outside the two phase region on a palladium-hydrogen phase diagram.

The composite can be treated by a method that comprises the step of treating a composite gas separation module with hydrogen gas at a temperature of up to about 250°C. The composite gas separation module may be formed using any technique known in the art. In one embodiment, the composite gas separation module is formed as described herein. Preferably, the composite gas separation module includes palladium or an alloy thereof.

In one embodiment, the temperature of the hydrogen gas is at least about 200°C. The pressure of the hydrogen gas can range up to about 8 bar (0.8 MPa). For example, the pressure of the hydrogen gas can be in the range from about 2 to about 3 bar (0.2 to 0.3 MPa). The composite gas-separation module can be treated with hydrogen gas, for example, for at least about 1 hour such as about 1 hour to about 4 hours or about 3 to about 4 hours. It is believed that by exposing newly formed palladium-containing membranes to hydrogen at a low temperature (*e.g.*, up to about 250°C such as about 200°C to about 250°C) and at a low pressure (*e.g.*, up to about 8 bar (0.8 MPa) such as up to about 2 or 3 bar (0.2 to 0.3 MPa)), palladium grain growth is slowed and membrane cracking is slowed or prevented. It is believed that suitable hydrogen temperatures and pressures for this treatment are those that lie outside the two phase region on a palladium-hydrogen phase diagram.

In one embodiment, a small quantity of the metal, sufficient to cover the pore walls of the substrate, for example less than about 10, 7, 5, 3 or 1 percent of the ultimate thickness of the dense gaseous membrane, is deposited on the porous substrate without a significant reduction of the substrate porosity. Typically, the deposition of palladium, gold and/or platinum on the porous substrate is made by surface activating and plating on the side of the substrate opposite to the side on which a gas-selective membrane will be formed. For example, in one embodiment, a deposit of palladium, gold and/or platinum is formed from the inside of a substrate tube (*e.g.*, using an electroless plating solution) and a dense gas-selective membrane is subsequently formed on the outside of the substrate tube.

The gas separation modules can also be fabricated by selectively surface activating a support proximate to a defect and preferentially depositing a material on the selectively surface activated portion of the support. The method is discussed in "Method for Curing Defects in the Fabrication of a Composite Gas Separation Module," U.S. Application Serial No. 10/804,848 filed March 19, 2004.

In one embodiment, the invention includes removing residual metal chlorides, for example, by treatment with an aqueous phosphoric acid solution, *e.g.*, 10% phosphoric acid solution. For example, the treatment can include application of 10% phosphoric acid solution at room temperature for a time sufficient to convert residual metal chlorides to metal phosphates, *e.g.*, about 30 minutes, followed by appropriate rinsing and drying, *e.g.*, rinsing with deionized water for about 30 minutes and drying at about 120°C for at least about 2 hours.

In some embodiments, the composite gas separation modules are made by one or more of the following steps:(i) substrate surface treatments by oxidizing the surface of the substrate or by forming a nitride layer, (ii) intermetallic diffusion barrier formation, (iii) surface activation of the support, e.g. with aqueous stannous chloride and palladium chloride prior to deposition of metal membrane, or (iv) metal deposition over the support or the intermediate layer, which steps are described in U.S. Patent No. 6,152,98, and also in U.S. Patent Application No.10/804,848, 10/804,846; U.S. Patent Application No. 10/804,847, entitled "Method for Fabricating Composite Gas Separation Modules," filed on March 19, 2004; and U.S. Patent Application No. 10/836,088, entitled "High Tamman Temperature Intermediate Layer", filed on April 30, 2004.

The following illustrative embodiments will serve to illustrate the invention disclosed herein. The examples are intended only as a means of illustration and should not be construed as limiting the scope of the invention in any way. Those skilled in the art will recognize many variations that may be made without departing from the spirit of the disclosed invention.

ILLUSTRATIVE EMBODIMENT 1

Figure 4 shows a schematic diagram of a multi-tubular, DC heated, radial flow, membrane, steam reforming reactor in accordance with the present invention. In the reactor shown in Figure 4, a vaporizable hydrocarbon and steam enter the reactor at inlet 69 and flow through the reforming catalyst bed 70 (which is in the form of an annulus) containing multiple membrane tubes 71 (made by a process as described in Illustrative Embodiment

11 or Illustrative Embodiment 12) and multiple DC tubes 72 surrounded by the catalyst bed. In this embodiment the feed gases and reaction gases flow through the catalyst bed radially from outside to inside. The multiple hydrogen-selective, hydrogen-permeable, membrane tubes 71 are disposed axially in concentric rows in the reforming catalyst bed and serve to remove hydrogen, which is produced by the reforming reactions. The multiple DC tubes (i.e., chambers) 72 are also disposed axially in concentric rows in the reforming catalyst bed (for example, in a ratio of 1:2 or other number of DC tubes to the number of membrane tubes). The multiple DC tubes are in contact with the reforming catalyst bed and provide a controlled, distributed heat flux to the catalyst bed sufficient to drive the reforming reactions. While the membrane tubes and the DC tubes are shown to be in concentric rows in Figure 4, other geometric arrangements of these tubes can be suitably employed, and are within the scope of the present invention.

The DC tubes 72 generally comprise a fuel conduit disposed within a larger tube with an inlet and flow path for a preheated oxidant (e.g., preheated air) and an outlet for combustion (flue) gas. The DC tubes may be closed ended with a fuel conduit, oxidant inlet and flow path, and flue gas outlet arranged as shown in Figure 6A, or may open ended with the fuel conduit, oxidant inlet and flow path arranged as shown in Figure 6B.

High purity hydrogen is removed from the multi-tubular, radial flow, reactor shown in Figure 8 via outlets 73, with the aid of vacuum. Optionally, a sweep gas may be used to promote the diffusion of hydrogen through the membranes of the membrane tubes 71. If a sweep gas is employed, the membrane tubes 71 may contain an outer sweep gas feed tube and an inner return tube for sweep gas and hydrogen as discussed in Figure 12. By-product gases, including unpermeated hydrogen, if not further used internally for heat production, e.g., combustion or heat exchange, exit the multi-tubular, radial flow, reactor via outlet 74. A hollow tube or cylinder 75 may optionally be used for flow distribution.

ILLUSTRATIVE EMBODIMENT 2

Figure 5 is a top cross-section view of the shell of the multi-tubular, DC heated, radial flow, membrane, steam reforming reactor of Figure 4. The cross sectional view of the reactor shows multiple membrane tubes 71 (made by a process as described in Illustrative Embodiment 11 or Illustrative Embodiment 12 and multiple DC tubes 72 dispersed in catalyst bed 70 with optional hollow tube or cylinder 75 being in the center of the reactor. In the example shown, the membrane tubes 71 have outside diameters (OD) of about one inch (2.54 cm) while DC tubes have an OD of approximately two inches (about

5.08 cm), although other sizes of these tubes can be suitably employed. If a sweep gas is employed, the membrane tubes 71 may contain an outer sweep gas feed tube and an inner return tube for sweep gas and hydrogen as shown in Figures 8 and 13. A larger shell containing more tubes duplicating this pattern can also be used.

ILLUSTRATIVE EMBODIMENT 3

Figures 6A and 6B are schematic diagrams showing an example of a "closed ended" and of an "open ended" distributed combustion tubular chamber which are used to drive the reforming reactions in various embodiments of the present invention. Referring to Fig. 6A, an oxidant (in this case preheated air) enters the DC tube at inlet 76 and mixes with fuel which enters the DC tube at inlet 77 and passes into fuel conduit 78 through nozzles 79 spaced along the length of the fuel conduit, whereupon it mixes with the air which has been preheated to a temperature such that the temperature of the resulting mixture of fuel and air is above the autoignition temperature of the mixture. The reaction of the fuel passing through the nozzles and mixing with the flowing preheated air at a temperature above the autoignition temperature of the mixture, results in distributed combustion which releases controlled heat along the length of the DC tube as shown, with no flames or hot spots. The combustion gases, (i.e., flue gas) exit the DC tube at outlet 80.

In the "open ended" DC tubular chamber shown in Fig. 6B, preheated air enters the DC tube at inlet 76 and the fuel at inlet 77, and the fuel passes through conduit 78 and nozzles 79, similar to "closed end" DC tube in Fig. 6A. However, in the case of the "open ended" DC tube, the flue gas exits the DC tube at open end 81, instead of outlet 80 as shown in Fig.6A.

ILLUSTRATIVE EMBODIMENT 4

Figure 7 is a schematic drawing of a multi-tubular, DC heated, axial flow, membrane, steam reforming reactor in accordance with the present invention. In the reactor shown in Figure 7, a vaporizable hydrocarbon and steam enter the reactor at inlet 69 and flow through the reforming catalyst bed 70 containing multiple hydrogen- selective membrane tubes 71 (made by a process as described in Illustrative Embodiment 11 or Illustrative Embodiment 12) and multiple DC tubes 72. In this embodiment the feed gases and reaction gases flow through the catalyst bed axially from the top of the catalyst bed to the bottom. The multiple hydrogen-selective membrane tubes 71 are disposed axially in the reforming catalyst bed and serve to remove hydrogen which is produced by the reforming reactions. In the embodiment shown the membrane tubes are closed at the top and a sweep gas (e.g. steam) is employed, which enters the reactor at inlet 85 into the bottom of the membrane tubes where it flows upward in the outer part of the membrane tube, counter-current to the hydrocarbon and steam feed. A stinger pipe fitted to the bottom of the permeate section may be used to distribute the sweep gas in the membrane tube. The permeated hydrogen and sweep gas flow downward in a return tube located in the center of the membrane tube and exit the reactor via outlet 86. The pressure drop in the permeate pipe section is significant when the length of the pipe relative to the diameter exceeds a given limit. Actually, the volumetric amount of hydrogen crossing the membrane is proportional to the membrane area, □*D*L and the multiplier is the velocity, which is fixed as a function relating to Sievert's law, the description of which can be found in US2003/0068269. The same hydrogen amount has to flow across the pipe cross section which is equal to $\pi * D^2/4$. The ratio of hydrogen velocities through the pipe and through the membrane respectively is proportional to $(\pi *D*L)/(\pi *D^2/4)$ or to L/D. Pressure drop increases with gas velocity. If this ratio exceeds a limit, then the velocity in the permeate pipe exceeds a limit too, since the velocity through the membrane is fixed. Then the pressure drop in the permeate pipe becomes high and it reduces the hydrogen flux by creating back pressure in the permeate section. In such a case, the reactor design has to accommodate either a higher membrane diameter, or a reduced length.

