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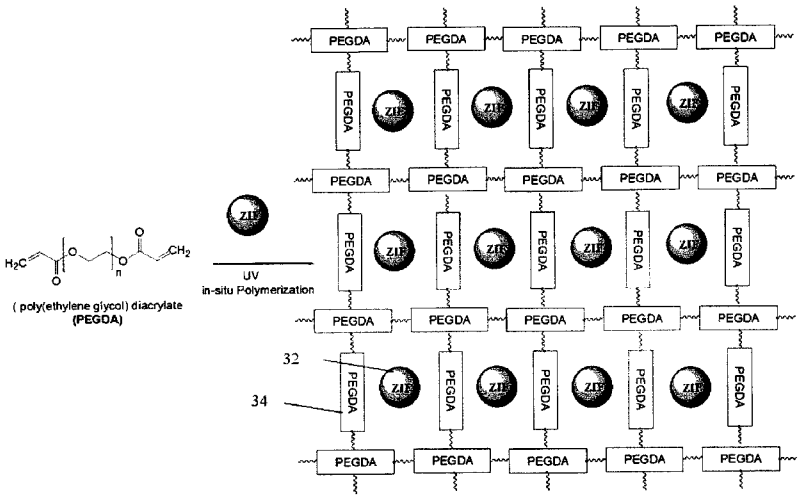


FIG. 3

(57) Abstract: Disclosed is a mixed matrix oligomeric material and methods for making and using the same. The material can include a cross-linked matrix and metal organic framework (MOFs) dispersed in the matrix, wherein the matrix includes cross-linked oligomers having a molecular weight of less than 3000 g/mole, and wherein the oligomers cross-link with one another through cross-linkable groups present on the oligomers.

WO 2017/003661 A1

CROSS-LINKED MIXED MATRIX MEMBRANES BY IN-SITU POLYMERIZATION

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority of U.S. Provisional Patent Application No. 62/187,695, filed July 1, 2015, which is hereby incorporated by reference in its entirety.

BACKGROUND OF THE INVENTION

A. Field of Invention

[0002] The present invention generally relates to cross-linked mixed matrix polymeric membranes formed via in-situ polymerization. By way of example, the membranes can be obtained by exposing a mixture of oligomers and ZIFs to ultraviolet radiation. The resulting mixed matrix membranes have good selectivity and permeability parameters for gas separation applications.

B. Description of Related Art

[0003] A membrane is a structure that has the ability to separate one or more materials from a liquid, vapor or gas. The membrane acts like a selective barrier by allowing some material to pass through (i.e., the permeate or permeate stream) while preventing others from passing through (i.e., the retentate or retentate stream). This separation property has wide applicability in both the laboratory and industrial settings in instances where it is desirable to separate materials from one another (e.g., removal of nitrogen or oxygen from air, separation of hydrogen from gases like nitrogen and methane, recovery of hydrogen from product streams of ammonia plants, recovery of hydrogen in oil refinery processes, separation of methane from the other components of biogas, enrichment of air by oxygen for medical or metallurgical purposes, enrichment of ullage or headspace by nitrogen in inerting systems designed to prevent fuel tank explosions, removal of water vapor from natural gas and other gases, removal of carbon dioxide from natural gas, removal of H2S from natural gas, removal of volatile organic liquids (VOL) from air of exhaust streams, desiccation or dehumidification of air, etc.).

[0004] Examples of membranes include polymeric membranes such as those made from polymers, liquid membranes (e.g., emulsion liquid membranes, immobilized (supported)

liquid membranes, molten salts, etc.), and ceramic membranes made from inorganic materials such as alumina, titanium dioxide, zirconia oxides, glassy materials, etc.

[0005] For gas separation applications, the membrane of choice is typically a polymeric membrane. One of the issues facing polymeric membranes, however, is their well-known trade-off between permeability and selectivity as illustrated by Robeson's upper bound curves (Robeson, *J Membr. Sci.* 1991, 62:165; Robeson, *J Membr. Sci.*, 2008, 320:390-400). In particular, there is an upper bound for selectivity of, for example, one gas over another, such that the selectivity decreases with an increase in membrane permeability.

[0006] Metal-organic frameworks (MOFs) such as zeolitic imidazolate frameworks (ZIFs) have been previously incorporated into polymeric membranes to create mixed matrix membranes. The purpose of the use of MOFs was to increase the permeability of said membranes. These mixed matrix membranes were prepared by blending ZIFs with polymers, in which no chemical reaction between the ZIFs and the polymers occurred. This allowed for an increase in the permeability of the membranes, due to the poor interaction between the ZIFs and polymers at the polymer–zeolite interface. In particular, non-selective interfacial voids were introduced in the membranes such that the voids allowed for increased permeability but decreased selectivity of given materials. This has been referred to as a "sieve-in-a-cage" morphology (Hillock *et al.*, *Journal of Membrane Science.* 2008, 314:193–199). FIGS. 1A-B illustrate prior art membranes exhibiting "sieve in a cage" morphology (Mahajan, *et al., J Appl. Polym. Sci.,* 2002, 86:881).

[0007] Such "sieve-in-a-cage" morphology has resulted in mixed matrix membranes that fail to perform above a given Robeson upper bound trade-off curve. That is, a majority of such membranes fail to surpass the permeability-selectivity tradeoff limitations, thereby making them less efficient and more costly to use. By way of example, PCT Publication WO 2012/159224 describes zeolitic imidazolate framework (ZIF) dispersed in a polydimethylsiloxane (PDMS) matrix for alcohol/water separation. A ZIF-8/6FDA-DAM mixed matrix membrane for propylene/propane separations has been reported by Koros, et al., *Journal of Membrane Science*, 389 (2012) 34-42. A thermal cross-linkable co-polyimide/ZIF-8 mixed matrix membrane for natural gas purification has been reported by Chung, et al., *Journal of Membrane Science*, 444 (2013) 173-183. All of these mixed matrix membranes, which were prepared by blending ZIFs with polymers, had voids or defects due

to the poor affinity between the ZIFs and polymers. Thus, the membranes failed to address the sieve-in-a-cage morphology problems discussed above.

SUMMARY OF THE INVENTION

[0008] A solution to the sieve-in-a-cage morphology problems discussed above has been discovered. The solution is premised on the use of oligomers or prepolymers rather than polymers in preparing mixed matrix membranes having MOFs such as ZIFs. In particular, it was discovered that a mixture of oligomers or prepolymers (e.g., poly(ethylene glycol) diacrylates (PEGDA) having a molecular weight of less than 3000 g/mole) and ZIFs (e.g., ZIF-8 or ZIF-8-90 or a combination thereof) can be subjected to electromagnetic radiation (e.g., ultraviolet (UV) radiation) such that in-situ polymerization of the oligomers occur in the presence of the ZIFs, thereby creating a cross-linked polymeric matrix from the oligomers that also includes ZIFs dispersed within the matrix. The resulting mixed matrix membranes produced from this process have been shown to have gas separation performances that can exceed a given Robeson's upper bound curve. Without wishing to be bound by theory, it is believed that the membranes prepared in this manner have a more consistent and structured interaction between the ZIFs and the polymeric matrix, thereby substantially reducing or even eliminating defects at the ZIF/polymer interface. Thus, the sieve-in-a-cage morphology issues seen with previous membranes can be addressed by the present invention. Furthermore, the cross-linking degree of polymer matrix can be adjusted by blending poly(ethylene glycol) diacrylates with some amount of mono-functional acrylates (e.g., poly(ethylene glycol) methyl ether acrylate (PEGMEA), ethylacrylate (EA), etc.) before the *in situ* polymerization step.

[0009] In one aspect of the present invention there is disclosed a mixed matrix oligomeric material that includes a cross-linked matrix and a metal organic framework (MOFs) dispersed in the matrix. The mixed matrix oligomeric material includes cross-linked oligomers having a molecular weight of less than 3000 g/mole, preferably 500 g/mole to 800 g/mole, and most preferably 725 g/mole to 775 g/mole, and the oligomers cross-link with one another through cross-linkable groups. The mixed matrix oligomeric material can include cross-linked oligomers having a repeating ethylene glycol unit and at least two cross-linkable groups. In some instances, at least two cross-linkable groups can each be an acrylate group and said acrylate group can be a poly(ethylene glycol) diacrylate. In the current embodiments, the MOFs can be zeolitic imidazolate frameworks (ZIFs). ZIFs have attractive properties such as

high specific surface area, temperature stability, and a chemically flexible framework that can be modified with functional group selection. The ZIF of the disclosed mixed matrix oligomeric material can include a methyl imidazole carboxyaldehyde, a methyl imidazole, or a combination thereof. Alternatively, the ZIF can be ZIF-8 or ZIF-8-90, or a combination thereof. The mixed matrix oligomeric material of the current invention can be formed by in-situ cross-linking of a mixture that includes the oligomers and MOFs. The in-situ formation of the mixed matrix oligomeric can include electromagnetic radiation such as, for example, ultraviolet (UV) radiation. The current invention provides a mixed matrix oligomeric material where the majority or substantially all of the cross-linking can be through cross-linkable groups present on the oligomers without the need or requirement of a separate cross-linking agent. The mixed matrix membrane can be characterized by Fourier Transform infrared radiation (FT-(IR) and peaks characteristic of acrylate groups (e.g., peaks at 811, 1196, and 1408 cm^{-1}) are absent or substantially absent. The mixed matrix oligomeric material can be in the form of a thin film membrane, a flat sheet membrane, a spiral membrane, a tubular membrane, or a hollow fiber membrane. The mixed matrix material can be used across a wide range of processes such as gas separation (GS) processes, vapor permeation (VP) processes, pervaporation (PV) processes, membrane distillation (MD) processes, membrane contactors (MC) processes, and carrier mediated processes. In some aspects, the mixed matrix oligomeric material provided is substantially void-free or a majority of the voids in the material is 5 or less Angstroms in diameter.

[0010] In another aspect of the present invention there is disclosed a method for separating at least one component from a mixture of components using the mixed matrix oligomeric material disclosed throughout this specification. In one instance, the process can be used to separate two materials, gases, liquids, compounds, etc. from one another. Such a process includes contacting a mixture of components on a first side of the cross-linked mixed matrix membrane, such that at least a first component is retained on the first side in the form of a retentate and at least a second component is permeated through the material to a second side in the form of a permeate. In this sense, the composition or method could include opposing sides, wherein one side is the retentate side and the opposing side is the permeate side. In particular instances, the process can be directed to removing at least one of N_2, H_2, CH_4, CO_2, C_2H_4, C_2H_6, C_3H_6, and/or C_3H_8 from a mixture. In preferred aspects, the first component can be a first gas, for example hydrogen, and the second component can be a second gas, for example propane, nitrogen, or methane. Alternatively the first gas can be, for example

carbon dioxide, and the second gas can be, for example methane or nitrogen. It one aspect the first gas is an olefin and the second gas is a paraffin, and in a further aspect the olefin is propylene and the second gas is propane. The disclosed method for separating at least one component from a mixture of components using the mixed matrix oligomeric membrane disclosed throughout this specification where a mixture is feed to the mixed matrix oligomeric membrane can be performed at a range of pressure and temperature. The feed pressure of the mixture to the membrane or the pressure at which the mixture is fed to the membrane can be 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 and 20 atmosphere (atm) or more or can range from 1 to 20 atm, 2 to 15 atm, or from 2 to 10 atm. Further the temperature during the separation step can be 20, 25, 30, 35, 40, 45, 50, 55, 60, or 65 °C or more or can range from 20 to 65 °C or from 25 to 65 °C or from 20 to 30 °C. The process can further include removing or isolating either or both of the retentate and/or the permeate from the composition or membrane. The retentate and/or the permeate can be subjected to further processing steps such as a further purification step (*e.g.*, column chromatography, additional membrane separation steps, etc.). Further, it is contemplated that at least 2, 3, 4, 5, or more of the same or different membranes disclosed herein can be used in series with one another to further purify or isolate a targeted liquid, vapor, or gas material. Similarly, the membranes disclosed herein can be used in series with other currently known membranes to purify or isolate a targeted material.

