



(51) International Patent Classification:

B01D 53/22 (2006.01) *B01D 69/10* (2006.01)
B01J 20/22 (2006.01) *B01D 71/00* (2006.01)
B01D 69/02 (2006.01) *C07F 15/04* (2006.01)

(21) International Application Number:

PCT/US2015/042036

(22) International Filing Date:

24 July 2015 (24.07.2015)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/028,699 24 July 2014 (24.07.2014) US

(71) Applicant: KING ABDULLAH UNIVERSITY OF SCIENCE AND TECHNOLOGY [SA/SA]; 4700 King Abdullah University of Science and Technology, Thuwal, 23955-6900 (SA).

(72) Inventor; and

(71) Applicant : EDDAOUDI, Mohamed [US/SA]; 4700 King Abdullah University of Science and Technology, Thuwal, 23955-6900 (SA).

(72) Inventors: SHEKHAH, Osama; 4700 King Abdullah University of Science and Technology, Thuwal, 23955-6900 (SA). BELMABKHOUT, Youssef; 4700 King Abdullah University of Science and Technology, Thuwal, 23955-6900 (SA).

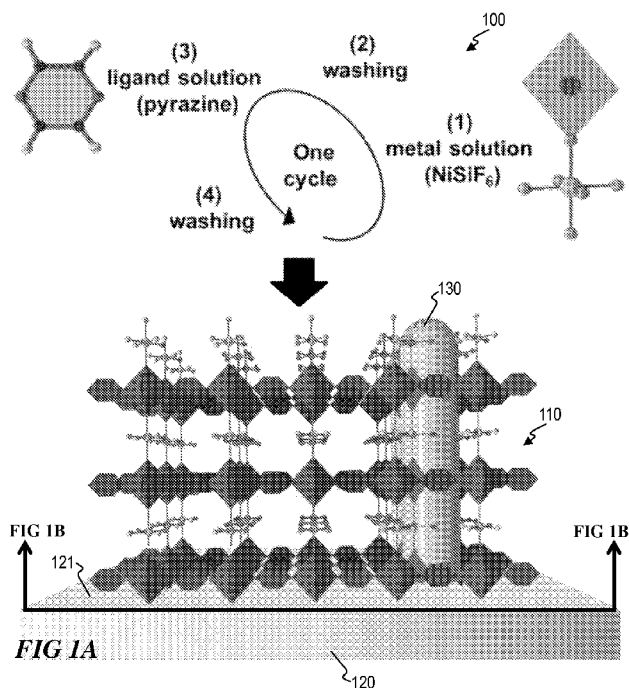
(74) Agents: ARMITAGE, Benjamin C. et al.; Billion & Armitage, 7401 Metro Blvd., Suite 425, Minneapolis, Minnesota 55439 (US).

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

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ,

[Continued on next page]

(54) Title: FABRICATION OF HIGHLY CO₂ SELECTIVE METAL ORGANIC FRAMEWORK MEMBRANE USING LIQUID PHASE EPITAXY APPROACH



(57) Abstract: Embodiments include a method of making a metal organic framework membrane comprising contacting a substrate with a solution including a metal ion and contacting the substrate with a solution including an organic ligand, sufficient to form one or more layers of a metal organic framework on a substrate. Embodiments further include a defect-free metal organic framework membrane comprising MSiF₆(pyz)₂, wherein M is a metal, wherein the thickness of the membrane is less than 1,000 μm, and wherein the metal organic has a growth orientation along the [110] plane relative to a substrate.



TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

FABRICATION OF HIGHLY CO₂ SELECTIVE METAL ORGANIC FRAMEWORK MEMBRANE USING LIQUID PHASE EPITAXY APPROACH

CROSS REFERENCE TO RELATED APPLICATION

5 This application claims benefit of US Provisional Application No. 62/028,699, filed on 24 July 2014 and which application is incorporated herein by reference. A claim of priority is made.

BACKGROUND

10 Today, environmental concerns and governmental regulatory schemes have challenged industry to reduce carbon dioxide emissions. For example, power plants are a major source of carbon dioxide emissions with worldwide emissions exceeding more than 2 billion tons of exhaust CO₂ annually. Suitable CO₂ capture processes require energy efficiency, and must exhibit targeted separation performance (e.g., high CO₂ selectivity). Membranes have shown
15 great promise in CO₂ emissions capture, particularly in CO₂ capture from power plant emissions, as a result of their operating simplicity and efficiency as compared to alternative separation technologies. Suitable separation membranes exhibit high permeance for undesirable species and the opposite for more valuable and/or favored species in order to concentrate the latter. For example, a practical membrane for CO₂ capture from
20 predominately H₂, N₂ and CH₄ containing gases should exhibit a high permeance for CO₂ as compared to CH₄ and H₂. In instances where permeation is adsorption-driven, the membrane necessarily exhibits high adsorption selectivity for the non-favored permeating species (e.g., CO₂), and/or slow adsorption selectivity for the favored species (e.g., CH₄ and H₂).

The unique properties of metal-organic frameworks (MOFs) have demonstrated
25 superiority over other gas separation and capture technologies due to their permanent porosity, ability to tune pore windows and cage-sizes, and chemical and thermal stability. MOFs are compounds including metal ions or clusters coordinated by organic ligands to form one-, two-, or three-dimensional porous structures. In the form of bulk solids and microcrystalline powder materials, MOFs have been used in many applications including sensing, gas storage
30 and separation, catalysis, and drug delivery. However, the use of MOFs as membranes for gas purification and separation depends on the fabrication of continuous and defect-free MOF thin-films with good adhesion to supports, which has thus far proved challenging. MOFs can be produced by methods, such as hydrothermal or solvothermal techniques whereby crystals are slowly grown from a hot solution, but such methods are not suitable for MOF membrane
35 fabrication.

SUMMARY

Embodiments herein provide porous, defect-free, highly CO₂ selective MOF membranes, and liquid phase epitaxy (LPE) fabrication methods for fabricating the same.

5 LPE fabrication methods yield continuous and defect-free MOF thin-films with good adhesion to substrates. While the MOFs and LPE fabrication methods are directed towards SIF-SIX MOFs with high CO₂ selectivity, the MOFs and LPE fabrication methods can be suitable for other applications.

10 In one embodiment, a method of making a CO₂ selective metal organic framework membrane based on hexafluorosilicate comprises contacting a substrate with a solution including a metal ion; and contacting the substrate with a solution including an organic ligand, sufficient to form one or more layers of a metal organic framework on a substrate. In such embodiments, the metal ion solution can include MSiF₆, wherein M is Ni, Cu, Zn, Fe, Al, Nb, Mn, or Co, and the organic ligand solution can comprise pyrazine.

15 In one embodiment, a metal organic framework membrane can comprise MSiF₆(Ligand)₂, wherein M is a metal, wherein the thickness of the membrane is less than 1,000 μm. In such embodiments, the metal can comprise one or more of Ni, Cu, Zn, Fe, Al, Nb, Mn and Co, and the ligand can comprise pyridine, 4,4'-Bipyridin, pyrazine, pyrimidine, pyridazine, triazine, thiazole, oxazole, pyrrole, imidazole, pyrazole, triazole, oxadiazole, 20 thiadiazole, quinoline, benzoxazole, benzimidazole, 1,4-Diazabicyclo[2.2.2]octane (DABCO), or 1,2-bis(4-pyridyl)acetylene (dpa). In such embodiments, the metal organic framework can be contiguous with a substrate, and the metal organic framework can have a growth orientation along the [110] plane relative to the substrate.

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

BRIEF DESCRIPTION OF THE DRAWINGS

30 FIG. 1A illustrates a liquid phase epitaxy method for preparing a MOF thin film, according to one or more embodiments of the disclosure.

FIG. 1B illustrates a top view normal to a substrate surface of a MOF thin-film deposited by a liquid phase epitaxy method, according to one or more embodiments of the disclosure.

35 FIG. 2 shows PXRD pattern of NiSiF₆(Pyz)₂ (SIFSIX-3-Ni) thin film grown on alumina support, according to one or more embodiments of the disclosure.

FIG. 3A illustrates a top view SEM images of a NiSiF₆(pyz)₂ thin film, according to one or more embodiments of the disclosure.

FIG. 3B illustrates a cross-sectional SEM image of a NiSiF₆(pyz)₂ thin film, according to one or more embodiments of the disclosure.

5 FIG. 4 shows single gas permeability vs. Lennard Jones diameter of He, H₂, CO₂, O₂, N₂, and CH₄ at 308 K with NiSiF₆(Pyz)₂ membranes, according to one or more embodiments of the disclosure.