There are also multiple DC tubes (i.e., chambers) 72 disposed axially in the reforming catalyst bed. In the embodiment shown the DC tubes are "closed ended" tubes with preheated air entering at inlet 76, fuel entering at 77 and combustion gas (i.e., flue gas) exiting the reactor at outlet 80. The multiple DC tubes are in heat transferring contact with the reforming catalyst bed 70 and provide a controlled, distributed heat flux to the catalyst bed sufficient to drive the reforming reactions. While the membrane tubes and the DC tubes are shown to be in a particular geometric pattern in Figure 11, it is understood that other geometric arrangements of these tubes may be used and are within the scope of the invention. While "closed ended" DC tubes are employed in the particular reactor shown in Figure 7, "open ended" DC tubes may be suitably employed as well. Also, the DC tubes and/or the membrane tubes may be surrounded by cylindrical screens (not shown) to protect them from getting in direct contact with the catalyst, and to allow insertion of these tubes even after the catalyst is loaded into the reactor.

The DC chamber must be free of obstructions and have a tubular dimension for the external or exterior tube of the DC chamber such that the length to diameter ratio is higher than a given limit, preferably more than 4. This ratio ensures that the air velocity in the chamber becomes higher than the flame velocity of the fuel and that turbulence is induced to improve heat transfer. In such a condition, no flames are created or stabilized. Any obstructions (like baffles) would create stagnation points where flames would form and stabilize.

High purity hydrogen, which diffuses through the membrane into the membrane tubes, is removed from the reactor via outlet(s) 86 together with the sweep gas (in this case steam). While outlet 86 is shown in Figure 7 to be located on the side of the reactor, this outlet may optionally be located at the bottom of the reactor thereby avoiding a bottom side exit manifold. A further option involves the use of a vacuum instead of a sweep gas to facilitate diffusion of the hydrogen through the membrane into the membrane tubes. Vacuum can be induced either mechanically with a pump or chemically with a metal hydride precursor which reacts away the hydrogen to form metal hydride. The hydride is on-line for a given period of time and when it is saturated, a parallel compartment can be put on-line, while the original compartment is isolated and heated to desorb and produce the hydrogen. This is advantageous in cases where the hydrogen needs to be stored and/or shipped to a customer or in cases where the cost of electrical energy for running a pump is higher than using waste energy to desorb the hydrogen from the hydride. Detailed economics will dictate the right choice.

In another embodiment of the reactor in Figure 7, the sweep gas inlet 85 and the hydrogen, sweep gas outlet 86 and their associated plenums, may be placed on the top of the reactor allowing easy access to the bottom of the reactor. In a further embodiment of the reactor of Figure 11, the preheated air inlet 76, the fuel inlet 77 and the flue gas outlet 80 and their associated plenums may be placed on the bottom of the reactor allowing easy access to the top of the reactor.

By-product gases, including carbon dioxide, steam, and minor amounts of carbon monoxide and unpermeated hydrogen, if not further used internally for heat production, e.g., combustion or heat exchange, exit the multi-tubular, axial flow, reactor via outlet 74. The reactor shown in Fig. 11 may be equipped with baffles and/or screens such as the baffles shown in Figures 13A and 13B or 13C and 13D.

ILLUSTRATIVE EMBODIMENT 5

Figure 8 is a top cross-section view of the shell of the multi-tubular, DC heated, axial flow, membrane reactor shown in Figure 7. In the embodiment shown multiple membrane tubes 71 (made by a process as described in Illustrative Embodiment 11 or Illustrative Embodiment 12) and multiple DC tubes 72 are dispersed in reforming catalyst bed 70. The multiple DC tubes employed in this embodiment are "closed ended" DC tubes as discussed above in connection with Figure 7. The membrane tubes are equipped with an outer sweep gas feed tube and an inner hydrogen, sweep gas return tube as discussed in connection with Figure 7. A typical reactor of the type shown in this Figure 8 may comprise, for example, 19 DC tubes of 5.5" outer diameter and 90 membrane tubes of 2" outer diameter enclosed in a shell of 3.5 ft diameter containing catalyst in the void spaces. Other shell sizes and numbers of tubes can be suitably employed depending on the capacity needed. The design parameter which is of utmost importance is the optimum gap between the membrane and the DC tubes. If a high gap is assumed, then heat transfer limitations occur since the flow of enthalpy from DC to the reforming reaction is slow. The membranes may not operate isothermally and cold spots may develop, thus reducing the reactor efficiency. If a small gap is assumed, then there may be problems with insufficient catalyst penetration in the gap, overheating of the membrane, or even touching of the hot DC tube with the membrane in conditions where the tubes are not perfectly straight. A narrow gap limitation will make reactor fabrication more expensive, since clearances are hard to achieve. Thus, an intermediate gap is more preferable. As a particular non-limiting example, the gap between the membrane and the DC tubes is from about ¼ inch (about 0.64 cm) to about 2 inches (about 5.08 cm), particularly from about ½ inch (about 1.27 cm) to about 1 inch (about 2.54 cm). The gap between the membrane tubes may be from about ¼ inch (about 0.62 cm) to about 2 inches (about 5.08 cm), particularly from about ½ inch to about 1 inch and this has to be also optimized. The hydrogen-permeable membrane tube has a ratio of length to diameter of less than about 500.

ILLUSTRATIVE EMBODIMENT 6

Figures 9A and 9B and 9C and 9D show two different configurations of baffles which may be employed in the multi-tubular, DC heated, axial flow, membrane steam reforming reactors of the invention to increase contact of the reactant gases with the catalyst in the catalyst beds. The baffle configuration shown in Figures 9A and 9B comprises a washer shaped baffle 87 and a disk shaped baffle 88 arranged in an alternating pattern. This baffle arrangement causes the feed and reactant gases to flow through the hole in the washer shaped baffle and be deflected by the disk shaped baffle thereby enhancing the contact of the reactant gases with the catalyst (not shown) which is packed in the area between the baffles.

The baffle arrangement shown in Figures 9C and 9D comprises truncated disks 89 which are placed in an alternating pattern (truncated left and truncated right) in the reactor thereby causing the feed and reactant gases to "zigzag" as they flow through the catalyst (not shown) which is packed in the area between the baffles.

The baffles in Figures 9A&B and 9C&D will have openings (not shown) to allow the DC tubes and membrane tubes to pass through them. Screens positioned in vertical alignment (not shown) may also be used to support the baffles and in some cases hold the catalyst away from the shell wall or from the center of the shell for better gas flow distribution.

ILLUSTRATIVE EMBODIMENT 7

Figure 13 is a top cross-section view of the shell of a multi-tubular reactor in accordance with one embodiment of the invention in which four membrane tubes 71 (made by a process as described in Illustrative Embodiment 11 or Illustrative Embodiment 12) are dispersed in the reforming catalyst bed 70 which is packed into reactor tube 82, while the DC chamber is in the form of an annulus surrounding the reforming catalyst bed. The tubular DC chamber (which is defined by outer wall 83 and the wall of the reactor tube 82) contains multiple fuel conduits 78 having nozzles (not shown) through which fuel flows and mixes with preheated air flowing in the DC chamber whereupon combustion occurs. If a sweep gas is employed, the membrane tubes 71 may contain an outer sweep gas feed tube and an inner return tube for sweep gas and hydrogen as shown in Figure 13. In one embodiment of the invention, the membrane tubes have an outer diameter of 2 inches, while the outer DC tube has an inner diameter (ID) of approximately 8.6 inches. However, other sizes can be suitably employed.

ILLUSTRATIVE EMBODIMENT 8

Figure 10 is a top cross-section view of the shell of another embodiment of the multi-tubular, axial flow, reactor of the invention in which multiple reactor tubes 82 packed with reforming catalyst are employed. In this example each of the six reactor tubes 82 contains a catalyst bed 70 and a membrane tube 71 (made by a process as described in Illustrative Embodiment 11 or Illustrative Embodiment 12) containing an outer sweep gas feed tube and an inner hydrogen, sweep gas return tube. Heat is provided to the reforming catalyst beds by the tubular DC chamber defined by outer wall 83 and inner wall 84. The

DC chamber contains multiple fuel conduits 78 dispersed at various intervals in the DC chamber. A hollow tube or cylinder defined by inner wall 84 may optionally be used for flow distribution.

ILLUSTRATIVE EMBODIMENT 9

Figure 12 is a top cross-section view of the shell of further embodiment of the multi-tubular, axial flow, reactor of the invention in which four membrane tubes are dispersed in each of six reactor tubes 82 containing catalyst beds 70. Heat is provided to the catalyst beds by DC chamber defined by outer wall 83 and inner wall 84. The DC chamber contains multiple fuel conduits 78 having nozzles 79 (not shown). If a sweep gas is employed, the membrane tubes 71 (made by a process as described in Illustrative Embodiment 11 or Illustrative Embodiment 12) may contain an outer sweep gas feed tube and an inner return tube for sweep gas and hydrogen as discussed shown and discussed above in connection with Figures 8 and 13. The hollow cylinder or tube defined by inner wall 84 may optionally be used for flow distribution.

ILLUSTRATIVE EMBODIMENT 10

Figure 12 is a top cross-section view of the shell of further embodiment of the multi-tubular, axial flow, reactor of the invention in which six membrane tubes **71** (made by a process as described in Illustrative Embodiment 11 or Illustrative Embodiment 12) are dispersed in each of the six reactor tubes 82 packed with reforming catalyst. Heat is provided to the reforming catalyst beds by the DC chamber defined by outer wall 83 and inner wall **84**. The DC chamber contains multiple fuel conduits **78**. Additional heat may be provided to the catalyst beds by employing a DC tube 72 in the center of each of the reactor tubes 82 as shown in Figure 12. The hollow tube or cylinder defined by inner wall 84 may optionally be used for flow distribution.

If a sweep gas is employed, the membrane tubes 71 may contain an outer sweep gas feed tube and an inner return tube for sweep gas and hydrogen as discussed in Figure 12.

ILLUSTRATIVE EMBODIMENT 11

This embodiment describes the fabrication of a composite structure which can be used for making the hydrogen selective and hydrogen-permeable membrane tubes for the reactors of Illustrative embodiments 1-10. It had a dense hydrogen-selective membrane, an intermediate layer that included a preactivated aluminum oxide (Al_2O_3) powder and a palladium binder, and a nominal 0.1 media grade porous 316L stainless steel ("PSS") support.

