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SUPERINDUSTRIA Y COMERCIO
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REF: EXPEDIENTE : **00032439**

SOLICITANTE: BP AMOCO CORPORATION

FECHA DE LA SOLICITUD: MAYO 05, 2000

TITULO: MATERIALES COMPUESTOS PARA REACTORES DE MEMBRANA

ASUNTO: SOLICITUD ESTUDIO DE FONDO

DILIA RODRÍGUEZ D´ALEMAN, en mi condición de apoderada de la Sociedad solicitante, por el presente escrito atentamente solicito a Usted que habiéndose surtido la publicación de la presente solicitud, en la Gaceta de la Propiedad Industrial N°.522 de fecha Noviembre 28 de 2002 se proceda con el estudio de Fondo.

Para tal fin me permito anexar la tasa correspondiente.

Agradezco continuar con el presente trámite.

Señor Jefe,

DILIA RODRÍGUEZ D´ALEMAN
T.P.No. 20824 del CSJ

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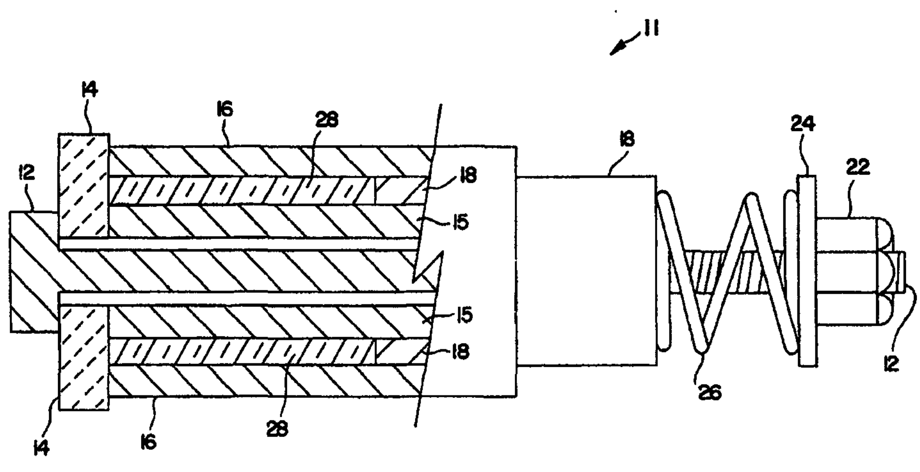

(57) Abstract

The present invention relates to composite materials for membrane reactors which include a gas–tight ceramic (28), a porous support (15, 16), and an interfacial zone therebetween. More particularly, this invention relates to composite materials using oxygen ion–conducting dense ceramic membranes (28) formed on a porous support (15, 16) comprising a metallic alloy to provide an interfacial zone identifiable by a gradient of composition in at least one metallic element across the interfacial zone between the dense ceramic membrane and the porous support. Processes using composite materials in accordance with the invention are, for example, used for production of synthesis gas comprising carbon monoxide and molecular hydrogen which synthesis gas is, advantageously, free of deleterious and/or inert gaseous diluents such as nitrogen.

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composite exhibits greater stability when exposed to a reducing gas environment and other operating conditions for extended time periods.

It is an object of the invention to overcome one or more of the problems described above.

Other objects and advantages of the invention will be apparent to those skilled in the art from a review of the following detailed description, taken in conjunction with the drawing and the appended claims.

Other objects and advantages of the invention will become apparent upon reading the following detailed description and appended claims.

Summary of the Invention

In broad aspect, the present invention is directed to composite materials for membrane reactors which include a gas-tight ceramic, a porous support, and an interfacial zone therebetween. More particularly, this invention relates to composite materials using oxygen ion-conducting dense ceramic membranes formed on a porous support comprising a metallic alloy to provide an interfacial zone of chemical interaction between the dense ceramic membrane and the porous support. Advantageously such composite materials are used for membrane reactors converting, for example, natural gas to synthesis gas by controlled partial oxidation and reforming reactions, and when desired subsequent conversion of the synthesis gas to added-value products, for example, by a water-gas shift process.

In one aspect, the invention is a composite material for membrane reactors, which composite material comprises:

A dense ceramic membrane comprising a crystalline mixed metal oxide which exhibits, at operating temperatures, electron conductivity, oxygen ion conductivity, and ability to separate oxygen from a gaseous mixture containing oxygen and one or more other components by means of the conductivities;

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A porous support comprising an alloy of at least two metallic elements which support exhibits mechanical stability at operating temperature; and

An interfacial zone of chemical interaction between the dense ceramic membrane and the porous support.

Preferably the dense ceramic membrane in the composite is made from a mixed metal oxide in a particulate form by compressing particulate oxide against the porous support at elevated temperatures, whereby chemical interactions between the porous alloy and the mixed metal oxide form an interfacial zone.

In another aspect, the invention is a hollow tube module for membrane reactors, which module comprises:

A dense ceramic membrane comprising a crystalline mixed metal oxide which exhibits, at operating temperatures, electron conductivity, oxygen ion conductivity, and ability to separate oxygen from a gaseous mixture containing oxygen and one or more other components by means of the conductivities;

An inner porous tube comprising an alloy of at least two metallic elements which tube exhibits mechanical stability at operating temperature;

A first interfacial zone between the dense ceramic membrane and the inner porous tube having, across the interfacial zone, a gradient of composition in at least one metallic element;

An outer porous tube comprising an alloy of at least two metallic elements which tube exhibits mechanical stability at operating temperature; and

A second interfacial zone between the dense ceramic membrane and the outer porous tube having, across the interfacial zone, a gradient of composition in at least one metallic element.

Preferably the dense ceramic membrane in the tube module is made from a mixed metal oxide in a particulate form compressing particulate oxide against the inner and outer porous (2)

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tubes at temperatures in a range from about 500° C to about 1250° C, whereby the gradients of composition defining the first and second interfacial zones are obtained.

In another aspect, the invention is a process to convert organic compounds into value-added porducts, which composite material comprises: by

Providing a membrane reactor comprising a plurality of the hollow tube module described herein above;

Contacting the outer porous tube of the hollow tube module with an oxygen-containing gaseous mixture having a relatively higher oxygen partial pressure;

Contacting the inner porous tube of the hollow tube module with a gaseous composition having a relatively lower oxygen partial pressure; and;

Permitting oxygen to be transported through the dense ceramic membrane by means of its electron conductivity and oxygen ion conductivity thereby separateing oxygen from the oxygen-containing gaseous mixture having a relatively higher oxygen partial pressure into the gaseous composition having a relatively lower oxygen partial pressure.