[0011] Also disclosed in the context of the present invention is a gas separation device that includes the current mixed matrix oligomeric material of the present invention. The gas separation device can include an inlet configured to accept feed material, a first outlet configured to expel a retentate, and a second outlet configured to expel a permeate. The gas separation device of can be configured to be pressurized so as to push feed material through the inlet, retentate through the first outlet, and permeate through the second outlet. The gas separation device can be configured to house and utilize a thin film membrane, a flat sheet membrane, a spiral membrane, a tubular membrane, or a hollow fiber membrane or the present invention.

[0012] In another aspect there is disclosed a method of making, *in situ*, the mixed matrix oligomeric materials of the present invention. The method can include subjecting a mixture of metal organic framework (MOFs) and oligomers having a molecular weight of less than 3000 g/mole, preferably 500 g/mole to 800 g/mole, and most preferably 725 g/mole to 775

g/mole, with ultraviolet (UV) radiation and forming an oligomeric matrix having MOFs dispersed in the matrix, wherein the oligomers cross-link with one another through cross-linkable groups present on the oligomer. The oligomeric matrix can be a polymeric matrix in which the polymers are made via polymerization/cross-linking of the oligomers. In a particular embodiment, UV radiation is applied at a wavelength of 400 to 100 nm, preferably 350 to 250 nm, or more preferably from 325 to 275 nm. In one instance, the wavelength used is about 312 nm. Photopolymerization can be performed for 1 hour at 3 mw/cm^2. In certain aspects, the oligomers to be polymerized/cross-linked with one another have a molecular weight of 500 to 800 g/mole or preferably 725 to 775 g/mole. The oligomers can have repeating ethylene glycol units and at least two cross-linkable groups. The at least two cross-linkable groups can each be acrylate groups. In a preferred embodiment, the oligomers can each have a poly(ethylene glycol) diacrylate. In certain aspects, the MOFs can be zeolitic imidazolate frameworks (ZIFs). The ZIFs can be a methyl imidazole carboxyaldehyde, a methyl imidazole, or a combination thereof. In certain preferred embodiments, the ZIFs can be ZIF-8 or ZIF-8-90, or a combination thereof. In some aspects, a majority or substantially all of the cross-linking/polymerization can be through the cross-linkable groups present on the oligomers. Therefore, and in certain aspects, separate cross-linking agents do not have to be used in the context of the present invention. The formed mixed matrix oligomeric material can be used as a thin film membrane, a flat sheet membrane, a spiral membrane, a tubular membrane, or a hollow fiber membrane. In some instances, the produced mixed matrix oligomeric material can be substantially void-free or a majority of the voids in the material is 5 or less Angstroms in diameter.

[0013] In the context of the present invention embodiments 1 to 39 are disclosed. Embodiment 1 is a mixed matrix oligomeric material that includes a cross-linked matrix and metal organic framework (MOFs) dispersed in the matrix, wherein the matrix includes cross-linked oligomers having a molecular weight of less than 3000 g/mole, and wherein the oligomers cross-link with one another through cross-linkable groups present on the oligomers. Embodiment 2 is the mixed matrix oligomeric material of embodiment 1, wherein the oligomers have a molecular weight of 500 to 800 g/mole or preferably 725 to 775 g/mole. Embodiment 3 is the mixed matrix oligomeric material of any one of embodiments 1 to 2, wherein the cross-linked oligomers have a repeating ethylene glycol unit and at least two cross-linkable groups. Embodiment 4 is the mixed matrix oligomeric material of embodiment 3, wherein the at least two cross-linkable groups are each an acrylate group.

Embodiment 5 is the mixed matrix oligomeric material of embodiment 4, wherein the oligomers are each a poly(ethylene glycol) diacrylate. Embodiment 6 is the mixed matrix oligomeric material of any one of embodiments 1 to 5, wherein the MOFs are zeolitic imidazolate frameworks (ZIFs). Embodiment 7 is the mixed matrix oligomeric material of embodiment 6, wherein the imidazole of the ZIFs is a methyl imidazole carboxyaldehyde, a methyl imidazole, or a combination thereof. Embodiment 8 is the mixed matrix oligomeric material of embodiment 7, wherein the ZIFs are ZIF-8 or ZIF-8-90, or a combination thereof. Embodiment 9 is the mixed matrix oligomeric material of any one of embodiments 1 to 8, wherein the material is the reaction product of in-situ cross-linking of a mixture that includes the oligomers and MOFs. Embodiment 10 is the mixed matrix oligomeric material of embodiment 9, wherein ultraviolet (UV) radiation is used for in-situ cross linking. Embodiment 11 is the mixed matrix oligomeric material of any one of embodiments 1 to 10, wherein a majority or substantially all of the cross-linking is through cross-linkable groups present on the oligomers. Embodiment 12 is the mixed matrix oligomeric material of embodiment 11, wherein the material does not include a separate cross-linking agent. Embodiment 13 is the mixed matrix oligomeric material of any one of embodiments 1 to 12, wherein the material is a thin film membrane, a flat sheet membrane, a spiral membrane, a tubular membrane, or a hollow fiber membrane. Embodiment 14 is the mixed matrix oligomeric material of any one of embodiments 1 to 13, wherein the mixed matrix oligomeric material is substantially void-free or a majority of the voids in the material is 5 or less Angstroms in diameter.

[0014] Embodiment 15 is a method for separating at least one component from a mixture of components. The method includes contacting a mixture of components on a first side of the cross-linked mixed matrix material of any one of embodiments 1 to 14, such that at least a first component is retained on the first side in the form of a retentate and at least a second component is permeated through the material to a second side in the form of a permeate. Embodiment 16 is the method of embodiment 15, wherein the first component is a first gas and the second component is a second gas. Embodiment 17 is the method of embodiment 16, wherein the first gas is hydrogen and the second gas is propane, nitrogen, or methane, or wherein the first gas is carbon dioxide and the second gas is methane or nitrogen. Embodiment 18 is the method of embodiment 17, wherein the first gas is an olefin and the second gas is a paraffin. Embodiment 19 is the method of embodiment 18, wherein the olefin is propylene and the second gas is propane. Embodiment 20 is the method of any one of

embodiments 15 to 19, wherein the pressure at which the mixture is feed to the material is from 1 to 20 atm at a temperature ranging from 20 to 65 °C. Embodiment 21 is the method of any one of embodiments 15 to 20, wherein the retentate and/or the permeate is subjected to a purification step.

[0015] Embodiment 22 is a gas separation device that includes the mixed matrix oligomeric material of any one of embodiments 1 to 14. Embodiment 23 is the gas separation device of embodiment 22, further including an inlet configured to accept feed material, a first outlet configured to expel a retentate, and a second outlet configured to expel a permeate. Embodiment 24 is the gas separation device of embodiment 23, configured to be pressurized so as to push feed material through the inlet, retentate through the first outlet, and permeate through the second outlet. Embodiment 25 is the gas separation device of embodiment 24, configured for using a thin film membrane, a flat sheet membrane, a spiral membrane, a tubular membrane, or a hollow fiber membrane.

[0016] Embodiment 26 is a method of making, in-situ, the mixed matrix oligomeric material of any one of embodiments 1 to 14. The method includes (a) subjecting a mixture that includes the metal organic framework (MOFs) and oligomers having a molecular weight of less than 3000 g/mole with ultraviolet (UV) radiation; and (b) forming an oligomeric matrix having MOFs dispersed in the matrix, wherein the oligomers cross-link with one another through cross-linkable groups present on the oligomer. Embodiment 27 is the method the method of embodiment 26, wherein the UV radiation is applied at a wavelength of 312 nm. Embodiment 28 is the method of any one of embodiments 26 to 27, wherein the photopolymerization is performed for 1 hour at 3 mw/cm^2. Embodiment 29 is the method of any one of embodiments 26 to 28, wherein the oligomers have a molecular weight of 500 to 800 g/mole or preferably 725 to 775 g/mole. Embodiment 30 is the method of any one of embodiments 26 to 29, wherein the cross-linked oligomers have a repeating ethylene glycol unit and at least two cross-linkable groups. Embodiment 31 is the method of embodiment 30, wherein the at least two cross-linkable groups are each an acrylate group. Embodiment 32 is the method of embodiment 31, wherein the oligomers are each a poly(ethylene glycol) diacrylate. Embodiment 33 is the method of any one of embodiments 26 to 32, wherein the MOFs are zeolitic imidazolate frameworks (ZIFs). Embodiment 34 is the method of embodiment 33, wherein the imidazole of the ZIFs is a methyl imidazole carboxyaldehyde, a methyl imidazole, or a combination thereof. Embodiment 35 is the method of embodiment

34, wherein the ZIFs are ZIF-8 or ZIF-8-90, or a combination thereof. Embodiment 36 is the method of any one of embodiments 26 to 35, wherein a majority or substantially all of the cross-linking is through cross-linkable groups present on the oligomers. Embodiment 37 is the method of embodiment 36, wherein the material does not include a separate cross-linking agent. Embodiment 38 is the method of any one of embodiments 26 to 37, wherein the mixed matrix oligomeric material is formed into a thin film membrane, a flat sheet membrane, a spiral membrane, a tubular membrane, or a hollow fiber membrane. Embodiment 39 is the method of any one of embodiments 26 to 38, wherein the mixed matrix oligomeric material is substantially void-free or a majority of the voids in the material is 5 or less Angstroms in diameter.

[0017] The term "oligomer" in the context of the present invention refers to a compound having a molecular weight of less than 3000 g/mole, preferably 500 g/mole to 800 g/mole, and most preferably 725 g/mole to 775 g/mole. Dimers, trimers, and tetramers are, for instance, are oligomers composed of two, three and four monomers, respectively. Oligomers, when heated or treated with ultraviolet radiation can polymerize to form a polymer of the oligomers. The term oligomer and prepolymer can be used interchangeably throughout the specification.

[0018] The terms "about," "approximately," and "substantially" are defined as being close to as understood by one of ordinary skill in the art, and in one non-limiting embodiment the terms are defined to be within 10%, preferably within 5%, more preferably within 1%, and most preferably within 0.5%.

[0019] The use of the word "a" or "an" when used in conjunction with the term "comprising" in the claims or the specification may mean "one," but it is also consistent with the meaning of "one or more," "at least one," and "one or more than one."

[0020] The words "comprising" (and any form of comprising, such as "comprise" and "comprises"), "having" (and any form of having, such as "have" and "has"), "including" (and any form of including, such as "includes" and "include") or "containing" (and any form of containing, such as "contains" and "contain") are inclusive or open-ended and do not exclude additional, unrecited elements or method steps.

[0021] The membranes, ingredients, components, compositions, or methods disclosed herein can "comprise," "consist essentially of," or "consist of" particular method steps,

ingredients, components, compositions, etc. disclosed throughout the specification. With respect to the transitional phase "consisting essentially of," in one non-limiting aspect, a basic and novel characteristic of the membranes disclosed herein are their improved selectivity parameters through the reduction of voids between the polymers and MOFs of the mixed matrix membranes.

[0022] Other objects, features and advantages disclosed herein will become apparent from the following figures, detailed description, and examples. It should be understood, however, that the figures, detailed description, and examples, while indicating specific embodiments of the invention, are given by way of illustration only and are not meant to be limiting. Additionally, it is contemplated that changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023] **FIG. 1A** is a schematic representation of an undesirable gap between the polymer matrix and the molecular sieve insert of the prior art, commonly referred to as "sieve in a cage" morphology.

[0024] **FIG. 1B** is a scanning electron microscope (SEM) image f zeolite particles of the prior art exhibiting "sieve-in-a-cage" morphology.

[0025] **FIGS. 2A-2C** are schematics of the synthesis of (A) ZIF-8, (B) ZIF-8-90, and (C) ZIF-8-90-EDA.

[0026] **FIG. 3** is a schematic illustration showing *in situ* polymerization of a mixture of PEGDA and a ZIF to form a cross-linked mixed matrix membrane of the present invention.

[0027] **FIG. 4** is a schematic illustration showing the preparation of the comparative polymeric membrane, cross-linked PEGDA (CL-PEGDA).

[0028] **FIG. 5** is a SEM image of ZIF-8 showing the particle size.