FIGS. 5A-C illustrate mixture permeation testing using a VP-continuous permeate composition analysis technique, according to one or more embodiments of the disclosure.

10 FIGS. 6A illustrates calculated diffusion coefficients for various gaseous species, according to one or more embodiments of the disclosure.

FIGS. 6B illustrates calculated sorption coefficients for various gaseous species, according to one or more embodiments of the disclosure.

15

DETAILED DESCRIPTION

The disclosure herein provides liquid phase epitaxy (LPE) fabrication methods for porous highly CO₂ selective MOFs, which yield continuous and defect-free MOF thin-films with good adhesion to supports (i.e., substrates). In particular, this disclosure provides
20 continuous and defect-free thin-film SIFSIX MOFs, and methods for fabricating the same, having characteristics highly suitable for many applications including gas capture and separation. Such continuous and defect-free thin-film SIFSIX MOFs exhibit high CO₂ adsorption selectivity advantageous for CO₂ adsorption-driven permeation. Additionally, such MOFs further exhibit high CO₂ selectivity vs. H₂S, unlike many other known MOF thin-
25 films.

Metal organic frameworks (MOFs) are a versatile and promising class of crystalline solid state materials which allow porosity and functionality to be tailored towards various applications. For example, MOF materials exhibit exceptionally high specific surface area, in addition to tunable pore size and functionality (e.g., CO₂ selectivity, and H₂S tolerance),
30 which make them suitable for many applications including gas storage, gas separation, catalysis, drug delivery, light-emitting devices, and sensing.

Generally, MOFs comprise a network of nodes and ligands, wherein a node has a connectivity capability at two or more functional sites, and a ligand has a connectivity capability at two functional sites each of which connect to a node. Nodes are typically metal
35 ions or metal containing clusters, and, in some instances, ligands with node connectivity

capability at two or more functional sites can also be characterized as nodes. In some instances, ligands can include two functional sites capable of each connecting to a node, and optionally one or more additional functional sites which do not connect to nodes within a particular framework. In some embodiments, ligands can be poly-functional, or polytopic, and comprise two or more functional sites capable of each connecting to a node. In some 5 embodiments, polytopic ligands can be heteropolytopic, wherein at least two of the two or more functional sites are different.

A MOF can comprise a metal-based node and an organic ligand which extrapolate to form a coordination network. Such coordination networks have advantageous crystalline and 10 porous characteristics affecting structural integrity and interaction with foreign species (e.g., gases). The particular combination of nodes and ligands within a framework will dictate the framework topology and functionality. Through ligand modification or functionalization, the environment in the internal pores can be modified to suit specific applications.

MOF can be represented by the formula $[(\text{node})_a(\text{ligand})_b(\text{solvent})_c]_n$, wherein n 15 represents the number of molecular building blocks. Solvent represents a guest molecule occupying pores within the MOF, for example as a result of MOF synthesis, and can be evacuated after synthesis to provide a MOF with unoccupied pores. Accordingly, the value of c can vary down to zero, without changing the definitional framework of the MOF. Therefore, in many instances, MOFs can be defined as $[(\text{node})_a(\text{ligand})_b]_n$, without reference 20 to a solvent or guest molecule component.

An example of a class of MOFs is SIFSIX- n - M , wherein n is at least two, and M can comprise Ni, Cu, Zn, Fe, Al, Nb, Mn or Co. More specifically, M can comprise Ni. The SIFSIX- n - M MOF class is isorecticular across its metal analogues (i.e., each M analogue has the same framework topology) and is characterized by periodically arrayed hexafluorosilicate 25 (SIFSIX) pillars. SIFSIX- n - M MOFs have many desirable characteristics, including tunable pore sizes, which lend the various analogues well to a number of industrial applications. Specific SIFSIX- n - M MOF analogues include SIFSIX-3-Cu, SIFSIX-3-Zn, and SIFSIX-3-Ni, among others.

SIFSIX- n - M MOFs can be coordinated by a variety of organic ligands. In some 30 embodiments, the ligand can be any bi-functional N-donor linkers based on monocyclic or polycyclic group (aromatic or not). In some embodiments, a ligand can comprise a polydentate, or poly-functional ligand, such as a bi-functional ligand, a tri-functional ligand, or ligands with four or more functional sites. In some embodiments, a ligand can comprise an N-donor linker. In some embodiments a ligand can comprise a poly-functional ligand. In 35 some embodiments, a ligand can comprise a plurality of N-donor functional groups. Pyrazine

is an example of a ligand with two N-donor functional groups. In some embodiments, a ligand can comprise a monocyclic or polycyclic group structure, wherein the cyclic groups can be aromatic or nonaromatic. In some embodiments, a ligand can comprise a nitrogen-containing monocyclic or polycyclic group structure. In some embodiments, a ligand can
5 comprise a nitrogen-containing heterocyclic ligand, including pyridine, 4,4'-Bipyridin, pyrazine, pyrimidine, pyridazine, triazine, thiazole, oxazole, pyrrole, imidazole, pyrazole, triazole, oxadiazole, thiadiazole, quinoline, benzoxazole, benzimidazole, 1,4-Diazabicyclo[2.2.2]octane (DABCO), 1,2-bis(4-pyridyl)acetylene (dpa), and tautomers thereof.

10 SIFSIX MOF structures as provided herein can exhibit a porosity of greater than 50% of the MOF crystal volume and surface area values ranging from 1000 to 10,000 m²/g, far exceeding those of traditional porous materials such as zeolites and carbons. In particular, SIFSIX-n-M MOFs are suitable for CO₂ removal applications, due to their strong/uniform CO₂ adsorption sites, including pre-combustion CO₂ capture, and post-combustion CO₂
15 capture, and natural gas, biogas upgrading and trace/low CO₂ removal applications. SIFSIX MOF materials exhibit very high (non-reactive) CO₂ energetics, but fully reversible physical driven adsorption-desorption operations at very mild conditions. The ideal combination of contracted pore size and the high charge density also provide high CO₂ adsorption selectivity over H₂, CH₄ and N₂ across a wide range of CO₂ concentrations. While SIFSIX MOFs have
20 been synthesized in the lab using solvothermal/hydrothermal synthesis techniques, such methods are not currently able to produce defect-free or substantially defect-free MOF thin-films and membranes. Accordingly, methods for synthesizing thin-film SIFSIX MOFs are needed in order to lend particular industrial utility to these materials in membrane technology

SIFSIX MOFs can be fabricated using epitaxial methods. Epitaxy generally refers to
25 crystalline material deposition on a crystalline substrate. The surface and lattice characteristics of the substrate affect the characteristics of crystalline growth thereon, and it is therefore often critical to ensure a suitable lattice match between the substrate and the growth layer material. For example, optoelectronics materials rely on careful lattice matching of semiconductor materials when epitaxially growing LED and LASER architectures. Epitaxial
30 growth can be accomplished by a number of methods, including physical vapor deposition and LPE. LPE is a method by which a crystalline layer is grown on a substrate through the solidification of a liquid phase growth material. LPE is predominately used to fabricate semiconductor and magnetic rare-earth iron materials. Longevity and performance of crystalline-based devices (e.g., microelectronic, photonic and magnetic devices) relate
35 directly to crystalline quality of grown materials, which are highly susceptible to minor flaws

in growth conditions. For example, trace concentrations of oxygen present during GaAs transistor fabrication can cause dislocations (i.e., crystalline defects) and undermine device performance.

LPE methods are described herein for fabricating MOF materials with high CO₂ selectivity over H₂S, among other advantageous characteristics. Moreover, LPE methods can be used to precisely fabricate defect-free MOF thin-films without the drawback of high susceptibility to minor flaws in growth conditions germane to the LPE growth process.

LPE growth can be used to prepare the SIFSIX-MOF thin-films. A LPE method for preparing an MOF thin-film on substrate is shown in FIG. 1A, and can include (1) contacting, such as immersing or spraying, a substrate with a metal ion solution, and (3) subsequently contacting, such as immersing or spraying, the substrate with an organic ligand solution. The metal ion solution can comprise $[(M)(SiF_6)]_xH_2O$, where M can comprise Ni, Cu, Zn, Fe, Al, Nb, Mn and Co, wherein x is an integer. The organic ligand solution can include pyrazine, bipyridine, or mixture of both, for example. The organic ligand solution can further alternatively include one or more SIFSIX-n-M MOF ligands as described above.