A 2.5 inch (6.35 centimeter (cm)) long, 0.5 inch (1.27 cm) outside diameter (O.D.) section of PSS tube, welded to a section of non-porous 316L stainless steel tube on one end and a non-porous cap on the other end, was obtained from Mott Metallurgical Corporation. Contaminants were removed by cleaning the tube in an ultrasonic bath with alkaline solution at 60°C for one hour. Tap water was flushed on both the inside and the outside of the tube for 5 hours to remove all the alkaline solution from the PSS pore system. The tube was then washed with distilled water 2 or 3 times in an ultrasonic bath (10 minutes each wash). Finally, the tube was rinsed with acetone for 10 minutes. The support was then dried at 120°C overnight. The tube was then oxidized in air at 500°C for 10 hours. After oxidation, the color of the porous substrate had changed from silver to gray-green and did not appear uniform. A second oxidation at 500°C for 10 hours was performed and the color of the support changed from gray-green to red and uniform.

Preactivated aluminum oxide (alumina) powder was formed by surface activating aluminum oxide powder using the following method. 5 grams (g) of Al_2O_3 powder with an average particle size of 5 microns (Buehler, Ltd., Lake Bluff, IL), 2.5 g of Al_2O_3 powder with a mean particle size of 3 microns (Buehler, Ltd.) and 1 g of Al_2O_3 powder with a mean particle size of 0.01-0.02 microns (Alfa Aesar; Ward Hill, MA) were cleaned in 200 milliliters (mL) of water solution with pH adjusted to 2 using 10 M HCl. The cleaning step was performed in an ultrasonic bath at 60°C for 1 hour. The cleaned alumina powder mixture was filtered using glass microfiber filter paper (WHATMAN® GF/F type, Whatman, Inc; Clifton, NJ) and an aspirator. The filter cake with the glass microfiber filter was then put in 200 mL of aqueous stannous chloride ($SnCl_2$) solution (1 g/L, pH=2) for sensitization. The sensitizing step was performed in an ultrasonic bath at 60°C for 10 minutes. The GF/F filter was removed from the solution using a glass rod and the sensitized powder mixture was filtered. The filter cake with the glass microfiber filter was placed in 200 mL aqueous palladium chloride ($PdCl_2$) (0.1g/L, pH=2) activation solution. The activation step was performed in an ultrasonic bath at 60°C for 10 minutes. Finally, the activated powder mixture was filtered, washed with distilled water, and dried overnight at 120°C. At the end of the activation procedure, a thin yellowish cake of preactivated aluminum oxide was formed on the glass microfiber filter.

0.5 g of the pre-activated mixture was mixed in 200 ml of water at pH 2 to form a slurry which was placed in ultrasonic bath for homogenization. The oxidized support was then placed in the slurry and a vacuum was pulled (using an aspirator) from the inside of the tube. After 30 seconds, a gray deposit formed on the porous section of the support.

Palladium adhesion to the support was increased by the presence of anchoring sites. Anchoring sites, such as the tips of the substrate particles (*e.g.*, the tips of PSS grains forming the PSS support), were not covered by the alumina powder to produce good adhesion between the palladium membrane and the support. To expose the anchoring sites, extra alumina cake was removed by gloved hand while gently rinsing with distilled water. The vacuum in the tube side was maintained during removal of the extra alumina. Alumina remained inside the pore mouths of the porous support.

The support was then palladium plated for 20-30 minutes while applying a vacuum to the tube side using the following procedure. The tube was immersed in a plating solution at room temperature. The plating solution was composed of 4 grams $Pd(NH_3)_4Cl_2 \cdot H_2O$/liter, 198 milliliters NH_4OH (28 weight percent)/liter, 40.1 grams Na_2EDTA/liter, and 6 milliliters aqueous H_2NNH_2 (1 M)/liter. The plating solution and tube were placed in a water bath at 60°C. During plating, the level of plating solution was kept constant by adding a small quantity of plating solution for loss of solution to the vacuum. After the palladium in the plating solution was depleted, the tube was removed and placed in deionized water at 60°C until the water temperature reached room temperature. The tube was rinsed with cold water 4 to 5 times. Then, the support was dried at 120°C overnight.

After the powder deposition, the support was surface activated by sequentially immersing the exterior of the support in aqueous baths of $SnCl_2$ and $PdCl_2$. The exterior of the tube was immersed in 140 mL of aqueous $SnCl_2$ (1 g/L) at 20°C for about 5 minutes and was subsequently rinsed with deionized water. The exterior of the tube was then immersed in 140 mL of aqueous $PdCl_2$ (0.1 g/L) at 20°C for about 5 minutes followed by rinsing first with 0.01 molar hydrochloric acid and then with deionized water. The above-described surface activation cycle was performed a total of three times.

The surface activated support was then plated with palladium for 3 hours (2 cycles of palladium plating, as described above). After the first cycle of palladium plating, a slight mechanical treatment was preformed on the palladium layer with 600 grit silicon carbide paper to smooth the palladium layer. A dense palladium film, 14.8 microns thick (determined gravimetrically), was achieved after a total plating time of 9 hours. This composite palladium membrane showed a hydrogen permeance of 22.7 $[m^3/(m^2 \text{ hour bar}^{0.5})]_{STP}$ at 500°C. The hydrogen permeance was stable during the total time of the experiment (70 hours) at 500°C. The selectivity (H_2/He) of this membrane at 500°C was 260.

ILLUSTRATIVE EMBODIMENT 12

This embodiment describes the fabrication of a composite structure which can be used for making the hydrogen selective and hydrogen-permeable membrane tubes for the reactors of Illustrative embodiments 1-10. It had a dense hydrogen-selective membrane, an intermediate layer that included preactivated aluminum oxide (Al_2O_3) powders and a palladium binder, and a nominal 0.1 media grade porous 316L stainless steel ("PSS") support.

A 2.5 inch (6.35 cm) long, 0.5 inch (1.27 cm) outer diameter section of PSS tube, welded to a section of non-porous 316L stainless steel tube on one end and a non-porous cap on the other end, was obtained from Mott Metallurgical Corporation. The support was cleaned and dried following the same procedure described in Example 1. The support was then oxidized at 500°C in air for 10 hours.

Three different mixtures of powders were prepared as described below.

Powder Mixture 1 included 65 wt% Al_2O_3 with an average particle size of 1 micron (Alfa Aesar); 30 wt% Al_2O_3 with an average particle size of 5 microns (Buehler, Ltd.), and 5 wt% Al_2O_3 with an average particle size of 3 microns (Buehler, Ltd.).

Powder Mixture 2 included 60 wt% Al_2O_3 with an average particle size of 0.3 micron (Alfa Aesar); 30 wt% Al_2O_3 with an average particle size of 3 microns (Buehler, Ltd.), and 10 wt% Al_2O_3 with an average particle size of 1 micron (Alfa Aesar).

Powder Mixture 3 included 60 wt% Al_2O_3 with an average particle size of 0.01-0.02 micron (Alfa Aesar); 30 wt% Al_2O_3 with an average particle size of 1 micron (Alfa Aesar), and 10 wt% Al_2O_3 with an average particle size of 0.3 micron (Alfa Aesar).

The fine and very fine mixtures of alumina powders (*i.e.*, Powder Mixtures 2 and 3) were activated separately following the procedure described in Example 1. The coarse powder (*i.e.*, Powder Mixture 1) was not activated to avoid subsequent deposition of palladium too deep into the pore system of the PSS support.

The oxidized PSS support was placed for 1 minute in a 200 mL water slurry at pH 2 that contained 0.5 g of Powder Mixture 1. A vacuum was applied to the tube side of the support and an alumina cake easily formed on the support. Extra alumina cake was removed by gloved hand while gently rinsing with distilled water while vacuum on the tube side was maintained. Alumina powder only remained in the pore mouths of the support. Following the deposition of Powder Mixture 1, the support was immersed for 1 minute in a 200 mL water slurry that contained 0.5 g of pre-activated Powder Mixture 2 while a vacuum was applied to the tube side of the support. Again, extra alumina cake was removed carefully by gloved hand as described above. After deposition of the pre-activated Powder Mixture 2, the support was placed in 140 mL of palladium plating solution (described in Example 1) for 5 minutes of palladium plating (with no vacuum applied to the tube side) to glue the alumina particles. Following deposition of Powder Mixture 2, the support was immersed in a 200 mL water slurry that contained 0.5 g of pre-activated Powder Mixture 3 for 1 minute while a vacuum was applied to the tube side of the support. Again, extra alumina cake was removed carefully by gloved hand. After deposition of pre-activated Powder Mixture 3, the support was immersed in 140 mL of palladium plating solution for 5 minutes of palladium plating (with no vacuum applied to the tube side). This process produced a graded support.

The graded support was then surface activated by performing two times the surface activation cycle described in Example 1. The surface activated support was then plated with palladium for 3 hours (2 cycles of palladium plating, as described in Example 1 with no vacuum applied). After the first cycle of palladium plating a slight mechanical treatment was preformed on the palladium layer with 600 grit silicon carbide paper to smooth the palladium layer. After the first two palladium plating cycles, the support was surface activated using one cycle without a vacuum applied and then two surface activation cycles with a vacuum applied to the tube side of the support. Following surface activation, palladium was plated for 3 hours while pulling a vacuum on the tube side of the support. The support was then surface activated again using 3 surface activation cycles and then plated with palladium for an additional 3 hours, both steps performed without vacuum. After a total plating time of 9 hours, the membrane was 14 microns thick (determined gravimetrically).

The permeance of this membrane reached 16 $[m^3/(m^2 \text{ hour bar}^{0.5})]_{STP}$ after 50 hours at 250°C, which was extremely high compared to the membrane of Example 1. The selectivity of this membrane at 250°C was measured to be 84. The low selectivity was likely due to an imperfection in the PSS support that could not be covered by palladium.

ILLUSTRATIVE EMBODIMENT 13

This embodiment describes the fabrication of a composite structure which can be used for making the hydrogen selective and hydrogen-permeable membrane tubes for the reactors of Illustrative embodiments 1-10. It had a dense hydrogen-selective membrane, an intermediate layer that included preactivated aluminum oxide (Al_2O_3) powders and a palladium binder, and a nominal 0.1 media grade porous HASTELLOY® C-22® support. (HASTELLOY® C-22® is a nickel-chromium-molybdenum-iron-tungsten alloy.)

A 6 inch (15.24 cm) long, 1 inch (2.54 cm) outer diameter section of HASTELLOY® tube, welded to a section of non-porous 316L stainless steel tube on one end and a non-porous cap on the other end, was obtained from Mott Metallurgical Corporation. The support was cleaned and dried following the same procedure described in Example 1. The support was then oxidized at 700°C in air for 12 hours. A graded support was then produced using the same procedures and the same alumina powder mixtures as described in Example 2.