In preferred embodiments of the invention the crystalline mixed metal oxide composition is selected from a class of materials which have an X-ray identifiable crystalline structure based upon the structure of the mineral perovskite, $CaTiO_3$.

In other preferred embodiments of the invention the crystalline mixed metal oxide composition is selected from a class of materials represented by

$$D_{\alpha} E_{\alpha+\beta} O_{\delta}$$

where D comprises at least one metal selected from the group consisting of magnesium, calcium, strontium, and barium, E comprises at least one element selected from the group consisting of vanadium, chromium, manganese, iron, cobalt, and nickel, α is a

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number in a range from about 1 to about 4, β is a number in a range from about 0.1 to about 20, such that

$$1.1 < (\alpha+\beta)/\alpha \leq 6,$$

and δ is a number which renders the compound charge neutral, wherein the crystalline mixed metal oxide composition has a crystalline structure comprising layers having a perovskite structure held apart by bridging layers having a different structure identifiable by means of powder X-ray diffraction pattern analysis, the composition such that a dense ceramic membrane comprising the composition exhibits electron conductivity and oxygen ion conductivity, and ability to separate oxygen from a gaseous mixture containing oxygen and one or more other volatile components by means of the conductivities.

The invention also includes use of the composite materials in membrane reactors for separation of oxygen from an oxygen-containing gaseous mixture. Typically in such processes the aforesaid composite materials are used in separation apparatus for transfer of oxygen from an oxygen-containing first gaseous mixture having a relatively higher oxygen partial pressure to a second gaseous mixture having a relatively lower oxygen partial pressure and preferably containing one or more components, more preferably including organic compounds which react with oxygen. An essential feature of such selectively permeable dense ceramic membrane of the composite materials is that it retain its ability to separate oxygen for an adequate period of time at the conditions of operation.

The present invention relates, also, to preparation, structure, and properties of dense ceramic membranes comprising mixed metal oxide compositions which exhibit electron conductivity and oxygen ion conductivity, and ability to separate oxygen selectively from a gaseous mixture containing oxygen and one or more other volatile components by means of the conductivities. An essential feature of such selectively permeable material is that it retain its ability to separate and transport oxygen for an adequate period of time.

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Brief Description Of The Drawing

The appended claims set forth those novel features which characterize the present invention. The present invention itself, as well as advantages thereof, may best be understood, however, by reference to the following brief description of preferred embodiments taken in conjunction with the annexed drawings, in which:

FIGURE 1 is a longitudinal view, in partial section, depicting apparatus for demonstrating aspects of a hollow tube module for membrane reactors using composite material comprising oxygen ion-conducting dense ceramic according to the present invention;

FIGURE 2 is a perspective view of a disc sectioned from apparatus depicted in FIGURE 1;

FIGURE 3 is a cross-sectional view of the disc depicted in FIGURE 2;

FIGURE 4 is a digital image, from a scanning electron microscope, showing position for linescan analysis across regions of mixed metal oxide, porous metallic support, and interfacial zone therebetween; and

FIGURE 5 is a graphical presentation of linescan analysis data at the position shown in FIGURE 4.

For a more complete understanding of the present invention, reference should now be made to the embodiments illustrated in greater detail in the accompanying drawing and described below by way of examples of the invention.

Brief Description of the Invention

As stated previously, dense ceramic membranes useful in accordance with this invention comprises a crystalline mixed metal oxide which exhibits, at operating temperatures, electron conductivity, oxygen ion conductivity and ability to separate oxygen from a gaseous mixture containing oxygen and one or more other volatile components by means of the conductivities.

A preferred class of oxygen ion-conducting dense ceramic materials is disclosed in commonly assigned U.S. Patent Nos.:

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5,580,497; 5,639,437 and (08/625,119) to Balachandran, Kleefisch, Kobylinski, Morissette and Pei, which patents are specifically incorporated herein in their entirety by reference.

Particularly useful crystalline mixed metal oxide compositions are selected from a class of materials represented by

$$D_{\alpha} E_{\alpha+\beta} O_{\delta}$$

where D comprises at least one metal selected from the group consisting of magnesium, calcium, strontium, and barium, E comprises at least one element selected from the group consisting of vanadium, chromium, manganese, iron, cobalt, and nickel, α is a number in a range from about 1 to about 4, β is a number in a range upward from 0.1 to about 20, such that

$$1.1 < (\alpha+\beta)/\alpha \leq 6,$$

and δ is a number which renders the compound charge neutral.

Dense ceramic membranes used in accordance with this invention advantageously and preferably comprise a crystalline mixed metal oxide composition which has a crystalline structure comprising layers having a perovskite structure held apart by bridging layers having a different structure identifiable by means of powder X-ray diffraction pattern analysis. the composition Such dense ceramic membranes exhibit electron conductivity and oxygen ion conductivity, and ability to separate oxygen from a gaseous mixture containing oxygen and one or more other volatile components by means of the conductivities

Useful dense ceramic membranes advantageously comprise the crystalline mixed metal oxide composition is represented by

$$(D_{1-y} M'_{y})_{\alpha} (E_{1-x} G_{x})_{\alpha+\beta} O_{\delta}$$

where D is a metal selected from the group consisting of magnesium, calcium, strontium, and barium, M' is a metal selected from the group consisting of magnesium, calcium, strontium,

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barium, copper, zinc, silver, cadmium, gold, and mercury, E is an element selected from the group consisting of vanadium, chromium, manganese, iron, cobalt, and nickel, G is an element selected from the group consisting of vanadium, chromium, manganese, iron, cobalt, nickel, niobium, molybdenum, technetium, ruthenium, rhodium, palladium, indium, tin, antimony, rhenium, lead, and bismuth, with the proviso that D, E, G and M' are different elements, y is a number in a range from about 0.1 to about 0.5, x is a number in a range from about 0.1 to about 0.8, α is a number in a range from about 1 to about 4, β is a number in a range from 0.1 to about 20, preferably β is a number in a range from about 0.1 to about 6, such that

$$1.1 < (\alpha+\beta)/\alpha \leq 6,$$

and δ is a number which renders the compound charge neutral.

In preferred embodiments of the invention the crystalline mixed metal oxide composition is represented by

$$Sr_{\alpha}(Fe_{1-x}Co_{x})_{\alpha+\beta}O_{\delta}$$

where x is a number in a range from 0.01 to about 1, α is a number in a range from about 1 to about 4, β is a number in a range from about 0.1 to about 20, such that

$$1 < (\alpha+\beta)/\alpha \leq 6,$$

and δ is a number which renders the compound charge neutral, and wherein the crystalline mixed metal oxide composition has a crystalline structure comprising layers having a perovskite structure held apart by bridging layers having a different structure identifiable by means of powder X-ray diffraction pattern analysis, the composition such that a dense ceramic membrane comprising the composition exhibits electron conductivity and oxygen ion conductivity, and ability to separate oxygen from a gaseous mixture containing oxygen and one or more other volatile components by means of the conductivities.