LPE method 100 can optionally include one or more solvent rinses or washes. In one embodiment, a LPE method for preparing an MOF thin film on a substrate can include (1) contacting a substrate with a metal ion solution, (2) subsequently washing the substrate with a solvent, and (3) subsequently immersing the substrate in an organic ligand solution. In one embodiment, a LPE method for preparing an MOF thin film on a substrate can include (1) contacting a substrate with a metal ion solution, (2) subsequently washing the substrate with a solvent, and (3) subsequently immersing the substrate in an organic ligand solution. In one embodiment, a LPE method for preparing an MOF thin film on a substrate can include (1) immersing a substrate in a metal ion solution, (2) subsequently washing the substrate with a solvent, (3) subsequently immersing the substrate in an organic ligand solution, and (4) subsequently washing the substrate with a solvent. Washing can remove physically adsorbed metal ions and/or organic ligands, for example. Washing can prepare a deposited layer for subsequent deposition of a next layer.

A pair of immersions in each respective metal solution and ligand solution, with or without one or more optional washings, constitute one growth cycle. LPE method 100 can comprise 1 or more growth cycles. LPE method 100 can comprise up to 5 growth cycles, up to 25 growth cycles, up to 50 growth cycles, up to 100 growth cycles, up to 150 growth cycles, up to 200 growth cycles, or greater than 200 growth cycles. The thin film thickness depends on the number of growth cycles. Accordingly, a method of fabrication can include any number or growth cycles required to achieve a desired film thickness. The number of

growth cycles can be increased to increase film thickness. In one embodiment, a LPE method for preparing an MOF thin film on a substrate can comprise one growth cycle. In another embodiment, a LPE method for preparing an MOF thin film on a substrate can comprise a plurality of growth cycles. In some embodiments, concentration of one or more
5 of the metal ion solution and the organic ligand solution can be increased to increase deposition rate. In some embodiments, temperature of one or more of the metal ion solution and the organic ligand solution can be increased to increase deposition rate. In some embodiments, temperature and concentration of one or more of the metal ion solution and the organic ligand solution can be increased to increase deposition rate.

10 The contact time can vary depending on the type of metal or ligand precursor used, and the respective concentrations of the metal ion solution and the organic ligand solution. In some embodiments, immersion in the metal ion solution can be about 1 minute to about 60 minutes. In some embodiments, immersion in the metal ion solution can be up to about 1 minute, up to about 5 minutes, up to about 10 minutes, up to about 15 minutes, up to about 20
15 minutes, up to about 40 minutes, up to about 60 minutes, or greater than about 60 minutes. In some embodiments, immersion in the metal ion solution can be less than about 60 minutes, less than about 45 minutes, less than about 30 minutes, less than about 25 minutes, less than about 20 minutes, less than about 15, or less than about 10 minutes. In some embodiment, immersion in the organic ligand solution can be about 1 minute to about 60 minutes. In
20 some embodiments, immersion in the organic ligand solution can be up to about 1 minute, up to about 5 minutes, up to about 10 minutes, up to about 15 minutes, up to about 20 minutes, up to about 40 minutes, up to about 60 minutes, or greater than about 60 minutes. In some embodiments, immersion in the organic ligand solution can be less than about 60 minutes, less than about 45 minutes, less than about 30 minutes, less than about 25 minutes, less than
25 about 20 minutes, less than about 15, or less than about 10 minutes.

The solvent for preparation and rinsing can be one or more of methanol, ethanol, acetonitrile, water, and DMF. Substrate 120 can include one or more of alumina, titanium oxide, polymer, copolymer, glass, ceramic, indium phosphide, metal or metal oxide, combinations thereof and composites thereof. An advantage of LPE method 100 is that
30 substrate 120 need not be lattice matched to the MOF deposition layer 110. Suitable substrates can be highly porous. Suitable substrates can comprise nucleation sites. An MOF thin-layer or thin-film grown on a substrate is contiguous with the substrate. Nucleation sites facilitate depositions of a first layer of metal ions or organic ligands such that MOF self-assembly can be achieved by subsequent deposition of one or more of metal ions and organic

ligands. Nucleation sites can comprise –OH sites. Nucleation sites can comprise –COOH sites. Nucleation sites can comprise –OH sites and –COOH sites.

FIG. 1A illustrates the fabrication of a SIFSIX-3-Ni MOF (i.e., NiSiF₆(pyz)(H₂O)₂) thin-film, but the method can be utilized to fabricate a variety of MOF thin films. For example, the method can be used to fabricate SIFSIX-n-M MOFs, wherein M can comprise one or more of Ni, Cu, Zn, Fe, Al, Nb, Mn or Co. The method can also be used to fabricate SIFSIX-n-M MOFs wherein the ligand comprises pyridine, 4,4'-Bipyridin, pyrazine, pyrimidine, pyridazine, triazine, thiazole, oxazole, pyrrole, imidazole, pyrazole, triazole, oxadiazole, thiadiazole, quinoline, benzoxazole, benzimidazole, 1,4-Diazabicyclo[2.2.2]octane (DABCO), 1,2-bis(4-pyridyl)acetylene (dpa), and tautomers thereof.

One advantageous aspect of the LPE method and SIFSIX thin-layer MOFs described herein includes well-defined film thicknesses, particularly as compared to known MOF fabrication methods. Depending on the preparation conditions, one deposition layer can range from about 1 nm to about 1000 nm. Repeating the growth cycle can create customizable membrane thickness depending on the number of layers formed. For example, a thin-film MOF thickness can be less than about 1000 μm, less than about 500 μm, less than about 250 μm, less than about 150 μm, less than about 100 μm, less than about 75 μm, less than about 50 μm, less than about 25 μm, less than about 20 μm, less than about 15 μm, less than about 10 μm, or less than about 5 μm.

A further advantage of the LPE method and SIFSIX thin-layer MOFs described herein includes a high degree of orientation within the deposited films and the absence of defects, such as pin-holes, cracks, or grain boundary dislocations. In many embodiments, perfectly crystalline SIFSIX MOF layers can be fabricated using the LPE method.

A further advantage the LPE method and SIFSIX thin-layer MOFs is the growth orientation of the MOF thin-layer relative to the substrate. FIG. 1B illustrates a top view normal to a substrate 120 surface 121 (shown in FIG. 1A) of a MOF thin-film 110 deposited by a LPE method. FIGS. 1A-B both illustrate the preferential orientation of growth along the [110] plane which advantageously aligns the larger channels of the SIFSIX-3-Ni structure perpendicular relative to a substrate surface 121. Such channels are the only accessible permeation pathway for gases. One such channel is shown occupied by guest molecule 130.

A further advantage the LPE method and SIFSIX thin-layer MOFs is high selectivity for CO₂ over relevant industrial gases such as O₂, H₂, N₂ and CH₄. Accordingly, a defect-free, crystalline SIF-SIX MOF thin-layer can be deposited on a substrate with a preferential

orientation of permeation channels, wherein the MOF exhibits high selectivity for CO₂ over one or more of O₂, H₂, N₂ and CH₄.

Generally, a defect-free SIF-SIX MOF thin-film membrane can be fabricated using LPE on substrate, wherein the MOF can be characterized by

5 [(M)(SiF₆)(Ligand)_n]_L · [Substrate], wherein M can comprise Ni, Cu, Zn, Fe, Mn, Al, Nb, or Co, Ligand can comprise pyridine, 4,4'-Bipyridin, pyrazine, pyrimidine, pyridazine, triazine, thiazole, oxazole, pyrrole, imidazole, pyrazole, triazole, oxadiazole, thiadiazole, quinoline, benzoxazole, benzimidazole, 1,4-Diazabicyclo[2.2.2]octane (DABCO), or 1,2-bis(4-

10 pyridyl)acetylene (dpa), and Substrate can comprise alumina, titanium oxide, polymer, copolymer, glass, ceramic, indium phosphide, metal or metal oxide, combinations thereof and composites thereof. In one embodiment, Ligand can optionally comprise or tautomers of pyridine, 4,4'-Bipyridin, pyrazine, pyrimidine, pyridazine, triazine, thiazole, oxazole, pyrrole, imidazole, pyrazole, triazole, oxadiazole, thiadiazole, quinoline, benzoxazole, benzimidazole, 1,4-Diazabicyclo[2.2.2]octane (DABCO), or 1,2-bis(4-pyridyl)acetylene (dpa). In one

15 particular example, a defect-free, pure phase NiSiF₆(pyz)₂ metal organic framework thin-film membrane can be fabricated with using a liquid-phase epitaxy growth method on an alumina substrate. For both pure and mixed gas feeds, the NiSiF₆(pyz)₂ MOF membrane can exhibit an adsorption-driven selectivity for carbon dioxide over relevant industrial gases such as O₂, H₂, N₂ and CH₄.