The graded support was then surface activated by performing two times the surface activation cycle described in Example 1. The surface activated support was then plated with palladium for 3 hours (2 cycles of palladium plating, as described in Example 1 with no vacuum applied). A third cycle of palladium plating was performed without vacuum for the first 40 minutes and pulling a vacuum in the tube side during the last 50 minutes.

After the last plating and rinsing with DI water, the membrane was dried for 2 hours at 120°C. The thickness of the palladium layer after these steps was 7.7 microns (determined gravimetrically). The helium leak of the membrane after the total of 4.5 hours of palladium plating was 8.9×10^{-4} $m^3/(m^2$ hour bar) and the membrane was considered dense.

The permeability of this membrane reached 21.5 $[m^3/(m^2 \text{ hour bar}^{0.5})]_{STP}$ at 250°C after 150 hours in hydrogen. The selectivity (H_2/He) at 250°C was 2016. The membrane showed hydrogen permeance of 28.5 $[m^3/(m^2 \text{ hour bar}^{0.5})]_{STP}$ at 300°C, 33.6 $[m^3/(m^2 \text{ hour bar}^{0.5})]_{STP}$ at 350°C, 38.3 $[m^3/(m^2 \text{ hour bar}^{0.5})]_{STP}$ at 400°C, 43.5 $[m^3/(m^2 \text{ hour bar}^{0.5})]_{STP}$ at 450°C, and 50 $[m^3/(m^2 \text{ hour bar}^{0.5})]_{STP}$ at 500°C. The selectivity of the membrane decreased from 2016 at 250°C to 42 at 500°C. However, the large helium leak was likely due to a blister in the welding between the porous part of the support and the non-porous part. The module was repaired as described in Example 14, below.

ILLUSTRATIVE EMBODIMENT 14

After hydrogen characterization (which lasted 743 hours), the membrane produced as described in Illustrative Embodiment 13 was repaired. The surface of the membrane was examined and large blisters were found at the interface between the porous parts and the non-porous parts of the support. The surface of the membrane was masked using polytetrafluoroethylene tape, and palladium was plated for 6 hours locally on the welds between the porous HASTELLOY® C-22® support and the non-porous parts. After local palladium plating of the two welds, the helium leak dropped to 0.006 $[m^3/(m^2 \text{ hour bar})]_{STP}$ at room temperature. Finally, the support was unmasked and the total surface was activated with three surface activation cycles using the procedure described in Example 1 while applying a vacuum to the tube side of the support and a last palladium plating cycle (1.5 hours) was performed. The thickness of the membrane after repair was about 10 microns and the helium leak was undetectable.

The permeability of this membrane reached 14.8 $[m^3/(m^2 \text{ hour bar}^{0.5})]_{STP}$ at 250°C after 47 hours in hydrogen. The membrane was then slowly heated (0.5°C/min) to 500°C and the hydrogen permeance was measured to be 40.6 $[m^3/(m^2 \text{ hour bar}^{0.5})]_{STP}$ at 500°C. After 200 hours in hydrogen at 500°C, helium was introduced in the reactor to measure the helium leak. The helium leak was 0.00064 $[m^3/(m^2 \text{ hour bar})]_{STP}$ so that the selectivity (H_2/He) was 27000. Hydrogen was then reintroduced for another 270 hours. After the 270 hours, the permeance was 41.2 $[m^3/(m^2 \text{ hour bar}^{0.5})]_{STP}$ and the selectivity (after switching to helium) was 2400. After another 285 extra hours in hydrogen (with 4 changes H_2-He-H_2), the membrane had a permeance of 42.5 $[m^3/(m^2 \text{ hour bar}^{0.5})]_{STP}$ and a selectivity of 600. To conclude, the repaired module was stable at 500°C for 755 hours and the final permeance was 42.5 $[m^3/(m^2 \text{ hour bar}^{0.5})]_{STP}$ with a selectivity of 600.

ILLUSTRATIVE EMBODIMENT 15

This embodiment describes the fabrication of a composite structure which can be used for making the hydrogen selective and hydrogen-permeable membrane tubes for the reactors of Illustrative embodiments 1-10. It had a dense hydrogen-selective membrane, an intermediate layer that included preactivated aluminum oxide (Al_2O_3) powders and a palladium binder, and a nominal 0.1 media grade porous HASTELLOY® C-22® support.

A 6 inch (15.24 cm) long, 1 inch (2.54 cm) outer diameter section of HASTELLOY® tube, welded to a section of non-porous 316L stainless steel tube on one end and a non-porous cap on the other end, was obtained from Mott Metallurgical Corporation. The support was cleaned and dried following the same procedure described in Example 1. The support was then oxidized at 700°C in air for 12 hours.

Three different powders were prepared as described below.

Powder No. 1 (coarse powder) was γ-alumina powder with an average particle size of 3 microns (SPA-Gamma-AF CERALOX® high purity aluminum oxide, Sasol North America, Inc., Houston, TX). Powder No. 2 (fine powder) was Al_2O_3 with an average particle size of 0.3 micron (10-20 γ (gamma) phase, Alfa Aesar). Powder No. 3 (very fine powder) was Al_2O_3 with an average particle size of 0.01-0.02 micron (80-95 γ (gamma) phase, Alfa Aesar).

10 g of the coarse powder, 10 g of the fine powder, and 5 g of the very fine powder were separately surface activated using the following procedure. Each powder was placed in a separate 500 mL cylinder containing 250 mL of aqueous $SnCl_2$ solution (1 g/L, pH=2). This step of sensitizing the powder was performed in an ultrasonic bath at 60°C for 10 minutes. After 10 minutes, 250 mL of aqueous $PdCl_2$ solution (0.1 g/L, pH=2) were added into the cylinder already containing the aqueous $SnCl_2$ solution and alumina powder. The resulting slurry, with a total volume of about 500 mL, became brown instantly. The slurry was placed in an ultrasonic bath at 60°C for 10 minutes. The resulting surface activated powder was then filtered from the slurry by using one filter paper (WHATMAN® GF/F type) for every 50 mL of slurry. Therefore, each filter paper contained about 1 g of preactivated coarse powder, about 1 g of preactivated fine powder, or about 0.5 g of preactivated very fine powder. The filter cakes, 30 in number, were dried at 120°C for 2 hours.

1 g of the pre-activated coarse powder (*i.e.*, 1 filter paper with its cake) was mixed with 450 mL of water at pH 2 to form a slurry which was then placed in ultrasonic bath to homogenize the alumina suspension. After 1 minute, the filter paper was removed from the slurry using a glass rod. The oxidized support was then placed into the slurry and a vacuum was pulled (using an aspirator) from the inside of the tube. After 30 seconds, a gray deposit formed on the porous section of the support. Extra alumina cake was removed by gloved hand while gently rinsing with distilled water while the tube side vacuum was maintained. The support was then dipped for 4 additional seconds in the slurry. Then, the support was plated with palladium for 15 minutes using a procedure similar to that described in Example 1 using 400 mL of plating solution and with no vacuum applied to the support.

Following deposition and plating of the preactivated coarse powder, the support was immersed for 20 to 30 seconds in a 450 mL water slurry containing 1 g of the preactivated fine powder while a vacuum was applied to the inside of the support. An alumina cake formed on the support. Extra alumina cake was removed by gloved hand while gently rinsing with distilled water while a vacuum was applied to the inside of the support. The support was then dipped for 5 additional seconds in the slurry. Then, the support was again plated with palladium, as described above, for 10 minutes.

Following the deposition and plating of the preactivated fine powder, the support was immersed for 30 seconds in a 450 mL water slurry containing 0.5 g of the preactivated very fine powder while a vacuum was applied to the inside of the support. No extra alumina cake seemed to form using the preactivated very fine powder. The support was again plated with palladium, as described above, for 10 minutes. The support became black in color. Underneath the black layer, shiny gray palladium could be seen. This black powdery layer was readily removed. With gloved hands the very fine black powder was used to polish the surface of the support. After 5-10 minutes of rubbing the surface, the support was rinsed with deionized water to remove the black particles. Once the shiny gray surface was visible, the support was plated with palladium for another 10 minutes. Finally, the support was dried at 120°C for 4 hours.

The support was then masked with polytetrafluoroethylene tape, letting only 2 mm of the porous section of the tube and 5 mm of the non-porous section of the tube visible. To increase the adhesion between palladium and the tube, the oxide layer on the tube weld was removed by dipping the masked support in 400 mL of 1 M HCl. The surface was gently rubbed with gloved hands to ease the oxide removal. The support was surface activated using with 2 activation cycles and palladium was plated to the welding zones for 1.5 hours using a procedure similar to that described in Example 1 under vacuum. Then, the support was dried at 120°C for 4 hours.

Finally, the support was unmasked and the surface was activated with two surface activation cycles using the procedure described in Example 1. Then, the support was palladium plated for 3 hours (2 cycles of 1.5 hours) wherein 400 mL of plating solution was used for each cycle. A third palladium plating cycle, lasting 1 hour, was performed while a vacuum was applied to the tube side of the support. A palladium layer formed that was only 3.9 microns thick (determined gravimetrically). The helium leak was measured to be 0.0024 $[m^3/(m^2 \text{ hour bar})]_{STP}$. The membrane was considered to be dense.

The ranges and limitations provided in the instant specification and claims are those, which are believed to particularly point out and distinctly claim the instant invention. It is, however, understood that other ranges and limitations that perform substantially the same function in substantially the same manner to obtain the same or substantially the same result are intended to be within the scope of the instant inventions defined by the instant specification and claim

The reference to any prior art in this specification is not, and should not be taken as an acknowledgement or any form of suggestion that the referenced prior art forms part of the common general knowledge in Australia.

In the specification the term “comprising” shall be understood to have a broad meaning similar to the term “including” and will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps. This definition also applies to variations on the term “comprising” such as “comprise” and “comprises.”

CLAIMS

1. A reactor, comprising:

   a) a reaction chamber comprising:
      a catalyst bed adapted to produce reaction products comprising hydrogen gas from a hydrogen-producing feedstock; and

   b) at least one hydrogen-selective, hydrogen-permeable gas separation module adapted to receive the reaction products from the catalyst bed and to separate the reaction products into (1) a product stream comprising hydrogen and (2) a byproduct stream, wherein the gas separation module comprises:

      (i) a porous substrate;

      (ii) an intermediate layer at the porous substrate that comprises particles and a binder metal, wherein the binder metal is distributed throughout the intermediate layer; and

      (iii) a hydrogen-selective membrane, wherein the hydrogen-selective membrane overlies the intermediate layer.