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In other preferred aspects of the invention the crystalline mixed metal oxide composition is represented by

$$(Sr_{1-Y}M_Y)_\alpha(Fe_{1-X}Co_X)_{\alpha+\beta}O_\delta$$

where and M is an element selected from the group consisting of yttrium, barium, and lanthanum, X is a number in a range from about 0.01 to about 0.95, preferably X is a number in a range from 0.1 to 0.8, Y is a number in a range from about 0.01 to about 0.95, preferably Y is a number in a range upward from 0.1 to about 0.5, α is a number in a range from about 1 to about 4, β is a number in a range from about 0.1 to about 20, preferably β is a number in a range from about 0.1 to about 6, such that

$$1.1 < (\alpha+\beta)/\alpha \leq 6,$$

and δ is a number which renders the compound charge neutral.

In yet other preferred aspects of the invention the crystalline mixed metal oxide composition is represented by

$$Sr\,Fe\,Co_{0.5}\,O_\delta\cdot$$

where δ is a number which renders the compound charge neutral, and wherein the composition has a powder X-ray diffraction pattern comprising significant lines substantially as described in Table I.

Table I
Principal XRD Lines

Interplanar Spacing d, Å [1]	Assigned Strength
9.52 ±.05	Weak
3.17 ±.05	Weak
2.77 ±.05	Medium-Strong
2.76 ±.05	Medium-Strong
2.73 ±.03	Very Strong
2.08 ±.03	Weak-Medium

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1.96 ±.02	Medium
1.90 ±.02	Weak-Medium
1.592 ±.01	Weak-Medium
1.587 ±.01	Medium
1.566 ±.01	Weak

[1]Angstroms

As is generally known, the assigned strengths in X-ray diffraction patterns may vary depending upon the characteristics of the sample. The observed line strength in any particular sample may vary from another sample, for example, depending upon the amounts of each crystalline phase, oxygen content, and/or amorphous material in a sample. Also, X-ray diffraction lines of a particular crystalline material may be obscured by lines from other materials present in a measured sample.

Useful crystalline mixed metal oxide compositions can, also, be selected from a class of materials known, generally, as perovskites which have an X-ray identifiable crystalline structure based upon the structure of the mineral perovskite, $CaTiO_3$. In its idealized form, the perovskite structure has a cubic lattice in which a unit cell contains metal ions at the corners of the cell, another metal ion in its center and oxygen ions at the midpoints of each cube edge. This cubic lattice is identified as an ABO_3-type structure where A and B represent metal ions. In the idealized form of perovskite structures it is required that the sum of the valences of A ions and B ions equal 6, as in the model perovskite mineral, $CaTiO_3$.

Preferred membranes include an inorganic crystalline material comprising strontium, iron, cobalt and oxygen, preferably having a powder X-ray diffraction pattern comprising significant lines substantially as described in Table I. Advantageously the crystalline mixed metal oxide demonstrates oxygen ionic conductivity and electronic conductivity. The invention includes method of preparation for the crystalline mixed metal oxide compositions containing at least strontium, cobalt, iron and oxygen.

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As mentioned above, the mixed metal oxide materials useful in dense ceramic membranes of this invention include any single phase and/or multi-phase, dense phase, intimate mixture of materials which has electron conductivity and oxygen ion conductivity. In relation to the solid metal oxide materials, the terms "mixture" and "mixtures" include materials comprised of two or more solid phases, and single-phase materials in which atoms of the included elements are intermingled in the same solid phase, such as in the yttria-stabilized zirconia. The term "multi-phase" refers to a material which contains two or more solid phases interspersed without forming a single phase solution. Useful core material, therefore, includes the multi-phase mixture which is "multi-phase" because the electronically-conductive material and the oxygen ion-conductive material are present as at least two solid phases, such that atoms of the various components of the multi-component solid are, primarily, not intermingled in the same solid phase.

Useful multi-phase solid core materials are described in European Patent Application number; 90305684.4, published on November 28, 1990, under Publication No. EP 0 399 833 A1 the disclosure of which is hereby incorporated herein by reference.

In the indirect method for making a dense ceramic membranes containing a mixed metal oxide material having crystalline structure according to the invention, a solid oxide is made and commuted to a powder, the powder is blended into a plastic mass with solvent liquid and optionally additives, a desired shape formed from the plastic mass, and the shape heated to temperatures sufficient to form a dense and solid ceramic having electron conductivity and oxygen ion conductivity. Typically, such ceramics are obtained at temperatures in a range upward from about 500° C, and generally at temperatures in a range upward from about 800° C.

solid oxide
plastic mass
solvent liq

Porous supports for use according to this invention can be made of any suitable alloy which exhibits mechanical stability at operating temperature. Particularly useful are alloys, such as nickel-base steel alloys. Suitable alloys advantageously and preferably have coefficients of expansion matching that of the ceamic employed, i.e. within a range of about 25 percent of the ceramic's coefficient of expansion, more preferably within about 15 percent. Preferred alloys include nickel-iron-chromium alloys having the following limiting chemical composition:

Element	Percent	Element	Percent
Nickel	30.0 - 35.0	Silicon	1.0 max.
Iron	39.5 min.	Copper	0.75 max.
Chromium	19.0 - 23.0	Aluminum	0.15 - 0.60
Carbon	0.06 - 0.10	Titanium	0.15 - 0.60
Manganese	1.50 max.	Al + Ti	0.85 - 1.20
Sulfur	0.015 max.		

Alloys having such chemical composition are commericially avaiable under the names INCOLY alloy 800 and INCOLY alloy 800HT.

Porous metal products are made by compacting and sintering (heating), and other well known methods (See, for example, Kirk-Othmer *Encyclopedia of Chemical Technology*, third edition, Vol. 19, pages 28 to 61, John Wiley & Sons, Inc. 1982). In porous materials, the void space that determines the porosity is controlled as to amount, type, and degree of interconnection. When in contact with gases containing oxygen and/or organic compounds over a long period of time at elevated temperature, suitable porous supports advantageously and preferably remain rigid, do not change porosity and are resistant to corrosion reactions such as oxidation and carbonization. Chromium in the alloy promotes formation of a protective surface oxide, and nickel provides good retention of the protective coating, especially during cyclic exposure to high temperatures.