20 SIF-SIX MOF thin-films as described herein are generally applicable to a wide range of gas capture and upgrading applications. In one example, the NiSiF₆(pyz)₂ MOF membrane embodies an MOF thin-film platform with a combination of tunable pore sizes (rather than large surface area) with requisite sorption chemistry exhibiting highly selective and fast (e.g., 10-100 times faster) CO₂ adsorption over N₂, O₂, CH₄ and H₂, and uniformly

25 aligned and strong adsorption sites (e.g., CO₂ adsorption sites). NiSiF₆(pyz)₂ membranes can be used to target different separation applications relating to CO₂ capture. Surface modules of a membrane can be reduced by using a CO₂ selective membrane. For example, in purifying syngas (30% CO₂ and ~70% H₂), an H₂-selective ZIF-8 membrane requires strict and complex requirement in terms of membrane surface. However, CO₂-selective NiSiF₆(pyz)₂

30 MOF membranes can purify syngas much more efficiently by permeating the smaller CO₂ fraction. Further, the CO₂-selective NiSiF₆(pyz)₂ MOF membranes exhibit a CO₂/H₂ selectivity of 13, thus requiring a smaller module and drastically simplifying the technology.

EXAMPLE 1: Preparation of defect-free pure phase NiSiF₆(Pyz)₂ MOF thin film

35 **membrane supported on porous alumina substrate via LPE**

A **SIFSIX-3-Ni** thin film was fabricated on a porous alumina substrate using an LPE method. A freshly cleaned and activated porous alumina substrate was immersed in a 0.13 M $\text{NiSiF}_6 \cdot 2\text{H}_2\text{O}$ and methanol solution for 10 minutes and subsequently rinsed with methanol. Next, the substrate was immersed in a 0.26 M pyrazine methanol solution for 10 minutes at 65 °C and
5 subsequently rinsed with methanol. This process was repeated for 25 and 30 growth cycles in two trials in order to increase the thickness of the thin film, yielding two thin-films having thicknesses of ~ 5 μm and ~ 7 μm , respectively.

The structure of the constructed **SIFSIX-3-Ni** thin film was confirmed by powder X-ray diffraction (PXRD) as shown in FIG. 2, which shows the PXRD pattern for the **SIFSIX-3-Ni** thin film 1. The PXRD patterns of the resultant thin film agree well with the calculated
10 PXRD pattern in term of peak positions, indicating that a pure phase **SIFSIX-3-Ni** was obtained. The peaks at $2\theta^\circ$ (theta angle) of 12.4° , which is assigned to the (100) planes of the **SIFSIX-3-Ni** crystal lattice, are relatively higher than the other peaks and thus indicative of a film growth with a preferential orientation growth along the [110] plane. This preferential
15 orientation growth along the [110] plane advantageously exposes the larger channels of the **SIFSIX-3-Ni** structure, which are the only accessible permeation pathway for gases.

FIG. 3A illustrates a top view SEM image of the $\text{NiSiF}_6(\text{pyz})_2$ thin film, and FIG. 3B illustrates a cross-sectional SEM image of the $\text{NiSiF}_6(\text{pyz})_2$ thin film. FIGS. 3A-B illustrate the growth of a homogenous and continuous **SIFSIX-3-Ni** thin film using the LPE method. The
20 thin film is composed of intergrown and densely packed small sized **SIFSIX-3-Ni** crystallites on the support surface with no evidence of macro sized cracks or defects like pin-holes. The cross-sectional SEM image of FIG. 3B supports the growth of a continuous thin film over a number of growth cycles. Further analyses of the SEM cross-sectional image in FIG. 3A reveals the absence of **SIFSIX-3-Ni** crystals growth inside the substrate pores. These unique
25 attributes, not yet observable with other growth techniques, corroborate the power of the LPE method for the growth of highly reproducible ultrathin, densely packed and continuous thin films with controllable thickness. SEM imaging determined a separating layer thickness of 5 μm .

Single gas permeation of He, H_2 , CO_2 , N_2 , O_2 , CH_4 , (>99.99%) was performed on the
30 **SIFSIX-3-Ni** membrane using a constant-volume/variable-pressure (CV/VP) permeation technique. Time-lag behavior was observed for almost all the tested gases indicating a defect-free film. An elevated O_2/N_2 selectivity of 1.5 is a further confirmation of the film's continuity. FIG. 4A shows single gas permeability vs. Lennard Jones diameter of He, H_2 , CO_2 , O_2 , N_2 , and CH_4 at 308 K with $\text{NiSiF}_6(\text{Pyz})_2$ membranes, illustrating a sharp maximum
35 in CO_2 permeability compared to all the other tested gases, with the exception of except H_2 .

In order to further confirm this selective permeation in favor of CO₂, CO₂/H₂:30/70 CO₂/CH₄:50/50 and CO₂/N₂:10/90 gas-mixture permeation experiments were carried out using mixture gas permeation combined with a continuous gas analysis setup. FIGS. 5A-C illustrate the results of these mixture permeation tests carried out using a VP-continuous permeate composition analysis technique at 308 K with 2 bar as a feed pressure. The experiments revealed a selectivity toward CO₂ of 13, 7 and 17 for the three gases systems, respectively, in stark contrast with the ideal selectivity of 0.8 for CO₂/H₂, 2 for CO₂/CH₄, 3.6 for CO₂/O₂, and 4 for CO₂/N₂, obtained from pure-gas permeation testing shown in FIG. 4. This shows the effect of gas sorption competition between the other gases and CO₂, and the high selectivity for CO₂ by the **SIFSIX-3-Ni** membrane.

The single gas permeation data were further analyzed using the solution-diffusion model, applicable to structures with nominal pore diameter less than 10Å. In this model, gas permeability through a dense or microporous framework is the product of diffusion and solubility effects. Diffusion is characterized by a diffusion coefficient, *D*, which is a measure of the kinetics of gas transport through the membrane (thin film) and can be correlated with molecular size of the gaseous species. *D* is calculated for each gaseous species from experimental permeation time-lags, and the results are illustrated in FIG. 6A. Solubility is characterized by a sorption coefficient, *S*, which comprises the framework interactions with the gases and can be correlated well with their condensability. *S* can be obtained indirectly from the solution-diffusion model via knowledge of *P* from FIG. 4 and *D* from FIG. 6A, wherein *S* was calculated as $S=P/D$ for each gaseous species and illustrated in FIG. 6B.