2. A steam reforming process for the production of hydrogen, comprising:

   (a) reacting steam with a hydrogen-producing feedstock at a temperature of from 200°C to 700°C and at a pressure of from 0.1MPa to about 20.0 MPa in a steam reforming reaction chamber containing a reforming catalyst to produce a mixture of primarily hydrogen and carbon dioxide, with a lesser amount of carbon monoxide; and

   (b) separating hydrogen from the mixture produced by the reforming reaction with a hydrogen-selective, hydrogen-permeable gas separation module; wherein the gas separation module comprises:

      (i) a porous substrate;

      (ii) an intermediate layer at the porous substrate that comprises particles and a binder metal, wherein the binder metal is distributed throughout the intermediate layer; and

      (iii) a hydrogen-selective membrane, wherein the hydrogen-selective membrane overlies the intermediate layer.

3. The reactor of claim 1 or process of claim 2 wherein the intermediate layer of the gas separation module comprises at least two sub-layers of particles and binder metal.

4. The reactor or process of any of claims 1-3 wherein at least one distributed combustion chamber is in a heat transferring relationship with said catalyst bed.

5. The reactor or process of any of claims 1-4 wherein the gas separation module is a tube.

6. The reactor or process of any of claims 1-5 wherein the intermediate layer of said gas separation module comprises a gradient of particle size from a surface of the intermediate layer proximate to the porous substrate to a surface of the intermediate layer distal to the porous substrate.

7. The reactor or process of any of claims 1-6 wherein a metal hydride precursor is separated from said reaction chamber by said gas separation module, said metal hydride precursor being in gaseous fluid communication with said gas separation module, where said metal hydride precursor is located to react with hydrogen permeating said gas separation module to form a metal hydride.

8. The reactor or process of any of claims 1-7 wherein the hydrogen-selective membrane is formed of palladium or an alloy thereof with at least one of the metals selected from the group consisting of copper, silver, gold, platinum, ruthenium, rhodium, yttrium, cerium and indium; and the porous substrate is a porous ceramic substrate or a porous metal substrate selected from the group consisting of stainless steel, an alloy comprising chromium and nickel, a nickel based alloy, and an alloy comprising chromium, nickel, and molybdenum.

9. The reactor or process of any of claims 1-8 wherein the binder metal is a hydrogen-selective hydrogen-permeable metal or an alloy thereof.

10. The reactor or process of any of claims 1-9 wherein the particles of the intermediate layer are selected from the group consisting of metal particles, metal oxide particles including aluminum oxide particles, ceramic particles, zeolite particles, and combinations thereof.

11. The reactor or process of any of claims 1-10 wherein the particles of the intermediate layer are a preactivated powder.

12. The reactor or process of any of claims 1-11 wherein the intermediate layer has an average thickness of from 0.3 micrometers to 3 micrometers.

13. The reactor or process of any of claims 1-12 further comprising additional particles deposited over the particles and binder metal and additional binder metal deposited onto the additional particles.

14. The reactor of claim 1 wherein the reactor is a steam reforming reactor and the catalyst bed is a steam reforming catalyst bed.

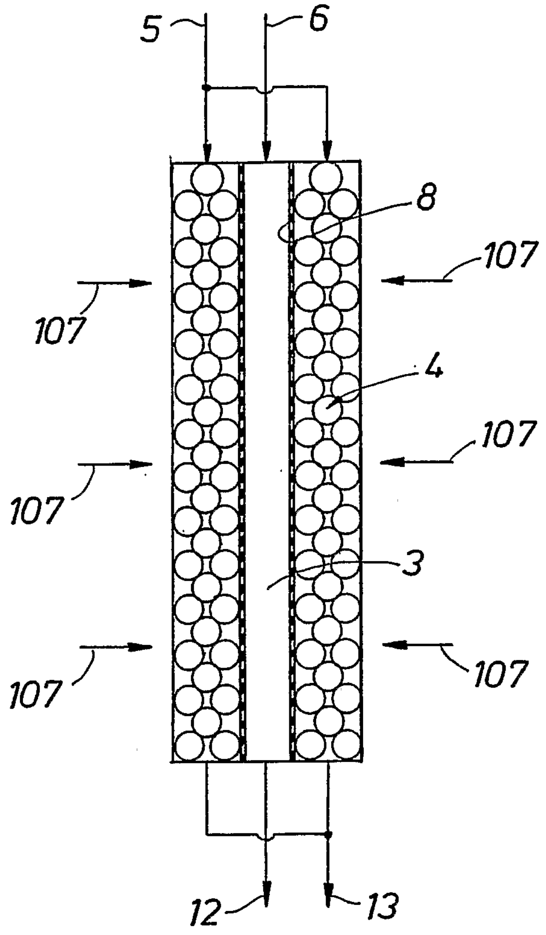
15. The reactor of claim 1 wherein the reactor is a dehydrogenation reactor and the catalyst bed is a dehydrogenation catalyst bed.

16. An integrated steam reforming reactor-hydrogen fuel cell comprising the reactor of claim 1 wherein the product stream containing hydrogen is delivered from the reactor to an anode compartment of a hydrogen fuel cell and the byproduct stream from the reactor is delivered to a cathode compartment of the hydrogen fuel cell.

17. A reactor substantially as hereinbefore described with reference to the examples and accompanying drawings.

18. A steam reforming process for the production of hydrogen substantially as hereinbefore described with reference to the examples and accompanying drawings.