[0029] **FIG. 6** is a X-ray diffraction (XRD) pattern of ZIF-8 as synthesized and as simulated.

[0030] **FIG. 7** are XRD patterns of mixed matrix membrane of the present invention, ZIF-8, and a comparative CL-PEGDA membrane.

[0031] **FIG. 8** are FT-IR spectra of PEGDA, comparative CL-PEGDA, mixed matrix membrane of the present invention, and ZIF-8.

[0032] **FIG. 9** are permeation and separation properties of the mixed matrix membrane of the present invention and a comparative CL-PEGDA membrane for CO_2/N_2 mixtures.

DETAILED DESCRIPTION OF THE INVENTION

[0033] Currently known mixed matrix membranes are prepared using a process that involves blending ZIFs with polymers and/or using cross-linking agents and/or a catalyst, in which some void and/or defect occurred due to the poor affinity between ZIFs and polymers. This leads to performance and cost inefficiencies when using such membranes in applications such as gas separation applications.

[0034] As discussed above, the mixed matrix membranes of the present invention provide a solution to such performance issues. In particular, it has been discovered that in-situ polymerization of a mixture of oligomers and ZIFs can produce mixed matrix membranes having the desired selectivity/permeability parameters for gas separation applications. As shown in a non-limiting embodiment in the Examples, the produced membranes can perform above a given Robeson's upper bound curve. Without wishing to be bound by theory, it is believed that the membranes prepared in this manner have a more consistent and structured interaction between the ZIFs and the polymeric matrix, thereby substantially reducing or even eliminating defects at the ZIF/polymer interface.

[0035] These and other non-limiting aspects of the present invention are discussed in the following subsections.

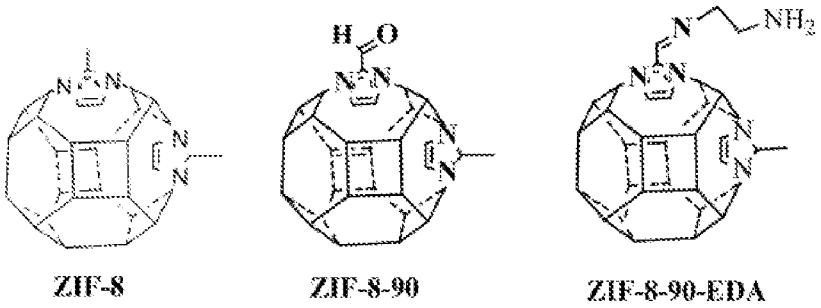
A. Metal-Organic Frameworks

[0036] MOFs are compounds having metal ions or clusters coordinated to organic molecules to form one-, two-, or three-dimensional structures that can be porous. By themselves, MOFs have been demonstrated to have very high gas sorption capacities, which suggest that gases generally will diffuse readily through MOFs if incorporated into a membrane. Zeolitic imidazolate frameworks (ZIFs) are a class of MOFs that are topologically isomorphic with zeolites and can also be used in membrane related applications such as separations, membrane reactors, and chemical sensors. ZIFs are composed of

tetrahedrally-coordinated transition metal ions (e.g. Fe, Co, Cu, Zn) connected by organic imidazole linkers. ZIF crystals are non-toxic and require little energy to create, making them an attractive possibility for carbon capture and storage. ZIFs are chemically and thermally stable materials and like zeolites and other porous materials, ZIF membranes are potentially attractive for the separation of gases because of their highly porous structure, large accessible pore volume with fully exposed edges and faces of the organic links, pore apertures in the range of the kinetic diameter of several gas molecules, and high CO_2 absorption capacity. ZIFs can be prepared with a range of imidazole ligands depending on the intended use of the ZIF.

[0037] In one aspect, ZIF-8 is a MOF prepared from a zinc salt and imidazole ligands (e.g., 2-methylimidazole). In some aspects, the zeolitic imidazolate frameworks are synthesized from zinc salts and mixed imidazole ligands. Non-limiting examples of such frameworks that can be used in the context of the present invention include ZIF-1, ZIF-2, ZIF-3, ZIF-4, ZIF-5, ZIF-6, ZIF-7, ZIF-8, ZIF-9, ZIF-10, ZIF-11, ZIF-12, ZIF-14, ZIF-60, ZIF-62, ZIF-64, ZIF-65, ZIF-67, ZIF-68, ZIF-69, ZIF-70, ZIF-71, ZIF-72, ZIF-73, ZIF-74, ZIF-75, ZIF-76, ZIF-77, ZIF-78, ZIF-79, ZIF-80, ZIF-81, ZIF-82, ZIF-86, ZIF-90, ZIF-91, ZIF-92, ZIF-93, ZIF-95, ZIF-96, ZIF-97, ZIF-100 and hybrid ZIFs, such as ZIF-7-8, ZIF-8-90, or ZIF-8-90-EDA. In some preferred embodiments, ZIF-8, ZIF-8-90, or ZIF-8-90-EDA can be used, with ZIF-8 being most preferred. ZIF-8 membranes display high CO_2 permeability for mixtures of CO_2 and CH_4. In general, it is possible to tune the properties of MOFs for specific applications using methods such as chemical modifications. One approach for chemically modifying a MOF is to use an imidazole that has a pendant functional group to affect the chemical/physical properties of the mixed matrix material or a further modifiable functional group that can be used in post-synthesis modification. In one aspect, ZIFs can contain imidazoles containing a functional groups that can be further modified in the mixed matrix material that can be used in combination with an imidazole that contains non-modifiable functional group or lacks a functional group that can be functionalized in the mixed matrix material, such as for example in ZIF-8, to form a hybrid mixed ZIF, such as ZIF-8-90.

[0038] In some aspects, ZIFs and hybrid ZIFs can be synthesized from zinc slats and imidazoles or mixed imadazoles. FIGS. 2(A)-(C) provide schematics of the synthesis of ZIF-8, ZIF-8-90, and ZIF-8-90-EDA, respectively, each of which have the following structures:



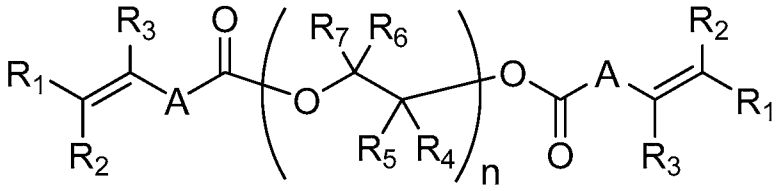
[0039] Other imidazole ligands with or without functional groups that can be functionalized in the mixed matrix material or with latent functional groups that cannot be functionalized to affect the chemical/physical properties of the mixed matrix material can be used in the preparation of ZIFs. These ligands may include, but are not limited to, one or more of imidazole, benzimidazole, 2-methylbenzimidazole, 5-methylbenzimidazole, 2-fluorobenzimidazole, 5-fluorobenzimidazole 2-chlorobenzimidazole, 5-chlorobenzimidazole, 4-azabenzimidazole, 5-azabenzimidazole, purin, 2-nitroimidazole, (1H-imidazol-2-yl)methanol, 4-methyl-5-imidazolecarboxaldehyde, 4-formylimidazole, 5-nitro-1H-benzimidazole, or 4,5-imidazoledicarboxylic acid.

[0040] In another aspect, any MOF either containing an appropriate functional group or that can be functionalized in the manner described herein can be used in the disclosed membranes. Examples include, but are not limited to, IRMOF-3, MOF-69A, MOF-69B, MOF-69C, MOF-70, MOF-71, MOF-73, MOF-74, MOF-75, MOF-76, MOF-77, MOF-78, MOF-79, MOF-80, DMOF-1-NH_2, UMCM-1-NH_2, and MOF-69-80.

[0041] In a further aspect, any zeolite/COF (covalent organic frameworks) either containing an appropriate functional group or that can be functionalized in the manner described herein can be used in the disclosed membranes.

B. Oligomers

[0042] In one aspect the invention, a prepolymer that functions as both as a cross-linker and as an oligomer in mixed matrix material formation is used to prepare the mixed matrix polymeric material. In some aspects of the invention, the oligomer has diacrylate groups that provide the functionality for cross-linking and polymerization. The oligomeric material can have a general structure (I):

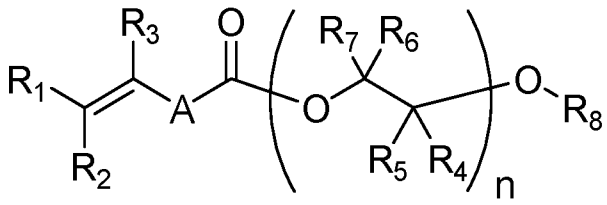


(I)

where n is greater than about 3 and less than about 100. The preferred molecular weight range of the oligomer material is greater than 300 g/mole and less than 4500 g/mole and still more preferably has a molecular weight for example, when R_1, R_2, R_3, R_4, R_5, R_6 or R_7 are all hydrogen, of less than 1000 g/mole where n would be less than 20, preferably 500 g/mole to 800 g/mole where n would be from about 9 to about 16, and most preferably 725 g/mole to 775 g/mole where n would be from about 14 to about 15. The oligomeric material can include a compound of formula (I) where R_1, R_2, R_3, R_4, R_5, R_6 or R_7 represents a hydrogen, an aryl, a cyano, or an alkyl group. The alkyl group may be a straight or branched chain group having from 1 to 10 carbon atoms, and examples include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, t-butyl, pentyl, isopentyl, neopentyl, hexyl, isohexyl, heptyl, octyl, 2-ethylhexyl, nonyl and decyl groups, of which those groups having from 1 to 6 carbon atoms are preferred, methyl and ethyl groups being more preferred and methyl group being most preferred. The aryl group can also be a heteroaryl and substituted with an ionic group, for example, a sulfonate or carboxylic group and a charge balancing cation. However, it is particularly preferred that R_1, R_2, R_3, R_4, R_5, R_6 or R_7 should all represent hydrogen atoms where A represents an alkylene group, this may be a straight or branched chain group having from 1 to 8 carbon atoms, and examples include the methylene, ethylene, propylene, trimethylene, tetramethylene, pentamethylene, hexamethylene, heptamethylene and octamethylene groups and such groups substituted by one or more alkyl groups. However, it is preferred that A should be a direct bond, i.e. compounds of formula (I) containing unsaturated conjugated carboxylic acid end groups that are the same as or different from each other. Specific examples of unsaturated conjugated and non-conjugated acids that may be represented by formula (I) and useful in the current invention include: acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid, 2-pentenoic acid, 3-pentenoic acid, 4-pentenoic acid, 2-hexenoic acid, 3-hexenoic acid, 4-hexenoic acid, 5-hexenoic acid, the heptenoic acids, the octenoic acids, the nonenoic acids, the decenoic acids, the undecenoic acids, the dodecenoic acids, the tridecenoic acids, the tetradecenoic acids, the pentadecenoic acids, the hexadecenoic acids, the heptadecenoic acids, the octadecenoic acids (especially oleic acid), the nonadecenoic acids and the icosenoic acids. Of these, the lower acids having

from 3 to 6 carbon atoms are preferred, acrylic acid and methacrylic acid being most preferred. In one aspect of the invention, the oligomer is poly(ethylene glycol) diacrylate (PEGDA) where the poly(ethylene glycol) diacrylate oligomers having a molecular weight of less than 1000 g/mole, 500 g/mole to 800 g/mole, or 725 g/mole to 775 g/mole or any value or range there between. PEGDA can be prepared from poly(ethylene glycol) diol by reaction thereof with acryloyl chloride or condensation of acrylic acid to form acrylate diesters of poly(ethylene glycol). Alternatively, PEGDA of desired molecular weight can be obtained commercially. A non-limiting example of a commercial source is Sigma Aldrich® (U.S.A).

[0043] In another aspect of the invention, the prepolymer can have a mono-acrylate group that provides the functionality to vary cross-link density of the resulted cross-linked polymeric matrix, or polymerize *in situ* to form an uncross-linked matrix. The oligomeric material can have a general structure (II):



(II)

where n is about from 1 to 100. The preferred molecular weight range of the oligomer material is greater than 200 g/mole and less than 4500 g/mole and still more preferably has a molecular weight for example, when R_1, R_2, R_3, R_4, R_5, R_6 or R_7 are all hydrogen, of less than 1000 g/mole. The oligomeric material can include a compound of formula (II) where R_1, R_2, R_3, R_4, R_5, R_6 or R_7 or R_8 represents a hydrogen, aryl, cyano or an alkyl group, and A is preferably a direct bond.

