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(54) Title: HIGHLY STABLE NI-M F6-NH₂O/ONPYRAZINE₂(SOLVENT)_x METAL ORGANIC FRAMEWORKS AND METHODS OF USE

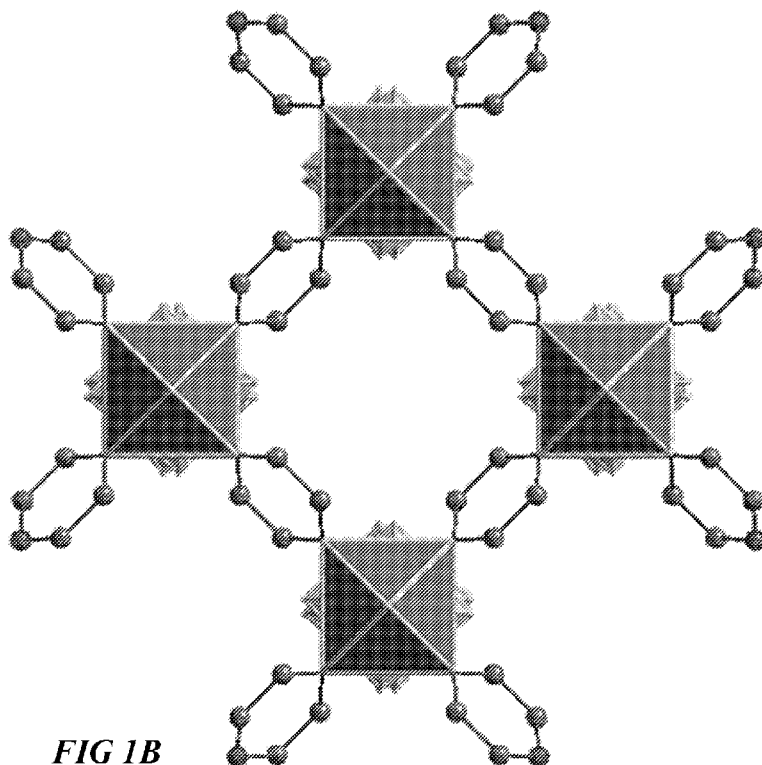


FIG 1B

(57) Abstract: Provided herein are metal organic frameworks comprising metal nodes and N-donor organic ligands. Methods for capturing chemical species from fluid compositions comprise contacting a metal organic framework characterized by the formula $[M_aM_bF_{6-n}(O/H_2O)_w(Ligand)_x(solvent)_y]_z$ with a fluid composition and capturing one or more chemical species from the fluid composition.



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SUMMARY

[0004] In general, this disclosure describes porous metal organic frameworks (MOFs). In particular, this disclosure describes MOFs suitable for the capture and removal of gases and/or vapors from fluids. It should be noted that although the embodiments of this disclosure are described with respect to examples for gas capture, the embodiments described herein are generally applicable to many fields including gas molecule separation, gas storage, catalysis, sensors, drug delivery, rare gas separation, and proton conductivity.

[0005] As provided herein, a method of capturing chemical species from a fluid composition can comprise contacting a metal organic framework characterized by the formula $[M_aM_bF_{6-n}(O/H_2O)_w(Ligand)_x(solvent)_y]_z$ with a fluid composition comprising two or more chemical species and capturing one or more captured chemical species from the fluid composition.

[0006] 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

[0007] The accompanying drawings illustrate non-limiting example embodiments of the invention.

[0008] **FIGS. 1A-B** illustrate schematic views of a metal organic framework, according to one or more embodiments of this disclosure.

[0009] **FIG. 2** illustrates a method for fabricating a metal organic framework, according to one or more embodiments of the disclosure.

[0010] **FIG. 3** illustrates a method for capturing chemical species from fluid compositions, according to one or more embodiments of the disclosure.

[0011] **FIGS. 4A-B** illustrate powder X-ray diffraction data of metal organic frameworks, according to one or more embodiments of this disclosure.

[0012] **FIG. 5A** illustrates propane sorption isotherm data of a metal organic framework, according to one or more embodiments of this disclosure.

[0013] **FIG. 5B** illustrates a method for utilizing a metal organic framework as a molecular sieve, according to one or more embodiments of this disclosure.

[0014] **FIGS. 6A-B** illustrate hydrocarbon sieving data, according to one or more embodiments of this disclosure.

[0015] FIG. 7A illustrates benzene sorption isotherm data of a metal organic framework, according to one or more embodiments of this disclosure.

[0016] FIGS. 8A-C illustrate H₂O sorption isotherm data of various metal organic frameworks, according to one or more embodiments of this disclosure.

5 [0017] FIG. 8D illustrates a comparison of the relationship between water uptake at 0.05 P/P₀, heat of sorption and regeneration temperature of various metal organic frameworks, according to one or more embodiments of this disclosure.

[0018] FIGS. 9A-C illustrate CO₂ sorption isotherm data of various metal organic frameworks, according to one or more embodiments of this disclosure.

10 [0019] FIGS. 9D-E illustrate CO₂ guest molecules inside a metal organic framework, according to one or more embodiments of this disclosure.

[0020] FIG. 9F illustrates CO₂ heat of sorptions of a metal organic framework, according to one or more embodiments of this disclosure.

[0021] FIG. 9G illustrates cyclic CO₂ /N₂ column breakthrough experiments for an MOF, according to one or more embodiments of this disclosure.

15 [0022] FIG. 9H illustrates a heat of adsorption-CO₂ uptake trade-off for a metal organic framework as compared to benchmark and new developed materials, according to one or more embodiments of this disclosure.

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DETAILED DESCRIPTION

[0023] Provided herein are a series of highly stable and highly tunable MOFs with high affinity and stability to water and H₂S. Such qualities allow for efficient and cost effective methods for dehydrating gases, vapors, and solvents capable of replacing many cumbersome and expensive industrial processes. Further, this novel series of MOFs can be
25 designed with a variety of pore sizes and assembled with and without open-metal sites, affording tunable properties for a variety of separation applications. For example, the MOFs provided herein can refine hydrocarbon fluids under conditions and in the presence of chemical species which render known technologies inefficient, impracticable, or inoperable. In particular, MOFs provided herein can perform molecular sieving of fluid mixtures such as
30 olefin/paraffin mixtures. In another example, the MOFs described herein are suitable for applications involving BTX removal from fluid compositions comprising H₂S, which offers enormous cost savings by protecting and maintaining the operation efficiency of Claus catalysts.

[0024] The present invention is described with reference to the attached figures, wherein like reference numerals are used throughout the figures to designate similar or equivalent elements. The figures are not drawn to scale and they are provided merely to illustrate the invention. Several aspects of the invention are described below with reference to example applications for illustration. It should be understood that numerous specific details, relationships, and methods are set forth to provide an understanding of the invention. One skilled in the relevant art, however, will readily recognize that the invention can be practiced without one or more of the specific details or with other methods. In other instances, well-known structures or operations are not shown in detail to avoid obscuring the invention. The present invention is not limited by the illustrated ordering of acts or events, as some acts may occur in different orders and/or concurrently with other acts or events. Furthermore, not all illustrated acts or events are required to implement a methodology in accordance with the present invention.

[0025] As used herein, "fluids" can refer to a gas, liquid, or combination thereof. A gas or liquid can include one or more components. For example, a fluid can include a gas stream comprising CO₂, H₂S and water vapor.

[0026] As used herein, "refining" refers to removing one or more unwanted components or separating one or more components from remaining components of a composition. For example, refining can include removing olefin chemical species from a fluid composition, such as a mixture of olefin and paraffin chemical species.

[0027] As used herein, "poly-functional" refers to the characteristic of having more than one reactive or binding sites. For example, a poly-functional ligand can attach to a metal ion in multiple ways, bridge multiple metal ions, or combinations thereof. Specifically, pyrazine is a poly-functional ligand.

[0028] As used herein, "olefin" refers to an unsaturated hydrocarbon molecule including a carbon-carbon double bond. Olefins are also referred to as alkenes. An example of an olefin is propene.

[0029] As used herein, "paraffin" refers to a saturated hydrocarbon molecule consisting of carbon and hydrogen atoms connected only by single bonds. Paraffins are also referred to as alkanes. An example of a paraffin is propane.

[0030] Gas storage and separation using porous materials has experienced significant development in recent years in various industrial applications related to energy, environment, and medicine. Among porous materials, 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. MOF crystal chemistry uses a molecular building block (MBB) approach that offers potential to construct MOFs where desired structural and geometrical information are incorporated into the building blocks prior to the assembly process.

5 [0031] Generally, MOFs comprise a network of nodes and ligands, wherein a node has a connectivity capability at three 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 ions or metal containing clusters, and, in some instances, ligands with node connectivity capability at three or more functional sites can also be characterized as nodes. In some 10 instances, ligands can include two functional sites capable of each connecting to a node, and one or more additional functional sites which do not connect to nodes within a particular framework. A MBB can comprise a metal-based node and an organic ligand which extrapolate to form a coordination network. Such coordination networks have advantageous crystalline and porous characteristics affecting structural integrity and interaction with 15 foreign species (e.g., gases). The particular combination of nodes and ligands within a framework will dictate the framework topology and functionality. While essentially limitless combinations of nodes and ligands exist, to date, very few MOF materials are H₂S stable which consequently preclude their use in gas separation.

[0032] As disclosed in co-owned U.S. Application No.: 62/044,928, a series of 20 isorecticular MOFs with periodically arrayed hexafluorosilicate (SiF₆) pillars, called **SIFSIX-2-Cu-i** and **SIFSIX-3-Zn**, **SIFSIX-3-Cu** and **SIFSIX-3-Ni** showed particularly high CO₂ selectivity and capture. These properties in **SIFSIX-3-M** materials suggest broad applications from ppm level CO₂ removal to bulk CO₂ separation. However, with the exception of **SIFSIX-3-Ni**, the **SIFSIX-3-M** materials were not tolerant to H₂S. And 25 although these materials exhibit high structural stability in the presence of CO₂, extensive exposure of all **SIFSIX-3-M** materials to moisture detrimentally induces a phase change and the formation of new 2D stable materials. These 2D materials exhibit relatively unaltered selectivity but diminished CO₂ uptake. This indicates that the **SIFSIX-3-M** materials series is not sufficiently robust to handle CO₂ and H₂S capture in most critical applications 30 throughout the oil and gas and renewable fuels industries, especially in applications which bring the materials into contact with moisture.