FIG.1



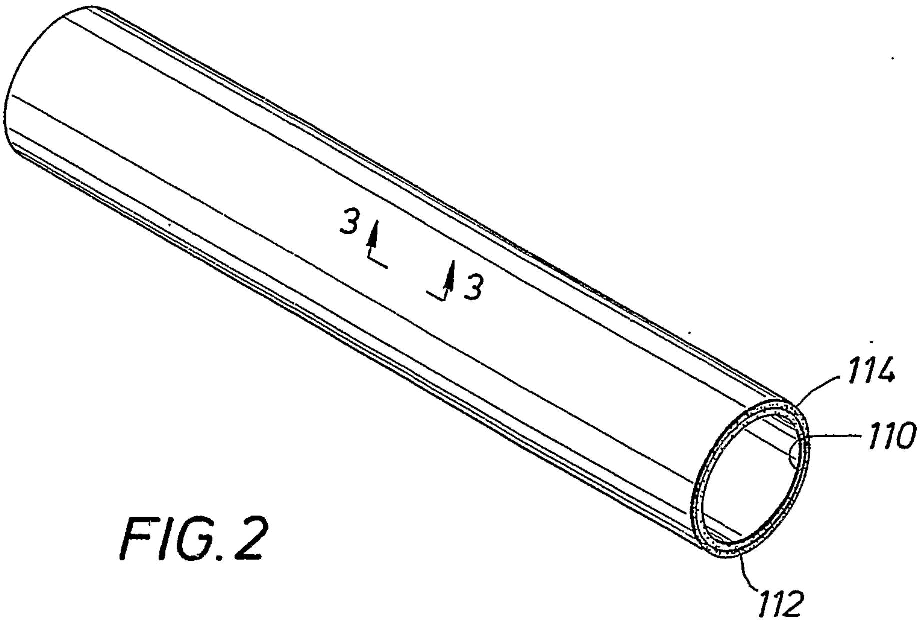


FIG.2

FIG. 3A

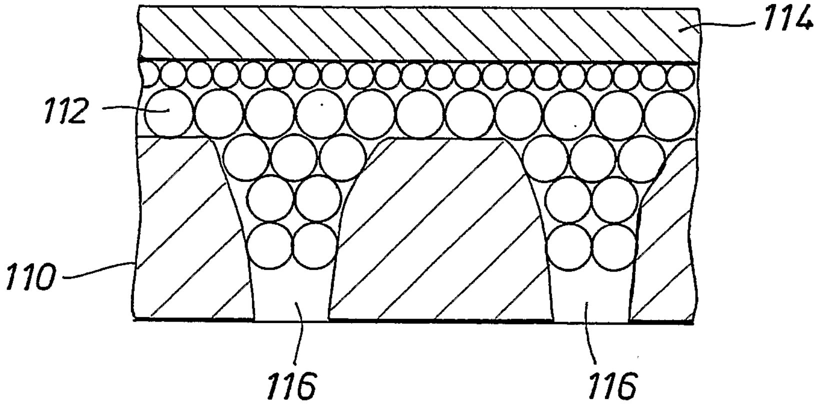


FIG. 3B

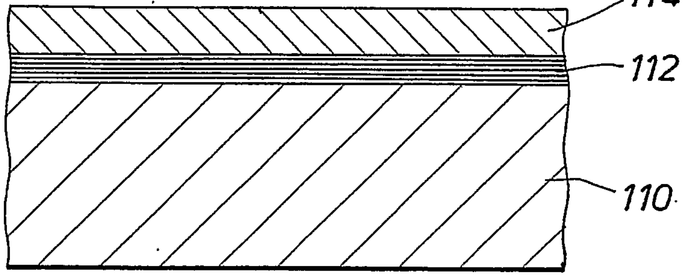


FIG.3C

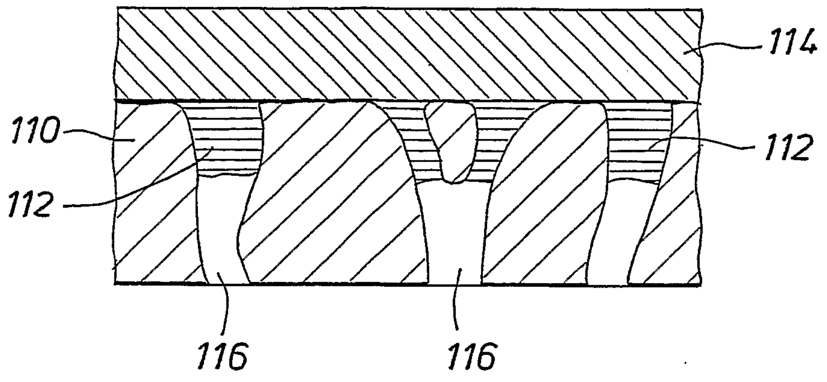


FIG.3D

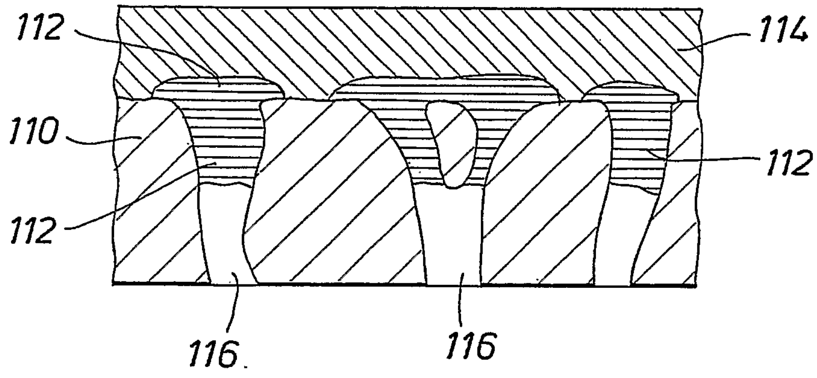
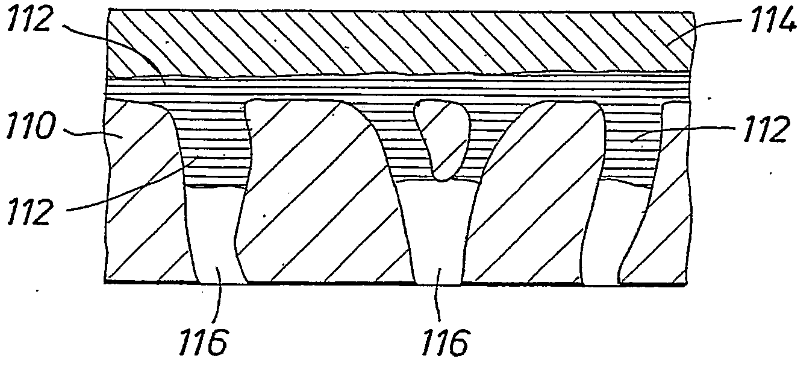