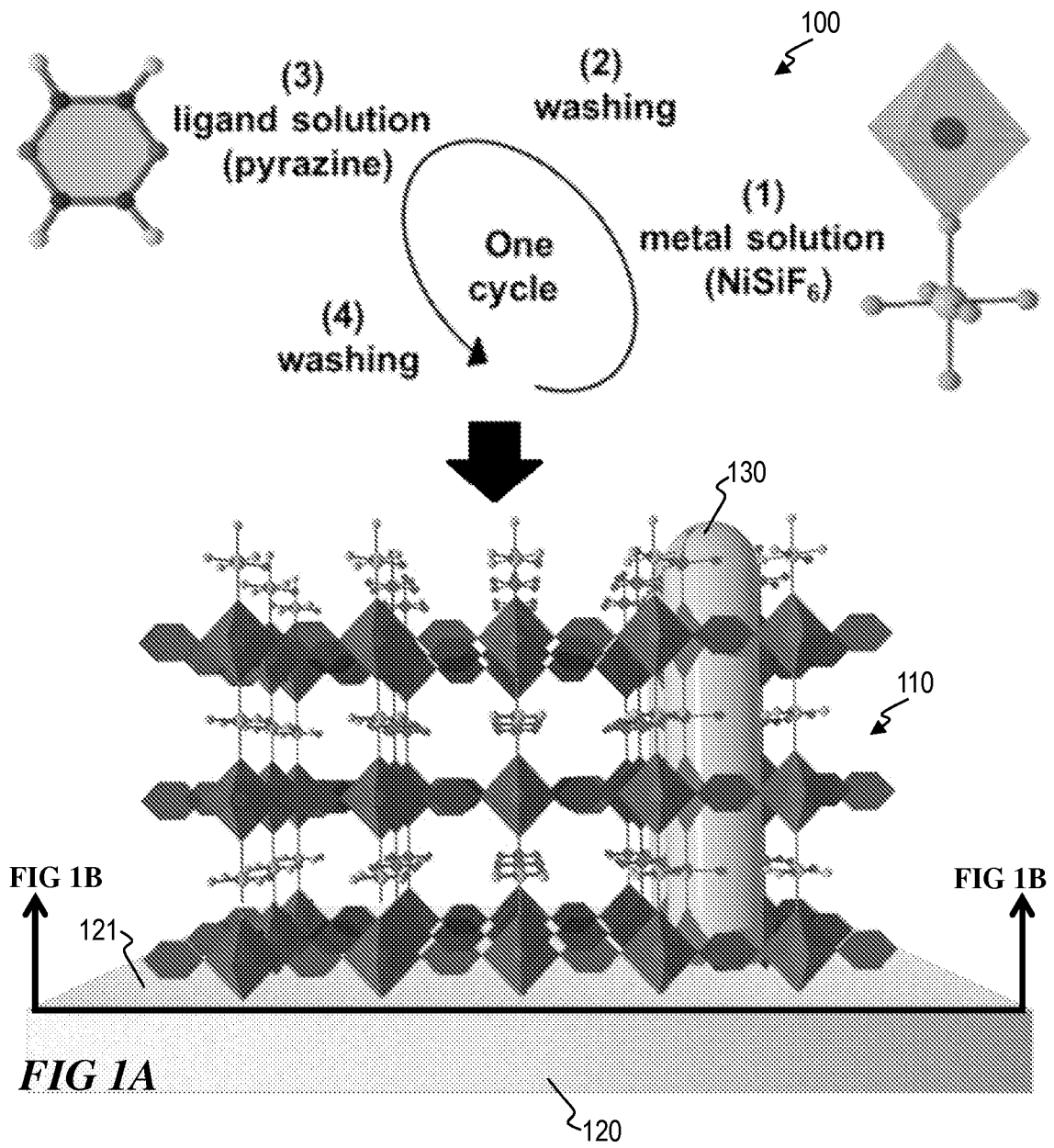
FIG. 4 demonstrates that all gas molecules tested experience more resistance to diffusion through the NiSiF₆(pyz)₂ framework, causing a general decline in diffusion coefficients with size (here used as Lennard Jones diameters). As the probe molecules approach the 3.8 Å pore aperture size estimated from crystal structure data, diffusion becomes more restricted. A 20-fold drop in *D* coefficients occurs from H₂ (2.8Å) through CO₂ (=4Å). With regards to the solubility coefficient, *S*, we observed a dramatic increase in case of CO₂, which is in a very good agreement with the adsorption measurements done over the powder material. The NiSiF₆(pyz)₂ demonstrates adsorption-driven permeation that generally trends with the condensability of the gas. This is similar to sorption coefficients that result in increased permeability for more condensable gases. The key observation, however, is that despite the restriction on the diffusion of CO₂ by the rigid and relatively small pore apertures, the remarkable affinity of NiSiF₆(pyz)₂ to CO₂ grants it the maximum, adsorption-driven, permeability of all tested gases.

35

WHAT IS CLAIMED IS:

1. A method of making a CO₂ selective metal organic framework membrane based on hexafluorosilicate comprising:
 - contacting a substrate with a solution including a metal ion, the metal ion solution including MSiF₆, wherein M is a metal; and
 - contacting the substrate with a solution including an organic ligand;wherein contacting the substrate with the metal ion solution and contacting the substrate with the organic ligand solution constitutes one growth cycle, and one growth cycle forms one or more layers of a metal organic framework on the substrate.
2. The method of claim 1, wherein contacting comprises immersing.
3. The method of claim 1, further comprising after contacting the substrate with the metal ion solution, the step of washing the substrate with a solvent.
4. The method of claim 1, further comprising after contacting the substrate with the organic ligand solution, the step of washing the substrate with a solvent.
5. The method of claim 1, wherein the metal comprises one or more of Ni, Cu, Zn, Fe, Al, Nb, Mn, and Co.
6. The method of claim 1, wherein the metal comprises Ni.
7. The method of claim 1, wherein the metal ion solution includes NiSiF₆.
8. The method of claim 1, wherein the organic ligand solution includes pyrazine.
9. The method of claim 1, wherein the substrate includes one or more of alumina, titanium oxide, polymer, copolymer, ceramic, glass, indium phosphide metal or metal oxide, combinations thereof and composites thereof.
10. The method of claim 1, wherein the metal organic framework is a defect-free NiSiF₆(pyz)₂ metal organic framework.

11. The method of claim 1, further comprising executing a plurality of growth cycles to grow a defect-free membrane.
12. A metal organic framework membrane comprising $MSiF_6(\text{Ligand})_2$, wherein M is a metal, and wherein the thickness of the membrane is less than 1,000 μm .
13. The metal organic framework membrane of claim 12, wherein the metal comprises one or more of Ni, Cu, Zn, Fe, Al, Nb, Mn and Co.
14. The metal organic framework membrane of claim 12, wherein the ligand comprises pyridine, 4,4'-Bipyridin, pyrazine, pyrimidine, pyridazine, triazine, thiazole, oxazole, pyrrole, imidazole, pyrazole, triazole, oxadiazole, thiadiazole, quinoline, benzoxazole, benzimidazole, 1,4-Diazabicyclo[2.2.2]octane (DABCO), or 1,2-bis(4-pyridyl)acetylene (dpa).
15. The metal organic framework membrane of claim 12, wherein the metal includes Ni and the ligand comprises pyrazine.
16. The metal organic framework membrane of claim 12, wherein the metal organic framework membrane is contiguous with a substrate, and the metal organic framework membrane has a growth orientation along the [110] plane relative to the substrate.
17. The metal organic framework of claim 16, wherein the substrate is alumina, titanium oxide, polymer, copolymer, glass, ceramic, indium phosphide, metal or metal oxide.
18. The metal organic framework of claim 16, wherein the substrate comprises one or more of $-\text{OH}$ nucleation sites and $-\text{COOH}$ nucleation sites.
19. The metal organic framework membrane of claim 12, wherein the membrane is CO_2 selective over one or more of O_2 , H_2 , N_2 and CH_4 .