[0033] MOFs, as provided herein, comprise one or more MBBs. Generally, a MBB, or a network of MBBs, can be represented by the formula [(node)_a(ligand)_b(solvent)_c]_n, n 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. In one example, an evacuated MOF can be subsequently enriched with a guest molecule compatible with the MOF framework and/or pores for a particular purpose (e.g., to outfit the MOF for use as a sensor). In other embodiments, guest molecules can include adsorbed gases, such as H₂S. While guest molecules can impart functionality onto a MOF, such are not a permanent fixture of the MOF. Accordingly, the value of c can vary down to zero, without changing the definitional framework of the MOF. Therefore in many instances, MOFs as provided herein will be defined as [(node)_a(ligand)_b]_n, without reference to a solvent or guest molecule component.

[0034] In some embodiments herein, MOFs can be characterized by the formula [(node)_a(ligand)_b(solvent)_c]_n. A non-limiting list of solvents can include one or more of H₂O, DMF, and DEF. In some embodiments, solvent can include a chemical species present after fabrication of the MOF. Some embodiments herein comprise a porous, uninhabited MOF characterized by the formula [(node)_a(ligand)_b]_n, wherein node comprises, generally, M_aM_bF_xO_y(H₂O)_z. In some embodiments, M_a comprises elements selected from periodic groups IB, IIA, IIB, IIIA, IVA, IVB, VIB, VIIB, or VIII. In some embodiments, M_b comprises elements selected from periodic groups IIIA, IIIB, IVB, VB, VIB, or VIII. In some embodiments, M_a comprises elements selected from periodic groups IB, IIA, IIB, IIIA, IVA, IVB, VIB, VIIB, or VIII and M_b comprises elements selected from periodic groups IIIA, IIIB, IVB, VB, VIB, or VIII. In some embodiments, M_a can comprise one of the following cations: Cu²⁺, Zn²⁺, Co²⁺, Ni²⁺, Mn²⁺, Zr²⁺, Fe²⁺, Ca²⁺, Ba²⁺, Pb²⁺, Pt²⁺, Pd²⁺, Ru²⁺, Rh²⁺, Cd²⁺, Mg⁺², Al⁺³, Fe⁺², Fe⁺³, Cr²⁺, Cr³⁺, Ru²⁺, Ru³⁺ and Co³. In some embodiments, M_b can be one of the following Al⁺³, Fe⁺², Fe⁺³, Cr²⁺, Cr³⁺, Ti³⁺, V³⁺, V⁵⁺, Sc³⁺, In³⁺, Nb⁵⁺, Y³⁺. In some embodiments, M_a can comprise one of the following cations: Cu²⁺, Zn²⁺, Co²⁺, Ni²⁺, Mn²⁺, Zr²⁺, Fe²⁺, Ca²⁺, Ba²⁺, Pb²⁺, Pt²⁺, Pd²⁺, Ru²⁺, Rh²⁺, Cd²⁺, Mg⁺², Al⁺³, Fe⁺², Fe⁺³, Cr²⁺, Cr³⁺, Ru²⁺, Ru³⁺ and Co³; M_b can be one of the following Al⁺³, Fe⁺², Fe⁺³, Cr²⁺, Cr³⁺, Ti³⁺, V³⁺, V⁵⁺, Sc³⁺, In³⁺, Nb⁵⁺, Y³⁺. In such embodiments, the ligand can be any bi-functional N-donor linkers based on monocyclic or polycyclic group (aromatic or not).

[0035] 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 some embodiments, a ligand can comprise a plurality of 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 non-aromatic. In some embodiments, a ligand can comprise a nitrogen-containing monocyclic or polycyclic group structure. In some embodiments, a ligand can comprise a nitrogen-containing heterocyclic ligand, including pyridine, pyrazine, pyrimidine, pyridazine, triazine, thiazole, oxazole, pyrrole, imidazole, pyrazole, triazole, oxadiazole, thiadiazole, quinoline, benzoxazole, benzimidazole, and tautomers thereof.

[0036] Some embodiments of suitable MOFs can be represented by the following general formula: $[M_a M_b F_x (O/H_2O)_z (\text{Ligand})_2]_n$ wherein M_a can be one of the following cations: Cu^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+} , Zr^{2+} , Fe^{2+} , Ca^{2+} , Ba^{2+} , Pb^{2+} , Pt^{2+} , Pd^{2+} , Ru^{2+} , Rh^{2+} , Cd^{2+} , Mg^{+2} , Al^{+3} , Fe^{+2} , Fe^{+3} , Cr^{2+} , Cr^{3+} , Ru^{2+} , Ru^{3+} and Co^3 ; M_b can be one of the following Al^{+3} , Fe^{+2} , Fe^{+3} , Cr^{2+} , Cr^{3+} , Ti^{3+} , V^{3+} , V^{5+} , Sc^{3+} , In^{3+} , Nb^{5+} , Y^{3+} ; and the ligand can be any bi-functional N-donor linkers based on monocyclic or polycyclic group (aromatic or not).

[0037] One MOF synthesis strategy provided herein comprises linking inorganic chains using appropriate N-donor based linkers to deliberately generate channels along one crystallographic direction. The inorganic chains are built up from the trans-connection between $M_a N_4 F_2$ and $M_b F_4 (H_2O)_2$ octahedra or between $M_a N_4 F_2$ and $M_b F_5 (H_2O)$ octahedra or between $M_a N_4 F_2$ octahedra and $M_b F_5 (O)$ octahedra. Figure 1A illustrates an example of an inorganic chain, built up from $M_a N_4 F_2$ and $M_b F_5 (H_2O)$ octahedra. The resulted inorganic chains are linked to each other using bi-functional N-donor organic ligands, thereby generating channels with different sizes and shapes depending on the nature of the organic linker. Figure 1B illustrates a schematic view of one embodiment of a MOF comprising a $\text{NiNbF}_5 \text{O}(\text{pyrazine})_2$ structure, viewed along the c-axis.

[0038] The utility of MOFs such as those provided herein are highly dependent upon the framework's structural features such as structural strength, density, functionality, pore aperture dimensions, pore dimensions, the ratio of pore aperture dimensions to pore dimensions, pore accessibility, and the presence of a plurality of pore dimensions and/or pore aperture dimensions (e.g., a poly-porous MOF). The originality of this new class of crystalline porous materials is based, in part, on the fact that the shape of cavities, (i.e. square or rectangle based channels), is controlled from a structural point of view using appropriate cations and organic linkers. The novel MOF architectures disclosed herein offer a novel improvement on some MOF architectures by replacing silicon components with other metals, such as Al^{3+} , Fe^{2+} , Fe^{3+} , V^{3+} , V^{4+} , V^{5+} , Nb^{5+} , to afford highly stable materials with or without open metals sites. In some embodiments, the use of specific cations, such as Al^{3+} , Fe^{2+} , Fe^{3+} ,

Cr²⁺, Cr³⁺, Ti³⁺, V³⁺, V⁵⁺, Sc³⁺, In³⁺, Y³⁺, in M_b site positions can introduce open-metal sites within the channels that enhance properties of gas capture.

[0039] These, and other features, collaborate to achieve MOFs with high affinity and stability to water and H₂S. Additionally, the novel series of MOFs structures disclosed herein can be designed with a variety of pore sizes and/or open-metal sites which afford tunable properties for a variety of gas/vapor/solvent separation applications. Tuning, in some embodiments, can include modification of the organic and/or inorganic components of the MOF. For example, lighter metal-based clusters can be used to lower the framework density and increase the relative wt. % of captured CO₂ and/or H₂S. Further, the MOF platforms as provided herein allow for an unprecedented high degree of tuning control at the molecular level, allowing the size and shape of channels within a MOF architecture to be rigorously controlled and adapted to specific separation of numerous gases, beyond CO₂ and H₂S.

[0040] In some embodiments, a representative

[M_aM_bF_{6-n}(O/H₂O)_w(Ligand)_x(solvent)_y]_z MOF structure can include a Ni M_a constituent, an M_b constituent group selected from one of Al, Fe, V, or Nb, and a Ligand comprising a pyrazine constituent group. All such embodiments offer high affinity and stability to water vapor and H₂S, unlike the Cu and Zn-based analogues of SIFSIX-3-M materials made with Si. In some embodiments a MOF characterized by the formula

[M_aM_bF_{6-n}(O/H₂O)_w(Ligand)_x(solvent)_y]_z wherein M_a equals Ni, M_b equals Al, Fe, V or Nb, and ligand equals pyrazine, the pore size (channel size) of the resulting MOF can be about 3.3 Å to about 3.8 Å, or about 2.8 Å to about 4.8 Å. In some embodiments, the channels are square/rectangular. In the same or in an alternative embodiment, a MOF can have a specific surface area of about 250 m²/g to about 500 m²/g. In either of the same MOFs or in an alternative embodiment, a MOF can have a pore volume of about 0.1 cm³/g to about 0.25 cm³/g. In a different embodiment, a more elongated ligand can provide an analogous MOF with much higher porosity.

[0041] In some embodiments, M_b and/or a ligand can be selected to hinder or allow rotation of a ligand. Altering the nature, shape, and dimensions of the (M_bOF₅)^{x-} pillars employed in [M_aM_bF_{6-n}(O/H₂O)_w(Ligand)_x(solvent)_y]_z MOFs can selectively hinder the free rotation of ligands and thus dictate the maximum and/or minimum opening of the pore aperture size. This approach offers potential to dial-in/command the passing-blocking of specific probe molecules. In some embodiments M_b and/or a ligand are selected to allow no rotation of a ligand. In some embodiments M_b and/or a ligand are selected to allow full

rotation of a ligand. In some embodiments M_b and/or a ligand are selected to allow partial rotation of a ligand.

[0042] In some embodiments, M_b and/or a ligand can be selected to hinder or allow rotation of a pillar. Altering the nature, shape, and dimensions of the $(M_bOF_5)^{x-}$ pillars employed in $[M_aM_bF_{6-n}(O/H_2O)_w(Ligand)_x(solvent)_y]_z$ MOFs can selectively hinder the free rotation of pillars and thus dictate the maximum and/or minimum opening of the pore aperture size. This approach offers potential to dial-in/command the passing-blocking of specific probe molecules. In some embodiments M_b and/or a ligand are selected to allow no rotation of a pillar. In some embodiments M_b and/or a ligand are selected to allow full rotation of a pillar. In some embodiments M_b and/or a ligand are selected to allow partial rotation of a pillar.