C. Photopolymerization

[0044] As discussed, current mixed matrix membranes are prepared using a process that involves blending ZIFs with polymers and/or using cross-linking agents and/or a catalyst, in which some void and/or defect has occurred due to the poor affinity between ZIFs and polymers. The prepolymer disclosed in the current embodiments is a photocurable oligomer or oligomers. A photocurable oligomer is an oligomer that changes its properties when exposed to light, often in the ultraviolet or visible region of the electromagnetic spectrum. Photopolymerization is an in-situ polymerization technique that has many advantages over thermal polymerization, including solvent-free systems, spatial and temporal control of

initiation, and high speed processing capabilities. In one aspect, the changes are manifested structurally, to provide a highly structured oligomer composite network as a result of cross-linking when exposed to ultraviolet radiation. Changes in structural and chemical properties can be induced internally by chromophores that are imbedded or part of the prepolymer, or externally by addition of photosensitive molecules. Photopolymerization involves a polymerizable radical or cationic matrix and a more or less complex photoinitiating system (PIS). In the current embodiments, free radical photopolymerization (FRP) using a photoiniator is preferred to cationic photopolymerization (CP). In one aspect a photoinitiator or mixtures of photoinitiators can be used in the current embodiments. Exemplary photoinitiating compounds include acetophenone, anisoin, anthraquinone, anthraquinone-2-sulfonic acid, sodium saltmonohydrate, (benzene) tricarbonylchromium, benzil, benzoin, benzoin ethyl ether, benzoin isobutyl ether, benzoin methyl ether, benzophenone, benzophenone / 1-hydroxycyclohexyl phenyl ketone, 3,3',4,4'-benzophenonetetracarboxylic dianhydride, 4-benzoylbiphenyl, 2-benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone, 4,4' Bis(diethylamino)benzophenone, 4,4'-Bis(dimethylamino)benzophenone, camphorquinone, 2-chlorothioxanthen-9-one, (cumene)cyclopentadienyliron(II) hexafluorophosphate, dibenzosuberenone, 2,2-diethoxyacetophenone, 4,4'-dihydroxybenzophenone, 2,2-dimethoxy-2-phenylacetophenone, 4-(dimethylamino)benzophenone, 4,4'-dimethylbenzil, 2,5-dimethylbenzophenone, 3,4-dimethylbenzophenone, diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide / 2-hydroxy-2-methylpropiophenone, 4'-ethoxyacetophenone, 2-ethylanthraquinone, ferrocene, 3'-hydroxyacetophenone, 4'-hydroxyacetophenone, 3-hydroxybenzophenone, 4-hydroxybenzophenone, 1-hydroxycyclohexyl phenyl ketone, 2-hydroxy-2-methylpropiophenone, 2-methylbenzophenone, 3-methylbenzophenone, methybenzoylformate, 2-methyl-4'-(methylthio)-2-morpholinopropiophenone, phenanthrenequinone, 4'-phenoxyacetophenone, thioxanthen-9-one, triarylsulfonium hexafluoroantimonate salts, and triarylsulfonium hexafluorophosphate salts. In preferred embodiments, a catalytic amount of 1-hydroxylcyclohexyl phenyl ketone (HCPK) is used as the photoinitiator. The wavelength selected to perform the photopolymerization of the oligomer can range based on the absorption of the PIS or photoinitiator. The wavelength can range from about 250 nm to about 450 mn, from about 275 nm to about 425 nm, from about 290 nm to about 400 nm, from about 300 nm to about 350 nm, or preferably from about 310 nm to about 330 nm. Photocurable oligomers undergo a process called curing, where oligomers are cross-linked upon exposure to electromagnetic radiation, forming what is

known as a network polymer. The result of in-situ photopolymerization of the photocurable oligomers in the presence of a ZIF, is the formation of a thermoset network of polymers having a cross-linked mixed matrix containing the ZIF. The free radical mechanism of radiation curable systems light absorbed by a photoinitiator generates free-radicals, which induce cross-linking reactions of a mixture of functionalized oligomers to generate a cured membrane. Photocurable oligomers that form through the free-radical mechanism undergo typical chain-growth polymerization, which includes the steps: initiation, chain propagation, and chain termination, where the propagation step is facilitated by the ethylenically unsaturated functionality of the photocurable oligomers. ZIF and the oligomer can be treated with ultraviolet radiation at a weight ratio of anywhere between from about 0 % wt/wt to about 100% wt/wt of ZIF to oligomer. The ZIF can be mixed, dissolved, or ground with sonication or heat, with the oligomer, followed by the mixture being sandwiched between two quartz plates separated by spacers to control film thickness at a weight/weight ratio of about 1%, of about 2%, of about 3%, of about 4%, of about 5%, of about 6%, of about 7%, of about 8%, of about 9%, or about 10%, of about 11%, of about 12%, of about 13%, of about 14%, of about 15%, of about 16%, of about 17%, of about 18%, of about 19%, or about 20%, of about 21%, of about 22%, of about 23%, of about 24%, of about 25%, of about 26%, of about 27%, of about 28%, of about 29%, or about 30%, of about 31%, of about 32%, of about 33%, of about 34%, of about 35%, of about 36%, of about 37%, of about 38%, of about 39%, or about 40%, of about 41%, of about 42%, of about 43%, of about 44%, of about 45%, of about 46%, of about 47%, of about 48%, of about 49%, or about 50%, of about 51%, of about 52%, of about 53%, of about 54%, of about 55%, of about 56%, of about 57%, of about 58%, of about 59%, or about 60%, of about 61%, of about 62%, of about 63%, of about 64%, of about 65%, of about 66%, of about 67%, of about 68%, of about 69%, or about 70%, of about 71%, of about 72%, of about 73%, of about 74%, of about 75%, of about 76%, of about 77%, of about 78%, of about 79%, or about 80%, of about 81%, of about 82%, of about 83%, of about 84%, of about 85%, of about 86%, of about 87%, of about 88%, of about 89%, or about 90%, of about 91%, of about 92%, of about 93%, of about 94%, of about 95%, of about 96%, of about 97%, of about 98%, or of about 99%, or any weight/weight ratio there between, for example without limitation, from about 30% wt/wt to about 70% wt/wt, or preferably from about 40% wt/wt to about 60% wt/wt, and most preferably from about 45% wt/wt to about 55% wt/wt. Without wishing to be bound by theory, it is believed that a material prepared in this manner provides a highly structured, composite thin film membrane. FIG. 3 is a schematic of the reaction of the ZIF with the oligomer to form the resulting mixed

membrane material. As shown in FIG. 3, the ZIFs (32) are evenly dispersed throughout the polymerized oligomers (34). This dispersion can be attributed to a variety of molecular forces depending of the ZIF employed, for example van der Waals forces. It was found that this mixed membrane material as shown in the Examples section had a gas separation performance superior to that of existing polymer-based membranes. FIG. 4 is an example of a polymeric material obtained through polymerization of the oligomer (34) in the absence of a ZIF. The spaces between the polymeric groups are voids. Without wishing to be bound by theory, it is believed that the ZIFs can fill the voids created during the polymerization and thus reducing the size of the void between the cross-linked polymers. In some embodiments, the mixed matrix material of the present invention is substantially void-free.

D. Membrane Applications

[0045] The membranes of the present invention have a wide-range of commercial applications. For instance, and with respect to the petro-chemical and chemical industries, there are numerous petro-chemical/chemical processes that supply pure or enriched gases such as He, N_2, and O_2, which use membranes to purify or enrich such gases. Further, removal, recapture, and reuse of gases such as CO_2 and H_2S from chemical process waste and from natural gas streams is of critical importance for complying with government regulations concerning the production of such gases as well as for environmental factors. In addition, efficient separation of olefin and paraffin gases is key in the petrochemical industry. Such olefin/paraffin mixtures can originate from steam cracking units (e.g., ethylene production), catalytic cracking units (e.g., motor gasoline production), or dehydration of paraffins. Membranes of the invention can be used in each of these as well as other applications. For instance, and as illustrated in the Examples, the treated membranes are particularly useful for H_2/N_2, H_2/CH_4, or CO_2/CH_4 gas separation applications.

[0046] The membranes of the present invention can be used in the purification, separation or adsorption of a particular species in the liquid or gas phase. In addition to separation of pairs of gases, the membranes can also be used to separate proteins or other thermally unstable compounds. The membranes may also be used in fermenters and bioreactors to transport gases into the reaction vessel and to transfer cell culture medium out of the vessel. Additionally, the membranes can be used to remove microorganisms from air or water streams, water purification, in ethanol production in a continuous fermentation/membrane

pervaporation system, and/or in detection or removal of trace compounds or metal salts in air or water streams.

[0047] In another instance, the membranes can be used in the separation of liquid mixtures by pervaporation, such as in the removal of organic compounds (e.g., alcohols, phenols, chlorinated hydrocarbons, pyridines, ketones) from water such as in aqueous effluents or process fluids. By way of example, a membrane that is ethanol-selective could be used to increase the ethanol concentration in relatively dilute ethanol solutions (e.g., less than 10% ethanol or less than 5% ethanol or from 5 to 10% ethanol) obtained by fermentation processes. A further liquid phase separation example that is contemplated with the compositions and membranes of the present invention includes the deep desulfurization of gasoline and diesel fuels by a pervaporation membrane process (see, e.g., U.S. Pat. No. 7,048,846, which is incorporated by reference). Compositions and membranes of the present invention that are selective to sulfur-containing molecules could be used to selectively remove sulfur-containing molecules from fluid catalytic cracking (FCC) and other naphtha hydrocarbon streams. Further, mixtures of organic compounds that can be separated with the compositions and membranes of the present invention include ethylacetate-ethanol, diethylether-ethanol, acetic acid-ethanol, benzene-ethanol, chloroform-ethanol, chloroform-methanol, acetone-isopropylether, allylalcohol-allylether, allylalcohol-cyclohexane, butanol-butylacetate, butanol-1-butylether, ethanol-ethylbutylether, propylacetate-propanol, isopropylether-isopropanol, methanol-ethanol-isopropanol, and/or ethylacetate-ethanol-acetic acid.

[0048] In particular instances, the membranes of the present invention can be used in gas separation processes in air purification, petrochemical, refinery, natural gas industries. Examples of such separations include separation of volatile organic compounds (such as toluene, xylene, and acetone) from chemical process waste streams and from Flue gas streams. Further examples of such separations include the separation of CO_2 from natural gas, H_2 from N_2, CH_4, and Ar in ammonia purge gas streams, H_2 recovery in refineries, olefin/paraffin separations such as propylene/propane separation, and iso/normal paraffin separations. Any given pair or group of gases that differ in molecular size, for example nitrogen and oxygen, carbon dioxide and methane, hydrogen and methane or carbon monoxide, helium and methane, can be separated using the mixed matrix membranes described herein. More than two gases can be removed from a third gas. For example, some

of the gas components which can be selectively removed from a raw natural gas using the membranes described herein include carbon dioxide, oxygen, nitrogen, water vapor, hydrogen sulfide, helium, and other trace gases. Some of the gas components that can be selectively retained include hydrocarbon gases. In further instances, the membranes can be used on a mixture of gases that include at least 2, 3, 4, or more gases such that a selected gas or gases pass through the membrane (e.g., permeated gas or a mixture of permeated gases) while the remaining gas or gases do not pass through the membrane (e.g., retained gas or a mixture of retained gases).

[0049] Additionally, the membranes of the present invention can be used to separate organic molecules from water (e.g., ethanol and/or phenol from water by pervaporation) and removal of metal (e.g., mercury(II) ion and radioactive cesium(I) ion) and other organic compounds (e.g., benzene and atrazene) from water.

[0050] A further use of the membranes of the present invention includes their use in chemical reactors to enhance the yield of equilibrium-limited reactions by selective removal of a specific product in an analogous fashion to the use of hydrophilic membranes to enhance esterification yield by the removal of water.