FIG.3E



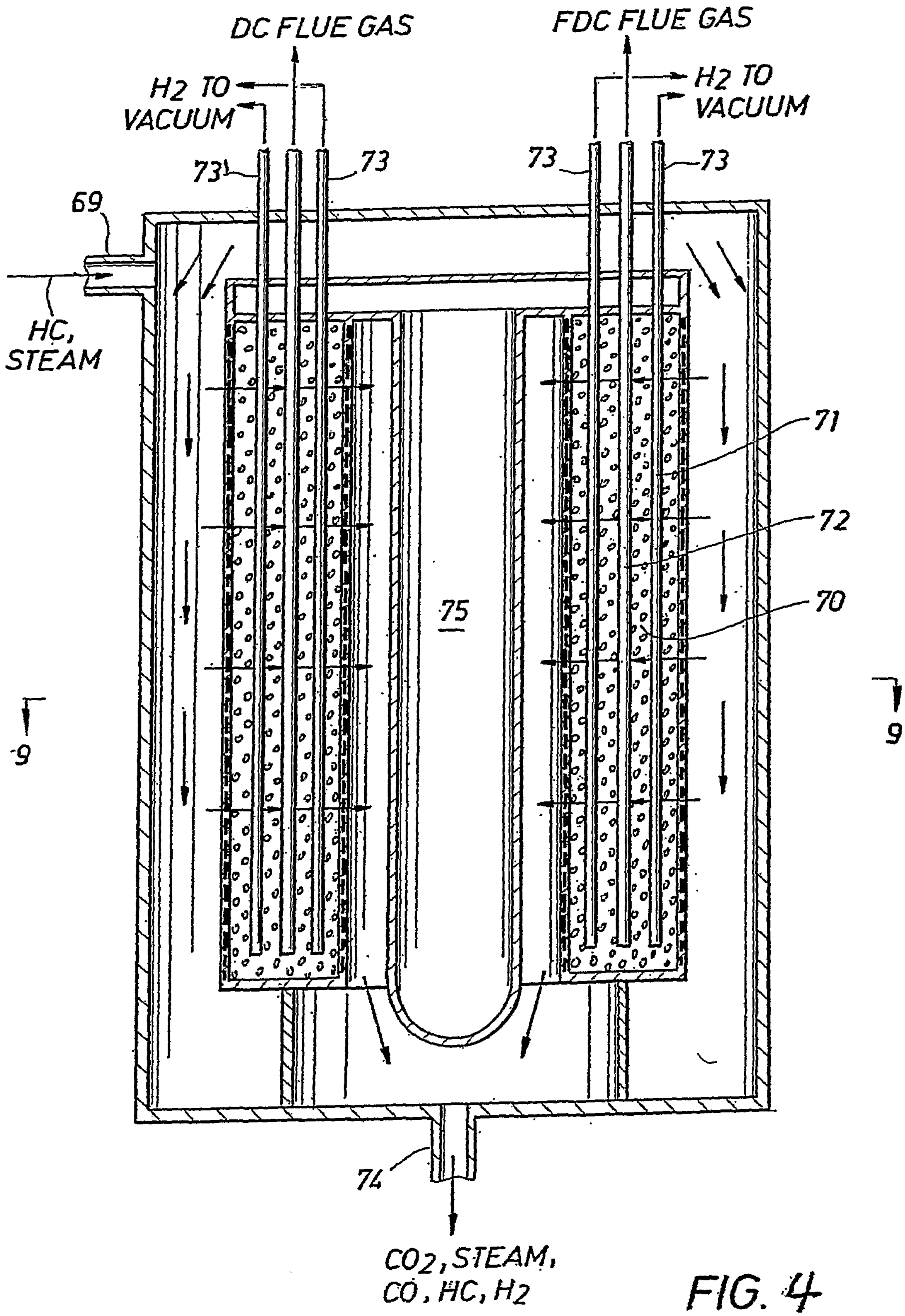

DC FLUE GAS
H2 TO VACUUM
73
73
FDC FLUE GAS
H2 TO VACUUM
73
73
69
HC, STEAM
71
72
70
75
9
9
74
CO2, STEAM, CO, HC, H2

FIG. 4

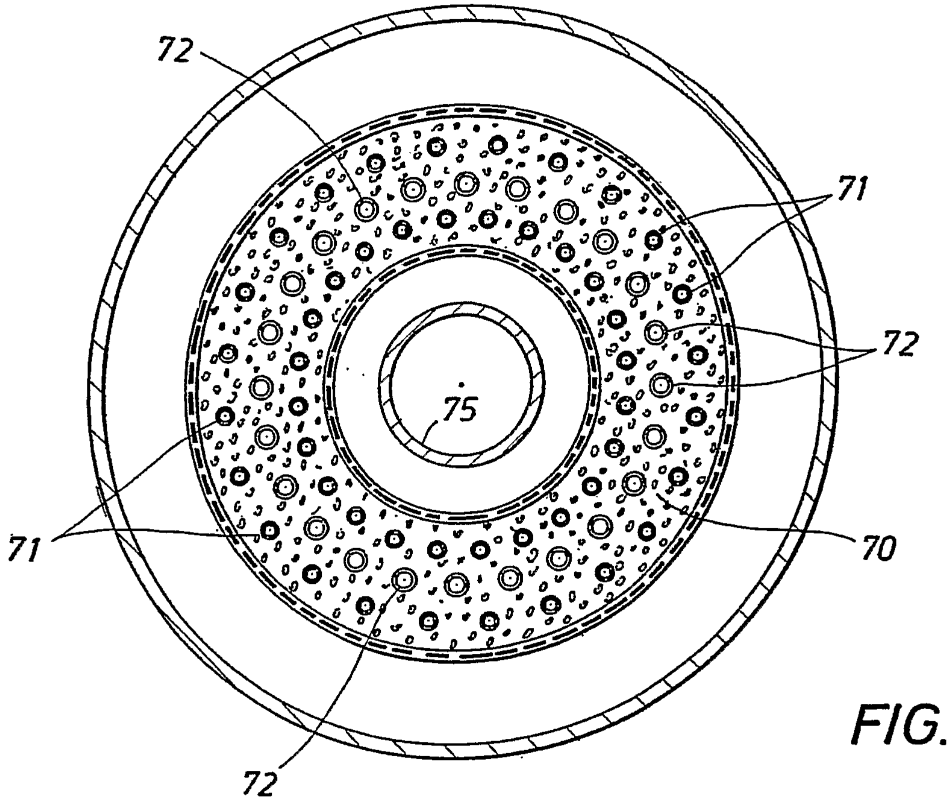


FIG. 5

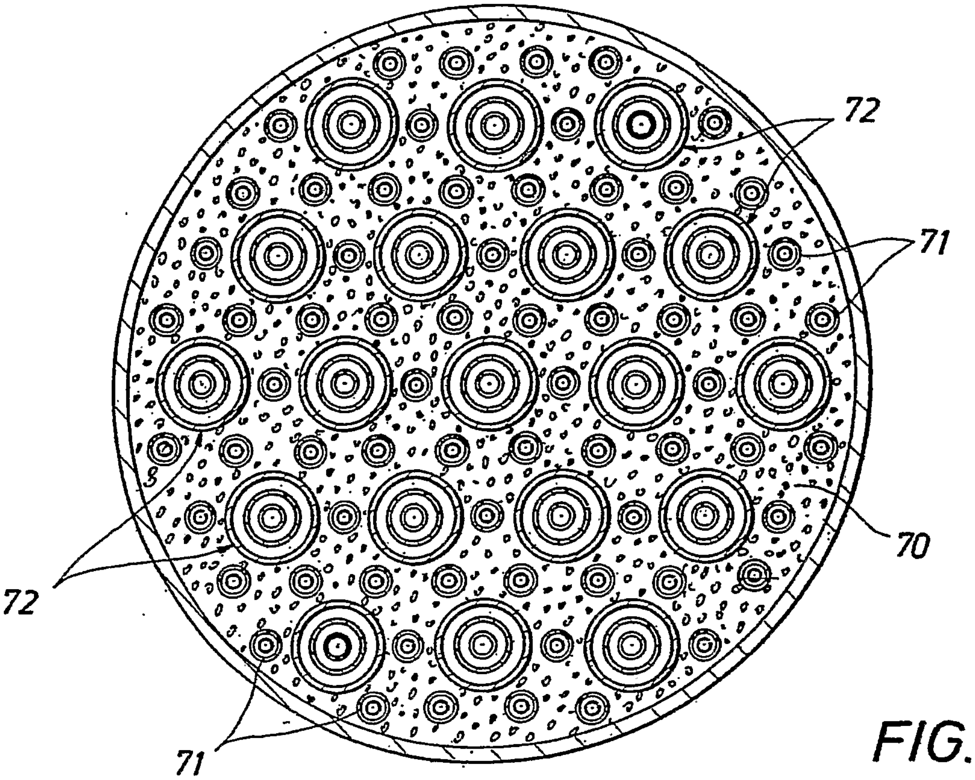


FIG. 8

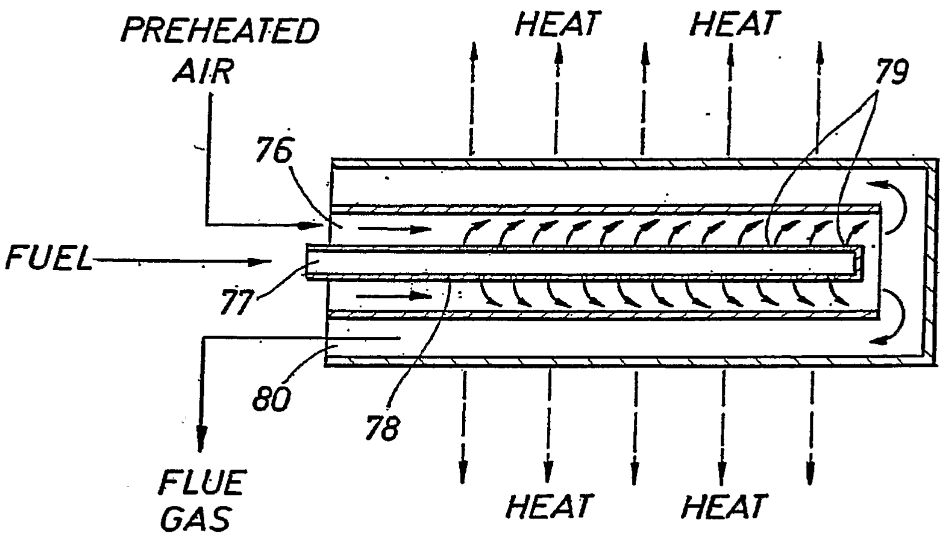

PREHEATED AIR
HEAT
HEAT
79
76
FUEL
77
80
78
FLUE GAS
HEAT
HEAT

FIG. 6A

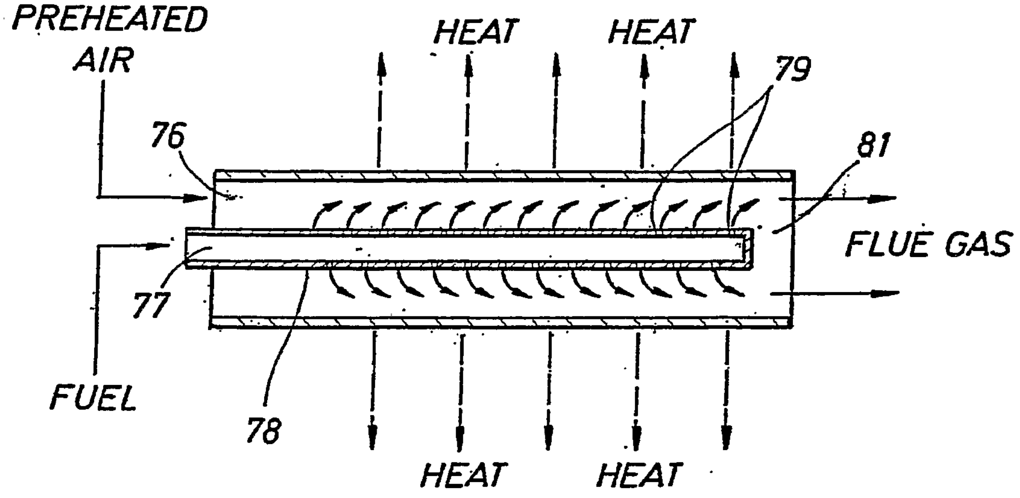

PREHEATED AIR
HEAT
HEAT
79
76
81
FLUE GAS
77
FUEL
78
HEAT
HEAT

FIG. 6B

FIG. 7

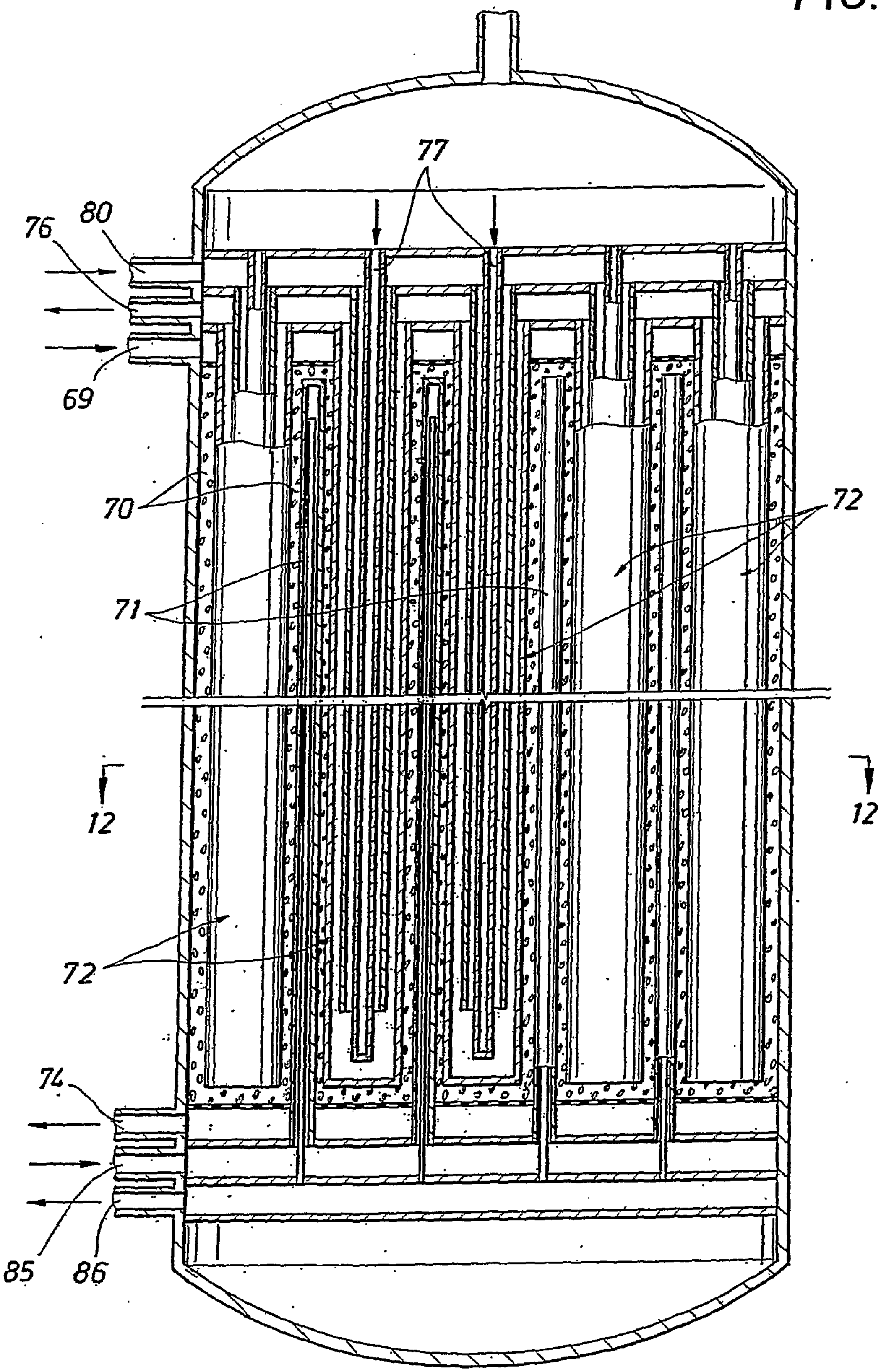


FIG. 9A

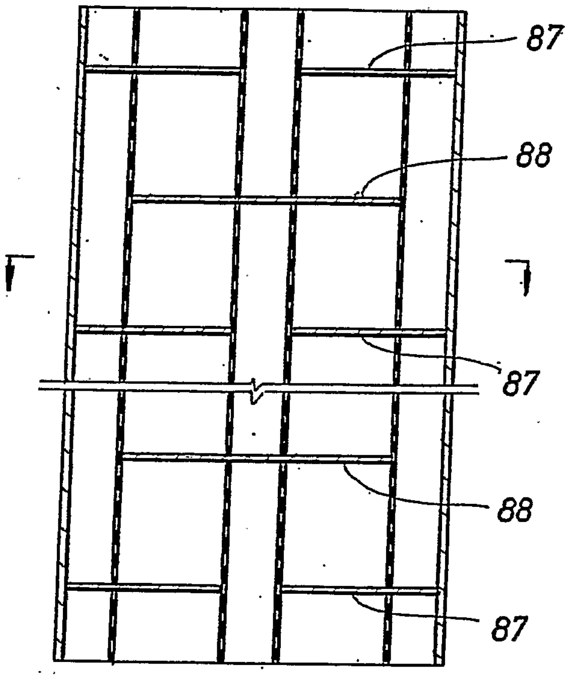


FIG. 9B

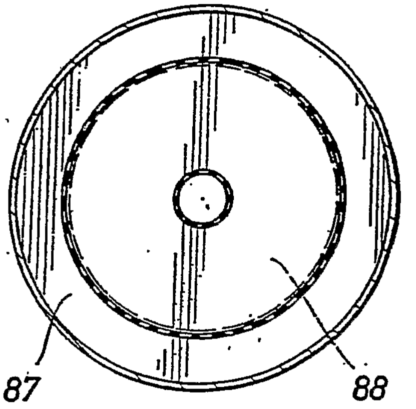


FIG. 9C

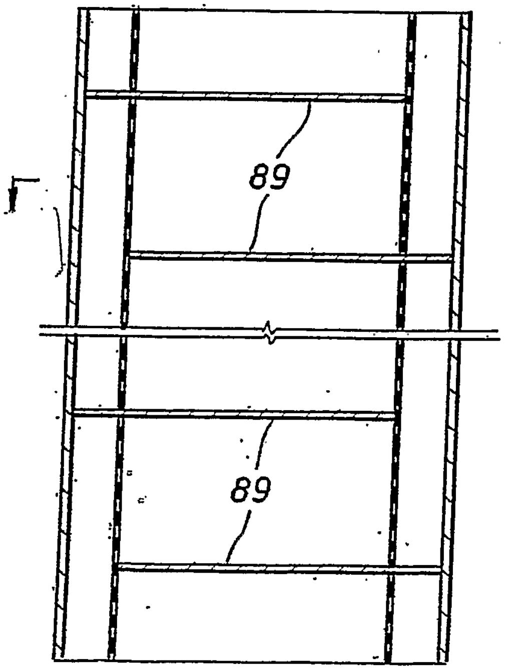
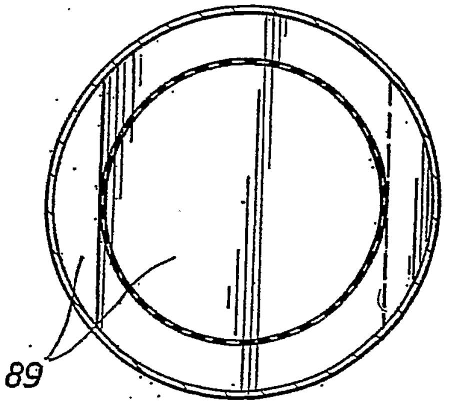