[0043] In some embodiments, M_b and/or a ligand can be selected to hinder or allow rotation of a ligand and a pillar. Altering the nature, shape, and dimensions of the $(M_bOF_5)^{x-}$ pillars employed in $[M_aM_bF_{6-n}(O/H_2O)_w(Ligand)_x(solvent)_y]_z$ MOFs can selectively hinder the free rotation of a ligand and a pillar and thus dictate the maximum and/or minimum opening of the pore aperture size. This approach offers potential to dial-in/command the passing-blocking of specific probe molecules. In some embodiments M_b and/or a ligand are selected to allow no rotation of a ligand and a pillar. In some embodiments M_b and/or a ligand are selected to allow full rotation of a ligand and a pillar. In some embodiments M_b and/or a ligand are selected to allow partial rotation of a ligand and a pillar.

[0044] A specific MOF characterized by the formula $[M_aM_bF_{6-n}(O/H_2O)_w(Ligand)_x(solvent)_y]_z$ is NbOFFIVE-1-Ni, wherein M_a comprises Ni and M_b comprises Nb. This MOF includes a $(NbOF_5)^{2-}$ inorganic pillar which, due to the larger Nb^{+5} , has a longer Nb-F bond length (1.905(1) Å) as compared to the Si-F bond length (1.681(1) Å) of the SIFSIX MOFs described above. The increased Nb-F bond length reduces the distance between the pendant fluorine in the channel, and the relatively increased nucleophile behavior of $(NbOF_5)^{2-}$ provides increased stability in the presence of water. Pyrazine is a suitable ligand for the NbOFFIVE-1-Ni MOF, among others as described herein. NbOFFIVE-1-Ni is a pillared sql-MOF based on $(NbOF_5)^{2-}$ pillars that connect a 2D square grid of Ni-(pyrazine)₂. The quadrangular-pillared sql-MOF can be viewed as a 3D MOF wherein each NiOF(pyrazine)₄ node serves as 6-connected node connected by $(NbOF_5)^{2-}$ pillars through fluorine/oxygen atoms giving rise to a pcu topology. It must be noted that the assignment of one oxygen and one fluorine atom in apical position within the pillar has been previously demonstrated in similar materials and confirmed with supporting techniques.¹²

The overall framework consists of square shaped open channels having slightly smaller diameters of about 3.175(1) Å (taking account of van der Waals radii) comparatively to the analogue material SIFSIX-3-Cu (3.980(1) Å).

[0045] A specific MOF characterized by the formula $[M_aM_bF_6$

5 $n(O/H_2O)_w(Ligand)_x(solvent)_y]_z$ is AlFFIVEH₂O-1-Ni, wherein M_a comprises Ni and M_b comprises Al. When utilizing a pyrazine ligand, this MOF can be characterized by the specific formula NiAlF₅(H₂O)(pyr)₂.2H₂O, although other ligands described herein can be suitable. Another specific MOF characterized by the formula $[M_aM_bF_6$

10 $n(O/H_2O)_w(Ligand)_x(solvent)_y]_z$ is FeFFIVEH₂O-1-Ni, wherein M_a comprises Ni and M_b comprises Fe. When utilizing a pyrazine ligand, this MOF can be characterized by the specific formula NiFeF₅(H₂O)(pyr)₂.4H₂O, although other ligands described herein can be suitable. AlFFIVEH₂O-1-Ni and FeFFIVEH₂O-1-Ni are isomorphs, and take advantage of the periodically arrayed fluorine combined with the adequate one dimensional channel size. In contrast to the Si of SIFSIX MOFs described above, the introduction of open metal sites

15 within the framework is concomitant with the utilization of an appropriate metal with the required oxidation state that allows the presence of a water molecule within the metal coordination sphere. Aluminum and Iron cations were used such that the MOF would adopt an octahedral fluorinated environment and lead to open metal sites after coordinated water removal via proper activation. Each isomorph utilizing pyrazine as a ligand exhibits a

20 primitive cubic (pcu) topology resulting from the pillaring of metal-pyrazine 2D square-grid moieties with $(MF_5H_2O)^{2-}$ (M= Al³⁺ or Fe³⁺) inorganic pillars.

[0046] Some such MOFs can be fabricated using a solvo(hydro)thermal synthetic procedure. As shown in Figure 2, a method for fabricating 200 a MOF 230 can include combining 205 reactants. Reactants can include one or more of a fluorhydric acid solution

25 206 with a Ni²⁺ source 207, a second metal source 208, and a solvent 209 to form a mixture 210. A Ni²⁺ source 207 can include one or more of nickel nitrate, hydrated nickel nitrate, nickel chloride, hydrated nickel chloride, nickel fluoride, hydrated nickel fluoride, nickel oxide, or hydrated nickel oxide. The second metal source 208 can include an Al³⁺ source, an Fe⁺² source, an Fe⁺³ source, a Cr²⁺ source, a Cr³⁺ source, a Ti³⁺ source, a V³⁺ source, a V⁵⁺

30 source, a Sc³⁺ source, an In³⁺ source, a Nb⁵⁺ source, or a Y³⁺ source, for example. These, metals can be in the form of nitrates, hydrated nitrates, chlorides, hydrated chlorides, fluorides, hydrated fluorides, oxides, hydrated oxides, and combinations thereof. The solvent 209 can include one or more of H₂O, dimethylformamide (DMF), and diethylformamide (DEF).

[0047] The method for fabricating 200 can further comprise to reacting 215 the mixture 210, sufficient to form a reacted mixture 220. Reacting 215 can include contacting the fluorhydric acid solution 206, the Ni²⁺ source 207, the second metal source 208, and the solvent 209. Reacting 215 can further comprise stirring or agitating the mixture 210, or heating the mixture 210. Heating the mixture 210 can comprise heating to a temperature between about 80 °C to about 200 °C. The reacted mixture 220 can be further processed 225 to provide a fabricated MOF 230. Processing 220 can include one or more of filtering the reacted mixture 220, rinsing the reacted mixture 220 with water, removing excess reactants from the reacted mixture 220. In some embodiments, guest molecules are optionally evacuated from a fabricated MOF 230. Guest molecules can include solvent guest molecules, or derivatives thereof.

[0048] Figure 3 illustrates a method 300 for capturing 320 one or more chemical species from a fluid composition 310 via a MOF 305. A method 300 for capturing 320 one or more chemical species from a fluid composition 310 can comprise contacting 315 a metal organic framework 305 characterized by the formula $[M_aM_bF_6_n(O/H_2O)_w(Ligand)_x(solvent)_y]_z$ with a fluid composition 310. Fluid composition 310 can comprise two or more chemical species. Method 300 can further comprise capturing 320 one or more captured chemical species from the fluid composition 310. In some embodiments, capturing 320 comprises physical adsorption of the one or more captured chemical species by the metal organic framework 305. In some embodiments, capturing 320 comprises chemisorption of the one or more captured chemical species by the metal organic framework. Chemisorption can occur by one or more captured chemical species chemically interacting with one or more open metal sites of the metal organic framework 305. In other embodiments, capturing 320 comprises physical adsorption and chemisorption of the one or more captured chemical species by the metal organic framework. Capturing can comprise wholly or partially containing a chemical species within a pore of a MOF. In some embodiments, capturing 320 consists of chemisorption. In some embodiments, capturing 320 consists of physical adsorption.

[0049] In some embodiments, the fluid composition 310 can comprise H₂S and one or more of benzene, toluene, xylene, ethylbenzene, naphthalene and styrene. In such embodiments, capturing 320 can comprise capturing one or more of benzene, toluene, xylene, ethylbenzene, naphthalene, and styrene. In a specific embodiment, M_a can comprise Ni²⁺ and M_b can comprise Nb⁵⁺.

[0050] In some embodiments, the fluid composition 310 can comprise breathable air. Breathable air can include atmospheric air, or life-supporting air in a confined space. In a non-limiting example, breathable air can include one or more of oxygen, nitrogen, carbon dioxide, and argon. In such embodiments, capturing 320 can comprise capturing carbon dioxide. In such embodiments, capturing 320 can consist of capturing carbon dioxide. In such embodiments, capturing 320 occurs in a confined space. Capturing 320 can comprise capturing trace amounts of carbon dioxide.

[0051] In some embodiments, the fluid composition 310 can comprise one or more of flue gas, syngas, biogas and landfill gas. In such embodiments, capturing 320 can comprise capturing carbon dioxide. In such embodiments, capturing 320 can consist of capturing carbon dioxide.

[0052] In some embodiments, the fluid composition 310 can comprise one or more gases, one or more vapors, one or more solvents, or combinations thereof. In such embodiments, capturing 320 can comprise capturing water. In such embodiments, capturing 320 can consist of capturing water. In one embodiment, M_a can comprise Ni^{2+} and M_b can comprise Fe^{+2} or Fe^{+3} .

[0053] In some embodiments, the fluid composition 310 can comprise one or more olefin species and one or more paraffin species. In such embodiments, capturing 320 can comprise capturing one or more olefins. In a particular embodiment, the one or more olefin species can comprise ethylene and the one or more paraffin species can comprise ethane. In another particular embodiment, the one or more olefin species can comprise propylene and the one or more paraffin species can comprise propane.

[0054] In some embodiments, the fluid composition 310 can comprise H_2S and one or more hydrocarbon species. In such embodiments, capturing 320 can comprise capturing H_2S . In such embodiments, capturing 320 can consist of capturing H_2S . In such embodiments, the one or more hydrocarbon species can comprise one or more open-chain hydrocarbons. In a particular embodiment, the one or more open-chain hydrocarbons can comprise propane, propene, ethane, ethene, and combinations thereof.

[0055] In some embodiments, one or more MOFs described herein are suitable for applications involving gas, vapor, and/or solvent dehydration. The particular outstanding properties of $NiM_bF_{6-2}O_w(H_2O)_x(Ligand)_y(solvent)_z$, wherein M_b can comprise Al, Fe, V, or Nb, for example, as compared to SIFSIX-3-M (Cu, Zn, Ni) materials, and others known in the art, in terms of stability to moisture, and H_2O uptake and affinity make these series of novel MOFs suitable for many industrial application where various degree of humidity need

to be removed. Furthermore, these materials are advantageous in that exposure to moisture in non-process settings (e.g., transport, installation, maintenance, etc.) will not affect performance.

[0056] In some embodiments, one or more MOFs described herein are suitable for applications involving CO₂ capture from flue gas, syngas, biogas and landfill gas. In particular,

MOFs, with and without open metal sites, characterized by the formula

$NiM_bF_6O_x(H_2O)_y(Ligand)_z$ exhibit a number advantageous of CO₂ properties (e.g., uptake, selectivity, and kinetics) at various concentrations (e.g., from 1% to 50%) and humidity values (e.g., up to ca. 100 % relative humidity) for a wide variety of relevant industrial gases.

