HYBRID ORGANIC-INORGANIC GAS SEPARATION MEMBRANES

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ABSTRACT

The invention discloses a composition comprising a hybrid composite organic-inorganic membrane. The hybrid organic-inorganic membrane according to the present invention may comprise an amorphous porous layer incorporating organic functionalities. The amorphous porous layer may be deposited on a porous alumina substrate by chemical vapor deposition (CVD). The amorphous porous layer may comprise a single top-layer (STL), multiple top-layers (MTL) or mixed top-layers (XTL). The substrate may comprise a single layer or multiple graded layers of alumina.

42 Claims, 17 Drawing Sheets
U.S. PATENT DOCUMENTS

OTHER PUBLICATIONS


* cited by examiner
FIG. 1. Graph of particle size distributions of three boehmite sols with a median particle
size of 40, 200 and 630 nm. These sols were used to prepare the gamma-alumina
multilayer substrate.
FIG. 3. Schematic of a suitable CVD apparatus for use in the deposition of hybrid organic-inorganic layers.
FIG. 4. Graph of permeation properties at different temperature for the CO$_2$-selective hybrid membrane STL-823-II prepared at 823 K using the CVD condition II with a medium PTES concentration of 0.19 mol m$^{-3}$. 
FIG. 5. Graph of permeation properties at different temperature for the CO$_2$-selective hybrid membrane STL-823-I prepared at 823 K using the CVD condition III with a low PTES concentration of 0.11 mol m$^{-3}$. 
FIG. 6. Graph of permeation properties at different temperature for the CO₂-selective hybrid membrane STL-773-I prepared at a low deposition temperature of 773 K using the CVD condition I with a low PTES concentration of 0.11 mol m⁻³.

Graph of permeation properties at different temperature for the CO₂-selective hybrid membrane STL-773-I prepared at a low deposition temperature of 773 K using the CVD condition I with a low PTES concentration of 0.11 mol m⁻³.
FIG. 7. Graph of permeation properties at different temperature for the CO₂-selective hybrid membrane STL-873-II prepared at a high deposition temperature of 873 K using the CVD condition II with a medium PTES concentration of 0.19 mol m⁻³.
FIG. 8. Graph of permeation properties at different temperature for the CO$_2$-selective hybrid membrane STL-823-IV prepared at 823 K using the CVD condition IV.

Diphenyldiethoxysilane (DPDES) was used as the Si source.
FIG. 9. Graph of permeances at different temperatures (473, 373 and 323 K) for different gas molecules through the CO₂-selective hybrid membrane STL-823-II. The membrane was prepared at 823 K with a medium PTES concentration of 0.19 mol m⁻³.
FIG. 10. Graph of permeances at different temperatures (373 and 323 K) for different gas molecules through the CO₂-selective hybrid membrane STL-823-IV. The membrane was prepared at 823 K with a medium DPDES concentration of 0.19 mol m⁻³.
FIG. 11. Graph of changes of permeances through the CO₂-selective hybrid membrane STL-823-II after calcined at different environment.
FIG. 12. Cross-sectional image of a hybrid membrane formed on a mesoporous alumina tube.
FIG. 13. FTIR spectra of the DPDES and PTES membrane samples and references.

- C=N str. vib (Ref.1, pp. 84)
- C=C str. (Ref.1, pp. 16)
- C=C aromatic str. (Ref.1, pp.17-18)
+ C-C str. (Ref.1, pp.19)
# P=O str. (Ref.1, pp.19)
- Si-O-C asym. str. (Ref.1, pp. 19, 244)
• C-H str., aromatic ring CH (Ref.1, pp. 15)
 v C-H asym. str., CH₃ (Ref.1, pp.16)
w C-H asym. str., CH₂-alkanes (Ref.1, pp. 16)

Ref.1:
FIG. 14. Graph of H$_2$ permeance through the membranes prepared from the mixed Si source containing different PTES content.
FIG. 15. Arrhenius plots for the permeance of $\text{H}_2$ through the PTES-derived membrane, PTES-TEOS-derived membranes and TEOS-derived membrane.
**FIG. 16.** Graph of changes of the H₂ permeance through two PTES-TEOS derived membranes and one silica membrane with the exposure time during. The hybrid membranes were exposed at 873 K to 78 mol% water vapor, while the silica membrane was exposed at 873 K to 16 mol% water vapor.
Figure 17. Permeation rates of various gases depending on size of the permeating gases

a) DPDES/(TEOS-DMDCS) = 0.05,

b) DPDES/(TEOS-DMDCS) = 0.1,

c) DPDES/(TEOS-DMDCS) = 0.15
HYBRID ORGANIC-INORGANIC GAS SEPARATION MEMBRANES

BACKGROUND OF THE INVENTION

Membranes may be defined as thin, solid materials that permit the selective transport of certain chemical species over others. This invention relates to hybrid organic-inorganic membranes for the separation of carbon dioxide or hydrogen from methane and other gases such as nitrogen. The composite membrane may comprise a nonporous layer being disposed on a porous substrate by chemical vapor deposition. Specifically, the invention comprises a single top-layer, multiple top-layers, or mixed top-layer silica membranes incorporating aromatic groups deposited on a porous substrate by chemical vapor deposition of gaseous precursors. The invention also concerns methods for preparing such composite membranes.

FIELD OF THE INVENTION

Membranes may be defined as thin, solid materials that permit the selective transport of certain chemical species over others. This invention relates to hybrid organic-inorganic membranes for the separation of carbon dioxide or hydrogen from methane and other gases such as nitrogen. The composite membrane may comprise an amorphous porous layer being disposed on a porous substrate by chemical vapor deposition. Specifically, the invention comprises a single top-layer, multiple top-layers, or mixed top-layer silica membranes incorporating aromatic groups deposited on a porous substrate by chemical vapor deposition of gaseous precursors. The invention also concerns methods for preparing such composite membranes.

BACKGROUND OF THE INVENTION

As energy prices rise, gas separation membrane technology has been receiving increasing attention because of its potential for reducing the environmental impact and costs of industrial processes. Gas separation membranes offer a number of benefits over other gas separation technologies such as low energy consumption and process simplicity because separation by membranes do not require a phase transformation.

Polymeric membranes are the most widely used commercially for gas separations. These membranes are generally highly selective but poorly permeable. In comparison, inorganic membranes are highly permeable but poorly selective. For better results, hybrid materials in which polymers and ceramics are dispersed at a molecular level have been investigated as gas separation membranes. The resulting hybrid membranes can sometimes retain the desirable properties of each material, for example, the flexibility and selectivity of polymers and the thermal stability of ceramics. There are several studies that have attempted to introduce organic functionalities on inorganic membrane surfaces to increase interactions with a particular gas. The introduction of organic functional groups sometimes also contributes to the modification of the molecular structure of the material, which results in favorable selectivity or permeability.

Hybrid organic-inorganic membranes are generally prepared by sol-gel methods because the low temperature processing chemistry allows the introduction of organic molecules inside an inorganic network. Okui et al. [T. Okui et al., J. Sol-Gel Sci. Technol. 5 (1995) 127] used the sol-gel and dip-coating technique to prepare a porous hybrid membrane composed of silica incorporating phenyl functional groups at 523 K on α-alumina porous substrates (mean pore size = 0.7 μm). Tetramethoxysilane (TMOS, Si(OC4H9)4) and phenyltrimethoxysilane (PTMOS, C6H5SiO(OC4H9)3) were the starting chemicals. Also, other functional groups such as methyl, propyl, 3-chloropropyl, 3,3,3-trifluoropropyl and octadecyl were introduced to study how changes in the affinity of these functional groups for permeating gases affects the permeation properties of the resulting materials. Among these organic functional groups, it was found that phenyl groups have the strongest affinity for CO2. Thus, silica membranes with phenyl groups had the best separation performance with values of permselectivity of 6.0 and 4.5 for CO2/N2 and CO2/CH4, with CO2 permeance of around 6.0×10^-10 mol·m^-2·s^-1·Pa^-1 at 298 K (calculated from the reported permeability coefficient of 6.7 cc (STP)·cm^-2·s^-1·cm Hg^-1 and a thickness of 3-4 μm). It was also reported that the phenyl group in the hybrid membrane remained undamaged at 723 K. Smaihi et al. [M. Smaihi et al., J. Membr. Sci. 116 (1996) 211] obtained an organic-inorganic gas separation membrane using a porous substrate and a thin organic-inorganic sol-gel layer as a permselective coating. These permselective layers were obtained by co-hydrolysis of tetramethoxysilane (TMOS) and phenyltrimethoxysilane (PTMOS) or diphenyldimethoxsilane (DPMOS, (C6H5)2SiO(OC4H9)2), followed by calcination at 773 K. It was found that DPMOS-DPMOS derived membranes exhibited higher permeance but selectivities in the Knudsen regime with CO2/N2=0.8, while PTMOS-DPMOS derived membranes with contents of PTMOS above 70 mol % showed much higher selectivity, around 15 for CO2/N2. The CO2 permeance through a 54% PTMOS-TMOS derived membrane was 6.0×10^-10 mol·m^-2·s^-1·Pa^-1 at 298 K while the selectivity of CO2/N2 was 4.0.