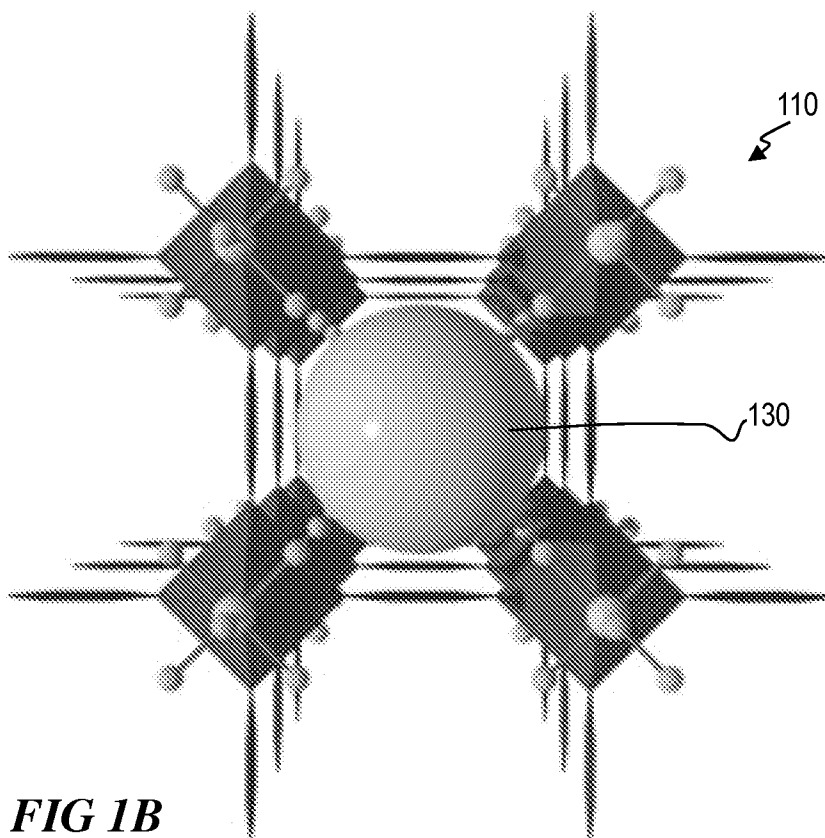


FIG 1B

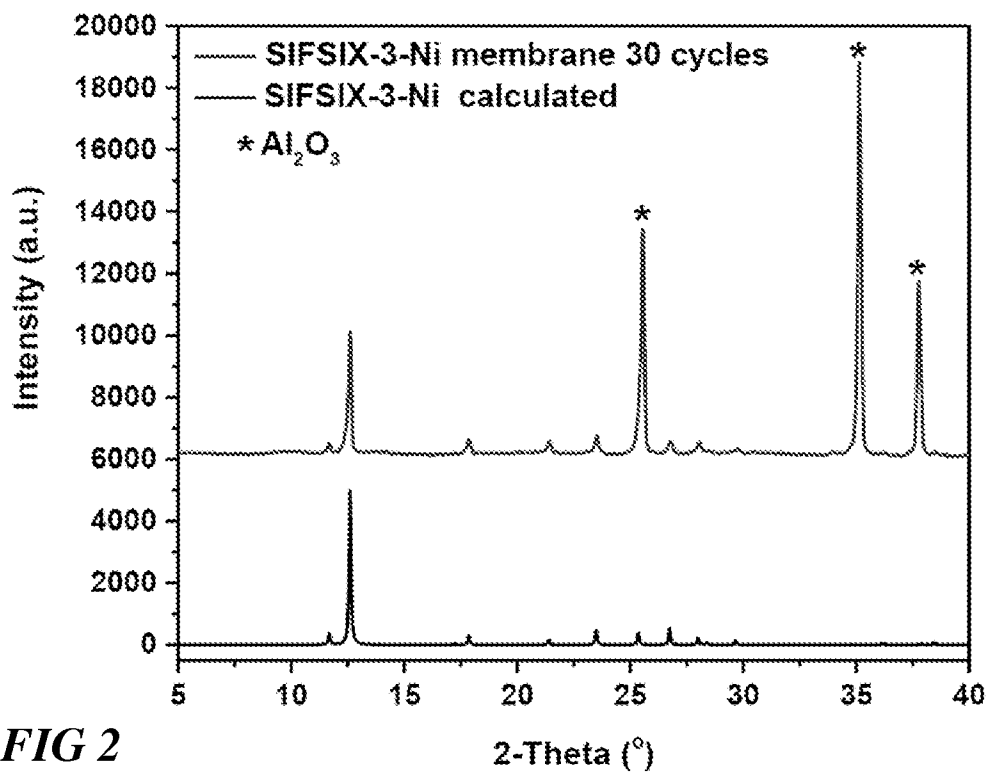


FIG 2

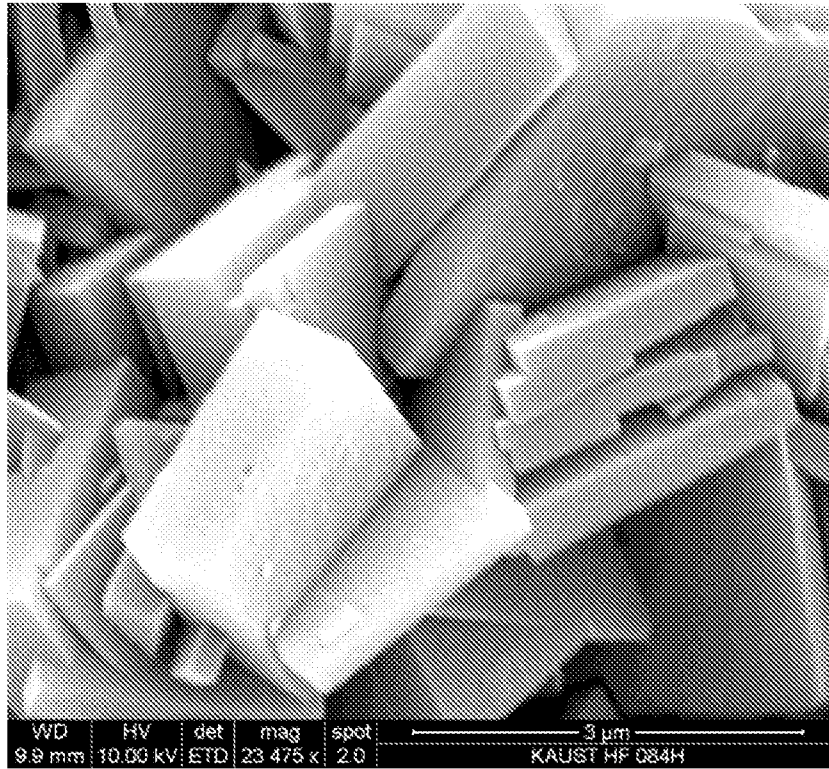


FIG 3A

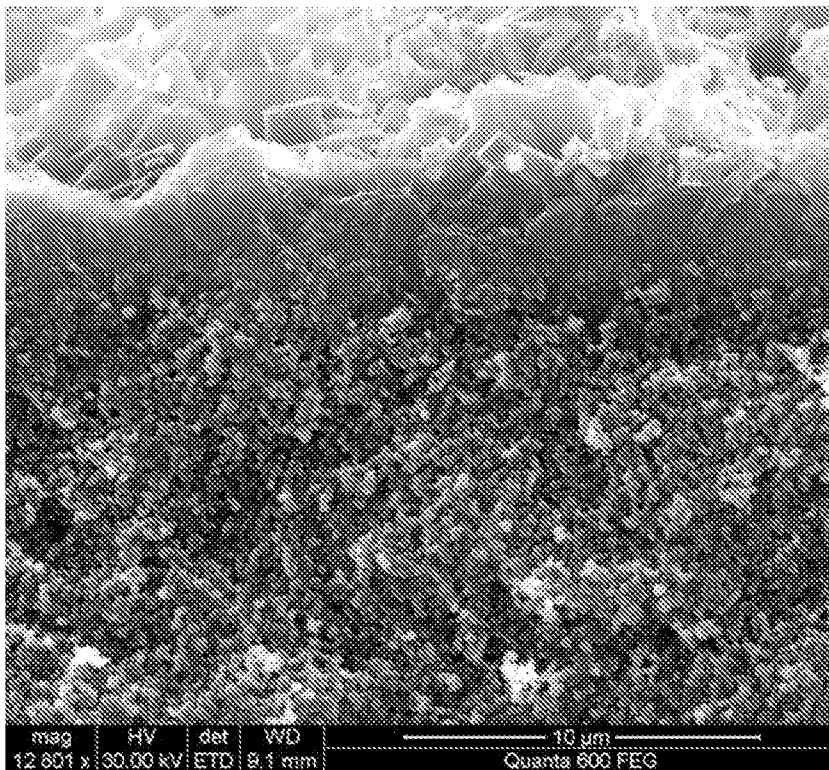


FIG 3B

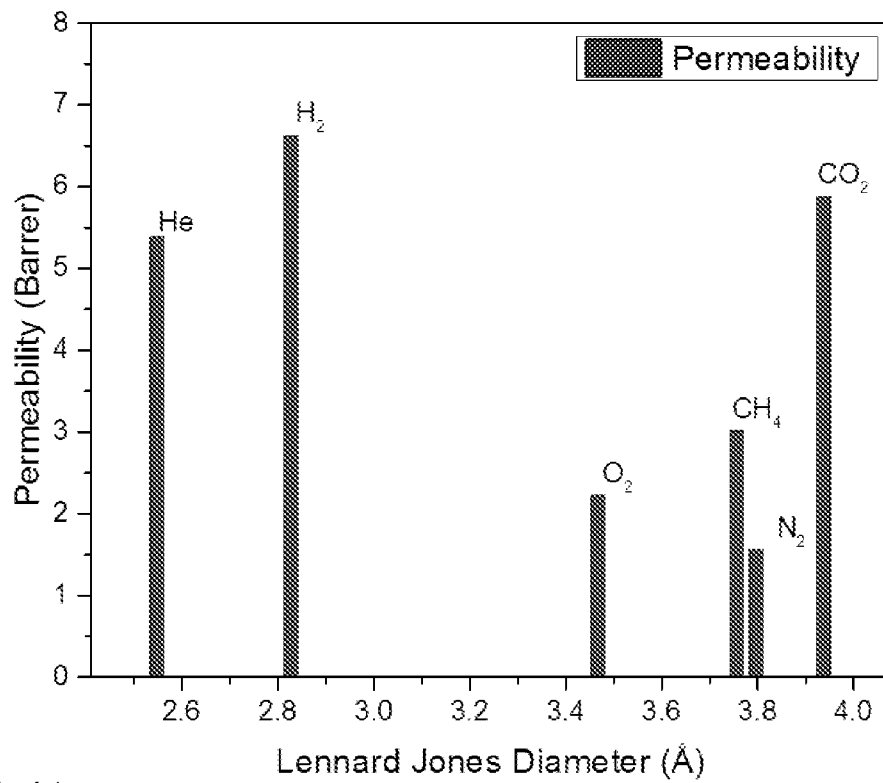


FIG 4A

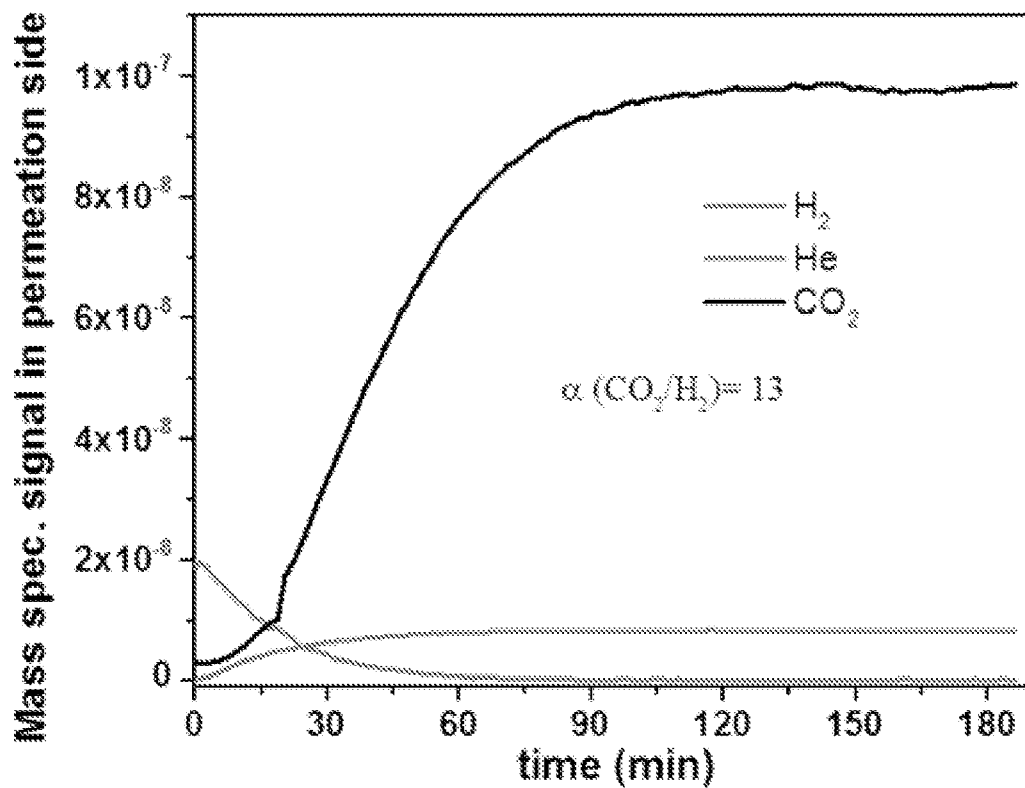


FIG 5A

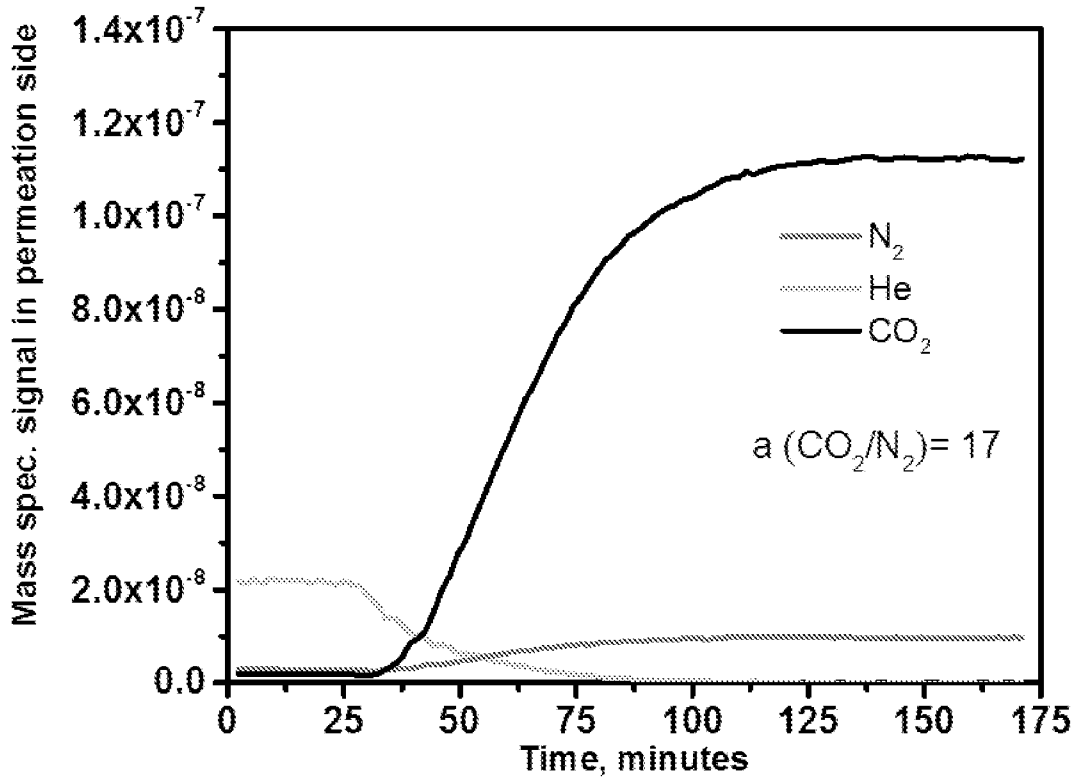


FIG 5B

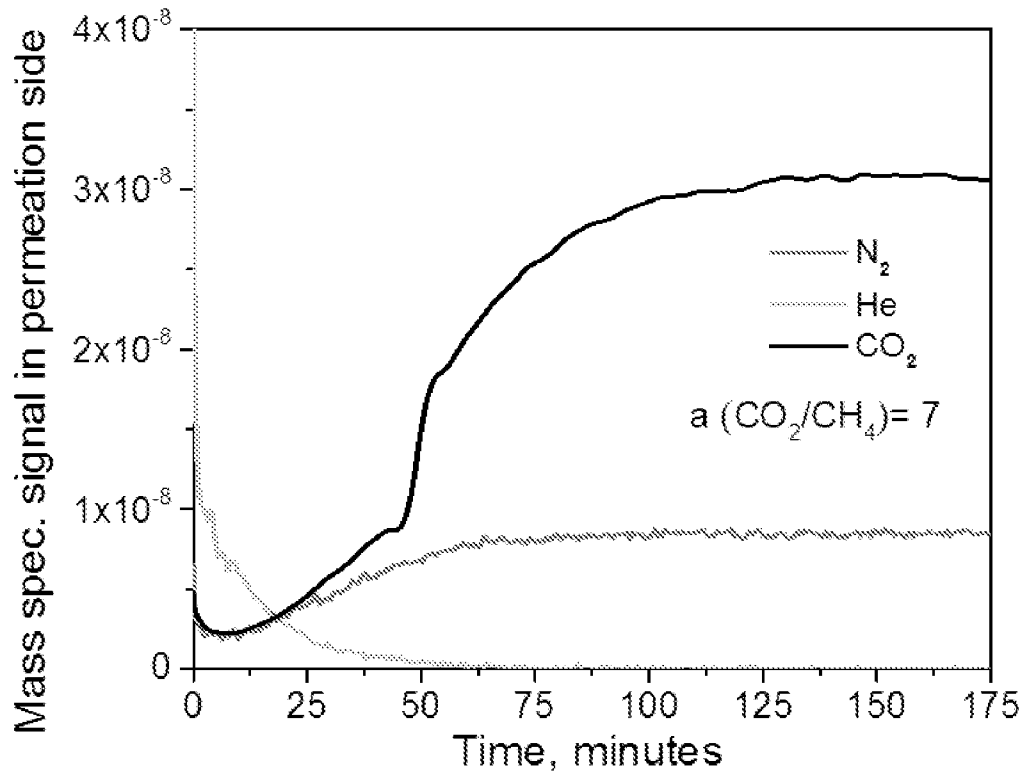


FIG 5C

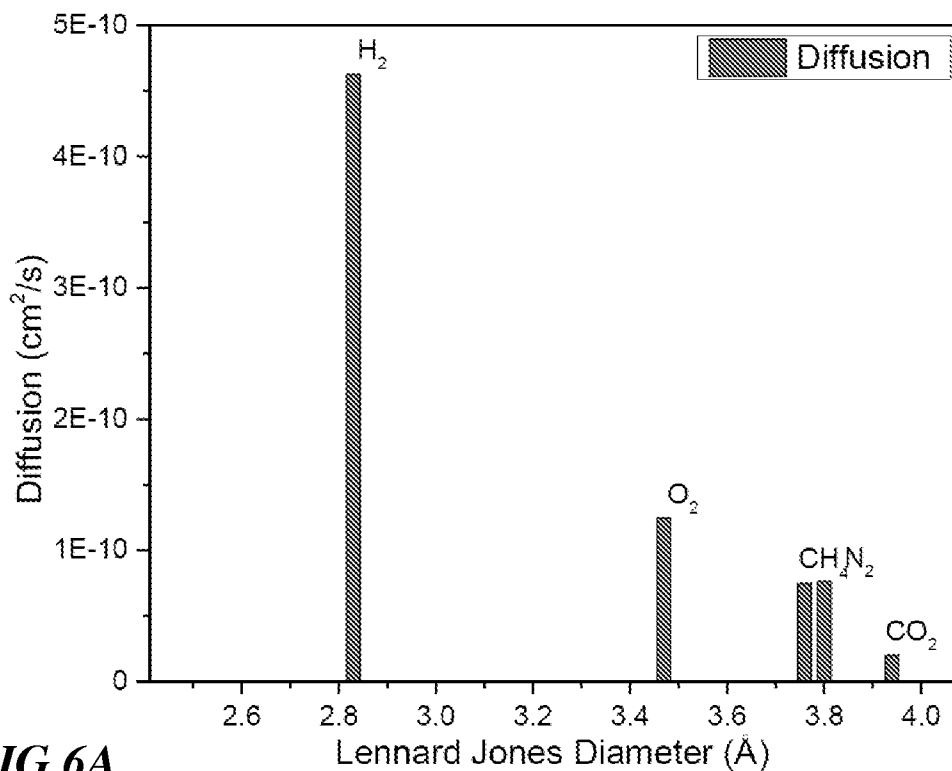


FIG 6A

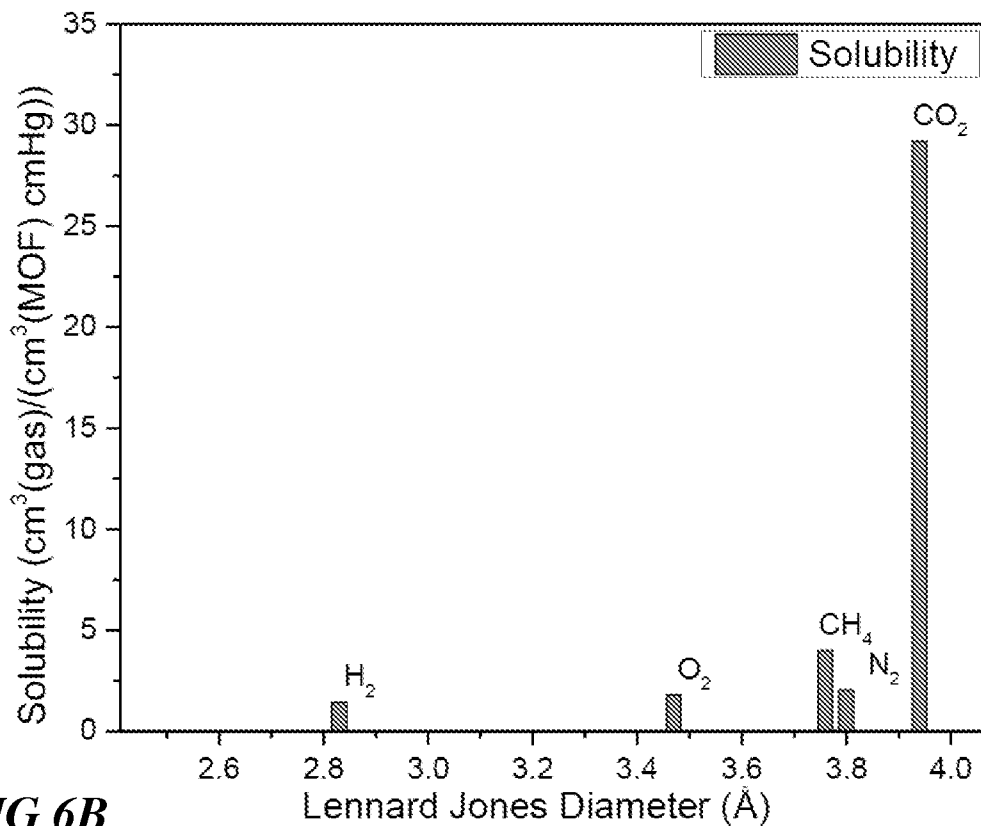


FIG 6B

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2015/042036

A. CLASSIFICATION OF SUBJECT MATTER
 INV. B01D53/22 B01J20/22 B01D69/02 B01D69/10 B01D71/00
 C07F15/04
 ADD.
 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)
 B01D B01J C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	MIRAL SHAH ET AL: "Current Status of Metal-Organic Framework Membranes for Gas Separations: Promises and Challenges", INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH, vol. 51, no. 5, 8 February 2012 (2012-02-08), pages 2179-2199, XP055127880, ISSN: 0888-5885, DOI: 10.1021/ie202038m abstract Chap. 5.5.1 Liquid phase epitaxy; page 2189 - page 2190 Chap. 5.2.1 Synthesis of MOF nanocrystals; page 2188 - column 2 ----- -/--	1-20