[0057] In some embodiments, one or more MOFs described herein are suitable for applications involving CO₂ removal in confined spaces. Efficient removal of CO₂ at low concentrations is vital for the proper operation of many confined-space systems, such as breathing systems. Confined spaces can include those found in submarines and aerospace craft. For example, in long-term space flight and submarine missions where air resupply opportunities are scarce, CO₂ must be removed from the air and recycled. An average crew member requires approximately 0.84 kg of oxygen and emits approximately 1kg of carbon dioxide per day. Thus the ability to continuously purify exhaled air to a maximum CO₂ concentration of 2-5% will lead to an optimal recycling and considerable reduction in fresh air supply in remote confined spaces. The shortcomings of existing technologies include a low daily capture capacity, due in part to the long temperature swing adsorption cycling (TSA) mode, which is determined mainly by absorbent reactivation. In case of low CO₂ concentration removal, chemical adsorbents (e.g., amine supported absorbents) are preferred with a heat of adsorption of 70-100 kJ/mol. The heat of adsorption indicates the energy required to clean the material after each adsorption cycle. The MOFs disclosed herein, such as NbOFFIVE-1-Ni, among others, operate purely on physical adsorption in processes such as VTSA or VSA (under mild vacuum), and therefore can both increase the daily CO₂ removal capacity and significantly decrease the energy needed for regeneration to lower than 2500 kJ/Kg CO₂. This is significantly lower than the 4,000 – 5,000 kJ/Kg CO₂ required by liquid amine scrubbing.

[0058] In one embodiment, a representative $M_aM_bF_xO_y(Ligand)_2$ MOF structure can include a Ni M_a constituent, a Nb M_b constituent group, and a Ligand comprising a pyrazine constituent group. Figure 4A illustrates powder X-ray diffraction data of NbOFFIVE-1-Ni, confirming the high stability of the MOF in the presence of water. Figure 4B illustrates

powder X-ray diffraction data of NbOFFIVE-1-Ni, confirming the high stability of the MOF in the presence of H₂S. Powder X-ray diffraction data for AlFFIVEH₂O-1-Ni and FeFFIVEH₂O-1-Ni similarly show high stability in the presence of water and H₂S.

[0059] Figure 5A illustrates H₂S and propane (C₃H₈) adsorption isotherms for NbOFFIVE-1-Ni. An adsorption isotherm determines the amount of adsorbed adsorbate over the dry mass of adsorbent as a function of its vapor pressure at constant temperature. The data in Figure 5A indicates an extremely high sorption of H₂S even at low pressure and essentially zero sorption of C₃H₈, even at over 2 bar at 298K. As shown in Figure 5A, one or more MOFs described herein are suitable for H₂S removal from polymer grade paraffins. In particular, one or more MOFs described herein are suitable for applications involving H₂S removal from propane. Single gas adsorption data revealed that the NbOFFIVE-1-Ni channels with restricted aperture-size allowed the adsorption of C₃H₆ but did not permit the C₃H₈ to diffuse/adsorb into the pore system at 298 K up to ca. 1 bar. Significantly, C₃H₆/C₃H₈: 50/50 mixed gas adsorption data, collected at 298 K (up to 0.5 bar partial pressure of C₃H₆), overlaid perfectly with the pure C₃H₆ adsorption isotherm and thus supported the molecular exclusion of propane from propylene. The concomitant aperture size and shape expressed in this new MOF adsorbent provided the requisite size/shape cut-off in adsorption, resulting in the observed unprecedented infinite C₃H₆/C₃H₈ selectivity. The infinite selectivity was further confirmed by performing C₃H₆/C₃H₈: 50/50 mixed-gas column breakthrough experiments, imitating the real conditions for the C₃H₆/C₃H₈ separation process, at room temperature and 1 bar in a packed column bed of ca. 1.4 g of NbOFFIVE-1-Ni. Markedly, using 4 cm³/min total gas flow, C₃H₈ was not adsorbed in the packed column bed while pure C₃H₆ was retained for ca. 480 seconds. Additionally, mixed-gas column breakthrough experiments were performed in dilute conditions using N₂ as a carrier inert gas, namely C₃H₆/C₃H₈/N₂: 5/5/90 and C₃H₆/C₃H₈/N₂: 25/25/90 mixtures. Noticeably, the pure C₃H₆ was retained in the packed column bed while N₂ and C₃H₈ were not adsorbed/retained by NbOFFIVE-1-Ni. Supportively, the regeneration/activation of the saturated adsorbent, desorption over a 10 minutes period, showed solely the propylene signal and thus confirming the non-adsorption/retention of the propane in the bed

[0060] To further support and confirm the complete molecular exclusion of C₃H₈ and the sole adsorption of C₃H₆, simultaneous calorimetric and gravimetric measurements (TG-DSC) were performed at 1 bar. This complementary study confirmed the complete exclusion of propane from propylene as evidenced by the no detection of noticeable heat of adsorption in the case of C₃H₈ and the quantified heat of adsorption for C₃H₆ of 57.4 kJ/mol. High

pressure adsorption studies confirmed the non-noticeable adsorption of C_3H_8 below 1.5 bar, only minor propane uptake was observed at around 1.5 bar (ca. 0.1 mol/Kg).

Noticeably, the resultant infinite propylene/propane selectivity has never been observed using adsorbent materials. Prior C_3H_6/C_3H_8 adsorption studies, using zeolite, carbon molecular sieves (CMS) or MOFs, revealed the plausible equilibrium and/or kinetic based separation but with a low to moderate separation factors.

[0061] Figure 5B illustrates a method for utilizing NbOFFIVE-1-Ni as a C_3H_8 sieve in a two-step CSA or VSA as compared to the five step Pressure Swing Adsorption (PSA) method required by zeolites such as zeolite 4A. Valuably, the prospective deployment of NbOFFIVE-1-Ni as a splitter agent/adsorbent, permitting the complete sieving of C_3H_8 from C_3H_6 , offers: (i) a simplified separation process based on a concentration swing recycling mode (CSRM) or a vacuum swing recycling mode (VSRM), where the ideal working C_3H_6 capacity can be accomplished by performing a desorption step with an inert gas (e.g. H_2 or N_2) purge at 1.2 bar or by simply reducing the pressure from 1.2 bar to 0.01 bar, (ii) the ability to eliminate the energy-demanding high pressure steps employed in the case of the zeolite 4A adsorbent, that is to say no pressurization (step 2), no purge (with N_2 , step 3) and no co-current blow down (step 4) will not be required in the projected concentration swing adsorption (CSA) or vacuum swing adsorption (VSA) system using the NbOFFIVE-1-Ni adsorbent. Markedly, the implementation of the VSA system based on NbOFFIVE-1-Ni as an adsorbent offers potential to considerably reduce the energy penalty associated with the conventional C_3H_6/C_3H_8 separation, and valuably recover both C_3H_6 and C_3H_8 separately in a high purity grade.

[0062] Correspondingly, subsequent mixed-gas (C_3H_6/C_3H_8 : 50/50) column breakthrough measurements were performed in order to corroborate the preservation of the adsorption properties and separation performance of the NbOFFIVE-1-Ni, namely the propylene adsorption uptake and the full molecular exclusion of propane from propylene at standard ambient temperature and pressure. Distinctively, the multiple adsorption/desorption measurements (over 10 cycles) using CSRM revealed that NbOFFIVE-1-Ni maintained its propylene adsorption capacity and its full molecular exclusion of propane. Detailed analysis of the data, for the C_3H_6/C_3H_8 : 50/50 mixed gas adsorption cycles in a bed comprised of 1.4 g of NbOFFIVE-1-Ni, indicated a C_3H_6 uptake of ca. 0.60 mol/kg for a given cycle based on an 8 min adsorption followed by a 10 min desorption using CSRM. Considerably, this result pinpoints the appropriateness of the NbOFFIVE-1-Ni as a stable separating agent for propylene/propane with a pronounced propylene uptake/recovery of ca. 2 mol/Kg/hour.

Markedly, the NbOFFIVE-1-Ni adsorbent offers potential to effectively separate propylene from propane with a reduced energy-footprint using a concentration swing adsorption (CSA). Perceptibly, the NbOFFIVE-1-Ni adsorbent proffers a plausible large propylene recovery/productivity and a marked higher purity than to the most prominent adsorbent for the said separation, namely the zeolite 4A using VSA at 423 K, offering only a limited 26% recovery for a propylene capacity of 1.03 mol/Kg/hour (0.13 mol/kg per cycle) with a 97% purity.

[0063] Figure 6A illustrates ethylene and ethane sorption isotherms for NbOFFIVE-1-Ni, which show a positive correlation between increased ethane and ethylene sorption and increased pressure at 298 K. Increased pressure increases the ethylene/ethane sorption ratio, which demonstrates the potential for NbOFFIVE-1-Ni in molecular sieving, particularly in olefin/paraffin separations. Similarly, Figure 6B illustrates propylene and propene sorption isotherms for NbOFFIVE-1-Ni, which show a positive correlation between increased propylene sorption and increased pressure and minimal propane sorption across all test pressures (0 – 800 Torr) at 298K. The propylene isotherms indicate Brunauer type-I adsorption characteristic of microporous adsorption at subcritical, near critical, and supercritical conditions, which is sometimes referred to as Langmuir adsorption. The plateau achieved at increasing pressure indicates monolayer coverage or complete saturation of the adsorbant, and can imply chemisorption. It can be noted that monolayer coverage, or near monolayer coverage, of propylene as shown in Figure 6B was achieved at a much lower pressure than ethylene, which, as shown in Figure 6A, has not achieved monolayer coverage, or near monolayer coverage, even at about 800 Torr. The similarity of the adsorption/desorption curves in Figures 6A-B for all species (ethylene, ethane, propylene, propane) suggest that there are no MOF structural changes during the adsorption process.

[0064] As shown in Figures 6A-B, one or more MOFs described herein are suitable for applications involving olefin/paraffin sieving separation. In particular, one or more MOFs described herein are suitable for applications involving propane/propene sieving separation. For example, NbOFFIVE-1-Ni shows full sieving of propene from propane. Such performance is unprecedented for any class MOFs both in industry and at the lab scale.

[0065] Similarly, one or more MOFs described herein are suitable for applications involving BTX removal from fluid compositions comprising H₂S. An example of a fluid composition comprising H₂S is sour gas, which is generally defined as having more than 5.7 milligrams of H₂S per cubic meter of gas. An example of sour gas is natural gas (CH₄) having more than 5.7 milligrams of H₂S per cubic meter of CH₄. Removing BTX, BTEX,

BTEXN, TEXS, and combinations thereof is critical to many industrial processes. For example, when H₂S is recovered in any industrial process, it is most commonly desulfurized by the Claus process which converts the gaseous H₂S to elemental sulfur. The Claus process includes a first thermal combustion step which typically achieves a 60-70% conversion of gaseous (H₂S) sulfur to elemental sulfur. A subsequent catalytic step converts the remaining gaseous H₂S and employs an activated aluminum(III) and/or titanium(IV) oxide catalyst. Claus catalysts can suffer from gradual surface area degradation in the presence of moisture, but are readily deactivated in the presence of BTX, BTEX, BTEXN, TEXS, and combinations thereof.