Another approach to enhance gas separation has been to prepare membranes containing large micropores by burning out functional groups attached to the silica. With plain silica membranes prepared by the decomposition of tetraethylorthosilicate (TEOS) [A. K. Prabhu, S. T. Oyama, J. Membr. Sci. 176 (2000) 233; S. Yan et al. Ind. Eng. Chem. Res. 33 (1994) 2096; H. Y. Ha et al. J. Membr. Sci. 85 (1993) 279], a microstructure is formed that allows the separation of small gaseous species like He and H2, but not CO2 or N2, from other gases. However, a silica membrane obtained by pyrolysis of phenyltriethoxysilane (PTES) or diphenyldimethoxsilane (DPPDS) showed good CO2 separation [B. K. Sea et al. J. Membr. Sci., 130 (1997) 41]. This silica membrane was prepared on a porous alumina support first by chemical vapor deposition (CVD) using PTES or DPPDS as the Si source at 773 K with the aid of evacuation, and then by calcination of the as-produced membrane in air at 673 K for 5 hours to remove the phenyl groups. The phenyl groups of PTES or DPPDS remained unaffected under the CVD conditions at 773 K and decreased the silica cross-link density, thus leading to a loose amorphous structure after subsequent calcination. The DPPDS-derived membrane had micropores larger than those of the TEOS-derived membrane, giving rise to a higher CO2 permeance of 8.1×10^-10 mol·m^-2·s^-1·Pa^-1 at 298 K with a CO2/CH4 selectivity of 11, in comparison to a permeance of 3.6×10^-10 mol·m^-2·s^-1·Pa^-1 and a selectivity of 0.66 for the TEOS-derived silica membrane.

SUMMARY OF THE INVENTION

One aspect of the invention discloses a composition comprising a hybrid composite organic-inorganic membrane. The hybrid organic-inorganic membrane according to the present invention may comprise an amorphous porous layer incorporating organic functionalities. The amorphous porous layer may further comprise silica. The amorphous porous layer may be deposited on a porous substrate by chemical vapor
deposition (CVD) in an atmosphere where the precursor concentration ranges from 1 to 100 volume % of the gas mixture at high temperature.

The organic functionalities according to the present invention may comprise at least one group selected from the aromatic groups, aliphatic groups, olefinic groups, heterocyclic groups, and any mixture thereof. The organic functionalities may comprise aromatic groups obtained from decomposition of phenyl-substituted silanes or siloxanes. The aromatic group may be obtained from the decomposition of phenyltriethoxysilane (PTES), diphenyldiethoxysilane (DPPES), triphenylethoxysilane (TPES), phenyltrimethoxysilane, diphenyldimethoxysilane, triphenylmethoxysilane, phenyltrimethylsilane, diphenylmethylsilane, triphenylmethylsilane, and any mixture thereof.

The porous substrate according to the present invention may comprise at least one layer selected from the group consisting of alumina, titania, silica, zirconia, boria, perovskites, spinels, pyrochlores, zeolites, stainless steel, and any combination thereof. The porous substrate may comprise a single layer of alumina prepared by coating a mesoporous support with a single dilute sol dipping solution followed by a calcination step.

The porous substrate may comprise multiple graded layers of alumina, with a gradually decreasing pore size structure, prepared by coating a macroporous support with a series of dilute sol dipping solutions containing boehmite sols of different particle followed by a calcination step.

An embodiment of a hybrid membrane according to the current invention exhibits a high permeance of greater than 3.0x10^-8 mol m^-2 s^-1 Pa^-1 at 873 K and the selectivity of greater than 9 with respect to gases selected from the group consisting of CH4, CH3OH, and CO2 for H2.

An embodiment of a hybrid membrane according to the current invention exhibits the selectivity for CO2 with respect to CH4 of greater than 10-39.

An embodiment of a hybrid membrane according to the current invention exhibits the permeance for CO2 of greater than 3.0x10^-8 mol m^-2 s^-1 Pa^-1 and the selectivity for CO2 with respect to CH4 of greater than 12-59.

An embodiment of a hybrid membrane according to the current invention exhibits the permeance for H2 of greater than 1.0x10^-7 mol m^-2 s^-1 Pa^-1 at 873 K.

An embodiment of a hybrid membrane according to the current invention exhibits the permeance for CH4 of greater than 3.0x10^-8 mol m^-2 s^-1 Pa^-1 and the permeance for H2 of greater than 1.0x10^-7 mol m^-2 s^-1 Pa^-1 at 873 K.

An embodiment of a hybrid membrane according to the current invention exhibits the selectivity for CO2 which is from 3.0x10^-8 to 12 with respect to CH4 from 273K to 403 K, respectively, and the permeance for CO2 of greater than 3.4x10^-8 to 8.7x10^-8 mol m^-2 s^-1 Pa^-1 from 273 K to 403 K, respectively.

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An embodiment of a hybrid membrane with a single top-layer is a membrane made by the decomposition of phenyltriethoxysilane (PTES). This membrane exhibits a high permeance at 273-403 K for CO2 from 3.0x10^-8 to 8.7x10^-8 mol m^-2 s^-1 Pa^-1 at 273-403 K.

An embodiment of a hybrid membrane with multiple top-layers (MTL) is a membrane made from the sequential decomposition of phenyltriethoxysilane (PTES), diphenyldiethoxysilane (DPPES), triphenylethoxysilane (TPES), phenyltrimethoxysilane, diphenyldiethoxysilane, triphenylmethoxysilane, phenyltrimethoxysilane, diphenylmethylsilane, triphenylmethylsilane, any phenyl-substituted silanes or siloxanes, and any mixture thereof.

Another aspect of the invention discloses a method for preparing a hybrid composite organic-inorganic membrane. The method according to the present invention may comprise a step of providing an amorphous porous layer incorporating organic functionalities. The method may further comprise a step of providing a porous substrate. The amorphous porous layer may be deposited on a porous alumina substrate by chemical vapor deposition (CVD) in an atmosphere where the precursor concentration ranges from 1 to 100 volume % of the gas mixture at high temperature.
Certain embodiments of the present invention are described in detail below with reference to the enclosed figures, wherein:

FIG. 1 is a graph of particle size distributions of three boehmite sols with a median particle size of 40, 200 and 630 nm. These sols were used to prepare the gamma-alumina multilayer substrate.

FIG. 2 is a schematic of dip-coating machine for use in preparation of gamma-alumina substrates.

FIG. 3 is a schematic of a suitable CVD apparatus for use in the deposition of hybrid organic-inorganic layers.

FIG. 4 is a graph of permeation properties at different temperatures for the CO$_2$-selective hybrid membrane STL-823-II prepared at 823 K using CVD condition II with a medium PTES concentration of 0.04 mol m$^{-3}$.

FIG. 5 is a graph of permeation properties at different temperatures for the CO$_2$-selective hybrid membrane STL-823-I prepared at 823 K using CVD condition III with a medium PTES concentration of 0.11 mol m$^{-3}$.

FIG. 6 is a graph of permeation properties at different temperatures for the CO$_2$-selective hybrid membrane STL-773-I prepared at a low deposition temperature of 773 K using CVD condition I with a low PTES concentration of 0.01 mol m$^{-3}$.

FIG. 7 is a graph of permeation properties at different temperatures for the CO$_2$-selective hybrid membrane STL-873-II prepared at a high deposition temperature of 873 K using CVD condition II with a medium PTES concentration of 0.19 mol m$^{-3}$.

FIG. 8 is a graph of permeation properties at different temperatures for the CO$_2$-selective hybrid membrane STL-873-IV prepared at 873 K using CVD condition IV. Diphenylidethoxysilane (DPDES) was used as the Si source.

FIG. 9 is a graph of permeances at different temperatures (473, 373 and 323 K) for different gas molecules through the CO$_2$-selective hybrid membrane STL-823-II. The membrane was prepared at 823 K with a medium PTES concentration of 0.19 mol m$^{-3}$.

FIG. 10 is a graph of permeances at different temperatures (373 and 323 K) for different gas molecules through the CO$_2$-selective hybrid membrane STL-823-IV. The membrane was prepared at 823 K with a medium DPDES concentration of 0.19 mol m$^{-3}$.

FIG. 11 is a graph of changes of permeance through the membrane with exposure time to H$_2$O. The hybrid membranes were exposed at 873 K to 78 mol % water vapor, while the silica membrane was exposed at 873 K to 16 mol % water vapor. R is the ratio of PTES to TEOS.

FIG. 12 is a cross-sectional image of a hybrid membrane formed on a mesoporous alumina tube. FIG. 13 is a FTIR spectra of the DPDES and PTES membrane samples and references. FIG. 14 is a graph of H$_2$ permeance through the membranes prepared from the mixed Si source containing different PTES amounts.

FIG. 15 is an Arrhenius plot of the permeance of H$_2$ through the PTES-derived membrane, PTES-TEOS-derived membranes and TEOS-derived membrane.

FIG. 16 is a graph of changes of the H$_2$ permeance through two PTES-TEOS derived membranes and one silica membrane with exposure time to H$_2$O. The hybrid membranes were exposed at 873 K to 78 mol % water vapor, while the silica membrane was exposed at 873 K to 16 mol % water vapor. R is the ratio of PTES to TEOS.

FIG. 17 is a graph of permeation rates of various gases depending on size of the permeating gases.

### Detailed Description of the Preferred Embodiments

The thin and defect-free hybrid membranes (silica with attached aromatic groups) of the present invention were formed on an intermediate alumina substrate which could be a single layer placed on a mesoporous alumina support or a multilayer with a gradually decreasing pore size structure placed on a macroporous alumina support. The intermediate alumina substrate was prepared by coating a mesoporous support with a single dilute sol dipping solution or by coating a macroporous support with a series of dilute sol dipping solutions containing boehmite sols of different particle sizes. Each coating step was followed by a calcination step.