The oxygen ion-conducting ceramic membrane provides a gas-tight partition between the outer porous tube and the inner porous tube of hollow tube module wherein the ceramic is impervious to the components of the oxygen-containing gaseous mixture at ambient temperature. When an oxygen-containing gaseous mixture having a suitably high partial pressure of oxygen, i.e., in a range upward from about 0.2 atm., is applied to of a dense ceramic membrane of this type (through the outer porous tube), oxygen will adsorb and dissociate on the surface, become ionized and diffuse through the ceramic to the other side and deionize, associate and desorb as separated oxygen into another gaseous mixture (through the inner porous tube) having a partial pressure of oxygen lower than that applied to the outer surface. The necessary circuit of electrons to supply this ionization/ deionization process is, advantageously, maintained internally in the oxide via its electronic conductivity.

Oxygen-containing gaseous mixtures suitable as feed streams to the present process typically contain between about 10 mole percent to 50 mole percent oxygen. Water, carbon dioxide, nitrogen and/or other gaseous components are typically present in feed mixtures. A preferred oxygen-containing gaseous mixture is atmospheric air. Volatile hydrocarbons which are converted to carbon dioxide and water under operating conditions of the process may be included in small amounts without causing adverse effect on the separation process. Representative of such hydrocarbons are linear and branched alkanes, alkenes and alkynes having from 1 to about 8 carbon atoms.

A difference in partial pressure of oxygen between the first and second zones, i.e., across the membrane, provides the driving force for separation of oxygen from an oxygen-containing gaseous mixture at process temperatures sufficient to cause oxygen in the first zone to adsorb, become ionized on the first surface and be transported through the ceramic membrane in ionic form toward the second surface of the ceramic membrane and the second zone where partial pressure of oxygen is lower than the first zone. Transported oxygen is collected and/or reacted in the second zone wherein ionic oxygen is converted into neutral form by release of electrons at the second surface.

An excess partial pressure of oxygen in the first zone over that in the second zone (positive oxygen partial pressure difference) can be created by compressing the gaseous mixture in the first zone to a pressure sufficient to recover transported oxygen, i.e., an oxygen permeate stream, at a pressure of greater than or equal to about one atmosphere. Typical feed pressures are in a range of from about 15 psia to abut 250 psia, depending largely upon the amount of oxygen in the feed mixture. Conventional compressors can be utilized to achieve the compression required to practice the present process.

Alternatively, a positive oxygen partial pressure difference between the first and second zones can be achieved by reaction of transported oxygen with an oxygen-consuming substance, such as a volatile organic compound, to form value added oxygen-containing products and/or by mechanically evacuation of the second zone to a pressure sufficient to recover transported oxygen. Advantageously, a gaseous mixture containing organic compounds such as methane, ethane, and other light hydrocarbon gases, for example natural gas under well-head pressures of several hundred psi, is fed into the second zone wherein at least one of the compounds reacts with the oxygen transferred into the zone to form value added oxidation products.

Oxygen-containing gas steams which flow across the first surface of dense ceramic membranes in gas separation apparatus of this invention can be air, pure oxygen, or any other gas containing at least about 1 mol percent free oxygen. In another embodiment, the oxygen-containing gas stream contains oxygen in other forms such as N_2O, NO, SO_2, SO_3, steam (H_2O), CO_2, etc. Preferably, the oxygen-containing gas steam contains at least about 1 mol percent free molecular oxygen (dioxygen) and more preferably the oxygen-containing gas steam is air.

As mentioned above, processes according to the present invention include processes for preparing synthesis gas by reacting oxygen from an oxygen-containing gas stream with a hydrocarbyl compound in another gas stream without contaminating the hydrocarbyl compound and/or products of oxidation with other gases from the oxygen-containing gas stream, such nitrogen from an air stream. Synthesis gas, a mixture of carbon monoxide (CO) and molecular hydrogen (H_2), is a valuable industrial feedstock for the manufacture of a variety of useful chemicals. For example, synthesis gas can be used to prepare methanol or acetic acid. Synthesis gas can also be used to prepare higher molecular weight alcohols or aldehydes as well as higher molecular weight hydrocarbons. Synthesis gas produced by the partial oxidation of methane, for example, is an exothermic reaction and produces synthesis gas having a useful ratio of hydrogen to carbon monoxide, according to the following equation:

$$CH_4 + 1/2O_2 \text{ ----------> } 2H_2 + CO$$

Preferred embodiments include processes for preparing synthesis gas by partial oxidation of any vaporizable hydrocarbyl compound. Hydrocarbyl compound used in processes of this invention suitably comprises one or more gaseous or vaporizable compounds that can be reacted with molecular oxygen or carbon dioxide to form synthesis gas. Most suitably, the hydrocarbyl compound is a hydrocarbon such as methane and/or ethane, however, various amounts of oxygen or other atoms can also be in the hydrocarbyl molecule. For example, hydrocarbyl compounds that can be converted to synthesis gas include methanol, dimethyl ether, ethylene oxide, and the like. However, the most preferable hydrocarbyl compounds are the low molecular weight hydrocarbons containing about 1 to about 20 carbons, more preferably 1 to about 10 carbon atoms. Methane, natural gas, which is mainly methane, or other light hydrocarbon mixtures which are readily available, inexpensive, are particularly preferred hydrocarbyl feed materials for processes of this invention. The natural gas can be either wellhead natural gas or processed natural gas. Composition of processed natural gas varies with the needs of the ultimate user. A typical processed natural gas composition contains, on a dry or water free basis, about 70 percent by weight of methane, about 10 percent by weight of ethane, 10 percent to 15 percent of CO_2, and the balance is made up of smaller amounts of propane, butane and

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nitrogen. Preferred hydrocarbyl feed materials also contain water at levels of about 15 percent which levels are useful to quench heat of any oxidation reactions. Mixtures of hydrocarbyl and/or hydrocarbon compounds can also be used.

Preferred Embodiments of the Invention

FIGURE 1 illustrates apparatus for demonstrating aspects of a hollow tube module for membrane reactors using composite material comprising oxygen ion-conducting dense ceramic according to the present invention. As depicted in partial sectional view **11** a device in accordance with this invention comprises a base fixture **14** to which an inner porous metallic tube **15** and an outer porous metallic tube **16** are attached, advantageously, by welding. The porous metallic tubes are sized and disposed to provide an annular cavity for forming and supporting a gas-tight ceramic **28** comprising a crystalline mixed metal oxide composition. The device is provided with a cylindrical die **18** which is closely sized to the annular cavity **28**, bolt **12**, nut **22**, washer **24** and spring **26**. During formation of composite materials of the invention at elevated temperatures, force is applied to particulate precursors of any desired ceramic by spring **26**. which is, advantageously, in a region of low temperature.