10 **[0066]** MOF's as provided herein, particularly those characterized by the formula NiM_bF_{6-n}(H₂O/O)_n(pyrazine)₂(solvent)_x, wherein M_b comprises Al, Fe, V, and Nb, offer an effective and unprecedented platform for moisture and BTX, BTEX, BTEXN, and TEXS extraction from H₂S fluid compositions, particularly including Claus process feed streams. In particular, Figure 7A shows benzene sorption isotherms at 293 K for NbOFFIVE-1-Ni. Benzene shows negligible adsorption, similar to the propane adsorption shown in Figure 6B, due in part to the large molecule size of benzene. Similar adsorption behavior can be assumed for toluene, xylene, styrene, ethylbenzene, and naphthalene, among others. Such negligible adsorption is in stark comparison to that of H₂S, as shown in Figure 6A. Therefore, NbOFFIVE-1-Ni is particularly suitable for removing H₂S from fluid compositions comprising BTX, BTEX, BTEXN, TEXS, and combinations thereof. Such MOFs offer an attractive alternative to the activated carbon beds currently used to remove BTX from Claus catalyst process feed streams. This is in part because activated carbon beds include a large range of microspores which allow competitive adsorption of BTX and H₂S, and thus low H₂S/BTX selectivity. Conversely, MOFs such as NbOFFIVE-1-Ni offer almost infinite H₂S selectivity.

[0067] Figure 8A illustrates H₂O sorption isotherms for NbOFFIVE-1-Ni, indicating an extremely high sorption of H₂O across all test pressures (0 – 1.2 Bar), and notably monolayer coverage, or near monolayer coverage, at low pressure (e.g., 0 Bar) at 298K.

[0068] Similarly suitable for such applications are AlFFIVEH₂O-1-Ni and FeFFIVEH₂O-1-Ni. Figure 8B illustrates variable temperature H₂O adsorption isotherms for AlFFIVEH₂O-1-Ni, and Figure 8C illustrates H₂O adsorption isotherms for FeFFIVEH₂O-1-Ni at 295 K. Both adsorption isotherms exhibit unprecedented steepness at very low partial pressure that supports their extremely high affinity for water. Moreover, AlFFIVEH₂O-1-Ni and FeFFIVEH₂O-1-Ni show exceptional adsorption saturation of 22 and 18 wt%,

respectively, at $P/P_0 = 0.05$ relative pressure and 293 K. Heats of adsorption for AlFFIVEH₂O-1-Ni and FeFFIVEH₂O-1-Ni were determined by TG-DSC experiments to be 63 kJ/mol and 64.7 kJ/mol respectively.

[0069] Figure 8D illustrates a comparison of the relationship between water uptake at 0.05 P/P_0 , heat of sorption and regeneration temperature of AlFFIVEH₂O-1-Ni and FeFFIVEH₂O-1-Ni with other well-known dehydrating agents. It is worth mentioning that the heat of H₂O adsorption at very low loading in case of the zeolite 5A is remarkably higher (80-120 kJ/mol) than MFFIVEH₂O-1-Ni (M=Al or Fe) series and consequently this behavior reflects the high desorption temperature 250°C (523K) needed to ensure optimal cyclic operations. MFFIVEH₂O-1-Ni (M=Al or Fe) have the greatest advantage to necessitate a much less demanding energy of H₂O vapour full desorption. In fact, activation/re-activation evaluation and adsorption/desorption cyclic properties of AlFFIVEH₂O-1-Ni demonstrated that the full dehydration is achievable after a simple heating at 95-105°C (368-378K) combined with flushing a less absorbable gas (such as N₂) or vacuum. The low temperature recycling feature is of prime importance as it prevents all the concerns with regards to coke formation, commonly occurring using zeolites, when the dehydration is carried out in the presence of hydrocarbon and/or VOC at high temperatures. Silica gel can be recycled by heating only at 90-100°C with a H₂O heat of adsorption of 43-50 kJ/mol, but it exhibits much lower H₂O adsorption uptake at low H₂O vapor partial pressures as it is shown in Figure 8D. Similar to the 3A, 4A, and 5A molecular sieves, MFFIVEH₂O-1-Ni MOFs exhibit an excellent rate of H₂O adsorption and much better adsorption kinetics than other types of desiccants.

[0070] Figure 9A illustrates a CO₂ isotherm up to 1 bar at 298K for NbOFFIVE-1-Ni and Figure 9B illustrates a variable temperature adsorption isotherm for NbOFFIVE-1-Ni at temperatures ranging from 258K to 348K. NbOFFIVE-1-Ni shows steep adsorption isotherms for CO₂. Figure 9C illustrates low pressure CO₂ isotherms for various MOFs, and shows that NbOFFIVE-1-Ni outperforms SIFSIX-3-Cu, the best known trace CO₂ capture MOF. NbOFFIVE-1-Ni absorbs 51.4 cm³/cm³ (1.3 mmol/g) CO₂ at 400 ppm and 298K as compared to 44.6 cm³/cm³ by SIFSIX-3-Cu, 15% higher than the best reported material. Consequently, NbOFFIVE-1-Ni is the best material for gravimetric and volumetric CO₂ capture at trace concentration, driven mainly by physisorption. The difference in uptake is observed even larger at higher temperatures where NbOFFIVE-1-Ni absorbs 63% more CO₂ at 400 ppm and 328K than SIFSIX-3-Cu. The volumetric uptake for well-known MOFs such

as Mg-MOF-74 is comparatively very small at 400 ppm ($\approx 1.7 \text{ cm}^3/\text{cm}^3$). In terms of gravimetric uptake both NbOFFIVE-1-Ni and SIFSIX-3-Cu have similar CO_2 capacity and adsorb $43 \text{ cm}^3 \text{ STP/g}$ at 1300 ppm and 298K, 300% higher than SAPO-34 (Sr^{2+}), a physical adsorbent candidate for CO_2 removal in long-duration crewed space exploration missions.

5 Recently, a copper silicate (SGU-29) was reported showing ca. $26 \text{ cm}^3/\text{cm}^3$ and $40 \text{ cm}^3/\text{cm}^3$ uptake at CO_2 concentration of 400 and 1000 ppm (single gas adsorption), respectively. The CO_2 volumetric and gravimetric uptakes of this purely inorganic CO_2 adsorbent is much lower than NbOFFIVE-1-Ni at very low CO_2 pressure.

[0071] Fourier difference data obtained through single crystal X-ray diffraction (SCXRD) of a degassed crystal of NbOFFIVE-1-Ni under 1bar CO_2 atmosphere at 298K, indicated a clearly localized CO_2 molecule within the 1D channels of the structure. Figures 9D and 9E provide direct visualization of CO_2 molecules inside the crystal structure of NbOFFIVE-1-Ni showing the energetically highly favorable arrangement of CO_2 molecules inside the channels along [010] and [001], respectively. CO_2 occupies highly energetically favorable position, where electropositive carbon of CO_2 is surrounded by four electronegative fluorine of $(\text{NbOF}_5)^{2-}$ groups (C...F distance = $3.04(1)\text{\AA}$) and electronegative oxygen atoms of CO_2 is surrounded by pyrazine hydrogens (C-H...O distance = $2.98(1)\text{\AA}$, angle = 119.9°). It can be inferred from the crystal structure that presence of strong complementary interactions at right position create energetically highly favorable 'sweet spot' for CO_2 that is responsible for uniquely strong physisorption-driven CO_2 capture features in this material. The highly favorable interactions for CO_2 in case of NbOFFIVE-1-Ni are reflected in the value of heat of CO_2 adsorption, shown in Figure 9F, which are comparable to that of SIFSIX-3-Cu. The heat of CO_2 adsorption for NbOFFIVE-1-Ni was determined using variable temperature isotherms and further confirmed by direct TG-DSC measurement.

25 **[0072]** Figure 9G illustrates cyclic CO_2 (1%)/ N_2 (99%) column breakthrough experiments at 298K in both dry and humid conditions. The breakthrough time under dry condition for 1% CO_2 in the gas stream with the flow rate of 10 cc/min was impressive 415 min/g (8.2 wt%). Advantageously, the presence of humidity (75%RH) did not significantly alter the CO_2 breakthrough time (283 min/g, uptake of 5.6 wt%). In addition, the CO_2 uptakes in dry and humid streams were reproducible after reactivation at 378K. Interestingly, the water vapor was retained in the column for 1100 min/g which corresponds to an uptake of 13.8wt%. Column breakthrough experiments were also carried out at trace concentration of CO_2 (1000 ppm CO_2) with the flow rate of $20 \text{ cm}^3/\text{min}$, proving that CO_2 could be retained in the column for 1880 min/g with an uptake of 7.4wt %.

[0073] For comparison purposes, NbOFFIVE-1-Ni was evaluated against other benchmark materials used in real world (both chemical and physical absorbents) as well as other newly developed promising materials, in terms of CO₂ heat of adsorption and CO₂ removal capacity during 1 day at around 1000 ppm CO₂. For practical purposes it was assumed that all sorbent were fully recyclable, with the exception of LiOH, which is a non-recyclable sorbent. The adsorption-desorption recycling was assumed to be 60 min (24 cycles a day) and the comparison was based on the CO₂ scrubbing requirement of 1kg of CO₂/1 day/1 person in confined spaces. The results in Figure 9H show that NbOFFIVE-1-Ni exhibits the best compromise between high CO₂ capacity in 1 day (24 cycles) at 1000 ppm CO₂ and optimal heat of adsorption (or energy required for regeneration) as compared to LiOH, liquid amine, amine supported solids, zeolites 5A (Ca²⁺), SAPO-34 (Sr²⁺) and the recently unveiled copper silicate (SGU-29). All the CO₂ adsorption capacities were determined at equilibrium.

[0074] The data in Figures 9A-G demonstrate the applicability of NbOFFIVE-1-Ni and other MOFs described herein for CO₂ capture applications in confined spaces and/or from ambient air. Moreover, new pcu-based MOFs, such as NbOFFIVE-1-Ni, using reticular chemistry are shown to be more efficient and stable than the best-known materials for CO₂ capture from atmospheric and confined space. Further, unlike many other MOFs, NbOFFIVE-1-Ni is easy to synthesize in large quantity (g to kg) in very economical manner, making it a commercially viable candidate.