[0051] The membranes of the present invention can also be fabricated into any convenient form such as sheets, tubes, spiral, or hollow fibers. They can also be fabricated into thin film composite membranes incorporating a selective thin layer that has been UV- and thermally-treated and a porous supporting layer comprising a different polymer material.

[0052] Further, it is contemplated that at least 2, 3, 4, 5, or more of the same or different membranes disclosed herein can be used in series with one another to further purify or isolate a targeted liquid, vapor, or gas material. Similarly, the membranes disclosed herein can be used in series with other currently known membranes to purify or isolate a targeted material.

[0053] Table 1 includes some particular non-limiting gas separation applications of the present invention.

Table 1

Gas Separation	Application
O_2/N_2	Nitrogen generation, oxygen enrichment
H_2/hydrocarbons	Refinery hydrocarbon recovery
H_2/CO	Syngas ratio adjustment
H_2/N_2	Ammonia purge gas
CO_2/hydrocarbon	Acid gas treating, enhanced oil recovery, landfill gas upgrading, pollution control
H_2S/hydrocarbon	Sour gas treating
H_2O/hydrocarbon	Natural gas dehydration
H_2O/air	Air dehydration
Hydrocarbons/air	Pollution control, hydrocarbon recovery
Hydrocarbons from process streams	Organic solvent recovery, monomer recovery
Olefin/paraffin	Refinery

EXAMPLES

[0054] The following examples are included to demonstrate certain non-limiting aspects of the invention. It should be appreciated by those of skill in the art that the techniques disclosed in the examples that follow represent techniques discovered by the applicants to function well in the practice of the invention. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments that are disclosed and still obtain a like or similar result without departing from the spirit and scope of the invention.

Materials and Testing

[0055] Zn(NO3)2·6H2O (≥99%, Sigma Aldrich®, U.S.A.), 2-methylimidazole (99%, Aldrich), poly(ethylene glycol) diacrylate (PEGDA, Mn = 700 g/mole, Aldrich) and solvents were used without further purification. X-ray diffraction (XRD) patterns were measured from a Bruker D8 Advance X-ray Diffractometer with CuKα radiation λ = 0.154056 nm. Scanning electron microscopy (SEM) images were obtained from a scanning electron microscope (SEM, Quantum 600, FEI) operating at 10 kV. The specific surface area and pore size of synthesized ZIF-8 particles were analyzed using Brunauer Emmet and Teller (BET) and HK nitrogen gas adsorption and desorption methods (ASAP 2020, Micromeritics, USA). Prior to the measurement the sample was degassed at 120 °C for 24 hours under vacuum. Sonication was performed using an ultrasonic cleaner (Model 8893, Cole-Parmer). Fourier transform infrared spectra (FT-IR) were acquired using a NICOLET-6700 FT-IR

spectrometer. Single-gas permeation was carried out by the vacuum permeation method. IS THIS A STANDARD METHOD?

Example 1
(Synthesis of ZIF-8 particles in methanol)

[0056] A solution of Zn(NO3)2·6H2O (5 g, 16.8 mmol) in 100 mL of methanol was rapidly poured into a solution of 2-methylimidazole (12 g, 146.2 mmol) in 150 mL of methanol under stirring. The mixture slowly turns turbid and after 3 h the particles are separated from the milky dispersion by centrifugation and washed 3 times with fresh methanol. The particles are dried at 100 °C under vacuum. The particle size is around 100 nm (FIG. 5). Its structure is confirmed by XRD (FIG. 6), which was the same as a simulated XRD pattern for ZIF-8. The BET surface area of the particles is around 1660.8 m2/g.

Example 2
(Preparation of comparative cross-linked poly(ethylene glycol diacrylate) membrane (CL-PEGDA))

[0057] A comparative sample of the cross-linked oligomer was prepared. Poly(ethylene glycol) diacrylate (PEGDA, 2 g, MW = 743 g/mole) and 1-hydroxylcyclohexyl phenyl ketone (HCPK, 2 mg) were mixed and stirred for 5 hours, and then sonicated for 45 minutes to eliminate bubbles. After sonication, the mixture was sandwiched between two quartz plates separated by spacers to control film thickness. The mixture was then polymerized by exposure to 312 nm UV light in a UV cross-linker apparatus (Model FB-UVXL-1000, Fisher Scientific) for 1 hour at 3 mw/cm^2. A colorless transparent film was obtained.

Example 3
(Preparation of mixed matrix membrane by *in situ* polymerization)

[0058] Poly(ethylene glycol) diacrylate (PEGDA, 2 g, MW = 743 g/mole), ZIF-8 (1 g, 2:1 ratio of oligomer to ZIF-8) and 1-hydroxylcyclohexyl phenyl ketone (HCPK, 2 mg) are mixed and stirred for 5 hours. Then the mixture was sonicated for 45 minutes to eliminate bubbles. After sonication, the mixture was sandwiched between two quartz plates separated by spacers to control film thickness. The mixture was then polymerized by exposure to 312 nm UV light in a UV Crosslinker reactor (Model FB-UVXL-1000, Fisher Scientific) for 1 hour at 3 mw/cm^2. A white film was obtained. FIG. 7 shows the XRD patterns of mixed matrix membrane, ZIF-8 and cross-linked poly(ethylene glycol diacrylate). From analysis of the XRD patterns, it was confirmed that the ZIF-8 particles in the mixed matrix membrane

are stable under the polymerization condition as the XRD pattern of the mixed matrix membrane of the present invention and the XRD pattern of the ZIF-8 of Example 1 were similar. FIG. 8 are FT-IR overlay spectra for PEGDA, cross-linked PEGDA membrane (CL-PEGDA), mixed matrix membrane and ZIF-8. The peaks at 811, 1196, and 1408 cm^{-1} are attributed to the characteristic peaks for the acrylate groups of monomer PEGDA. Such peaks are absent in the FT-IR spectra of the comparative CL-PEGDA and mixed matrix membrane, which indicates that the reaction conversion of PEGDA was high under photocatalytic conditions. Thus, it was concluded that the ZIF does not interfere in the polymerization of the oligomer (prepolymer).

Example 4
(Permeability and selectivity data)

[0059] The gas transport properties were measured using the variable pressure (constant volume) method. Ultrahigh-purity gases (99.99%) were used for all experiments. The membrane is mounted in a permeation cell prior to degassing the whole apparatus. Permeant gas is then introduced on the upstream side, and the permeant pressure on the downstream side is monitored using a pressure transducer. From the known steady-state permeation rate, pressure difference across the membrane, permeable area and film thickness, the permeability coefficient is determined (pure gas tests). The permeability coefficient, P [cm^3(STP)·cm/cm^2·s·cmHg], is determined by the following equation:

$$\mathbf{P} = \frac{\mathbf{1}}{\mathbf{760}} \times \frac{\mathbf{V}}{\mathbf{A}} \times \frac{\mathbf{273}}{\mathbf{273 + T}} \times \frac{\mathbf{L}}{\mathbf{760p}} \times \frac{\mathbf{dp}}{\mathbf{dt}}$$

where A is the membrane area (cm^2), L is the membrane thickness (cm), p is the differential pressure between the upstream and the downstream (MPa), V is the downstream volume (cm^3), R is the universal gas constant (6236.56 cm3·cmHg/mol·K), T is the cell temperature (°), and dp/dt is the permeation rate.

[0060] The gas permeabilities of polymer membranes are characterized by a mean permeability coefficient with units of Barrer. 1 Barrer = 10-10 cm^3(STP) ·cm/cm^2·s·cmHg. The gas permeability coefficient can be explained on the basis of the solution-diffusion mechanism, which is represented by the following equation:

$$P = D \times S$$

where D (cm^2/s) is the diffusion coefficient; and S (cm3 (STP)/ cm3·cmHg) is the solubility coefficient.

[0061] The diffusion coefficient was calculated by the time-lag method, represented by the following equation:

$$\mathbf{D} = \frac{\mathbf{L}^2}{\mathbf{6\theta}}$$

where θ(s) is the time-lag. Once P and D were calculated, the apparent solubility coefficient S (cm^3(STP)/ cm^3·cmHg) may be calculated by the following expression:

$$\mathbf{S} = \frac{\mathbf{P}}{\mathbf{D}}$$

[0062] In gas separation, the membrane selectivity is used to compare the separating capacity of a membrane for 2 (or more) species. The membrane selectivity for one component (A) over another component (B) is given by the ratio of their permeabilities:

$$\alpha_{A/B} = \frac{P_A}{P_B}$$

[0063] Selectivity obtained from ratio of pure gas permeabilities is called the ideal membrane selectivity or the ideal permselectivity. This is an intrinsic property of the membrane material. The ideal selectivity of a dense membrane for gas A to gas B is defined as follows:

$$\alpha = \frac{P_A}{P_B} = \frac{D_A}{D_B} * \frac{S_A}{S_B}$$

[0064] Table 2 shows gas permeability of the mixed matrix membrane measured at 21 °C, 2 Bar and compared to the comparative CL-PEGDA membrane. FIG. 9 shows graphs of CO_2/N_2 ideal selectivity versus CO_2 pressure in Barreres. This data represents the permeation and separation performance of mixed matrix membrane and a comparative CL-PEGDA membrane for CO_2/N_2 mixtures. The black line represents the Robeson upper bound limit for the polymers. From analysis of the data in Table 2 and FIG. 9, it was concluded that the mixed matrix membrane of the present invention surpass the Robeson upper bound permeability-selectivity of the comparative material.

Table 2

	Permeability (Barrier)				Ideal Selectivity					Thick-ness (μm)
Sample	N_2	CH_4	H_2	CO_2	CH_4/N_2	H_2/N_2	H_2/CH_4	CO_2/CH_4	CO_2/N_2	
Example 2	1.32	3.69	10.68	97.47	2.80	8.09	2.89	26.4	73.86	128
Example 3	4.91	14.29	51.50	334.95	2.91	10.50	3.61	23.45	68.27	202

CLAIMS

1. A mixed matrix oligomeric material comprising a cross-linked matrix and metal organic framework (MOFs) dispersed in the matrix, wherein the matrix includes cross-linked oligomers having a molecular weight of less than 3000 g/mole, and wherein the oligomers cross-link with one another through cross-linkable groups present on the oligomers.

2. The mixed matrix oligomeric material of claim 1, wherein the oligomers have a molecular weight of 500 to 800 g/mole or preferably 725 to 775 g/mole.

3. The mixed matrix oligomeric material of claim 1, wherein the cross-linked oligomers have a repeating ethylene glycol unit and at least two cross-linkable groups.

4. The mixed matrix oligomeric material of claim 3, wherein the at least two cross-linkable groups are each an acrylate group, preferably, a poly(ethylene glycol) diacrylate group.

5. The mixed matrix oligomeric material of claim 1, wherein the MOFs are zeolitic imidazolate frameworks (ZIFs).

6. The mixed matrix oligomeric material of claim 5, wherein the imidazole of the ZIFs is a methyl imidazole carboxyaldehyde, a methyl imidazole, or a combination thereof.

7. The mixed matrix oligomeric material of claim 6, wherein the ZIFs are ZIF-8 or ZIF-8-90, or a combination thereof.

8. The mixed matrix oligomeric material of claim 1, wherein the material is the reaction product of in-situ cross-linking of a mixture comprising the oligomers and MOFs.

9. The mixed matrix oligomeric material of claim 1, wherein a majority or substantially all of the cross-linking is through cross-linkable groups present on the oligomers.

10. The mixed matrix oligomeric material of claim 9, wherein the material does not include a separate cross-linking agent.

11. The mixed matrix oligomeric material of claim 1, wherein the mixed matrix oligomeric material is substantially void-free or a majority of the voids in the material are 5 or less Angstroms in diameter.

12. A method for separating at least one component from a mixture of components, the method comprising contacting a mixture of components on a first side of the cross-linked mixed matrix material of claim 1, such that at least a first component is retained on the first side in the form of a retentate and at least a second component is permeated through the material to a second side in the form of a permeate.