Other suitable metodes for forming the supported gas-tight ceramic include melting particulate ceramic of sources of ceramic at elevated temperature, for example about 1200° C, CVD, plasma spray, etc.

Suitable porous metallic materials must have coefficients of thermal expansion not too different from that of the ceramic at operating temperatures, preferably within about 10 percent of the ceramic's coefficient of thermal expansion. Useful porous metallic materials comprise, typically, an alloy of at least two metallic elements which alloy exhibits mechanical stability at operating temperature.

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In a cross-sectional view perpendicular to the section of FIGURE 1 the gas-tight ceramic can have any closed geometric form, which is, preferably, selected from circular, square or rectangular, and is, more preferably, circular. Preferred hollow tube module for membrane reactors of this invention comprise dense ceramic membrane and porous metallic tubes which form concentric cylinders.

While we have described a present preferred embodiment of the invention, it is to be distinctly understood that the invention is not limited thereto, but may be otherwise embodied and practiced within the scope of the following claims.

Examples of the Invention

The following Examples will serve to illustrate certain specific embodiments of the herein disclosed invention. These Examples should not, however, be construed as limiting the scope of the novel invention as there are many variations which may be made thereon without departing from the spirit of the disclosed invention, as those of skill in the art will recognize.

Example 1

This example demonstrates preparation of a hollow tube module using apparatus depicted in FIGURE 1 porous tubes of 316 stainless steel alloy having with outer diameters (OD) of 1/4" and 1/2" and 5 μm pore size.

The annular cavity between the coaxially disposed tubes (about 3" long) was loaded with particulate precursors of a desired ceramic comprising a fine agglomerate having stoichiometry $Sr\ Fe\ Co_{0.5}\ O_{\delta}$, but not yet formed into a single crystalline phase. This agglomerate was purchased to specification from Praxair Specialty Ceramics of, Seattle, Washington. The entire apparatus was placed in a closed alumina tube (1" OD) which was then evacuated by means of a vacuum pump. The alumina tube containing the apparatus was inserted into a furnace which has heated at a rate of 5° C per minute to 1000° C, held at 1000° C for 2 days and cooled a rate of 5° C per minute under vacuum. A diamond saw was used to cross section the resulting composite material into thin discs for analysis.

FIGURE 2 is a perspective view of a disc sectioned from apparatus. A first interfacial zone was formed between the inner porous tube **15** and ceramic **28** having, across the interfacial zone, a gradient of composition. Likewise a second interfacial zone was formed between the ceramic **28** and the outer porous tube **16**.

Chemistry across these interfacial zones was studied by electron microscopy. One of the discs was embedded in methylmethacrylate resin. A polished cross section was prepared using standard metallographic techniques and the polished cross section was coated with carbon by vacuum evaporation. A scanning electron microscope (SEM) was operated in the backscattered electron imaging mode (BSEI), which shows, primarily, compositional contrast (higher atomic number compositions are brighter). Energy-dispersive X-ray spectrometry (EDXS) analysis was done in the SEM with the electron probe scanning a field, identified "F", a partial field, identified "PF", or a stationary probe on a spot, identified "S". SEM/EDXS analysis can detect all elements boron and heavier. The evaporated carbon coating makes a minor contribution to the C signals in the spectra. Elemental distributions across the stainless steel/ceramic interface were determined by obtaining linescan profiles for O, Sr, Cr, Fe, Co, and Ni.

FIGURE 4 is a digital image, from a scanning electron microscope , showing position for linescan analysis across regions of mixed metal oxide, porous metallic support, and interfacial zone therebetween. Ceramic is on the left side and porous steel is on the right.

The interfacial zone, which is about 10 μm thick, appears to be two layers -- the BSEI-brighter layer (ceramic side) appears to have a uniform, dense composition, and the BSEI-darker layer

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(steel side) appears porous and more complex. The linescan covering about 125 μm (see FIGURE 5 which is a graphical presentation of linescan analysis data at the position shown in FIGURE 4). The digital BSEI image has a horizontal line which shows the location of the linescan (100 analysis points from one end point to the other), and the cross-hair marker on each linescan corresponds to the position of the vertical line on each corresponding elemental linescan profile. As shown the cross hair is at the boundary between the interfacial zone and the stainless steel.

The line scan extends from a region of ceramic on the left through an interfacial zone (about 5 μm), and on the right, steel with two pores (about 5 μm and about 15 μm from the cross-hair marker). The 5 μm distance is close enough to the ceramic that the surface of the pore is coated with a Sr-Cr-O species, while the more distant pore (15 μm) exhibits a Sr-O species. The regions of steel have characteristics of the alloy with the Ni concentration increasing at the interface. Ni concentration drops because of the Sr-Cr oxide crust on the surface in the pores. The interfacial zone is predominately a Cr-Fe-O system with Cr higher at the right side of the interfacial zone. An inverse relationship between the Cr and Fe appears in the region.

Some observations which can be made from these linescan data are as follows: (1) the ceramic appears to have a fairly uniform Sr-Fe-Co-Ba-0 composition, except that the Co level appears to vary significantly; (2) the steel has a uniform Fe-Cr-Ni-Mo composition, except that the Mo and Ni levels rise over the last couple micrometers up to the interfacial zone boundary; (3) the ceramic side of the interfacial zone is rich in O, Fe, and Co, whereas the stainless steel side of the interfacial zone is rich in 0 and Cr and some Mo; (4) there appears to be very little Sr in the interfacial zone, but some is observed in pores within the stainless steel layer; (5) although part of the carbon signal is from the evaporated carbon coating, there appears to be slightly more carbon in the ceramic than in the stainless steel, and even more carbon in the interfacial zone.

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For the purposes of the present invention, "predominantly" is defined as more than about fifty per cent. 'Substantially" is defined as occurring with sufficient frequency or being present in such proportions as to measurably affect macroscopic properties of an associated compound or system. Where the frequency or proportion for such impact is not clear substantially is to be regarded as about twenty per cent or more. The term "Essentially" is defined as absolutely except that small variations which have no more than a negligible effect on macroscopic qualities and final outcome are permitted, typically up to about one percent.

Examples have been presented and hypotheses advanced herein in order to better communicate certain facets of the invention. The scope of the invention is determined solely by the scope of the appended claims.

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That which is claimed is:

1. A composite material for membrane reactors, which composite material comprises:

(a-1) a dense ceramic membrane comprising a crystalline mixed metal oxide which exhibits, at operating temperatures, electron conductivity, oxygen ion conductivity, and ability to separate oxygen from a gaseous mixture containing oxygen and one or more other components by means of the conductivities;

(b-1) a porous support comprising an alloy of at least two metallic elements which support exhibits mechanical stability at operating temperature; and

(c-1) an interfacial zone of chemical interaction between the dense ceramic membrane and the porous support.