[0075] AlFFIVEH₂O-1-Ni and FeFFIVEH₂O-1-Ni are similarly suitable for CO₂ adsorption applications, particularly for adsorbing CO₂ from natural gas, flue gas and syngas, as these materials show selectivity for CO₂ over N₂, CH₄ and H₂. The heat of adsorption of CO₂, determined from variable temperature adsorption isotherms for AlFFIVEH₂O-1-Ni and FeFFIVEH₂O-1-Ni, is 45 kJ/mol and 48 kJ/mol, respectively. This was further confirmed by direct calorimetric measurement of CO₂ adsorption for the aluminum (43 kJ/mol) and iron (45.3 kJ/mol) analogues. By comparison with the Q_{st} associated to H₂O adsorption, it is clear that the framework-CO₂ interactions (45 kJ/mol) are much weaker than the framework-H₂O interactions, which is mainly due to water coordination to the available open metal site in the highly confined pores.

[0076] With the aim to study the dehydration performance of MFFIVEH₂O-1-Ni for CO₂ containing gas streams in general and NG in particular, breakthrough adsorption column experiments were carried out on AlFFIVEH₂O-1-Ni for single water vapor in the presence of N₂, CH₄ and CO₂ using the same total flow (23cm³/min) and relative humidity (75%RH).

Interestingly, the H₂O retention time in the column was similar (500-600 min/g within experimental error) independently if CH₄ and CO₂ are present or not in the CO₂/CH₄: 1/99 mixture. Further investigation using CO₂/N₂ mixture systems with increasing CO₂ concentration at 1, 10 and 50% showed no changes for the water vapor retention time in the column (500-600 min/g within experimental error). All these results prove that the same water vapor adsorption behavior and uptake occurred independently on the CO₂ composition and the type of mixtures tested (CO₂/CH₄:1/99, CO₂/N₂:1/99, CO₂/N₂:10/90 and CO₂/N₂:50/50).

[0077] On the other hand, while N₂ and CH₄ did not show any noticeable uptake in both dry and humid conditions, the retention time in the column for CO₂ during moisture containing tests was only slightly different (within experimental error) compared to the corresponding dry tests for all the mixtures studied.). Although the AIFIVEH₂O-1-Ni framework is energetically favorable for H₂O adsorption, these results show that CO₂ is still adsorbing in the presence of moisture.

[0078] To delineate further the mechanism occurring during the simultaneous CO₂ adsorption in hydrated CO₂/N₂ and CO₂/CH₄ mixtures, post in-situ temperature programmed desorption (after water vapor saturation) in the case of CO₂/N₂/H₂O mixture was carried by heating progressively at 55°C, 85°C and 95°C. It was observed that H₂O and CO₂ still desorb from the column, indicative of residual adsorbed CO₂ remaining in the pores of AIFIVEH₂O-1-Ni even at 95°C. These result show that AIFIVEH₂O-1-Ni could potentially adsorb CO₂ and H₂O simultaneously. In addition, calorimetric measurements of hydrated CO₂/N₂:1/99 showed similar CO₂ and H₂O heat of adsorption as compared to the corresponding values for single H₂O vapor and CO₂. These results represent a breakthrough/unprecedented finding in material development for CO₂ capture and NG upgrading in hydrated gas streams.

[0079] Because H₂O/CO₂ separation system on AIFIVEH₂O-1-Ni is mainly being driven by thermodynamics (no kinetic barrier), where CO₂ and H₂O can access the pore system easily, we intended to find the cut-off molecular size imposed by the access to the pores channels. In light of the theoretically (from crystal structure) slightly large aperture size in case of MFFIVEH₂O-1-Ni as compared to the previously reported NbOFFIVE-1-Ni suitable for C₃H₈ full sieving, we targeted to explore the adsorption of slightly bigger probe molecules such as n-C₄H₁₀, iso-C₄H₁₀, 1-propanol and iso-propanol. AIFIVEH₂O-1-Ni showed increasing selectivity for isobutene, n-butane, and 1-butene. FeFFIVEH₂O-1-Ni

showed increasing selectivity for isobutene and n-butane. AlFFIVEH₂O-1-Ni and FeFFIVEH₂O-1-Ni each showed increasing selectivity for isopropanol, 1-propanol, and ethanol. Interestingly AlFFIVEH₂O-1-Ni and FeFFIVEH₂O-1-Ni showed no adsorption for iso-butane and iso-propanol indicative of evident efficient dehydration, via full sieving, of gases/vapors with equal and larger sizes than iso-butane and iso-propanol.

[0080] These results demonstrate the value of the MOF embodiment characterized by the formula Ni(Al, Fe, V, or Nb)F₅O(pyrazine)₂(solvent)_x as a platform for refining a number of valuable hydrocarbon gases and fluids, including methane and propane. Further, these results suggest this MOF can be used to refine other hydrocarbon gases and fluids, including ethane, butane, and others. The data in Figure 6A also suggests NbOFFIVE-1-Ni can further be used for achieving a particularized fluid mixture. For example, a fluid stream containing initial ethylene and ethane amounts can be altered by varying the pressure at which the fluid contacts the MOF. The exemplary performance and properties of the Nb⁵⁺ based MOFs disclosed herein are notably achieved in spite of having no open metal sites. These and other results can be expected in similar other embodiments, with or without open metal sites, such as MOF structure characterized by the formula NiM_bF₅O(pyrazine)₂, wherein M_b can be one of the following Al⁺³, Fe⁺², Fe⁺³, Cr⁺², Cr⁺³, Ti⁺³, V⁺³, V⁺⁵, Sc⁺³, In⁺³, Nb⁺⁵, Y⁺³. These and other results can be expected in similar other embodiments, with or without open metal sites, such as MOF structure characterized by the formula M_aNbF₅O(pyrazine)₂, wherein M_a can be one of the following cations: Cu²⁺, Zn²⁺, Co²⁺, Ni²⁺, Mn²⁺, Zr²⁺, Fe²⁺, Ca²⁺, Ba²⁺, Pb²⁺, Pt²⁺, Pd²⁺, Ru²⁺, Rh²⁺, Cd²⁺, Mg⁺², Al⁺³, Fe⁺², Fe⁺³, Cr⁺², Cr⁺³, Ru²⁺, Ru³⁺.

EXAMPLE 1: Aperture size modification

[0081] Altering the nature, shape, and dimensions of the pillars employed in [M_aM_bF_{6-n}(O/H₂O)_w(Ligand)_x(solvent)_y]_z MOFs can selectively hinder the free rotation of ligands and thus dictate the maximum and/or minimum opening of the pore aperture size. This approach offers potential to dial-in/command the passing-blocking of specific probe molecules. The (NbOF₅)²⁻ pillaring inorganic building block of NbOFFIVE-1-Ni utilizing a pyrazine ligand demonstrates this approach. Analysis of the NbOFFIVE-1-Ni structure (collected at 100K) revealed the plausible smallest pore window opening associated with the relatively hindered rotation of the (NbOF₅)²⁻ pillars and the presence of hydrogen bond interactions. As a result, the hydrogen atoms of the pyrazine linkers circumference the resultant rectangular aperture size of 2.838(1) Å prohibiting the diffusion of any molecule other than water. In order to gain a better insight on the plausible rotation and tilting of the

pyrazine linker and subsequently derive a relative maximum opening of the window, providing a gate limit for the largest molecule to pass through, the same structure was collected and analysed at room temperature. Noticeably, at room temperature, the pyrazine molecules are perceived to freely rotate along the N...N axis, while the $(\text{NbOF}_5)^{2-}$ pillars rotate along the 4-fold axis. The concurrent pyrazine and pillars $(\text{NbOF}_5)^{2-}$ mobility afforded a maximum window aperture size of 4.752(1) Å.

[0082] To further confirm the restricted pore size opening due the hindered rotation of pyrazine ligands at low temperature, we performed adsorption studies on the fully evacuated **NbOFFIVE-1-Ni**. As anticipated, **NbOFFIVE-1-Ni** did not adsorb N_2 at 77K, indicating the restricted access to N_2 at this low cryogenic temperature due to the contracted window aperture size. On the other hand, adsorption studies performed at room temperature using CO_2 as the adsorbate molecule revealed that **NbOFFIVE-1-Ni** is microporous with a BET surface area of 280 m^2/g and a pore volume of 0.095 cm^3/g .

WHAT IS CLAIMED IS

1. A method of capturing chemical species from a fluid composition, the method comprising contacting a metal organic framework characterized by the formula $[M_a M_b F_6 \cdot n(O/H_2O)_w (Ligand)_x (solvent)_y]_z$ with a fluid composition comprising two or more chemical species; and capturing one or more captured chemical species from the fluid composition.
2. The method of claim 1, wherein M_a comprises elements selected from periodic groups IB, IIA, IIB, IIIA, IVA, IVB, VIB, VIIB, and VIII, M_b comprises elements selected from periodic groups IIIA, IIIB, IVB, VB, VIB, and VIII, Ligand comprises an organic, poly-functional, N-donor ligand
3. The method of claim 1, wherein M_a comprises Cu^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+} , Zr^{2+} , Fe^{2+} , Ca^{2+} , Ba^{2+} , Pb^{2+} , Pt^{2+} , Pd^{2+} , Ru^{2+} , Rh^{2+} , Cd^{2+} , Mg^{+2} , Al^{+3} , Fe^{+2} , Fe^{+3} , Cr^{2+} , Cr^{3+} , Ru^{2+} , Ru^{3+} or Co^{3+} , and M_b comprises Al^{+3} , Fe^{+2} , Fe^{+3} , Cr^{2+} , Cr^{3+} , Ti^{3+} , V^{3+} , V^{5+} , Sc^{3+} , In^{3+} , Nb^{5+} , or Y^{3+} .
4. The method of claim 1, wherein M_a comprises Ni^{2+} and M_b comprises Al^{+3} , Fe^{+2} , Fe^{+3} , V^{3+} , V^{5+} , or Nb^{5+} .
5. The method of claim 1, wherein the ligand comprises pyridine, pyrazine, pyrimidine, pyridazine, triazine, thiazole, oxazole, pyrrole, imidazole, pyrazole, triazole, oxadiazole, thiadiazole, quinoline, benzoxazole, or benzimidazole.
6. The method of claim 1, wherein capturing comprises physical adsorption of the one or more captured chemical species by the metal organic framework.
7. The method of claim 1, wherein capturing comprises chemisorption of the one or more captured chemical species by the metal organic framework.
8. The method of claim 7, wherein chemisorption occurs by one or more captured chemical

species chemically interacting with one or more open metal sites of the metal organic framework.