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "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 28 September 2015	Date of mailing of the international search report 08/10/2015
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Lançon, Eveline

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2015/042036

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>OSAMA SHEKHAH ET AL: "Made-to-order metal-organic frameworks for trace carbon dioxide removal and air capture", NATURE COMMUNICATIONS, vol. 5, 25 June 2014 (2014-06-25), XP055209187, DOI: 10.1038/ncomms5228 abstract page 2, lines 4-8 - column 2 paragraph 3; page 2 - column 2 Chapter "Preparation and characterization of SIFSIX-3-Cu analogue"; page 2 - column 2</p> <p style="text-align: center;">-----</p>	1-20
Y	<p>ZHANG ET AL: "Gas permeability properties of Matrimid(>R) membranes containing the metal-organic framework Cu-BPY-HFS", JOURNAL OF MEMBRANE SCIENCE, ELSEVIER BV, NL, vol. 313, no. 1-2, 16 January 2008 (2008-01-16), pages 170-181, XP022526542, ISSN: 0376-7388, DOI: 10.1016/J.MEMSCI.2008.01.005 abstract Chapter 2.4 Membrane formation; page 172 - column 1</p> <p style="text-align: center;">-----</p>	1-20
X	<p>SONGJIE FAN ET AL: "Facile synthesis of a continuous thin Cu(bipy)2(SiF6) membrane with selectivity towards hydrogen", JOURNAL OF MATERIALS CHEMISTRY A, vol. 1, no. 37, 1 January 2013 (2013-01-01), page 11438, XP055216119, ISSN: 2050-7488, DOI: 10.1039/c3ta11604b</p> <p style="text-align: center;">-----</p>	13-20