Boehmite sols with different particle size were prepared by carefully controlling the hydrolysis of aluminum alkoxides and the subsequent acid peptization of the boehmite precipitate obtained. The general procedure for preparing boehmite sols was as follows. A quantity of 0.2 mol of aluminum isopropoxide (Aldrich, 98.4%) was added to 300 ml of distilled water at room temperature. The mixture was quickly heated to 353 K within 0.5 hour with high speed stirring and was maintained at this temperature for 3-24 h for the hydrolysis of the isopropoxide and the formation of a boehmite (AIOOH) precipitate. The precipitate was then heated to 365 K and was peptized using a quantity of acetic acid (GR, 99.7%) with a molar ratio of H$^+$/Alkoxide in the range of 0.04-0.15. Peptization refers to the breakup of large oxide precipitate particles by acid treatment. The solution was refluxed at 365 K for 20 hour to get a clear or slightly translucent sol. The concentration of the resulting boehmite sols was calculated from the volume of the liquid and the known quantity of isopropoxide used. A dynamic light scattering analyzer (Horiba Model LB-500) was used to measure the particle size of the boehmite sols: these sols remained stable for more than 3 months. Three boehmite sols with a median particle size of 40, 200 and 630 nm were used in the present invention to prepare the gamma-alumina multilayer support. FIG. 1 shows the particle size distributions of these three boehmite sols.

A thin and defect-free intermediate ungraded substrate with one layer of gamma-alumina employed in the present invention was prepared on a mesoporous gamma-alumina support by the dipping-calcining method described in U.S. patent (S. T. Oyama, Y. Gu, D. Lee; US. Pat. No. 7,279,325 Feb. 20, 2007). The dip-coating of the support was carried out with a dilute dipping solution containing boehmite sols of particle sizes of 40 nm. A commercial alumina membrane tube (PALL Corporation, Membralox® T1-70-25G Membrane Tube, I.D. = 7 mm, O.D. = 10 mm) with a nominal pore size of 5 nm was used as the support. The preparation involved several steps. First, the alumina tube was cut to a length of 3-4 cm with a diamond saw and was connected to non-porous alumina tubes at both ends with ceramic joints. The ceramic joints were made with a glaze (Duncan IN 1001) fired at 1153 K for 0.5 h. Second, a dilute dipping solution was prepared by mixing a boehmite sol with a polyvinyl alcohol (PVA, M.W.=72,000) solution and diluting with distilled water to obtain a 0.15 M concentration of the sol and a 0.35 wt. % concentration of the PVA. Third, the alumina support was dipped into the dipping solution and was withdrawn after 10 seconds at a rate of 0.01 m s$^{-1}$ using a motor-driven dip-coating machine. The machine was built in-house and used a stepping motor drive (FIG. 2). Fourth, the dip-coated
alumina was dried in ambient air for 12-24 h, and then was heated to 873-923 K in air at a rate of 1 K min\(^{-1}\) and calcined at 873-923 K for 2-5 h.

A thin and defect-free gamma-alumina graded multilayer substrate employed in the present invention was prepared on a macroporous alpha-alumina support by the dipping-calcing method similar to the one described in U.S. patent (S. T. Oyama, Y. Gu, D. Lee; U.S. Pat. No. 7,270,325 Feb. 20, 2007). The dip-coating of the substrate was carried out with three dilute dipping solutions containing boehmite sols of different particle sizes. A commercial alumina membrane tube (PALL Corporation, Membralox® Ti-70-25Z Membrane Tube, I.D.=7 mm, O.D.=10 mm) with a nominal pore size of 100 nm was used as the substrate. The preparation involved the same steps as for the one-layer intermediate substrate described above except that the dipping and calcination steps were repeated three times using dipping solutions containing boehmite sols of progressively smaller particle sizes. The boehmite sols had particle sizes of 630, 200 and 40 nm.

The hybrid organic-inorganic membranes with a single top-layer (STL) were prepared as follows. The silica top-layer incorporating aromatic groups of the present invention was placed on top of the previously described gamma-alumina substrates by the deposition of a thin silica layer with attached aromatic groups by the chemical vapor deposition (CVD) method. The chemicals used in the CVD step were phenyltriethoxysilane (PTES) or diphenyldiethoxysilane (DPDES), and were decomposed at high temperature in an atmosphere where the precursor concentration ranges from 1 to 100 volume % of the gas mixture.

The setup is shown in FIG. 3, and the CVD process parameters are listed in Table 1. The support covered with the gamma-alumina intermediate layers was installed concentrically inside a piece of glass tubing of 14 mm inside diameter using machined Swagelok fittings with Teflon ferrules. After placing the assembly in an electric furnace and heating it to 773-873 K at a heating rate of 1 K min\(^{-1}\), an argon gas flow (balance gas) was introduced on the outer shell side and an argon gas flow (flush gas) was passed on the inner tube side. After 30 minutes the flush argon gas flow was stopped and a carrier gas flow containing PTES or DPDES was introduced to the inside of the support. The PTES or DPDES were introduced through a bubbler maintained at a temperature range of 356-371 K. The deposition time was varied from 8 to 78 h. After the CVD process was finished, the assembly was purged with the balance and flush gas flows for 30 minutes: Gas permeation measurements were generally conducted at 873 K for H\(_2\), CH\(_4\), and CO\(_2\) by the same method described previously. The selectivities for H\(_2\)/CH\(_4\) and H\(_2\)/CO\(_2\) were calculated as the ratio of the single-gas permeances of H\(_2\) to CH\(_4\) and CO\(_2\).

The hybrid organic-inorganic membranes with mixed top-layers (MTL) were prepared as follows. The membranes used as substrates the same combination of intermediate gamma-alumina layers on top of a macroporous support that were described previously. A thin mixed layer was placed on this substrate by a dual-component CVD method. This process places a silica layer incorporating aromatic groups on the surface of the substrate by the simultaneous thermal decomposition of TEOS and PTES or DPDES at high temperature.

The hybrid organic-inorganic membrane with mixed top-layers (XTL) were prepared as follows. The membranes used as substrates the same combination of intermediate gamma-alumina layers on top of a macroporous support that were described previously. A thin mixed layer was placed on this substrate by a dual-component CVD method. This process places a silica layer incorporating aromatic groups on the surface of the substrate by the simultaneous thermal decomposition of TEOS and PTES or DPDES at high temperature.

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The setup is shown in FIG. 3, and the CVD process parameters are listed in Table 3. The support covered with the gamma-alumina layers was installed as shown in the figure and was heated to 873 K as described previously. An argon gas flow was introduced on the outer shell side and a dilute argon gas flow was passed on the inner tube side. After 30 minutes a TEOS carrier gas flow was passed through a bubbler filled with TEOS at 296 K and a separate PTES carrier gas flow was passed through a bubbler filled with PTES at a higher temperature in the range of 331-356 K. The two carrier gases were then premixed with the dilute Ar flow before introduction to the inside of the support. The molar percent of PTES in the Si source can be adjusted by carefully controlling the flow rates of the carrier gases and the temperature of PTES. The deposition time was 3 hours. After the CVD process was finished, the assembly was purged with the balance and dilute gas flows for 30 minutes. Gas permeation measurements were generally conducted at 873 K for H\(_2\), CH\(_4\) and CO\(_2\) by the same method described previously. The selectivities for H\(_2\)/CH\(_4\) and H\(_2\)/CO\(_2\) were calculated as the ratio of the single-gas permeances of H\(_2\) to CH\(_4\) and CO\(_2\).

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The cross-sectional microstructure of the hybrid membrane was characterized using a field emission scanning electron microscope (FESEM Leo 1550). The samples were sputtered with gold before measurement with the electron microscope. The thickness of the membranes was obtained from high resolution cross-sectional images.

Hydrothermal stability tests were carried out on the hybrid membranes under an argon flow containing 78 mol % water vapor at 873 K up to 200 h. First, an argon flow at 15 \(\mu\)mol s\(^{-1}\) (flow rates in \(\mu\)mol\(s^{-1}\) can be converted to cm\(^3\) (NTP) min\(^{-1}\) by multiplication by 1.5) was passed through a heated bubbler containing distilled water and was then introduced on the inner side of the membrane tube to directly contact the fresh as-prepared membranes, while another argon flow also at 15 \(\mu\)mol s\(^{-1}\) was maintained on the outer shell side. The H\(_2\) permeation rate was measured periodically during the hydrothermal stability test to monitor the changes in the permeance. To make the measurements water vapor was shut off for about 30 min to dry the membranes under a dry argon flow. The wet argon flow was resumed immediately after the permeance measurements.
First, the dipping solution D840 containing the boehmite sol was prepared. The dipping solution made using the boehmite sol was faulted from dipping solution D840 with a sol particle concentration of 0.15 M. After 4 h, a clear solution with a PVA weight concentration of 3.5% was obtained. Then, 77 ml of 0.80 M boehmite sol B840 were vigorously mixed with 283 ml of distilled water and 40 ml of 3.5 wt % PVA solution were added and refluxed at 95 °C for 2 h. The final concentrations of PVA and boehmite sol were 0.35 wt% and 0.15 M. The solution was cooled to room temperature at quiescent conditions for 1 h and was set aside for the preparation of the gamma-alumina membranes.

Dipping solutions DS630 and DS200 were obtained by the same procedure using the boehmite sols BS630 and BS200 with medium particle sizes of 630 and 200 nm described previously.

Example 2

This example describes the preparation of two kinds of intermediate gamma-alumina substrates. One is the one-layer gamma-alumina substrate made on a mesoporous support. The other is the three-layer gamma-alumina substrate with a graded structure made on a macroporous support.