9. The method of claim 1, wherein the fluid composition comprises H₂S, and one or more of benzene, toluene, xylene, ethylbenzene, naphthalene and styrene, and the one or more captured chemical species consist of benzene, toluene, xylene, ethylbenzene, naphthalene, styrene, and combinations thereof.

10. The method of claim 9, wherein M_a comprises Ni²⁺ and M_b comprises Nb⁵⁺.

11. The method of claim 1, wherein the fluid composition comprises breathable air and the one or more captured chemical species consist of carbon dioxide.

12. The method of claim 10, wherein capturing occurs in a confined space.

13. The method of claim 1, wherein the fluid composition comprises one or more of flue gas, syngas, biogas and landfill gas, and the captured chemical species consists of carbon dioxide.

14. The method of claim 1, wherein the fluid composition comprises water and one or more of a gas, a vapor, and a solvent, and the captured chemical species consists of water.

15. The method of claim 13, wherein M_a comprises Ni²⁺ and M_b comprises Fe⁺² or Fe⁺³.

16. The method of claim 1, wherein the fluid composition comprises one or more olefin species and one or more paraffin species, and the one or more captured chemical species consist of one or more olefins.

17. The method of claim 15, wherein the one or more olefin species comprise ethylene and the one or more paraffin species comprise ethane.

18. The method of claim 15, wherein the one or more olefin species comprise propylene and the one or more paraffin species comprise propane.

19. The method of claim 1, where the fluid composition comprises H₂S and one or more hydrocarbon species, and the captured chemical species consists of H₂S.

20. The method of claim 18, wherein the one or more hydrocarbon species comprise one or more open-chain hydrocarbons.

21. The method of claim 19, wherein the one or more open-chain hydrocarbons comprise propane, propene, ethane, ethene, and combinations thereof.