Y	<p>abstract Chapter "Synthesis"; page 11439, column 2 last line of second last paragraph; page 11440, column 1</p> <p style="text-align: center;">-----</p> <p style="text-align: center;">-/--</p>	1-12

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2015/042036

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>ANGLIQUE BTARD ET AL: "Fabrication of a CO-selective membrane by stepwise liquid-phase deposition of an alkylether functionalized pillared-layered metal-organic framework [CuLP] on a macroporous support", MICROPOROUS AND MESOPOROUS MATERIALS, ELSEVIER SCIENCE PUBLISHING, NEW YORK, US, vol. 150, 3 September 2011 (2011-09-03), pages 76-82, XP028328135, ISSN: 1387-1811, DOI: 10.1016/J.MICROMESO.2011.09.006 [retrieved on 2011-09-10] abstract Chap. 2.2 Preparation of MOF membranes; page 77</p> <p style="text-align: center;">-----</p>	1-12
A	<p>US 2013/313193 A1 (NAIR SANKAR [US] ET AL) 28 November 2013 (2013-11-28) abstract claim 1</p> <p style="text-align: center;">-----</p>	1-12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2015/042036

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2013313193 A1	28-11-2013	US 2013313193 A1	28-11-2013
		WO 2013177199 A1	28-11-2013