The one-layer gamma-alumina substrate was prepared using a commercial alumina membrane tube with a nominal pore size of 5 nm as a support by the deposition of one gamma-alumina layer on top of the support, where the layer was faulted from dipping solution DS40 with a sol particle size of 40 nm. The support was used in sections of 3-4 cm length connected with non-porous alumina tubing at both ends by ceramic joints. A dip-coating method was employed to coat the alumina supports with the sol and binder materials. First, the dipping solution DS40 containing the boehmite sol with medium particle size of 40 nm described in Example 1 was designated as D840. 400 ml of the dipping solution DS40 were prepared as follows. First, 3.5 g of PVA (Fluka, M.W.: 72,000) and 5 ml of 1 M HNO₃ were added to 95 ml of boiling water with vigorous stirring and refluxing. After 4 h, a clear solution with a PVA weight concentration of 3.5% was obtained. Then, 77 ml of 0.80 M boehmite sol B840 were vigorously mixed with 283 ml of distilled water and 40 ml of the 3.5 wt % PVA solution were added and refluxed at 323 K for 2 h. The final concentrations of PVA and boehmite sol were 0.35 wt% and 0.15 M. The solution was cooled to room temperature at quiescent conditions for 1 h and was set aside for the preparation of the gamma-alumina membranes.

Dipping solutions DS630 and DS200 were obtained by the same procedure using the boehmite sols BS630 and BS200 with medium particle sizes of 630 and 200 nm described previously.
was used. The support was dipped at a speed of 0.01 m s⁻¹ in the dipping solution DS40, was held for 10 seconds, and was withdrawn at the same speed. Use was made of the mechanical dip-coating machine shown in FIG. 2. The sol-coated tube was dried in ambient air for 24 h, heated up 923 K at a heating rate of 1 K min⁻¹ and calcined for 5 h or 2 h. The calcination temperature and time depended on the subsequent deposition temperature for the hybrid membranes. A calcination at 873 K for 5 h was employed when the deposition of hybrid membranes was carried out at 773-823 K, while 923 K for 2 h was used in the case of the deposition of hybrid membranes at 873 K.

The three-layer gamma-alumina substrate was prepared using a commercial alumina membrane tube with a nominal pore size of 100 nm as a support by the deposition of three gamma-alumina layers on top of the support, where the layers were faulted from dipping solutions with decreasing sol particle concentrations. The previously described dip-coating method was employed to coat the alumina supports with the sol and binder materials. The sol-coated tube was dried in ambient air for 24 h, heated up 923 K at a heating rate of 1 K min⁻¹ and calcined for 2 h. Second, the dip-coating procedure was repeated using the dipping solution DS200 except for a longer dipping time of 25 seconds. Third, the as-calcined tube was dipped in the dipping solution DS40 and held for 50 seconds. The sol-coated tube was dried in ambient air for 24 h. The calcination temperature and time depended on the subsequent deposition temperature for the hybrid membranes. A calcination at 873 K for 5 h was employed in the case of the deposition temperature at 773-823 K, while 923 K for 2 h was used in the case of the deposition temperature at 873 K. As described in Example 2, the solutions DS630, DS200 and DS40 contained the sols with median particle sizes of 630, 200 and 40 nm, respectively.

### Example 3

This example describes the preparation of a single top-layer (STL) hybrid membrane by a chemical vapor deposition (CVD) technique. The hybrid organic-inorganic membrane composed of silica with phenyl groups was deposited on the one-layer alumina substrate calcined at 873 K for 5 hours, as described in Example 2. The CVD process was conducted at 823 K by employing CVD Condition II with a medium Si source concentration as listed in Table 1. The resulting hybrid membrane was designated STL-823-II. The Si source was phenyltriethoxysilane (PTES) vapor and was introduced using a bubbler at 365 K with argon as a carrier gas at a flow rate of 17.3 mol m⁻³ s⁻¹. The PTES flow with a medium concentration of 0.19 mol m⁻³ was passed on the tube (inner) side of the tubular membrane, while a flow of argon at a rate of 17.3 mol m⁻³ was maintained on the shell (outer) side of the reactor assembly. The CVD process was conducted at 823 K for 5, 15, 35 and 78 h with the apparatus shown in FIG. 3. Before and after CVD, the assembly was purged with flows of flush argon gas and balance argon gas at a rate of 17.3 mol m⁻³.

The permeation properties at 823 K before and after CVD are listed in Table 4. Before CVD, the permeance follows the order of gas molecular weight, which is H₂ > CH₄ > CO₂. The selectivities CO₂/CH₄ and H₂/CH₄ for the membrane substrate were 0.64 and 2.6, which are close to the values predicted by the Knudsen diffusion mechanism. As the deposition progressed, the permeance decreased slightly for all three gases, but relatively faster for CH₄, so the selectivity of CO₂/CH₄ was increased to above 1. The permeance follows the order of molecular size of H₂ > CO₂ > CH₄. The kinetic diameters of H₂, CO₂, and CH₄ were 0.29, 0.33 and 0.38 nm, respectively. After 78 h of deposition, the selectivities of CO₂/CH₄ and H₂/CH₄ were 1.2 and 6.1, respectively. The CO₂ and H₂ permeance were high, 4.4 x 10⁻⁷ and 2.2 x 10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹, respectively.

The permeation properties of the STL-823-II membrane were tested at different temperature. Table 5 and FIG. 4 show the CO₂ and CH₄ permeance and the CO₂/CH₄ selectivity at temperatures in the range of 297 K and 823 K (24° C. and 550° C.). The CO₂ permeance through the membrane increased with decreasing permeation temperature, and reached a maximum at around 473 K, and then decreased with decreasing temperature. The CH₄ permeance had a similar trend, but decreased much faster with decreasing temperature below 473 K, thus leading to a large increase in the selectivity. At 297 K, the CO₂ permeance was 5.8 x 10⁻⁸ mol m⁻² s⁻¹ Pa⁻¹, and the CO₂/CH₄ selectivity was 380. This membrane had a highest CO₂ permeance of 7.2 x 10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹ at 473 K, but it shows the best CO₂/CH₄ selectivity at lower temperature, especially in the range of 297-323 K (24-50° C.).

### TABLE 4

<table>
<thead>
<tr>
<th>Permeance properties</th>
<th>5 h-CVD</th>
<th>15 h-CVD</th>
<th>35 h-CVD</th>
<th>78 h-CVD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeance (mol m⁻² s⁻¹</td>
<td>2.5 x 10⁻⁷</td>
<td>9.7 x 10⁻⁸</td>
<td>9.7 x 10⁻⁵</td>
<td>1.5 x 10⁻⁶</td>
</tr>
<tr>
<td>CO₂</td>
<td>3.8 x 10⁻⁶</td>
<td>2.6 x 10⁻⁷</td>
<td>3.6 x 10⁻⁷</td>
<td>3.6 x 10⁻⁷</td>
</tr>
<tr>
<td>CH₄</td>
<td>6.2 x 10⁻⁶</td>
<td>2.3 x 10⁻⁶</td>
<td>1.3 x 10⁻⁷</td>
<td>3.2 x 10⁻⁷</td>
</tr>
<tr>
<td>Selectivity CO₂/CH₄</td>
<td>0.64</td>
<td>0.61</td>
<td>0.68</td>
<td>0.9</td>
</tr>
<tr>
<td>H₂/CH₄</td>
<td>2.6</td>
<td>2.6</td>
<td>2.5</td>
<td>4.2</td>
</tr>
</tbody>
</table>

### TABLE 5

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>CO₂ permeance (mol m⁻² s⁻¹ Pa⁻¹)</th>
<th>CH₄ permeance (mol m⁻² s⁻¹ Pa⁻¹)</th>
<th>CO₂/CH₄ selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>823</td>
<td>4.4 x 10⁻⁷</td>
<td>3.6 x 10⁻⁷</td>
<td>1.2</td>
</tr>
<tr>
<td>573</td>
<td>5.5 x 10⁻⁷</td>
<td>3.3 x 10⁻⁷</td>
<td>1.7</td>
</tr>
<tr>
<td>473</td>
<td>7.2 x 10⁻⁷</td>
<td>2.6 x 10⁻⁷</td>
<td>2.8</td>
</tr>
<tr>
<td>373</td>
<td>3.3 x 10⁻⁷</td>
<td>1.3 x 10⁻⁷</td>
<td>26</td>
</tr>
</tbody>
</table>
TABLE 5—continued

<table>
<thead>
<tr>
<th>Permeation temperature (K)</th>
<th>Permeance (mol m⁻² s⁻¹ Pa⁻¹)</th>
<th>Selectivity CO₂/CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>323</td>
<td>1.0 x 10⁻⁷</td>
<td>91</td>
</tr>
<tr>
<td>297</td>
<td>5.8 x 10⁻⁸</td>
<td>380</td>
</tr>
</tbody>
</table>

Example 4

This example describes the preparation of another single top-layer (STL) hybrid membrane deposited on the same one-layer gamma-alumina substrate calcined at 873 K for 5 hours, as described in Example 2. Differing from Example 3, this example used CVD process parameters denoted as Condition I with a low phenyltriethoxysilane (PTES) concentration of 0.11 mol m⁻³ (Table 1). The resulting hybrid membrane was designated STL-823-I. The CVD process was carried out for 10, 20, 30 and 41 hours, respectively in a similar manner as described in Example 3. Table 6 shows the changes in permeation properties at 823 K before and after CVD. After 41 h of deposition, the selectivities of CO₂/CH₄ and H₂/CH₄ were doubled and tripled, respectively. The CO₂ and H₂ permeance were 1.8 x 10⁻⁷ and 1.1 x 10⁻⁸ mol m⁻² s⁻¹ Pa⁻¹ at 823 K, a little lower than the membrane STL-823-II in Example 3.

Table 7 and FIG. 5 show the permeances for CO₂ and CH₄ and the selectivity of CO₂ over CH₄ at temperatures in the range of 323 K and 873 K (50° C. and 550° C.). Similar to the membrane STL-823-II in EXAMPLE 4, the membrane STL-823-I showed a permeance maximum at 473 K for both CO₂ and CH₄, and an increasing selectivity of CO₂/CH₄ with decreasing permeation temperature. At 323 K, the CO₂ permeance was 8.9 x 10⁻⁸ mol m⁻² s⁻¹ Pa⁻¹ and the CO₂/CH₄ selectivity was 32.