13. The method of claim 12, wherein the first component is a first gas and the second component is a second gas.

14. The method of claim 13, wherein the first gas is hydrogen and the second gas is propane, nitrogen, or methane, or wherein the first gas is carbon dioxide and the second gas is methane or nitrogen.

15. The method of claim 14, wherein the first gas is an olefin, preferably, propylene, and the second gas is a paraffin, preferably, propane

16. A gas separation device comprising the mixed matrix oligomeric material of claim 1.

17. A method of making, in-situ, the mixed matrix oligomeric material of claim 1, the method comprising:

(a) subjecting a mixture comprising metal organic framework (MOFs) and oligomers having a molecular weight of less than 3000 g/mole to ultraviolet (UV) radiation; and

(b) forming an oligomeric matrix having MOFs dispersed in the matrix, wherein the oligomers cross-link with one another through cross-linkable groups present on the oligomer.

18. The method of claim 17, wherein the UV radiation is applied at a wavelength of 312 nm.

19. The method of claim 17, wherein the photopolymerization is performed for 1 hour at 3 mw/cm^2.

20. The method of claim 17, wherein the oligomers have a molecular weight of 500 to 800 g/mole or preferably 725 to 775 g/mole.

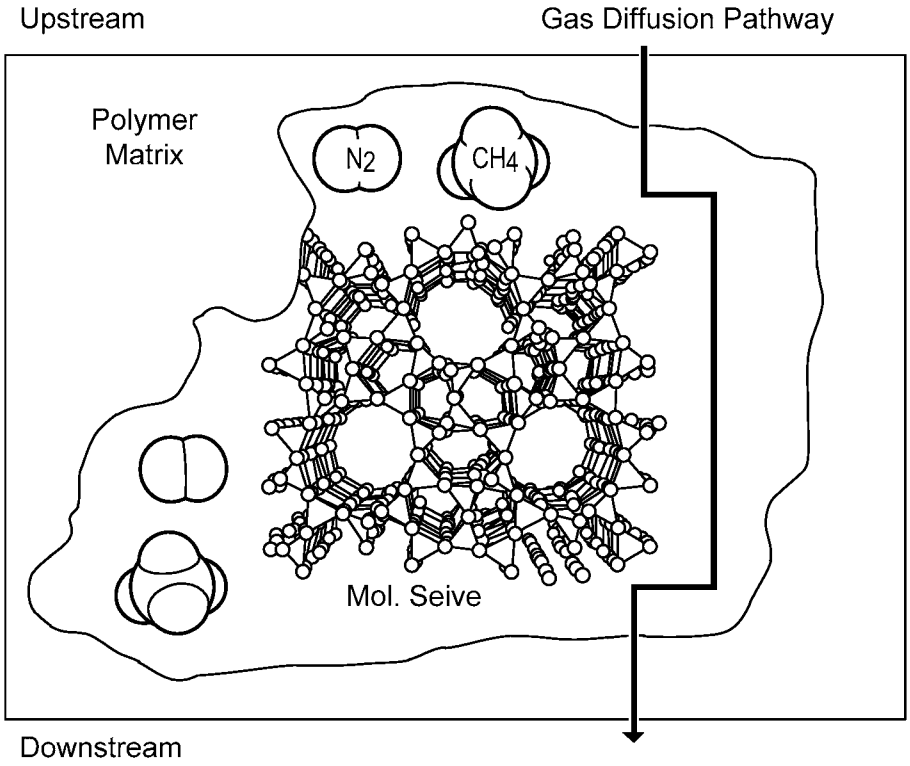


FIG. 1A
(Prior Art)

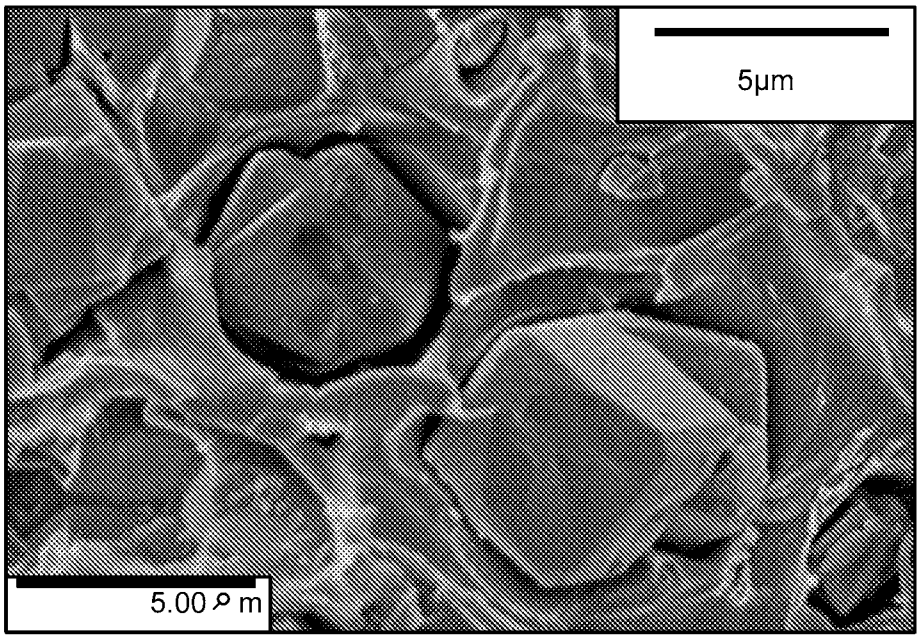


FIG. 1B
(Prior Art)

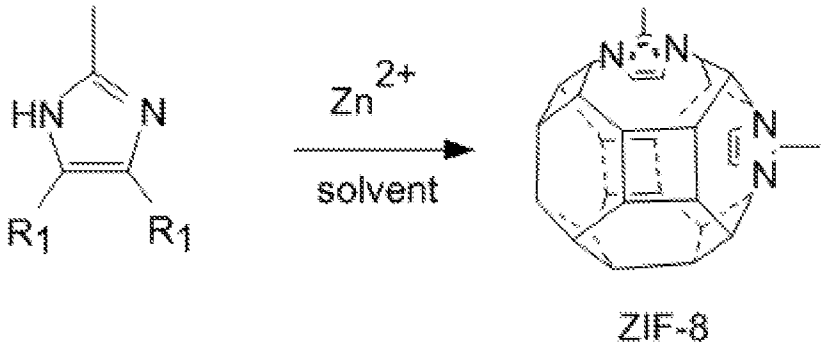


FIG. 2A

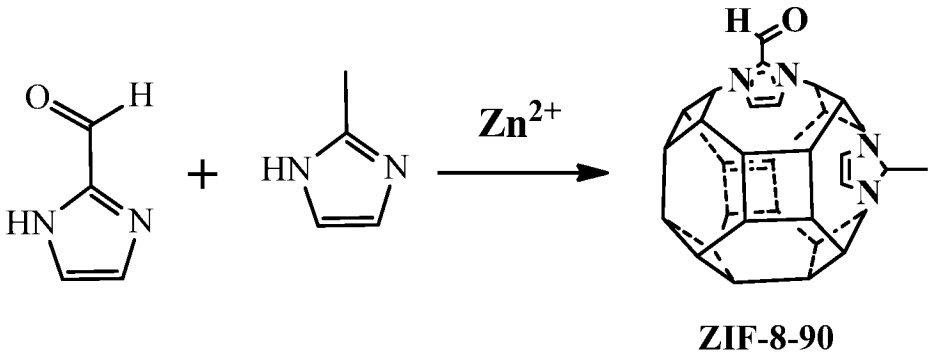


FIG. 2B

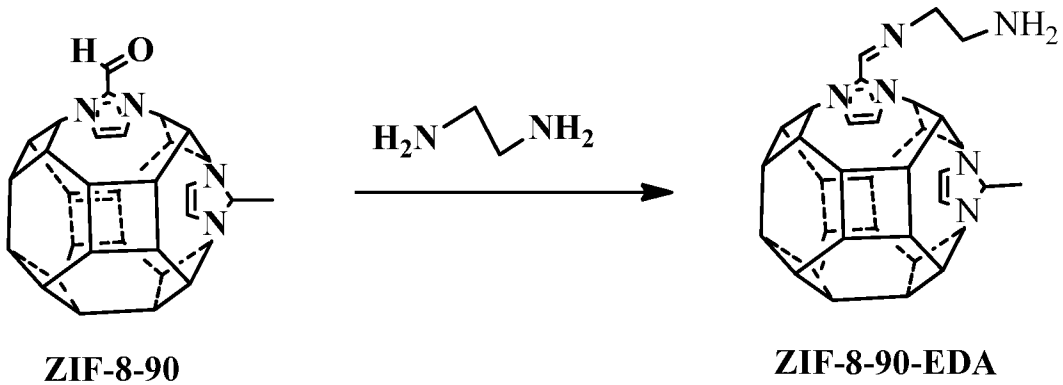


FIG. 2C

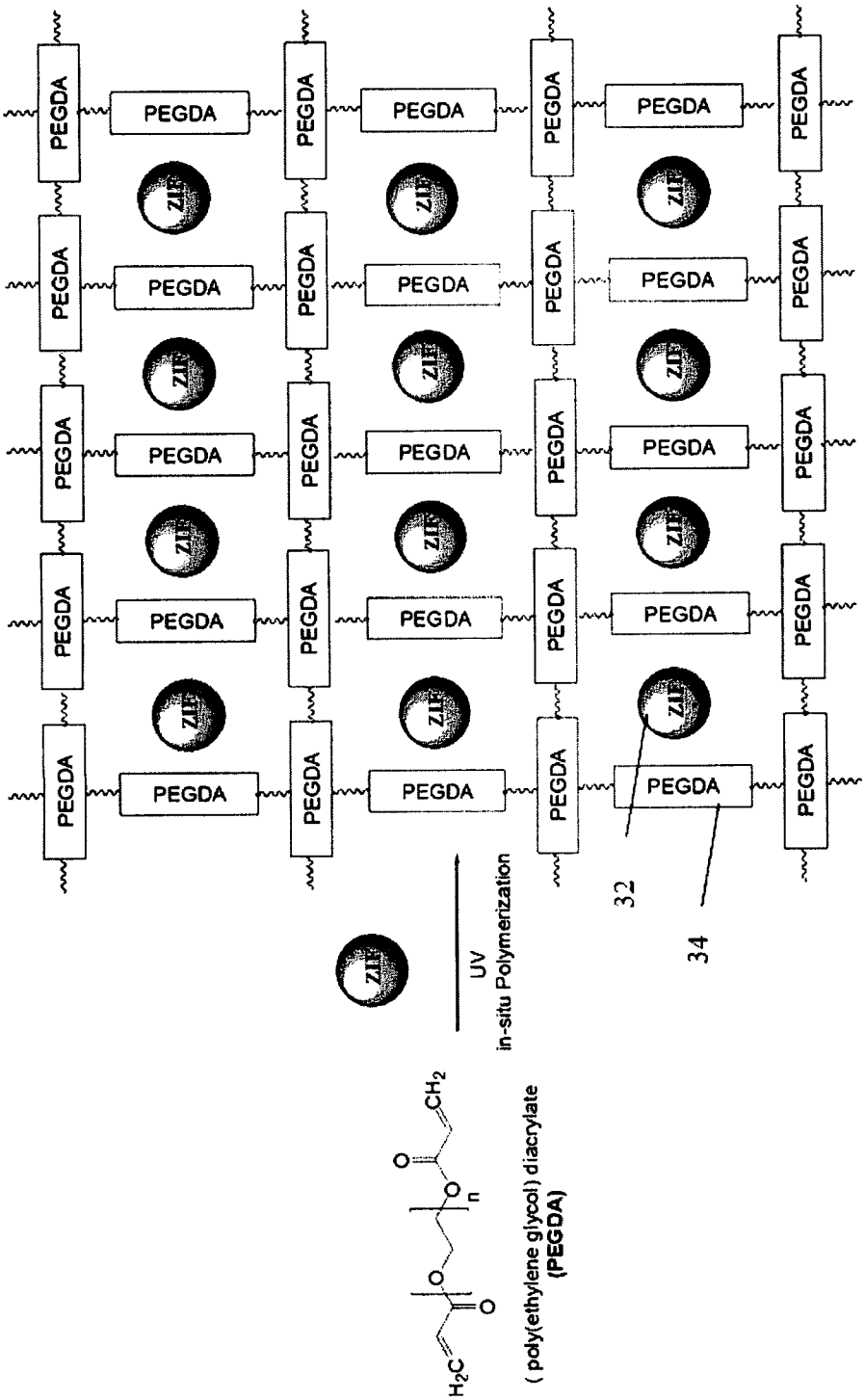

PEGDA
ZIF
UV
in-situ Polymerization
32
34
(polyethylene glycol) diacrylate
(PEGDA)