2. The composite material according to claim 1 wherein the dense ceramic membrane is made from mixed metal oxide in a particulate form by compressing particulate oxide against the porous support at elevated temperatures, whereby the chemical interaction defining the interfacial zone is obtained.

3. The composite material according to claim 1 wherein the crystalline mixed metal oxide composition is selected from a class of materials which have an X-ray identifiable crystalline structure based upon the structure of the mineral perovskite, $CaTiO_3$.

4. The composite material according to claim 1 wherein the crystalline mixed metal oxide composition is represented by

$$D_{\alpha} E_{\alpha+\beta} O_{\delta}$$

where D comprises at least one metal selected from the group consisting of magnesium, calcium, strontium, and barium, E comprises at least one element selected from the group consisting of vanadium, chromium, manganese, iron, cobalt, and nickel, α is a number in a range from about 1 to about 4, β is a number in a range from about 0.1 to about 20, such that

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$$1.1 < (\alpha+\beta)/\alpha \leq 6,$$

and δ is a number which renders the compound charge neutral, wherein the crystalline mixed metal oxide composition has a crystalline structure comprising layers having a perovskite structure held apart by bridging layers having a different structure identifiable by means of powder X-ray diffraction pattern analysis, the composition such that a dense ceramic membrane comprising the composition exhibits electron conductivity and oxygen ion conductivity, and ability to separate oxygen from a gaseous mixture containing oxygen and one or more other volatile components by means of the conductivities.

5. The composite material according to claim 1 wherein the crystalline mixed metal oxide composition is represented by

$$Sr\,Fe\,Co_{0.5}\,O_{\delta}$$

where δ is a number which renders the compound charge neutral, and wherein the composition has a powder X-ray diffraction pattern comprising significant lines substantially as described in Table I.

6. A hollow tube module for membrane reactors, which module comprises:

(a-6) a dense ceramic membrane comprising a crystalline mixed metal oxide which exhibits, at operating temperatures, electron conductivity, oxygen ion conductivity, and ability to separate oxygen from a gaseous mixture containing oxygen and one or more other components by means of the conductivities;

(b-6) an inner porous tube comprising an alloy of at least two metallic elements which tube exhibits mechanical stability at operating temperature;

(c-6) a first interfacial zone between the dense ceramic membrane and the inner porous tube having, across the interfacial zone, a gradient of composition in at least one metallic element;

(d-6) an outer porous tube comprising an alloy of at least two metallic elements which tube exhibits mechanical stability at operating temperature; and

(e-6) a second interfacial zone between the dense ceramic membrane and the outer porous tube having, across the interfacial zone, a gradient of composition in at least one metallic element.

7. The hollow tube module according to claim 6 wherein the dense ceramic membrane is made from the crystalline mixed metal oxide in a particulate form by compressing particulate oxide against the inner and outer porous tubes at temperatures near the melting point temperature of the desired ceramic, whereby the gradients of composition defining the first and second interfacial zones are obtained.

8. The hollow tube module according to claim 7 wherein the alloy is a high temperature steel comprising at least nickel, and chromium.

9. The hollow tube module according to claim 8 wherein the crystalline mixed metal oxide composition is represented by

$$Sr\,Fe\,Co_{0.5}\;O_{\delta}$$

where δ is a number which renders the compound charge neutral, and wherein the composition has a powder X-ray diffraction pattern comprising significant lines substantially as described in Table I.

10. A process to convert organic compounds into value-added porducts, which composite material comprises: by

(a-10) Providing a membrane reactor comprising a plurality of hollow tube module according to claim 6;

(b-10) Contacting the outer porous tube of the hollow tube module with an oxygen-containing gaseous mixture having a relatively higher oxygen partial pressure;

(c-10) Contacting the inner porous tube of the hollow tube module with a gaseous composition having a relatively lower oxygen partial pressure; and;

(d-10) Permitting oxygen to be transported through the dense ceramic membrane by means of its electron conductivity and oxygen ion conductivity thereby separateing oxygen from the oxygen-containing gaseous mixture having a relatively higher oxygen partial pressure into the gaseous composition having a relatively lower oxygen partial pressure.