TABLE 6

<table>
<thead>
<tr>
<th>Permeation properties substrate</th>
<th>10 h-CVD</th>
<th>20 h-CVD</th>
<th>30 h-CVD</th>
<th>41 h-CVD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeance</td>
<td>H₂</td>
<td>2.5 x 10⁻⁵</td>
<td>5.5 x 10⁻⁶</td>
<td>1.6 x 10⁻⁶</td>
</tr>
<tr>
<td></td>
<td>CH₄</td>
<td>9.7 x 10⁻⁶</td>
<td>2.0 x 10⁻⁶</td>
<td>4.1 x 10⁻⁷</td>
</tr>
<tr>
<td>Selectivity</td>
<td>CO₂/CH₄</td>
<td>0.64</td>
<td>0.67</td>
<td>0.78</td>
</tr>
<tr>
<td></td>
<td>H₂/CH₄</td>
<td>2.6</td>
<td>2.8</td>
<td>3.8</td>
</tr>
</tbody>
</table>

Example 5

This example describes the preparation of another single top-layer (STL) hybrid membrane deposited on the same one-layer gamma-alumina substrate calcined at 873 K for 5 hours, as described in Example 2. Differing from Example 3, this example used CVD process parameters denoted as Condition III with a high phenyltriethoxysilane (PTES) concentration of 0.26 mol m⁻³ (Table 1). The resulting hybrid membrane was designated STL-823-III. The CVD process was conducted at 823 K for 5, 11 and 20 hours, respectively in a similar manner as described in Example 3. Table 8 shows the changes in permeation properties at 823 K before and after CVD. After 20 h of deposition, the selectivities of CO₂/CH₄ and H₂/CH₄ were improved to 0.95 and 4.1, respectively, and the CO₂ and H₂ permeance were 2.7 x 10⁻⁷ and 1.2 x 10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹ at 823 K. The selectivity was not good as in Examples 3 and 4.

TABLE 7—continued

<table>
<thead>
<tr>
<th>Permeance (mol m⁻² s⁻¹ Pa⁻¹)</th>
<th>Selectivity CO₂/CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>373</td>
<td>2.1 x 10⁻⁷</td>
</tr>
<tr>
<td>323</td>
<td>8.9 x 10⁻⁸</td>
</tr>
</tbody>
</table>
**Example 6**

This example describes the preparation of another single top-layer (STL) hybrid membrane deposited on the same one-layer gamma-alumina substrate calcined at 873 K for 5 hours, as described in Example 2. Differing from Examples 3, 4 and 5, this example used a low deposition temperature of 773 K and the CVD Condition I with a low PTES concentration of 0.11 mol m\(^{-3}\) (Table 1). The resulting hybrid membrane was designated STL-773-I. The CVD process was conducted for 10, 15, 25 and 45 hours, respectively in a similar manner as described in Example 3. Table 9 shows the changes in the permeation properties at 823 K before and after CVD. After 45 h of deposition, the selectivities of CO\(_2\)/CH\(_4\) and H\(_2\)/CH\(_4\) were improved by 2-5 times, and the CO\(_2\) and H\(_2\) permeances were 1.8x10\(^{-7}\) and 1.1x10\(^{-6}\) mol m\(^{-2}\) s\(^{-1}\) Pa\(^{-1}\) at 783 K.

**Table 10**

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>CO(_2)</th>
<th>CH(_4)</th>
<th>CO(_2)/CH(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>473</td>
<td>3.8x10(^{-7})</td>
<td>1.2x10(^{-7})</td>
<td>3.2</td>
</tr>
<tr>
<td>373</td>
<td>1.0x10(^{-7})</td>
<td>8.9x10(^{-8})</td>
<td>1.2</td>
</tr>
<tr>
<td>303</td>
<td>8.3x10(^{-8})</td>
<td>9.9x10(^{-8})</td>
<td>0.8</td>
</tr>
</tbody>
</table>

**Example 7**

This example describes the preparation of another single top-layer (STL) hybrid membrane deposited on the three-layer gamma-alumina substrate with the third layer calcined at 923 K for 2 h, as described in Example 2. Differing from Examples 3, 4 and 5 and 6, this example used a high deposition temperature of 873 K and the CVD Condition II with a medium PTES concentration of 0.19 mol m\(^{-3}\) (Table 1). The resulting hybrid membrane was designated STL-873-II. The CVD process was conducted for 8 hours in a similar manner as described in Example 3. Table 11 shows the changes in permeation properties at 873 K before and after CVD. After 8 h of deposition, the selectivities of CO\(_2\)/CH\(_4\) and H\(_2\)/CH\(_4\) were 1.9 and 20, which are higher compared with the membranes prepared at lower temperature (773-823 K) in Examples 3, 4, 5 and 6. However, the permeance for CO\(_2\) and H\(_2\) were lower, 8.7x10\(^{-8}\) and 9.4x10\(^{-7}\) mol m\(^{-2}\) s\(^{-1}\) Pa\(^{-1}\), respectively at 873 K, even though a shorter deposition time was employed. A shorter deposition time was required because at the higher deposition temperature, the deposition rate was faster.

**Table 11**

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>CO(_2)/CH(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>773</td>
<td>1.6x10(^{-6})</td>
</tr>
<tr>
<td>673</td>
<td>1.9x10(^{-7})</td>
</tr>
<tr>
<td>573</td>
<td>2.3x10(^{-7})</td>
</tr>
</tbody>
</table>

**Table 12**

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>CO(_2)/CH(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>773</td>
<td>1.6x10(^{-6})</td>
</tr>
<tr>
<td>673</td>
<td>1.9x10(^{-7})</td>
</tr>
<tr>
<td>573</td>
<td>2.3x10(^{-7})</td>
</tr>
</tbody>
</table>

CH\(_4\) showed a similar trend as the membranes prepared at lower deposition temperatures of 773 K and 823 K in Examples 3, 4, 5 and 6. As the permeation temperature increased, the permeance increased and then decreased with a peak at around 473 K. Since the permeance of CH\(_4\) decreased much faster than that of CO\(_2\) with decreasing temperature below 473 K, the selectivity of CO\(_2\) over CH\(_4\) sub.4 increased with decreasing temperature, and jumped at temperatures below 473 K. Compared with the membrane prepared at lower temperature in Examples 3, 4 and 6, the membrane in this example showed a lower CO\(_2\) permeance. At 323 K, the CO\(_2\) permeance was 1.6x10\(^{-8}\) mol m\(^{-2}\) s\(^{-1}\) Pa\(^{-1}\) and the
CO₂/CH₄ selectivity was 180. This membrane had a highest CO₂ permeance of 4.7x10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹ at 473 K with a CO₂/CH₄ selectivity of 10.

Table 11 shows changes of permeation properties at different permeation temperatures in the range 299 K-823 K (26° C-600° C). The CO₂ permeance through the membrane increased with decreasing permeation temperature, and reached a maximum at around 373 K, and then decreased with decreasing temperature. The CH₄ permeance had a very similar trend, but decreased much faster with decreasing temperature below 373 K, thus leading to a quick increase of the selectivity below 373 K. At 299 K, the CO₂ permeance was 3.4x10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹ and the CO₂/CH₄ selectivity was 59. Compared with the PTES-derived hybrid membrane described in Example 3, the DPDES-derived hybrid membrane had higher CO₂ permeance but lower selectivity. On the other hand, the membrane in this example exhibited a highest CO₂ permeance of 8.7x10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹ at 373 K with a CO₂/CH₄ selectivity of 12.

Table 12 shows changes of permeation properties for CO₂ and CH₄ and the selectivity of CO₂/CH₄ with different permeation temperature through the single top-layer (STL) CO₂-selective hybrid membrane STL-873-IV. The CO₂ permeance through the membrane was in the order of CO₂:CH₄ gas molecular size. At 323 K, the permeance for CO₂ was higher than that for CH₄, even though the CO₂ molecule is lighter and smaller than the CO₂ molecule. This suggests that surface diffusion contributes to the permeation mechanism for some gases such as CO₂ at low temperature. The strong surface flow for CO₂ is caused by the strong affinity between

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>CO₂</th>
<th>CH₄</th>
<th>CO₂/CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>873</td>
<td>8.7 x 10⁻⁷</td>
<td>4.6 x 10⁻⁸</td>
<td>1.9</td>
</tr>
<tr>
<td>473</td>
<td>4.7 x 10⁻⁷</td>
<td>4.6 x 10⁻⁸</td>
<td>10</td>
</tr>
<tr>
<td>373</td>
<td>2.6 x 10⁻⁷</td>
<td>1.4 x 10⁻⁸</td>
<td>19</td>
</tr>
<tr>
<td>323</td>
<td>1.6 x 10⁻⁷</td>
<td>8.8 x 10⁻¹⁰</td>
<td>180</td>
</tr>
</tbody>
</table>

Example 3

Example 9

Example 10

CO₂ separation at different permeation temperature through the single top-layer (STL) CO₂-selective hybrid membrane STL-823-IV.
the CO₂ molecule and the aromatic groups present in the membrane: Therefore, both molecular sieving and surface diffusion make these hybrid membranes highly selective for CO₂ over CH₄ at low temperature.