FIG. 3

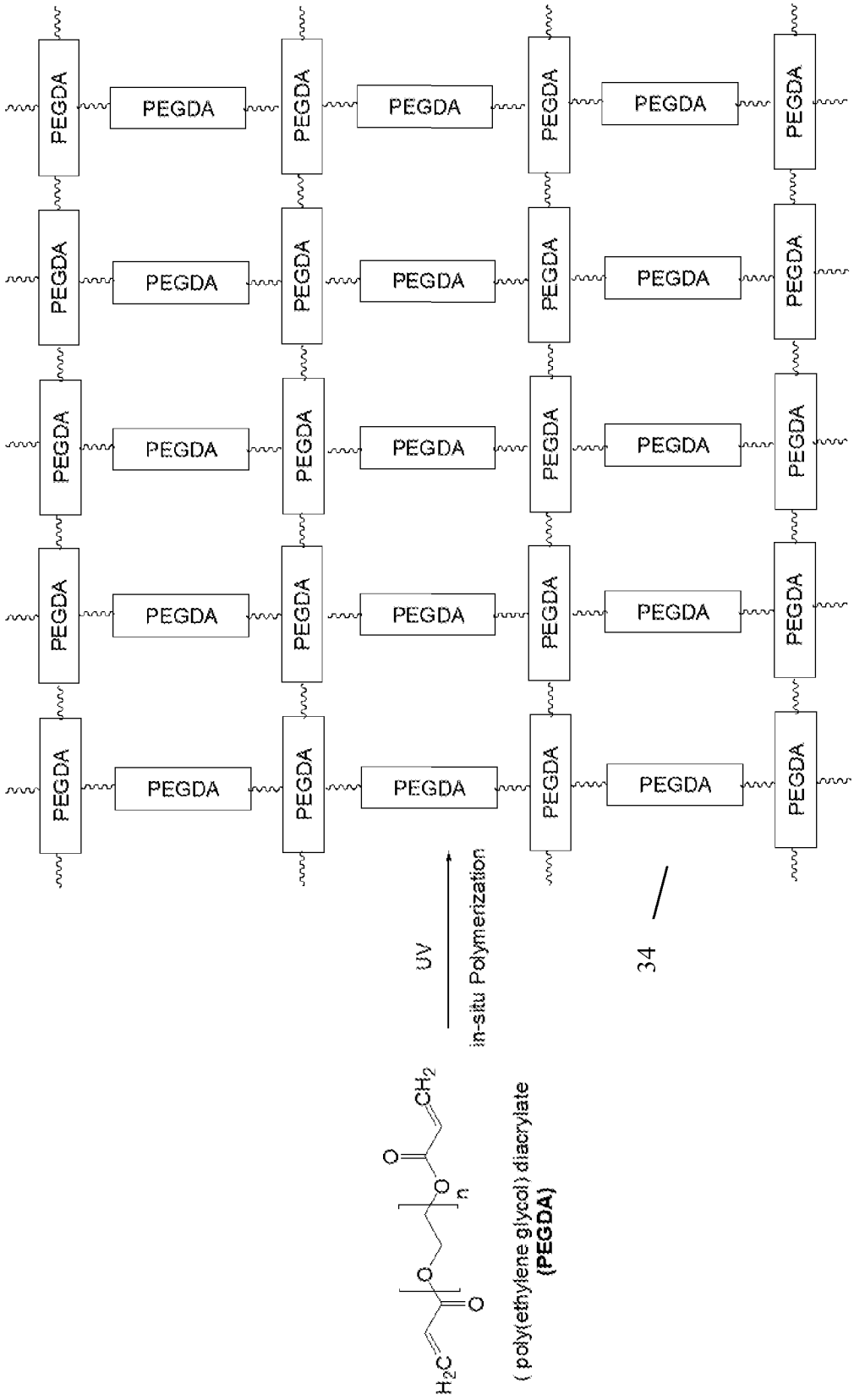

PEGDA
UV
in-situ Polymerization
34
(polyethylene glycol) diacrylate
(PEGDA)

FIG. 4

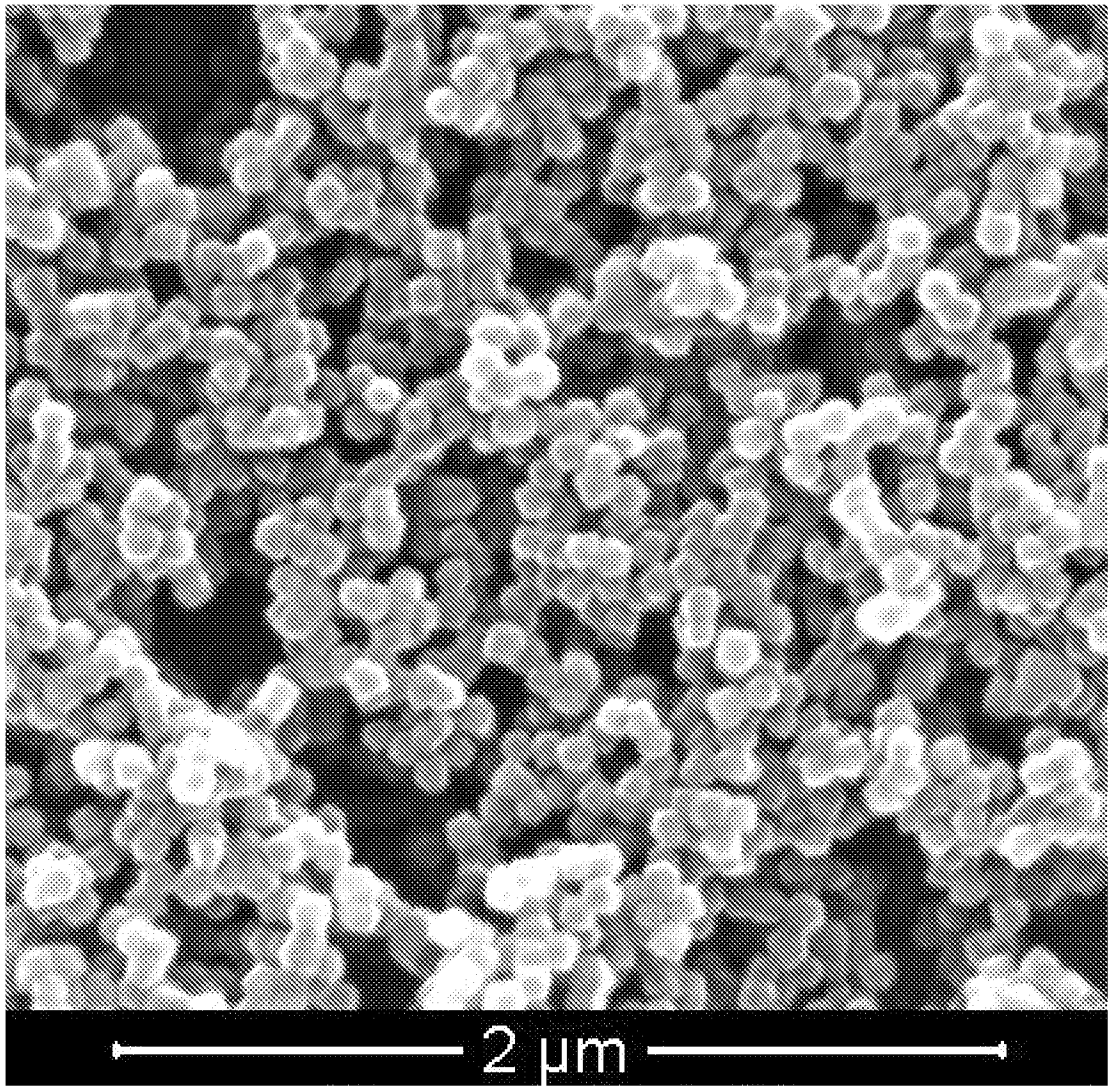


FIG. 5

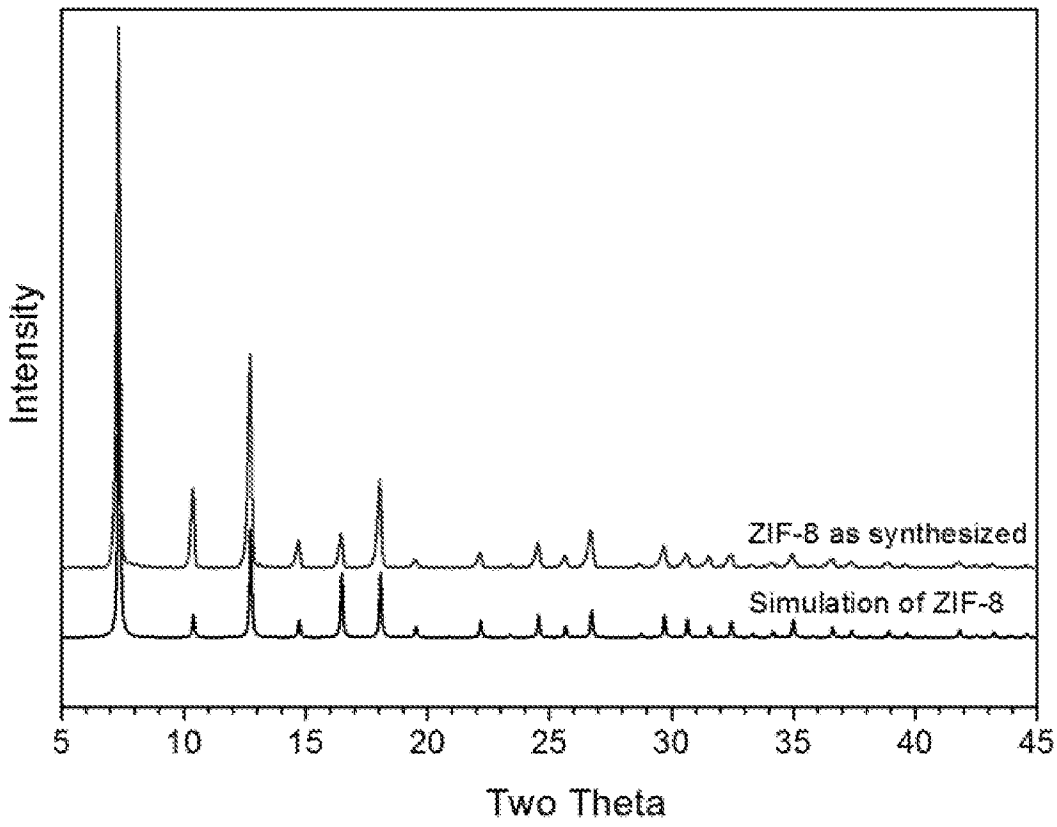

Intensity
ZIF-8 as synthesized
Simulation of ZIF-8
5
10
15
20
25
30
35
40
45
Two Theta