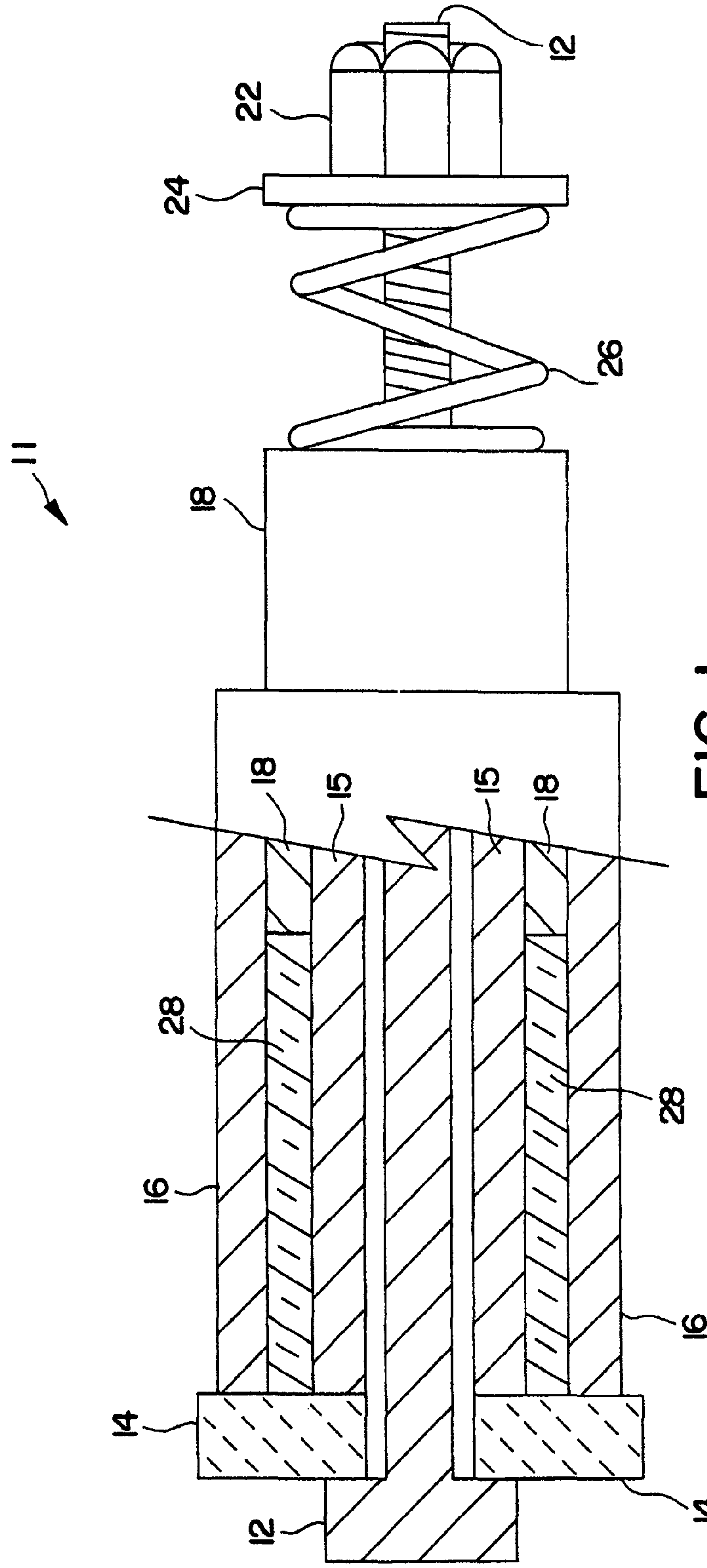

FIG. I

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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES

375
2006-02-16

2020
Bogotá, D.C.,

Doctora (señora): Oficio N° 1763
Dilia María Rodríguez D´Aleman

REFERENCIA:	Radicación No.	00-32439.
	Trámite	002.
	Evento	001.
	Actuación	430.
	Folios	005.

Realizado el examen de patentabilidad de la presente solicitud según el artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, "**art. 45**.- *Si la oficina nacional competente encontrara que la invención no es patentable o que no cumple con alguno de los requisitos establecidos en esta Decisión para la concesión de la patente, lo notificará al solicitante. Este deberá responder a la notificación dentro del plazo de sesenta días contados a partir de la fecha de la notificación. Este plazo podrá ser prorrogado por una sola vez por un período de treinta días adicionales.*
Cuando la oficina nacional competente estimara que ello es necesario para los fines del examen de patentabilidad, podrá notificar al solicitante dos o más veces conforme al párrafo precedente.
Si el solicitante no respondiera a la notificación dentro del plazo señalado, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, la oficina nacional competente denegará la patente." se notifica el siguiente Concepto Técnico:

1. DOCUMENTOS ESTUDIADOS

❖ Para el presente estudio se tuvo en cuenta el capítulo descriptivo, folios 69 a 108 y reivindicaciones 1 a 15, folios 109 a 1114 anexados como respuesta al requerimiento formal; lo cual fue aceptado dado que éste no implica una ampliación de la solicitud originalmente presentada conforme lo establece el artículo 34 de la decisión 486 de la Comisión de la Comunidad Andina "**art. 34**.- *El solicitante de una patente podrá pedir que se modifique la solicitud en cualquier momento del trámite. La modificación no podrá implicar una ampliación de la protección que correspondería a la divulgación contenida en la solicitud inicial.*
Del mismo modo, se podrá pedir la corrección de cualquier error material.".
❖ Se acepta reivindicación de prioridad US 09/306 945 del 7 de mayo de 1999.

2. OBJETO DE LA INVENCIÓN

- Título: Materiales compuestos para reactores de membrana
- La invención consiste en:

Reivindicaciones 1 a 11: Material compuesto de reactores de membrana cuyo compuesto comprende: a-1) una membrana de cerámica densa incluyendo un óxido de metal mezclado cristalino, el cual a temperatura de operación muestra conductividad electrónica, conductividad al ión oxígeno y capacidad para separar al oxígeno de la mezcla gaseosa que contiene oxígeno y uno o varios más componentes por medio de las conductividades; b-1) un soporte poroso que comprende la aleación de por lo menos dos elementos metálicos, cuyo soporte muestra estabilidad mecánica a temperatura de operación, y c-1) una zona interfacial de por lo menos 5 micras, que muestra interacción química entre la membrana de cerámica densa y el soporte poroso. Donde dicho óxido en forma de partículas es comprimido contra los tubos porosos internos y externos a temperaturas cercanas a las temperaturas del punto de fusión de dicha cerámica, mediante lo cual se obtienen los gradientes de composición que definen la primera y segunda zonas interfaciales. Adicionalmente la composición del óxido está definido por las fórmulas visibles en los folios 110 a 114.

Reivindicación 12 a 15: Un método para preparar el material compuesto que comprende:

i) añadir un solvente, un dispersante, un enlazante, un agente de plasticidad, y

ii) extruir dicho material a través de un molde a alta presión para producir un módulo de tubo hueco para reactores de membrana.

Donde el óxido es sometido a aspersión por encima de 500° C contra la superficie externa del soporte poroso.

- La clasificación según la IPC correspondiente al objeto de la solicitud es B01D 71/02.

3.CLARIDAD DE LA SOLICITUD

De acuerdo a la Decisión 486 de la Comisión de la Comunidad Andina en su Artículo 30.- "*Las reivindicaciones definirán la materia que se desea proteger mediante la patente. Deben ser claras y concisas y estar enteramente sustentadas por la descripción*", en este sentido se anota que no obstante el solicitante envió un nuevo capítulo reivindicatorio, la presente solicitud le falta claridad puesto que:

Incluye términos ambiguos "por lo menos", que no definen de manera precisa los intervalos de las variables. Además en algunas reivindicaciones se confunde el signo $\propto$ con el σ, lo cual se debe corregir porque ellos definen parámetros de las fórmulas del óxido cristalino.

6. DETERMINACIÓN DEL ESTADO DE LATÉCNICA

- La fecha a partir de la cual se realizó la búsqueda de anterioridades corresponde al 6 de mayo de 1999.
- Con base a lo anterior y la definición dada en el **art. 16.- "**Una invención se considerará nueva cuando no está comprendida en el estado de la técnica.
  El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización, comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida.
  Sólo para el efecto de la determinación de la novedad, también se considerará dentro del estado de la técnica, el contenido de una solicitud de patente en trámite ante la oficina nacional competente, cuya fecha de presentación o de prioridad fuese anterior a la fecha de presentación o de prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido esté incluido en la solicitud de fecha anterior cuando ella se publique o hubiese transcurrido el plazo previsto en el artículo 40." , se realizó la búsqueda de anterioridades en los archivos con que cuenta esta Oficina y se encontró el siguiente documento relacionado con la materia de la presente solicitud:

N°	DOCUMENTO	TÍTULO	FECHA DE PUBLICACIÓN
D1	WO 99/21640	Composite materials for membrane reactors	1999-05-06

4.EVALUACIÓN DE LOS REQUISITOS DE PATENTABILIDAD

El artículo 14 de la Decisión 486 de la Comisión de la Comunidad Andina establece que: "Los Países Miembros otorgarán patentes para las invenciones, sean de producto o de procedimiento, en todos los campos de la tecnología , siempre que sean nuevas, tengan nivel inventivo y sean susceptibles de aplicación industrial."