FIG. 10 shows the gas permeance as a function of kinetic diameters at 373 and 323 K through the hybrid membrane STL-823-IV. As described in Example 8, the membrane was prepared at 823 K by the CVD of diphenyldiethoxysilane (DPDES) using CVD condition IV listed in Table 1. It can be concluded that the permeation mechanism through the DPDES-derived hybrid membranes at low temperature is also molecular sieving and surface diffusion. The critical size of this hybrid material is also around 0.4 nm. Compared with FIG. 9, it was also found that the surface diffusion flow in the DPDES-derived membrane was stronger than in the PTES-derived membrane, leading to higher permeate at low temperature. At 373 K, the permeance for CO₂ through the DPDES-derived membrane was 8.7 × 10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹ in comparison to 3.3 × 10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹ for the PTES-derived membrane.

To investigate the thermal stability of the hybrid membranes, a series of measurements were conducted on a hybrid membrane STL-823-11 prepared using the method described in Example 3. First, the permeances for H₂, CO₂, CH₄ and SF₆ were measured at 473 K on the fresh hybrid membrane. Second, the membrane was cooled to room temperature, then heated to 823 K, and then cooled down to room temperature again at a rate of 1 K min⁻¹. Some specific temperatures were kept for periods of several hours to one day for other tests. After several cycles for a total of two weeks, the membrane was taken out from the furnace, wrapped with plastic wrap, and stored at ambient conditions for a month. Then, the membrane was calcined at 823 K for 2 h with flushing Ar and cooled down to 473 K. The permeation measurement was then taken again at 473 K using H₂, CO₂, CH₄ and SF₆. At last, the same membrane was calcined at 823 K for 2 h in air and the permeance were measured again at 473 K. The results are shown in FIG. 11. The small change in permeance after storage and calcination in Ar indicates good long-term stability of the hybrid membranes. Different results were obtained after calcination in air. Here it was found that the permeance increased substantially and the selectivity decreased. This is due to the combustion of the aromatic groups present in the membrane, thus leading to an increase in the pore size of the membrane. It is concluded that the hybrid membranes exhibit good thermal stability except in an oxidative environment.

FIG. 12 is a high-resolution electron micrograph of an STL-823-11 CO₂-selective hybrid membrane prepared using the method described in Example 3. There is clearly a thin layer at the very top with a different contrast from the alumina particle layer. This is the hybrid layer, of thickness 30 nm. Careful examination on the alumina layer reveals a separate alumina layer with smaller alumina particles and denser texture. This is the 1-layer alumina substrate with a thickness of 170 nm, which was prepared by dipping-calcination of the boehmite sol. Below the 1-layer alumina substrate is the commercial porous alumina support with a pore size of 5 nm.

FIG. 13 shows Fourier transform infrared (FTIR) spectra of STL membranes with various reference compounds. The membrane samples were obtained by scratching off the membrane material from the support with a stainless steel blade. These and other samples were mixed with KBr and pressed into pellets at 1.4 tons pressure with a hydraulic press (Carver). The FTIR spectra were obtained with a Bio-Rad Model FTS 3000MX instrument at a resolution of 4 cm⁻¹ using 64-1024 scans/spectrum. The samples prepared with DPDES (FIG. 13a) and PTES (FIG. 13b) (STL-823-IV and STL-823-11, respectively) were physically mixed with 4 wt% tetracyanoethylene used as an internal standard.

Comparison of the spectra with the references triphenylphosphine oxide/tetraethyldisilane (FIG. 13c), tetracyanoethylene (FIG. 13d), liquid DPDES (FIG. 13f), and liquid PTES (FIG. 13g) allows assignment and quantification of the bands. In the tetracyanoethylene spectrum (FIG. 13d) the peak at 2253 cm⁻¹ is due to C=N bond stretching, the peak at 2226 cm⁻¹ is due to the C=C bond stretching, and the peaks at 1152, 1116, and 1089 cm⁻¹ are due to C=C bond stretching. In the triphenylphosphine spectrum (FIG. 13e) the broad feature at 3054 cm⁻¹ is due to aromatic C-H bond in the peak at 1586, 1488, 1343 cm⁻¹ are due to aromatic C=C stretching, the peaks at 1191 and 1119 cm⁻¹ due to P-O bond stretching, and the peaks at 1164 and 1074 cm⁻¹ are due to C-C bond stretching. The spectra of liquid DPDES (FIG. 13f) and liquid PTES (FIG. 13g) are very similar. The peaks close to 3066 cm⁻¹ are due to aromatic C-H stretches, the peak at 2979 cm⁻¹ is due to the C-H stretch of the terminal CH₃ group, the peaks at 2925 and 2889 cm⁻¹ are due to the C-H stretch in CH₂ groups, the peaks at 1593, 1484, 1439, and 1386 cm⁻¹ are due to aromatic C=C stretching, the peaks at 1170 and 1080 cm⁻¹ are due to Si-O-C asymmetric stretches, and the peaks at 1143 and 1098 cm⁻¹ are due to C-C stretches. In the membrane materials the peaks at 1622, 1504, and 1396 cm⁻¹ can be assigned to aromatic C=C stretches. The liquid DPDES and PTES references show weak aromatic C=C stretches in comparison to the strong aliphatic C-H stretches. In the membrane materials no C-H stretches are visible. This may be due to the weakness of these bands or because the heat treatment in the preparation decomposed the phenyl groups into dehydrogenated graphite-like groups.

The bands in the aromatic C=C region of the membrane materials allow estimation of the amount of aromatic groups retained in the silica matrix. The calculation is made using the intensity of the aromatic C=C bands in triphenylphosphine oxide as a basis, with the C=N bands in tetracyanoethylene serving as a common standard in the materials. The ratio of Si/phenyl in the PTES membrane is 3.6 while in the DPDES it is 2.3. Thus, a substantial amount of aromatic carbon is present in the membrane materials.

Example 10

This example describes the preparation of a hybrid membrane with a multiple top-layer (MTL) structure deposited on the one-layer gamma-alumina substrate. The membrane is composed of two top-layers prepared by a first deposition of phenylriethoxysilane (PTES) and a subsequent second deposition of tetraethyloxydisilicate (TEOS) both at high temperature in an atmosphere where the precursor concentration ranges from 1 to 100 volume % of the gas mixture.

The substrate employed in this example was a one-layer gamma-alumina substrate calcined at 923 K, as described in Example 2. The deposition for the first top layer was carried out at 873 K on the alumina substrate using CVD condition II with a medium PTES concentration of 0.19 mol m⁻³ as listed in Table 1. The CVD process was conducted for 8 hours in a similar manner as described in Example 7. After the permeances for H₂, CH₄ and CO₂ were measured at 873 K, the resulting membrane was used as a new substrate for the deposition of the second top-layer. This second deposition was carried out at 873 K using CVD condition V with a TEOS concentration of 0.019 mol m⁻³ listed in Table 2. The CVD apparatus shown in FIG. 3 was used. The CVD process was conducted at 873 K in a similar manner as described in U.S. Pat. No. 6,527,833. The assembly was first purged with the balance and dilute gas flows (17.2 and 13.5 μmol s⁻¹) for 30
minutes, then a TEOS carrier gas flow of 3.7 μmol s⁻¹ was passed through a bubbler filled with TEOS at 296 K and was premixed with the dilute argon gas flow before introduction to the inside of the support. The resulting TEOS concentration was 0.0193 mol m⁻³. The deposition times were 2, 2.8, 3.8 and 4.1 hours, respectively. After the CVD process was finished, the assembly was purged with the balance and dilute gas flows for 30 minutes. The membrane was designated MTL-873-II-V. Gas permeation measurements were conducted at 873 K on H₂, CH₄, and CO₂.

The permeation properties at 873 K before and after CVD of TEOS are listed in Table 15. After 3.8 hours of CVD, the H₂ permeance through the multiple top-layer (MTL) composite membrane remained high at 1.0 x 10⁻⁸ mol m⁻² s⁻¹ Pa⁻¹ at 873 K while the H₂ selectivities over CH₄ and CO₂ were good, 32 and 17, respectively. The CVD process was continued for another 20 minutes, the H₂ selectivity over CH₄ increased to 56 but the H₂ permeance was reduced to 8.7 x 10⁻⁹ mol m⁻² s⁻¹ Pa⁻¹.

Example 11

This example describes the preparation of another multiple top-layer (MTL) hybrid membrane. The top layers were deposited by a first CVD of phenyltriethoxysilane (PTES) and subsequently by a second CVD of tetraethylorthosilicate (TEOS) both at high temperature in an atmosphere where the precursor concentration ranges from 1 to 100 volume % of the gas mixture.

Differing from Example 10, the substrate employed in this example had a graded three-layer gamma-alumina intermediate layer with the third layer calcined at 923 K for 2 h, as described in Example 2. The preparation involved two steps as in Example 10. First an initial deposition of PTES was conducted at 873 K for 16 hours using CVD condition II listed in Table 1 and then a second deposition of TEOS was carried out at 873 K for 2.2, 4.2, 5.5 and 7.5 hours, respectively using CVD condition V. The membrane was denoted MTL-873-II-V. The permeation properties at 873 K before and after CVD of TEOS are listed in Table 16. After 7.5 hours of CVD, the resulting composite membrane exhibited extremely high H₂ permeance, 3.5 x 10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹ at 873 K while the H₂ selectivity over CH₄ was 27.
Excellent H₂ separation properties with H₂ selectivities of over 3000 and a H₂ permeance of 1.6×10⁻⁵ mol m⁻² s⁻¹ Pa⁻¹ at 873 K. These values are similar to those for TEOs-derived silica membranes formed on one-layer alumina substrates, as described in U.S. Pat. No. 6,527,833.