FIG. 9D



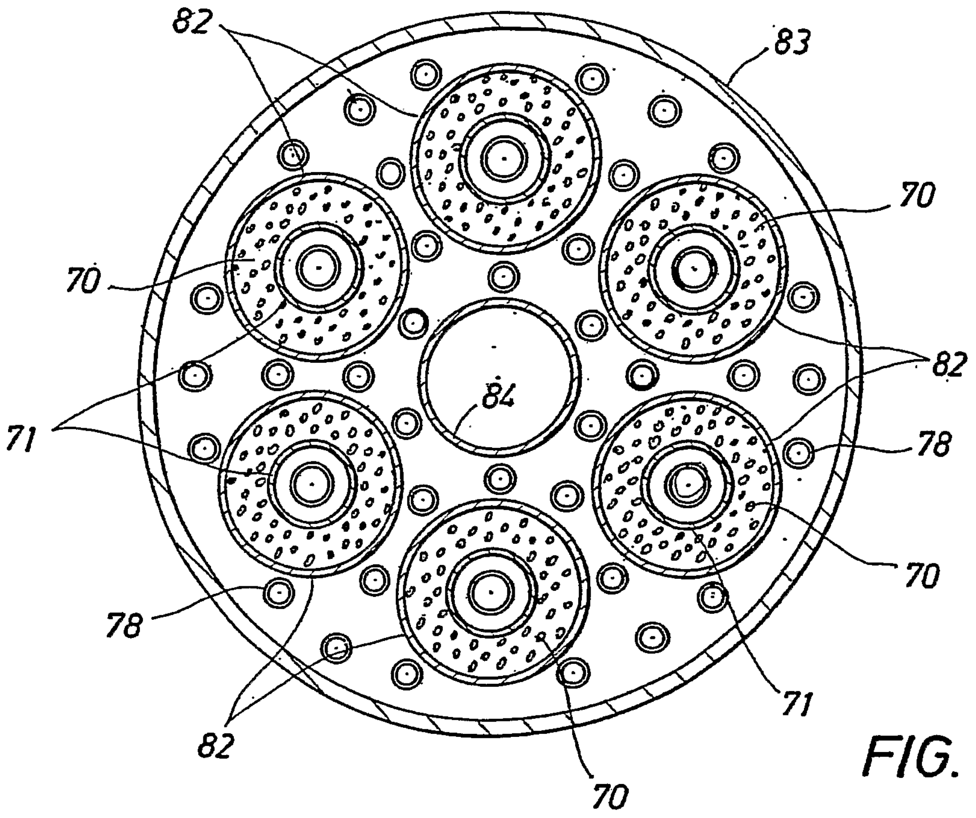

82
83
70
70
82
71
84
78
70
78
82
71
70

FIG. 10

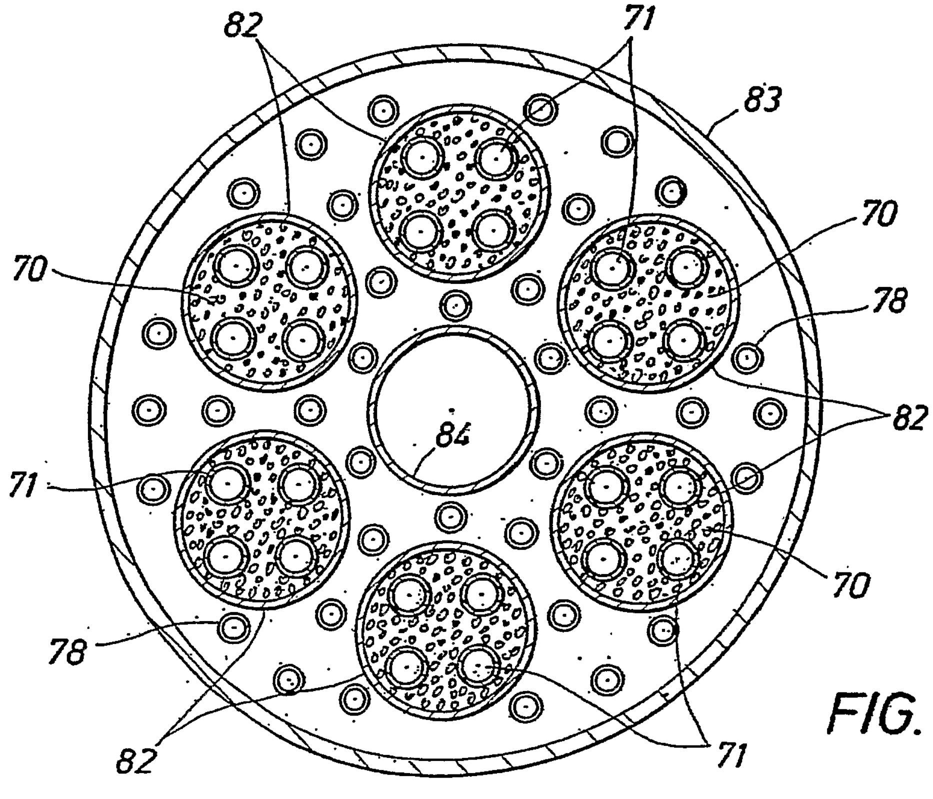

82
71
83
70
70
78
82
84
71
70
78
82
71

FIG. 11

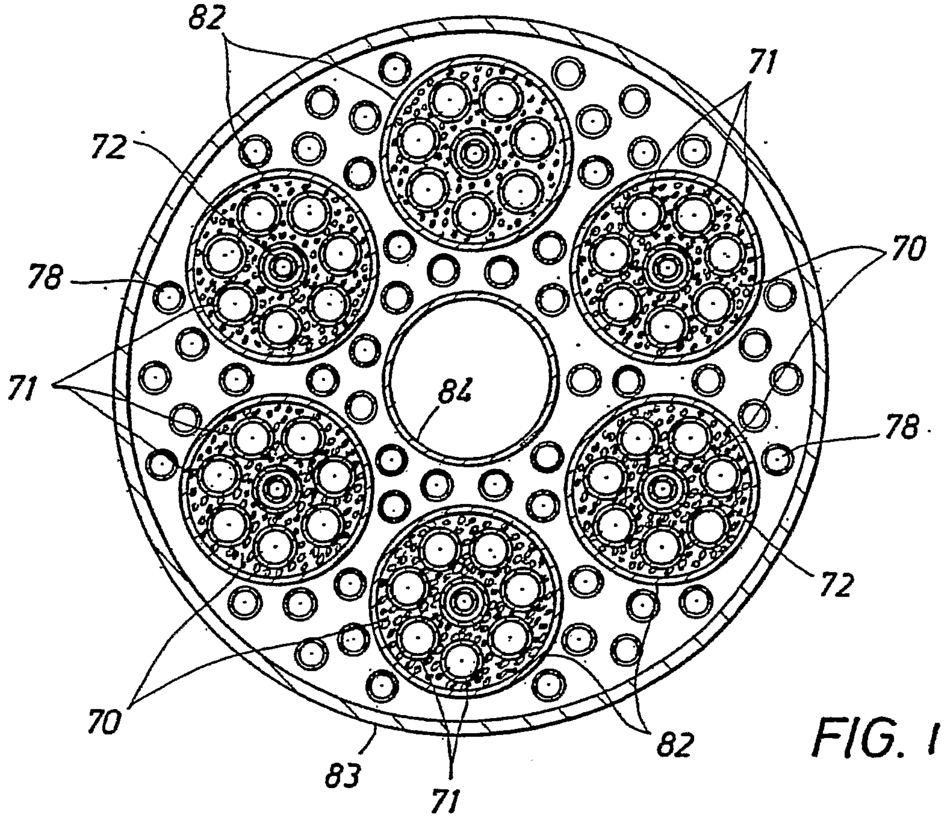


FIG. 12

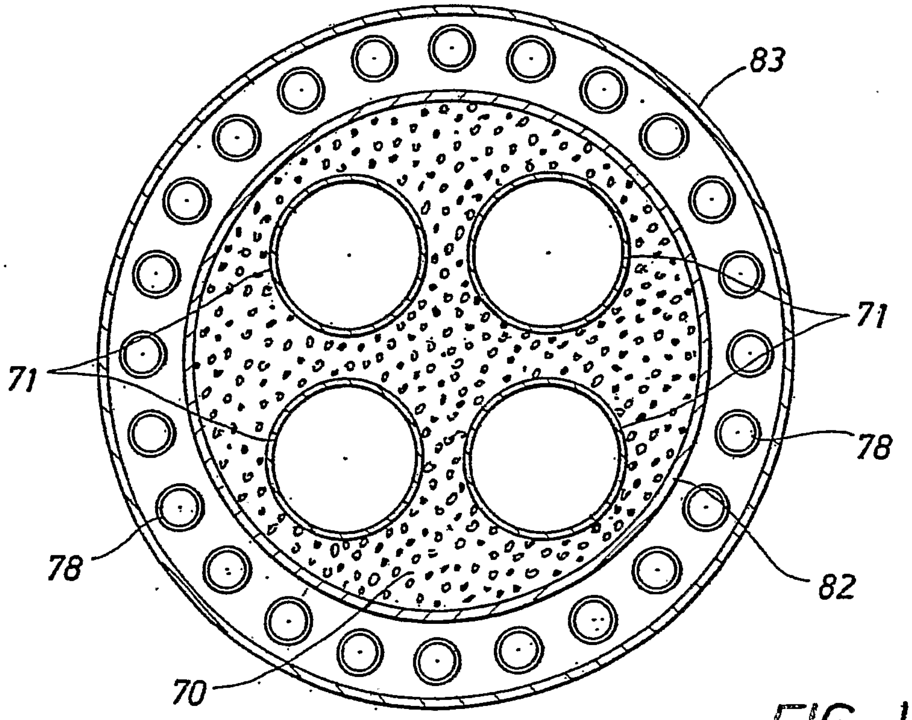


FIG. 13

FIG. 14