FIG. 6

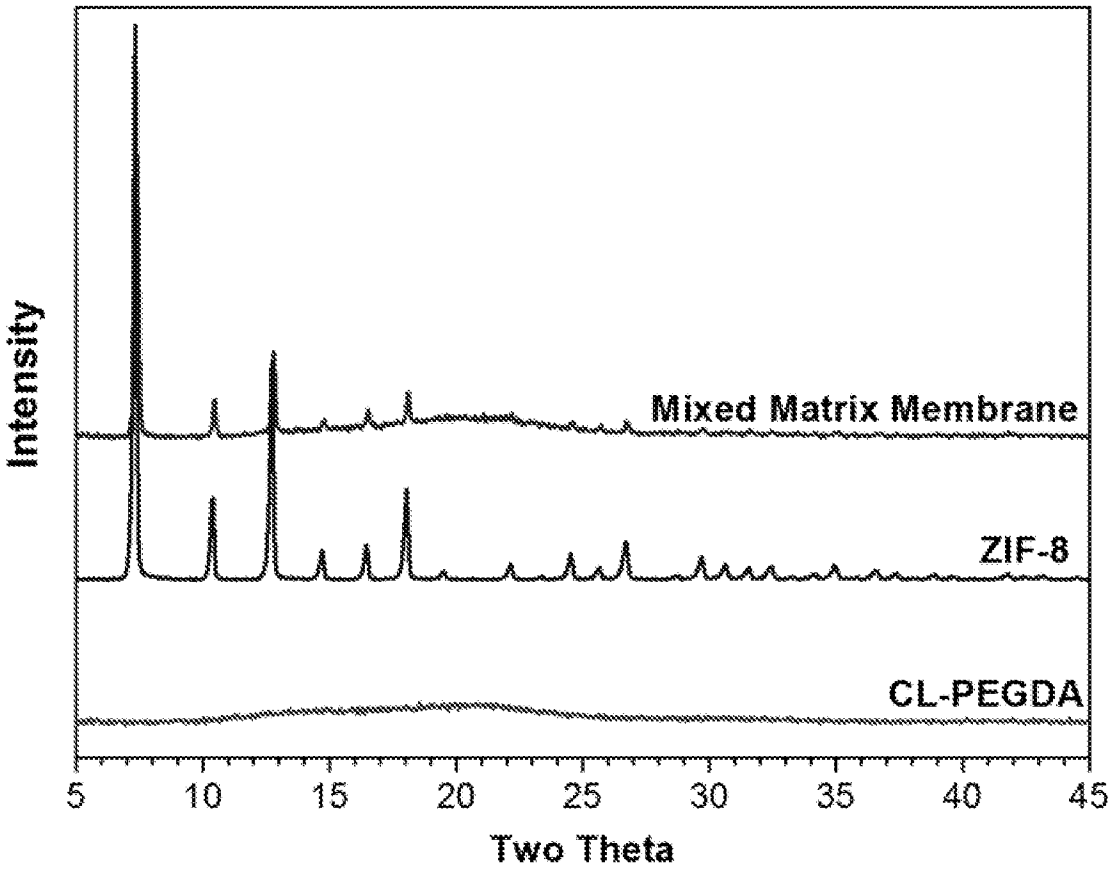

Intensity
Mixed Matrix Membrane
ZIF-8
CL-PEGDA
5
10
15
20
25
30
35
40
45
Two Theta

FIG. 7

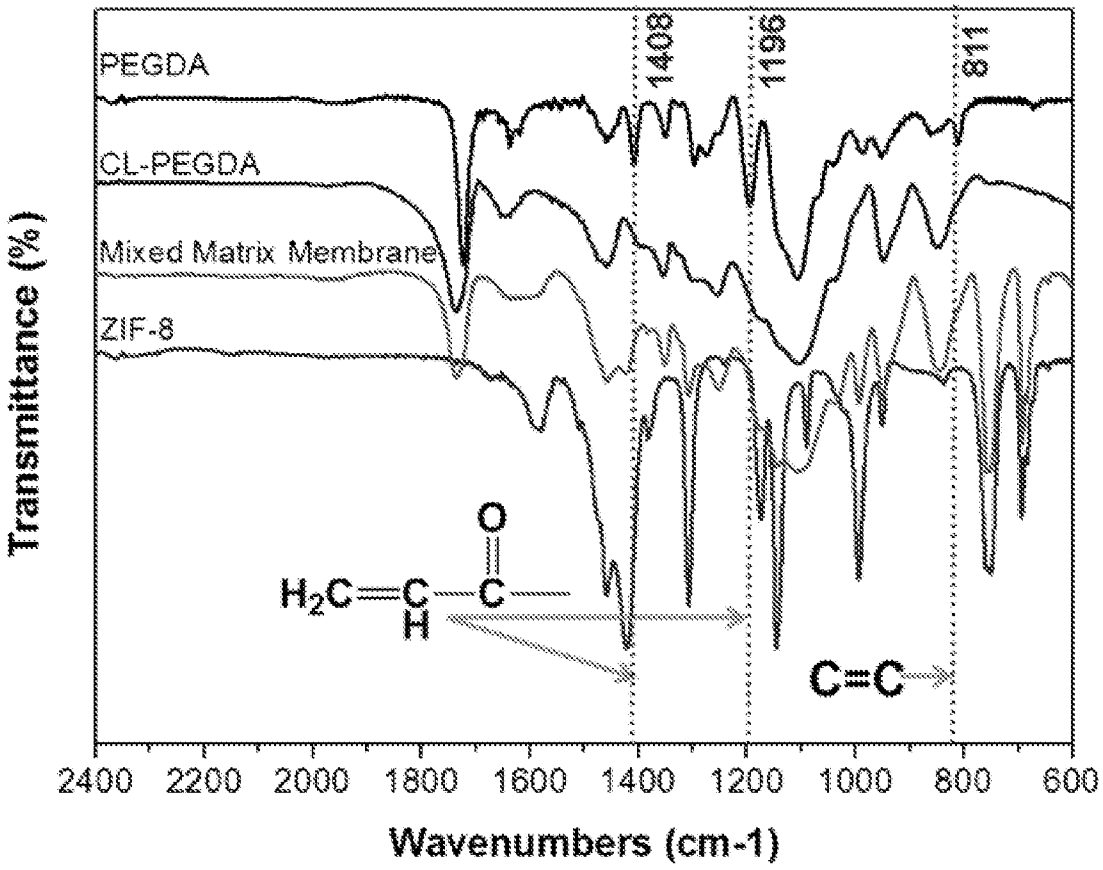

PEGDA
CL-PEGDA
Mixed Matrix Membrane
ZIF-8
1408
1196
811
Transmittance (%)
2400 2200 2000 1800 1600 1400 1200 1000 800 600
Wavenumbers (cm-1)
C=C

FIG. 8

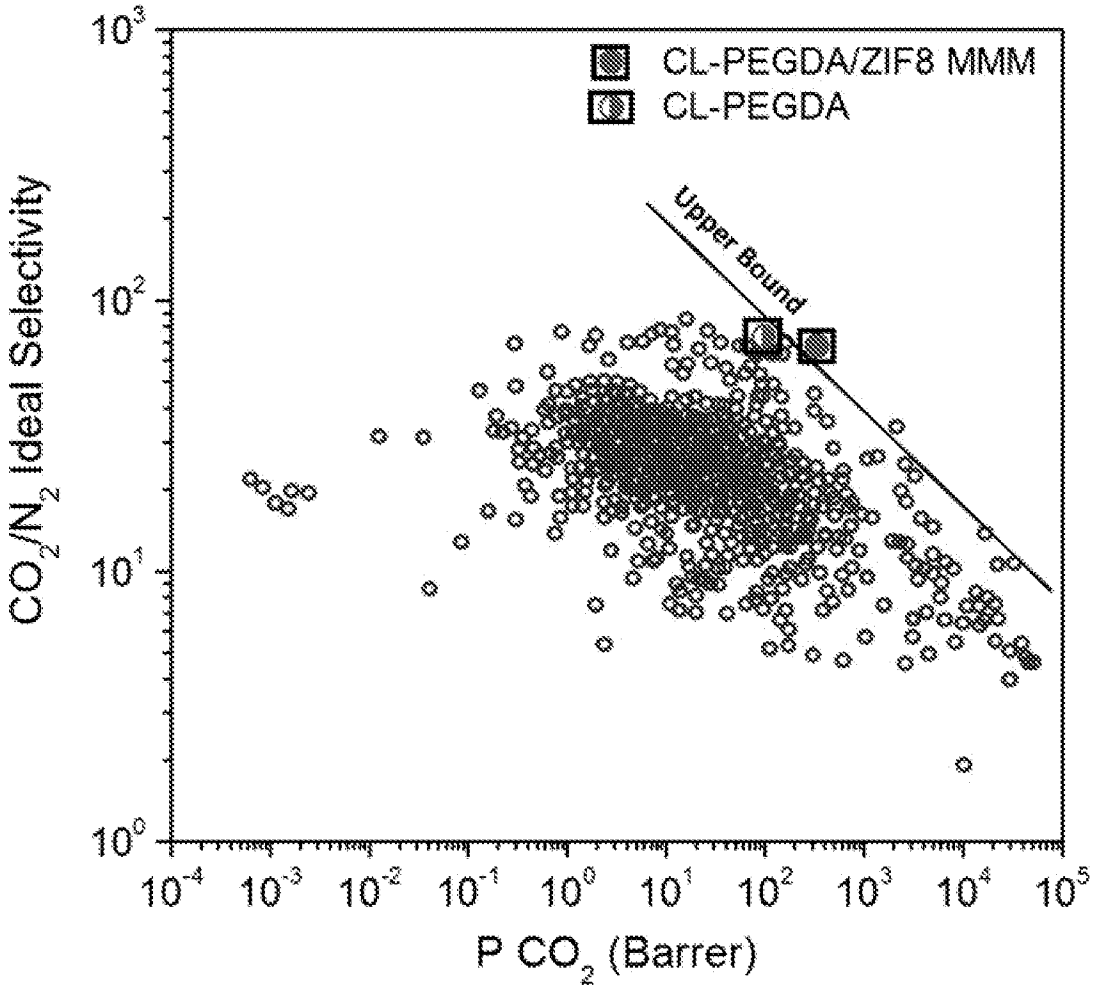

CL-PEGDA/ZIF8 MMM
CL-PEGDA
Upper Bound
CO_2/N_2 Ideal Selectivity
P CO_2 (Barrer)
10^0
10^1
10^2
10^3
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^4
10^5

FIG. 9

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/036726

A. CLASSIFICATION OF SUBJECT MATTER

C08J 5/20(2006.01)I, B01D 69/14(2006.01)I, C08J 3/24(2006.01)I, C08J 3/28(2006.01)I, C08F 8/42(2006.01)I, B01J 20/18(2006.01)I, B01J 20/22(2006.01)I, B01J 20/28(2006.01)I

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08J 5/20; B01D 63/00; B01D 71/40; B01D 69/12; C08J 9/36; B01D 71/06; B01D 69/14; C08J 3/24; C08J 3/28; C08F 8/42; B01J 20/18; B01J 20/22; B01J 20/28

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: mixed matrix oligomeric material, cross-linked matrix, metal organic framework, gas separation, ultraviolet radiation

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	HILLOCK et al., Crosslinked mixed matrix membranes for the purification of natural gas: Effects of sieve surface modification, Journal of Membrane Science, 2008, Vol. 314, No. 1, pp. 193-199 See abstract; and pages 193-199.	1-20
Y	HUNGER et al., Investigation of cross-linked and additive containing polymer materials for membranes with improved performance in pervaportion and gas separation, Membranes, 2012, Vol. 2, No. 4, pp. 727-763 See abstract; and pages 727-752.	1-20
A	ORDONEZ et al., Molecular sieving realized with ZIF-8/Matrimid□ mixed-matrix membranes, Journal of Membrane Science, 2010, Vol. 361, No. 1, pp. 28-37 See abstract; and pages 28-36.	1-20
A	US 7758751 B1 (LIU et al.) 20 July 2010 See the whole document.	1-20

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
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"E" earlier application or patent but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 August 2016 (24.08.2016)	**24 August 2016 (24.08.2016)**

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/036726

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	REZAKAZEMI et al., State-of-the-art membrane based CO2 separation using mixed matrix membranes (MMMs): an overview on current status and future directions, Progress in Polymer Science, 2014, Vol. 39, No. 5, pp. 817-861 See the whole document.	1-20
A	JP 2013-111565 A (FUJIFILM CORP.) 10 June 2013 See the whole document.	1-20
PX	WO 2015-129925 A1 (KYOTO UNIVERSITY) 03 September 2015 See pages 15-40; claims 1-12; and figures 1-26.	1-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2016/036726

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 7758751 B1	20/07/2010	None	
JP 2013-111565 A	10/06/2013	WO 2013-080890 A1	06/06/2013
WO 2015-129925 A1	03/09/2015	None	