Example 13

This example describes the preparation of three other mixed top-layer hybrid membranes using different molar ratio of PTES to TEOs. The hybrid membranes were deposited at 873 K on the same one-layer alumina substrate calcined at 923 K for 2 h described in Example 2, but using different CVD process parameters denoted as Condition VI, Condition VIII and Condition IX, and listed in Table 3. The PTES contents in the Si source TEOs were 17%, 50% and 60% for Conditions VI, VIII and IX, respectively. The resulting hybrid membranes were designed as XTL-873-VI, XTL-873-VIII, and XTL-873-IX, correspondingly. The permeation properties were measured and are listed in Table 18. It was found that the hybrid membrane prepared with increasing PTES content showed increasingly high H₂ permeance but decreasing H₂ selectivity. This trend is also clearly demonstrated in Fig. 14. When the molar ratio of PTES to TEOs was 1.4, the resulting membrane XTL-873-IX had a high H₂ permeance of 4.4×10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹ but the selectivities of H₂ over CH₄ and CO₂ were 7.5 and 13. As described previously, compared with the TEOS-derived silica membrane, the PTES-derived hybrid membrane has a looser structure and bigger pore size, thus leading to high H₂ permeance but low H₂ selectivity. The higher PTES content employed, the higher the permeance but the lower selectivity of the resulting membrane obtained.

The membrane with a loose structure and bigger pore size has low activation energy for gas permeance. Fig. 15 compares Arrhenius plots for the permeance of H₂ through the PTES-derived membrane, PTES-TEOS-derived membranes and TEOs-derived membrane. It is clear that the membrane obtained using more PTES content has higher permeance and lower activation energy for H₂. The TEOs-derived membrane had lowest permeance of 1.2×10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹ at 873 K and highest activation energy of 15 kJ mol⁻¹ for H₂, J. Membr. Sci., 231 (2004) 117. While the PTES-derived membrane exhibited the highest permeance of 2.2×10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹ at 823 K and lowest activation energy of 3.9 kJ mol⁻¹ for H₂.

Example 14

This example describes the hydrothermal stability of mixed top-layer hybrid membranes prepared by the dual-precursor CVD of PTES and TEOs. The hybrid membranes used in this example were fresh samples of XTL-873-VII and XTL-873-IX deposited on one-layer gamma-alumina substrate using the mixed Si sources containing 37 mol % and 60 mol % PTES as described in Examples 12 and 13. The hydrothermal stability test was carried out as previously described on these hybrid membranes at 873 K for 130-200 h under harsh conditions with 78 mol % water vapor. To compare with the hybrid membranes, one TEOs-derived silica membrane was prepared at 873 K on a three-layer alumina substrate by CVD of TEOs as described in U.S. patent (S. T. Oyama, Y. Gu, D. Lee, US. Pat. No. 7,179,325B2, Feb. 20, 2007). The test on the silica membrane was conducted at the same temperature (873 K) but under a gentle environment containing only 16 mol % water vapor in argon. Table 19 and Fig. 16 show changes in the H₂ permeance through these two PTES-TEOS-derived membranes and one silica membrane with exposure time. The majority of the reduction of the permeance was found for all membranes in the first 10 h. After 40 h of exposure to water vapor, the permeance became stable or decreased very slowly. However, the degree of reduction was different between the hybrid membranes and silica membrane. Although the hybrid membranes were exposed to much harsh conditions (78 mol % steam vs. 16 mol % steam), the H₂ permeance through these two hybrid membranes was reduced by 50-70% after 200 h-exposure in comparison to 90% for the TEOs-derived silica membrane. Among the hybrid membranes, the membrane prepared with higher PTES content exhibited less reduction in H₂ permeance (50% vs. 70% for a 130 h-exposure). In summary, PTES-TEOS derived hybrid membranes show better hydrothermal stability than the TEOs-derived silica membrane. Higher PTES content results in better hydrothermal stability.

The hydrophilicity of the TEOs-derived silica membrane is due to the presence of a large number of Si—OH groups on the surface of silica clusters. The attachment of hydrophilically stable Si-aromatic group to the silica clusters results in hydrophobic membranes that better withstand moisture. The more PTES used, the more aromatic groups remaining in the membrane and thus the stronger the resistance to densification.
Changes of $P_H$ permeance with the exposure time for two hybrid membranes and one silica membrane. The hybrid membranes were exposed at 873 K to 78 mol % water vapor, while the silica membrane was exposed at 873 K to 16 mol % water vapor.

<table>
<thead>
<tr>
<th>Hybrid membranes</th>
<th>Permeance $(\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>XTL-873-IX (60% PTES)</td>
</tr>
<tr>
<td>Original</td>
<td>$3.37 \times 10^{-7}$</td>
</tr>
<tr>
<td>2 h- Exposure</td>
<td>$(3.37 \times 10^{-7})$</td>
</tr>
<tr>
<td>(change)</td>
<td>$(-30.3%)$</td>
</tr>
<tr>
<td>40 h- Exposure</td>
<td>$1.17 \times 10^{-7}$</td>
</tr>
<tr>
<td>(change)</td>
<td>$(-49.0%)$</td>
</tr>
<tr>
<td>130 h- Exposure</td>
<td>$1.69 \times 10^{-8}$</td>
</tr>
<tr>
<td>(change)</td>
<td>$(-49.9%)$</td>
</tr>
<tr>
<td>200 h- Exposure</td>
<td>n/a</td>
</tr>
<tr>
<td>(change)</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Example 15

This example describes the use of the precursor diphenyldiethoxysilane (DPDES), a molecule analogous to phenyltriethoxysilane (PTES), except that another phenyl group substitutes for one of the ethyl groups. The purpose is to investigate the possibility of further size control of precursors to improve permeability.

DPDES-TEOS-DMDCS membranes were prepared by three component chemical vapor deposition of diphenyldiethoxysilane (DPDES, Aldrich, 98%), tetraethylorthosilicate (TEOS; Aldrich, 98%) and dimethyldichlorosilane (DMDCS, Aldrich, 98%) in a flow at 823 K simultaneously. A TEOS-DMDCS solution was again prepared at a molar ratio of 3/1 by mixing them in the same bubbler which was kept at 298 K as described earlier. The molar ratio of DPDES/TEOS-DMDCS was adjusted by changing the temperature of the oil bath. The DPDES bubbler temperature was set at 393 K to 413 K to obtain a molar ratio range of 0.05 to 0.15.

The permeation rates of DPDES-TEOS-DMDCS membranes are presented for various gases at different temperatures in Fig. 17. The permeation of gases followed the order of size through all types of DPDES-TEOS-DMDCS membranes, and they decreased slightly with decreasing temperature. Higher molar ratios of DPDES/TEOS-DMDCS resulted in higher CO$_2$/CH$_4$ selectivities, which were in the range 15-20. There were more phenyl groups in the membrane matrix resulted in a less dense structure. Thus, the permeation of gases through the DPDES-TEOS-DMDCS membranes was higher when compared to the PTES-TEOS-DMDCS with similar CO$_2$/CH$_4$ selectivities.

While the various embodiments of the present invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention.

Accordingly, the scope of protection is not limited by the description set out above, but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims. Each and every claim is incorporated into the specification as an embodiment of the present invention. Thus the claims are a further description and are an addition to the preferred embodiments of the present invention.

The discussion of a reference in the Background of the Invention is not an admission that it is prior art to the present invention, especially any reference that may have a publication date after the priority date of this application. The disclosures of all patents, patent applications and publications cited herein are hereby incorporated herein by reference, to the extent that they provide exemplary, procedural or other details supplementary to those set forth herein.

What is claimed is:

1. A composition comprising a hybrid composite organic-inorganic membrane wherein said membrane comprises:

- an amorphous porous layer comprising silica incorporating organic functionalities selected from the group consisting of aromatic groups, olefinic groups, and alicyclic groups; and
- a porous substrate;

wherein said amorphous porous layer is deposited on said porous substrate by chemical vapor deposition of gaseous precursors in an atmosphere where the precursor concentration ranges from 1 to 100 volume % of the gas mixture at a temperature from 673 K to 1173 K.

2. The hybrid composite organic-inorganic membrane of claim 1, wherein said organic functionalities comprise aromatic groups obtained from decomposition of phenyl-substituted silanes or siloxanes.

3. The hybrid composite organic-inorganic membrane of claim 1, wherein said organic functionalities comprise aromatic groups obtained from the decomposition of phenyltriethoxysilane (PTES), diphenyldiethoxysilane (DPDES), triphenylethoxysilane (TPES), phenyltrimethoxysilane, diphenylmethoxysilane, phenyltrimethoxysilane, diphenylmethoxysilane, and any mixture thereof.

4. The hybrid composite organic-inorganic membrane of claim 2, wherein said phenyl-substituted silanes is selected from the group consisting of phenyltriethoxysilane (PTES), diphenyldiethoxysilane (DPDES), and any mixture thereof.

5. The hybrid composite organic-inorganic membrane of claim 1, wherein said silica is formed from at least one silica precursor selected from the group consisting of alkoxydes of silicon, chlorosilanes, and any mixture thereof, wherein said alkoxydes of silicon including tetramethyldichlorosilicates (tetramethoxysilanes), tetraethlylorthosilicates (tetratetraethylsilanes) and tetrapropylorthosilicates (tetrapropylsilanes), said chlorosilanes including chloro-, dichloro-, trichloromethylsilanes, ethylsilanes, and propylsilanes.

6. The hybrid composite organic-inorganic membrane of claim 1, wherein said amorphous porous layer comprises a single top-layer (STL) made by the decomposition of a silica precursor, wherein said silica precursor selected from the group consisting of phenyltriethoxysilane (PTES), diphenyldiethoxysilane (DPDES), phenyltrimethoxysilane, diphenylmethoxysilane, trimethylmethoxysilane, phenyltrimethoxysilane, and any mixture thereof.