En cumplimiento del artículo 14 de la Decisión 486, se procedió a evaluar los requisitos de novedad, nivel inventivo y aplicación industrial con el fin de establecer la patentabilidad de la invención reivindicada en la solicitud en estudio.

4.1Evaluación de la NOVEDAD

La Decisión 486 de la Comisión de la Comunidad Andina establece en su art. 16.- "*Una invención se considerará nueva cuando no está comprendida en el estado de la técnica.*

El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización, comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida.

Sólo para el efecto de la determinación de la novedad, también se considerará dentro del estado de la técnica, el contenido de una solicitud de patente en trámite ante la oficina nacional competente, cuya fecha de presentación o de prioridad fuese anterior a la fecha de presentación o de prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido esté incluido en la solicitud de fecha anterior cuando ella se publique o hubiese transcurrido el plazo previsto en el artículo 40."

D1 afectaría la novedad de las reivindicaciones 1 a 11 puesto que el material compuesto que se reclama fue divulgado por este documento en su totalidad tal como se puede leer cuando D1 define un material compuesto para reactores de membrana en las páginas 9 a 27 de esta anterioridad correspondiente a la descripción. En consecuencia la materia reclamada no sería nueva.

D1 puso en evidencia en la página 9 a 10 un material compuesto por tres partes, donde dichos componentes coinciden con los reclamados en la presente solicitud tanto en su composición como en sus características.

De otro lado, las características precisadas en las reivindicaciones 2 y 3 se encuentras reveladas en las líneas 12 a 36 de la página 10 de D1 tal y como se reclaman en esta solicitud.

Lo mismo ocurre en cuanto a la definición del óxido metálico en el que sus características completas ya habían sido divulgadas por D1 a lo largo de las páginas 11 a 17 en las que incluso se puede encontrar la misma tabla que indica el patrón de DRX.

En cuanto al método que se reclama en las reivindicaciones 12 y 13 también está afectado en su novedad por D1, ya que se revela en la página 18 un método indirecto de hacer la cerámica densa en el que se mezclan un óxido sólido, una masa plástica, un solvente líquido y aditivos para luego darle una forma deseada por encima de 500°C. Ello correspondería efectivamente a la materia que se reclama y por lo tanto no sería nueva

4.2Evaluación del NIVEL INVENTIVO

De acuerdo al **art. 18.-** "*Se considerará que una invención tiene nivel inventivo, si para una persona del oficio normalmente versada en la materia técnica correspondiente, esa invención no hubiese resultado obvia ni se hubiese derivado de manera evidente del estado de la técnica.*", se conceptúa:

D1 afectaría el nivel inventivo de las reivindicaciones 14 y 15 porque en el último párrafo de la página 18 de este documento publicó un tipo de aleaciones útiles de acero basadas en níquel, e incluso se refiere a las de níquel- hierro – cromo.

Como se puede observar, el método para preparar el material compuesto consiste en las mismas etapas bajo las mismas condiciones sólo que en lugar de utilizar un tipo de aleación específica de níquel-cromo ya había sido revelada una basada en níquel y en las que también se había ensayado el cromo.

Es bien claro, para cualquier persona con los mínimos conocimientos en este arte que a partir de ensayos sistemático llegar a la aleación de acuerdo a la tabla que se presenta en la página 19 sin que ello constituya un salto en la formulación de la regla técnica y mucho menos una actividad creadora del hombre que amerite el privilegio solicitado.

Además se debe tener en cuenta que el tipo de aleación no caracteriza de manera determinante al método de preparación del material sino al material mismo. En consecuencia, estas reivindicaciones no tendrían nivel inventivo.

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de sesenta días contados a partir de la fecha de la notificación de la presente comunicación. **En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente**.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2,literal e), del capítulo quinto del título primero de la circular única No. 10 de 2001.

ALIX CARMENZA CÉSPEDES DE VERGEL
Jefe de la División de Nuevas Creaciones.

El anterior requerimiento fue notificado por fijación en lista, de fecha 16 FEB. 2006

CONCEPTO TÉCNICO N° 166 (2006-02-03)	**EXAMINADOR TÉCNICO CÓDIGO 202001**	**EXAMINADOR JURÍDICO CÓDIGO**

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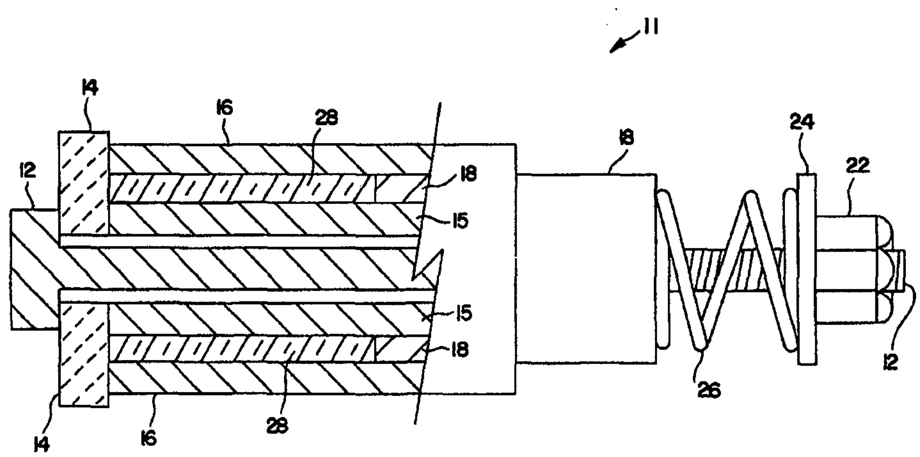

(57) Abstract

The present invention relates to composite materials for membrane reactors which include a gas-tight ceramic (28), a porous support (15, 16), and an interfacial zone therebetween. More particularly, this invention relates to composite materials using oxygen ion-conducting dense ceramic membranes (28) formed on a porous support (15, 16) comprising a metallic alloy to provide an interfacial zone identifiable by a gradient of composition in at least one metallic element across the interfacial zone between the dense ceramic membrane and the porous support. Processes using composite materials in accordance with the invention are, for example, used for production of synthesis gas comprising carbon monoxide and molecular hydrogen which synthesis gas is, advantageously, free of deleterious and/or inert gaseous diluents such as nitrogen.