7. The hybrid composite organic-inorganic membrane of claim 1, wherein said amorphous porous layer comprises a single top-layer (STL) made by the decomposition of a silica precursor, wherein said silica precursor selected from the group consisting of phenyltriethoxysilane (PTES), diphenyldiethoxysilane (DPDES), phenyltrimethoxysilane, diphenylmethoxysilane, trimethylmethoxysilane, phenyltrimethoxysilane, and any mixture thereof.
8. The hybrid composite organic-inorganic membrane of claim 1, wherein said amorphous, porous layer comprises a single top-layer (STL) made by the decomposition of phenyltriethoxysilane (PTES).

9. The hybrid composite organic-inorganic membrane of claim 1, wherein said amorphous porous layer comprises a single top-layer (STL) made by the decomposition of diphenylidethoxysilane (DPDES).

10. The hybrid composite organic-inorganic membrane of claim 1, wherein said amorphous porous layer comprises multiple top-layers (MTL) prepared by successive use of a phenyl group precursor, a silica precursor, and any mixture thereof, wherein said phenyl group selected from the group consisting of phenyltriethoxysilane (PTES), diphenylidethoxysilane (DPDES), triphenylethoxysilane (TPES), phenyltrimethoxysilane, diphenylmethoxysilane, phenyltrimethylsilane, diphenylmethyldimethylsilane, triphenylmethoxylsilane, and any combination thereof; said silica precursor selected from the group consisting of alkoxides of silicon, chlorosilanes, and the mixture thereof, wherein said alkoxides of silicon including tetramethylorthosilicates (tetramethoxysilanes), tetraethylorthosilicates (tetraethoxysilanes) and tetrapropylorthosilicates (tetrapropoxysilanes); said chlorosilanes including chloro-, dichloro-, trichloro-methylsilanes, ethylsilanes, and propylsilanes.

11. The hybrid composite organic-inorganic membrane of claim 1, wherein said amorphous porous layer comprises multiple top-layers (MTL) made from the sequential decomposition of phenyltriethoxysilane (PTES) and tetraethylorthosilicate (TEOS).

12. The hybrid composite organic-inorganic membrane of claim 1, wherein said amorphous, porous layer comprises multiple top-layers (MTL) made from the sequential decomposition of diphenylidethoxysilane (DPDES) and tetraethylorthosilicate (TEOS).

13. The hybrid composite organic-inorganic membrane of claim 1, wherein said amorphous porous layer comprises mixed top-layers (XTL) obtained from the simultaneous use of two or more different silica precursors selected from a first group, a second group, and any mixture thereof, wherein said first group consisting of phenyltriethoxysilane (PTES), diphenylidethoxysilane (DPDES), triphenylethoxysilane (TPES), phenyltrimethoxysilane, diphenylmethoxysilane, phenyltrimethylsilane, diphenylmethyldimethylsilane, triphenylmethoxylsilane, and any combination thereof; said second group consisting of alkoxides of silicon, chlorosilanes, and the mixture thereof, wherein said alkoxides of silicon including tetramethylorthosilicates (tetramethoxysilanes), tetraethylorthosilicates (tetraethoxysilanes) and tetrapropylorthosilicates (tetrapropoxysilanes); said chlorosilanes including chloro-, dichloro-, trichloro-methylsilanes, ethylsilanes, and propylsilanes.

14. The hybrid composite organic-inorganic membrane of claim 1, wherein said amorphous porous layer comprises mixed top-layers (XTL) made by the simultaneous decomposition of phenyltriethoxysilane (PTES) and tetraethylorthosilicate (TEOS).

15. The hybrid composite organic-inorganic membrane of claim 1, wherein said amorphous porous layer comprises mixed top-layers (XTL) made by the simultaneous decomposition of diphenylidethoxysilane (DPDES) and tetraethylorthosilicate (TEOS).
providing a porous substrate;
wherein said amorphous porous layer is deposited on said porous substrate by chemical vapor deposition of gaseous precursors in an atmosphere where the concentration of the gas ranges from 1% to 100% at temperature from 673 K to 1173 K.

30. The method for preparing a hybrid composite organic-inorganic membrane of claim 29, wherein said organic functionalities comprise aromatic groups obtained from the group consisting of phenyltrimethoxysilane, diphenyldimethoxysilane, phenyltrimethylsilane, diphenylmethoxysilane, phenyltrimethoxysilane, triphenylmethoxysilane, diphenylmethoxysilane, and any mixture thereof.

31. The method for preparing a hybrid composite organic-inorganic membrane of claim 29, wherein said silica is formed from at least one silica precursor selected from the group consisting of phenyltrimethoxysilane (PTES), diphenyldimethoxysilane (DPDES), triphenylethoxysilane (TPES), phenyltrimethoxysilane, diphenylmethoxysilane, triphenylmethoxysilane, phenyltrimethylsilane, diphenyltrimethoxysilane, triphenylmethyldimethylsilane, and any mixture thereof.

32. The method for preparing a hybrid composite organic-inorganic membrane of claim 29, wherein said silica is formed from at least one silica precursor selected from the group consisting of alkoxydes of silicon, chlorosilanes, and any mixture thereof, wherein said alkoxydes of silicon including tetramethylohlorosilicates (tetramethoxyxilicates), tetraethylchlorosilicates (tetraethoxyxilicates) and tetrapropylchlorosilicates (tetrapropoxyxilicates); said chlorosilanes including chloro-, dichloro-, trichloro-methyl silanes, ethyl silanes, and propylsilanes.

33. The method for preparing a hybrid composite organic-inorganic membrane of claim 29, wherein said amorphous porous layer comprises a single top-layer (STL) made by the decomposition of a silica precursor, wherein said silica precursor selected from the group consisting of phenyltrimethoxysilane (PTES), diphenyldimethoxysilane (DPDES), triphenylethoxysilane (TPES), phenyltrimethoxysilane, diphenylmethoxysilane, triphenylmethoxysilane, phenyltrimethylsilane, diphenyltrimethoxysilane, triphenylmethyldimethylsilane, and any mixture thereof.

34. The method for preparing a hybrid composite organic-inorganic membrane of claim 29, wherein said amorphous porous layer comprises multiple top-layers (MTL) prepared by successive use of a phenyl group precursor, an alkoxides of silicon, chlorosilanes, and the mixture thereof, wherein said alkoxydes of silicon including tetramethylohlorosilicates (tetramethoxyxilicates), tetraethylchlorosilicates (tetraethoxyxilicates) and tetrapropylchlorosilicates (tetrapropoxyxilicates); said chlorosilanes including chloro-, dichloro-, trichloro-methyl silanes, ethyl silanes, and propylsilanes.

35. The method for preparing a hybrid composite organic-inorganic membrane of claim 29, wherein said amorphous porous layer comprises mixed top-layers (XTL) obtained from the simultaneous use of two or more different silica precursors selected from a first group, a second group, and any mixture thereof, wherein said first group consisting of phenyltrimethoxysilane (PTES), diphenyldimethoxysilane (DPDES), triphenylethoxysilane (TPES), phenyltrimethoxysilane, diphenylmethoxysilane, triphenylmethoxysilane, phenyltrimethylsilane, diphenyltrimethoxysilane, triphenylmethyldimethylsilane, and any combination thereof; said second group consisting of alkoxydes of silicon, chlorosilanes, and any mixture thereof, wherein said alkoxydes of silicon including tetramethylohlorosilicates (tetramethoxyxilicates), tetraethylchlorosilicates (tetraethoxyxilicates) and tetrapropylchlorosilicates (tetrapropoxyxilicates); said chlorosilanes including chloro-, dichloro-, trichloro-methyl silanes, ethyl silanes, and propylsilanes.

36. The method for preparing a hybrid composite organic-inorganic membrane of claim 29, wherein said porous substrate comprises at least one layer selected from the group consisting of alumina, titania, silica, zirconia, boria, perovskites, spinels, pyrochlores, zeolites, stainless steel, and any combination thereof.

37. The method for preparing a hybrid composite organic-inorganic membrane of claim 29, wherein said porous substrate comprise multiple graded layers of alumina with a gradually decreasing pore size structure.

38. The method for preparing a hybrid composite organic-inorganic membrane of claim 29, wherein said porous substrate comprise multiple graded layers of alumina with a gradually decreasing pore size structure.

39. The hybrid composite organic-inorganic membrane of claim 22, wherein the permeance at 273 K to 403 K of said membrane for CO₂ is at least 3.0×10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹ and the selectivity for CO₂ with respect to CH₄ is at least 59.

40. The hybrid composite organic-inorganic membrane of claim 24, wherein the permeance for CO₂ is at least 8.7×10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹ from 273 K to 403 K, respectively.

41. The hybrid composite organic-inorganic membrane of claim 25, wherein the permeance for CO₂ is at least 3.0×10⁻⁹ mol m⁻² s⁻¹ Pa⁻¹ at 273 K to 403 K, and the selectivity for CO₂/CH₄ at least 380.

42. The hybrid composite organic-inorganic membrane of claim 26 wherein the permeance for CO₂ is at least 2.0×10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹ at 773 K to 823 K, and the selectivity for H₂/CH₄ is at least 10.

* * * * *
It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Title page, Item (75) Inventors, the last inventor Scott A. Scholten should have residence in Ponca City, OK (US), and should read as follows

--(75) Inventors: Shigeo Ted Oyama, Blacksburg, VA (US);
Yunfeng Gu, Painted Post, NY (US);
Joe D. Allison, Ponca City, OK (US);
Garry C. Gunter, Ponca City, OK (US);
Scott A. Scholten, Ponca City, OK (US)-->.

Signed and Sealed this
Tenth Day of July, 2012

David J. Kappos
Director of the United States Patent and Trademark Office