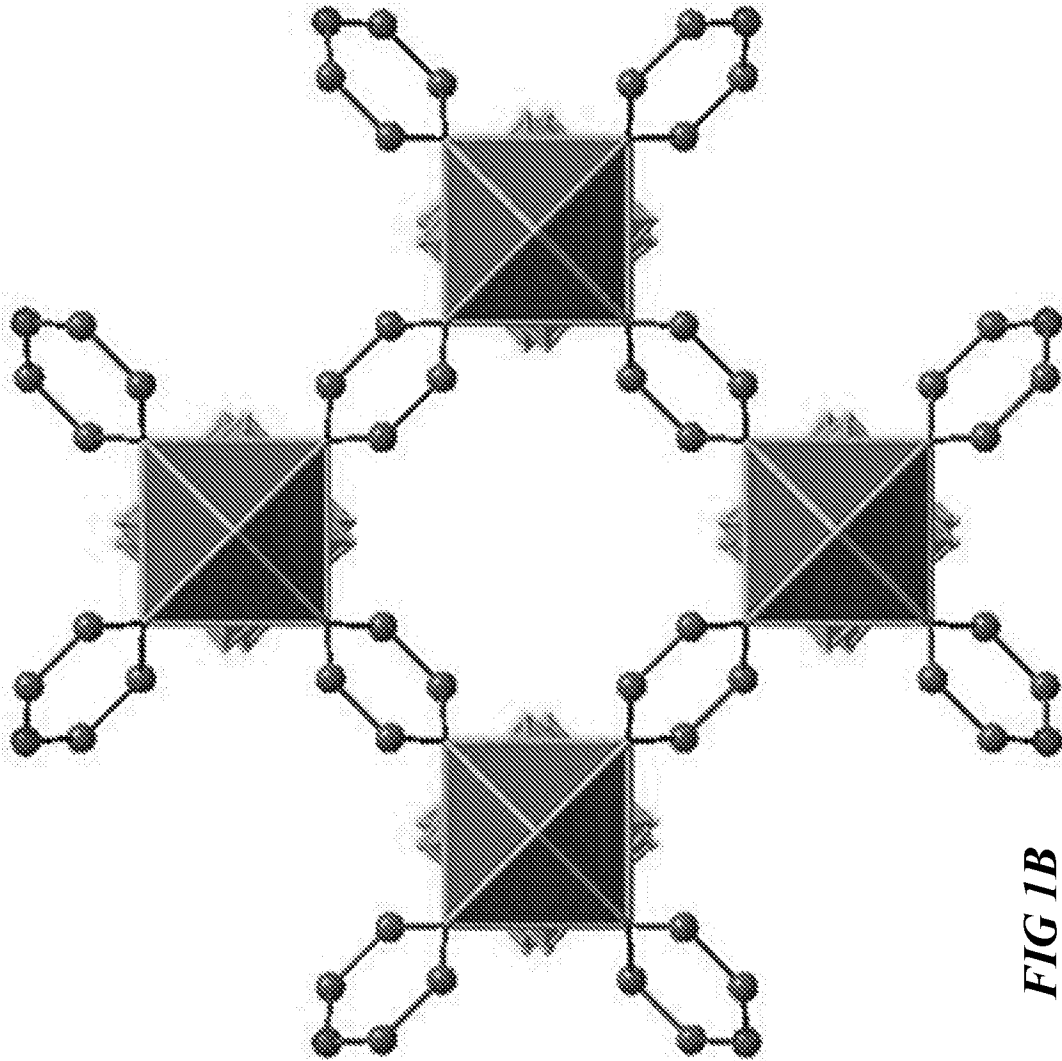


FIG 1B

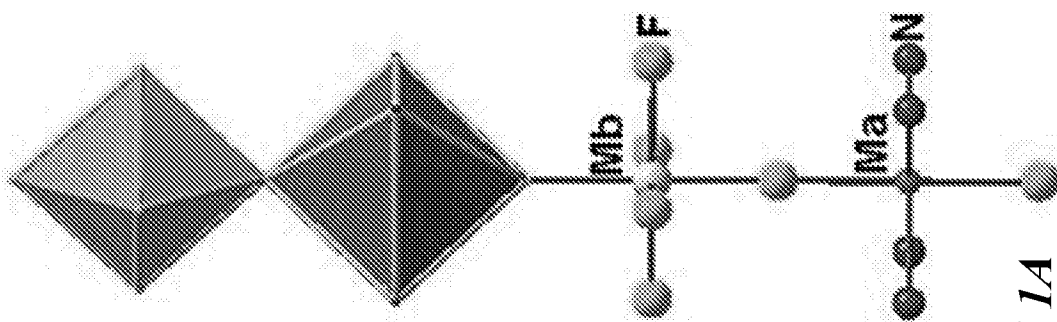


FIG 1A

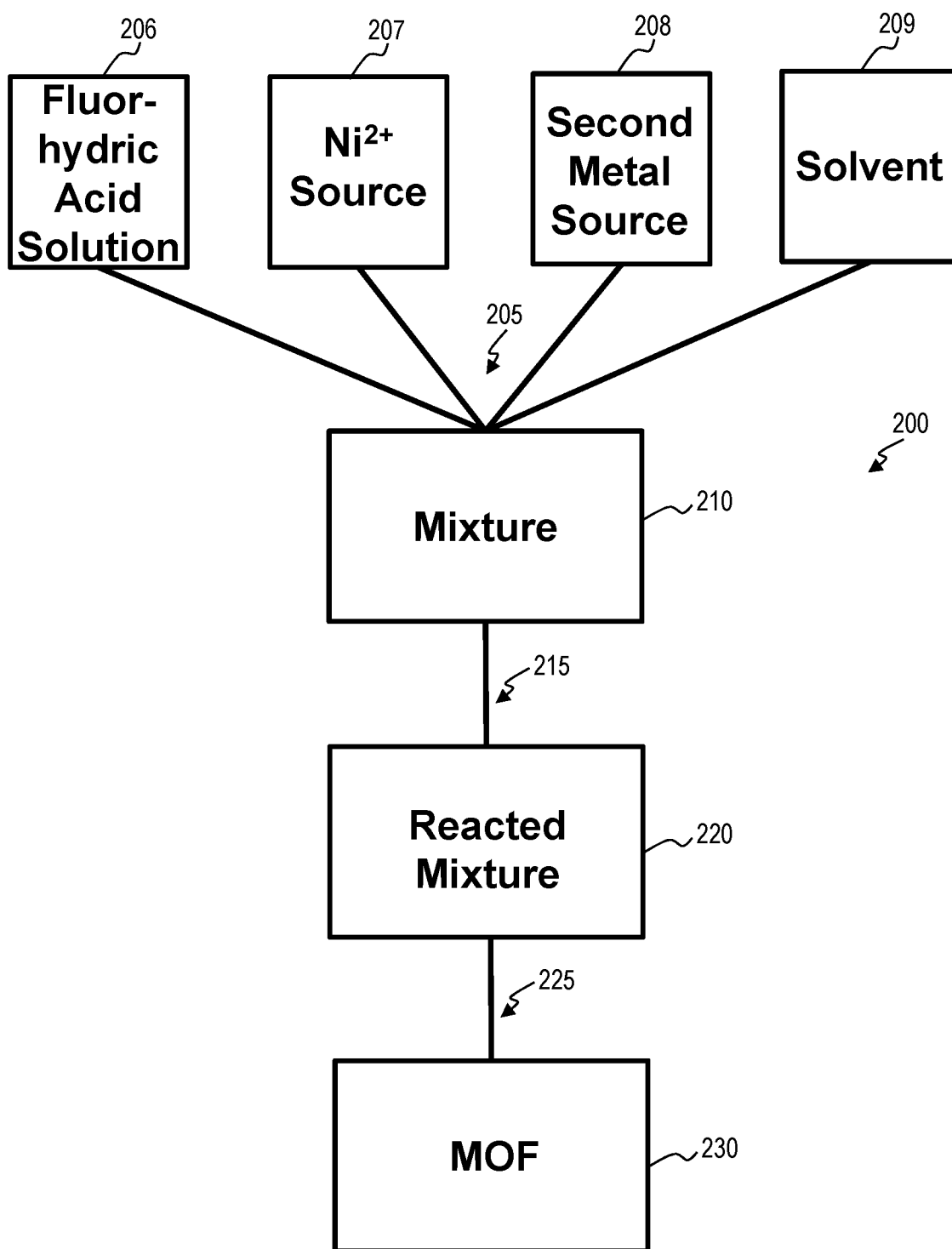


FIG 2

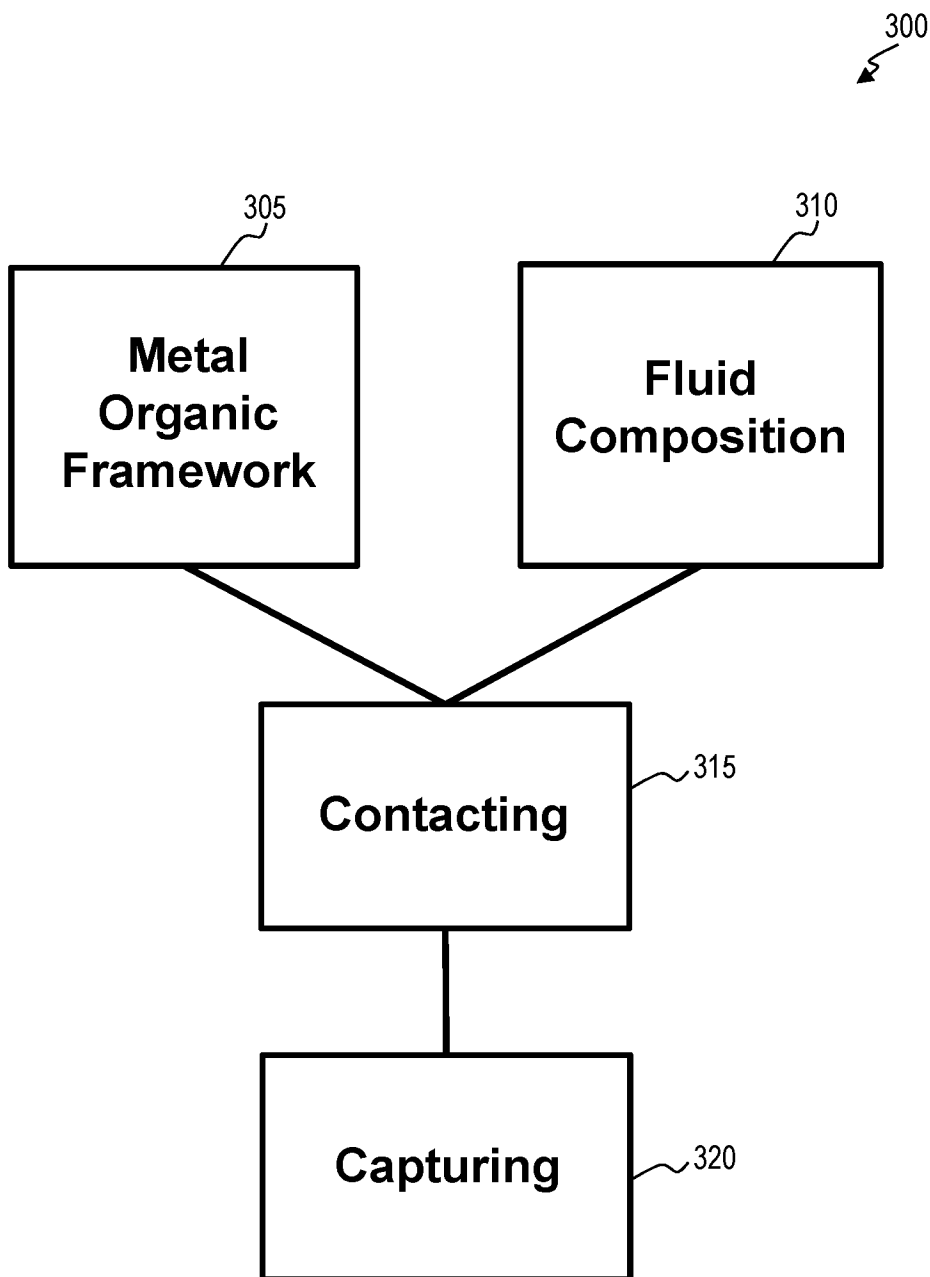


FIG 3

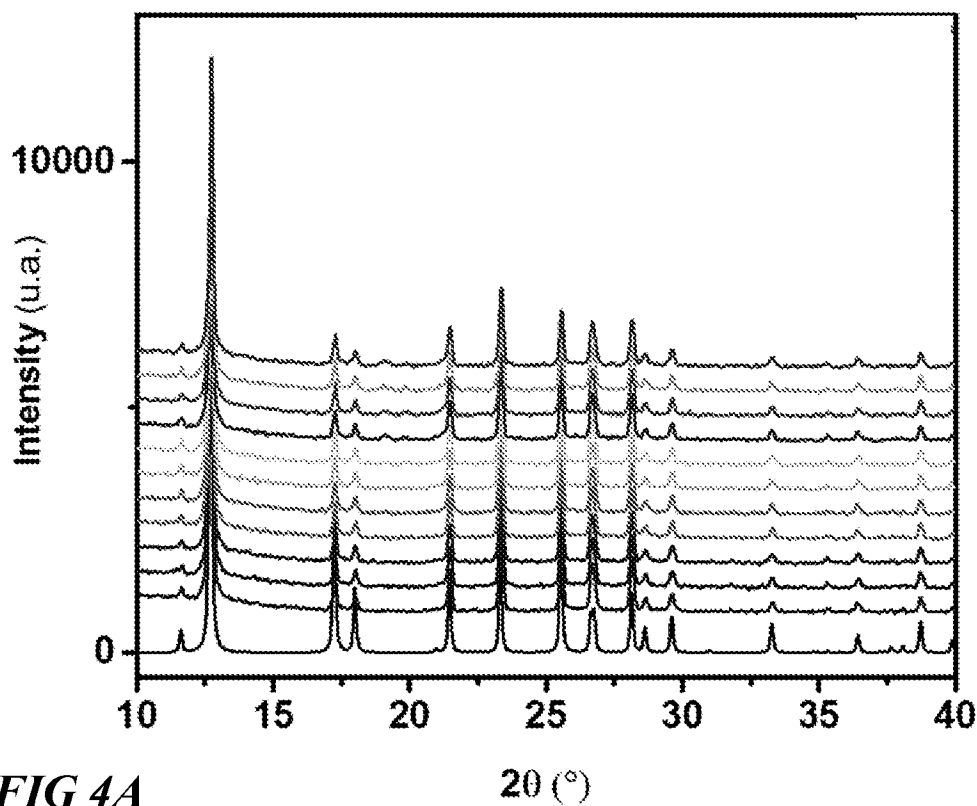


FIG 4A

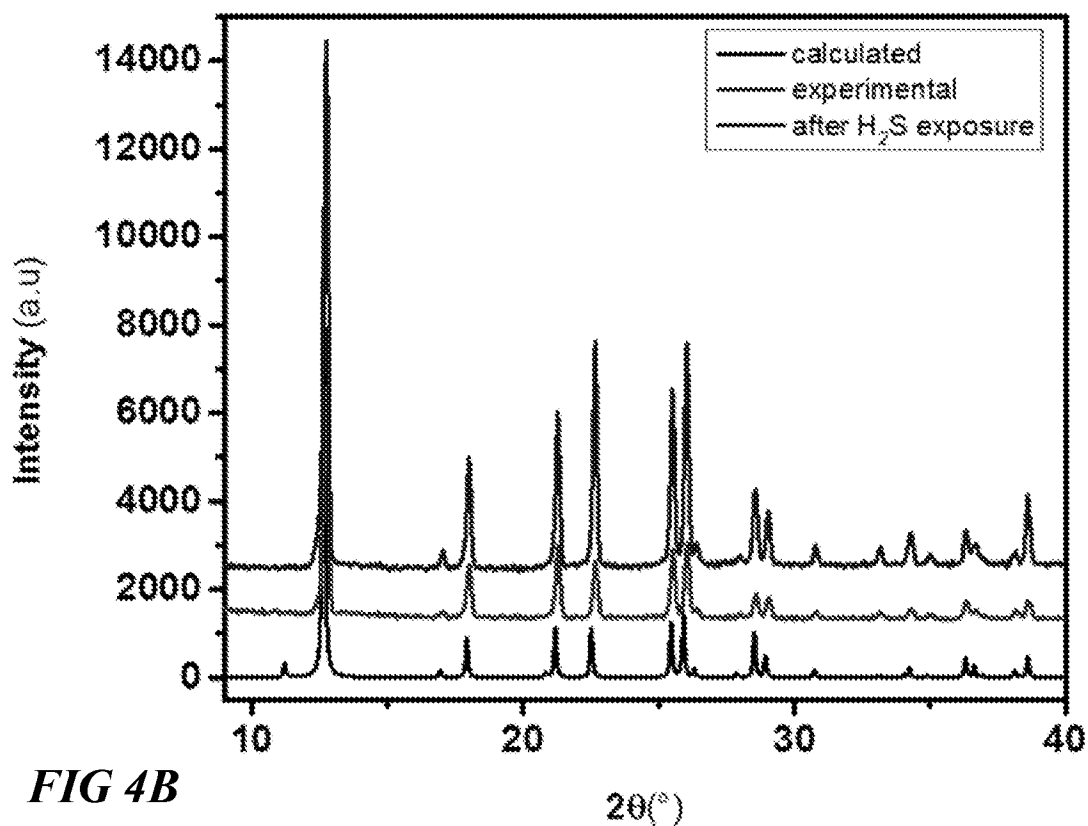


FIG 4B

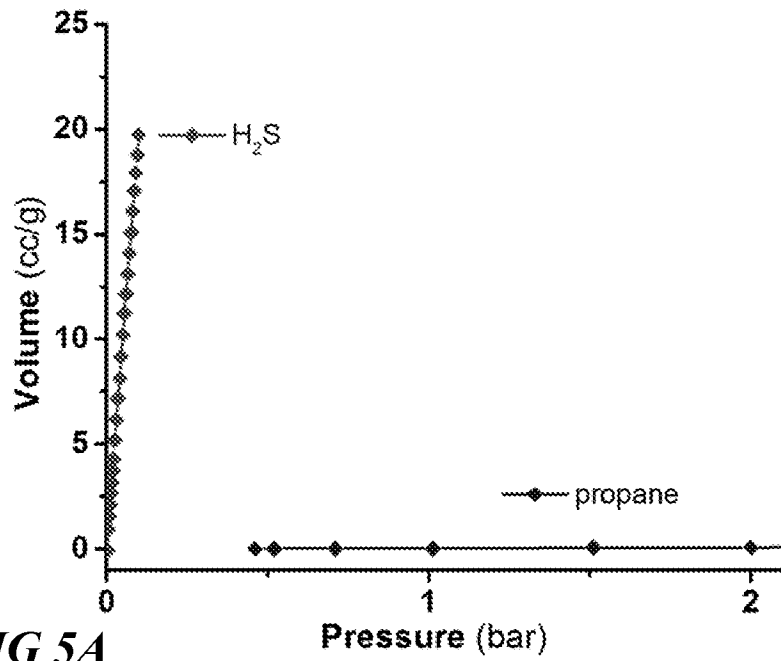


FIG 5A

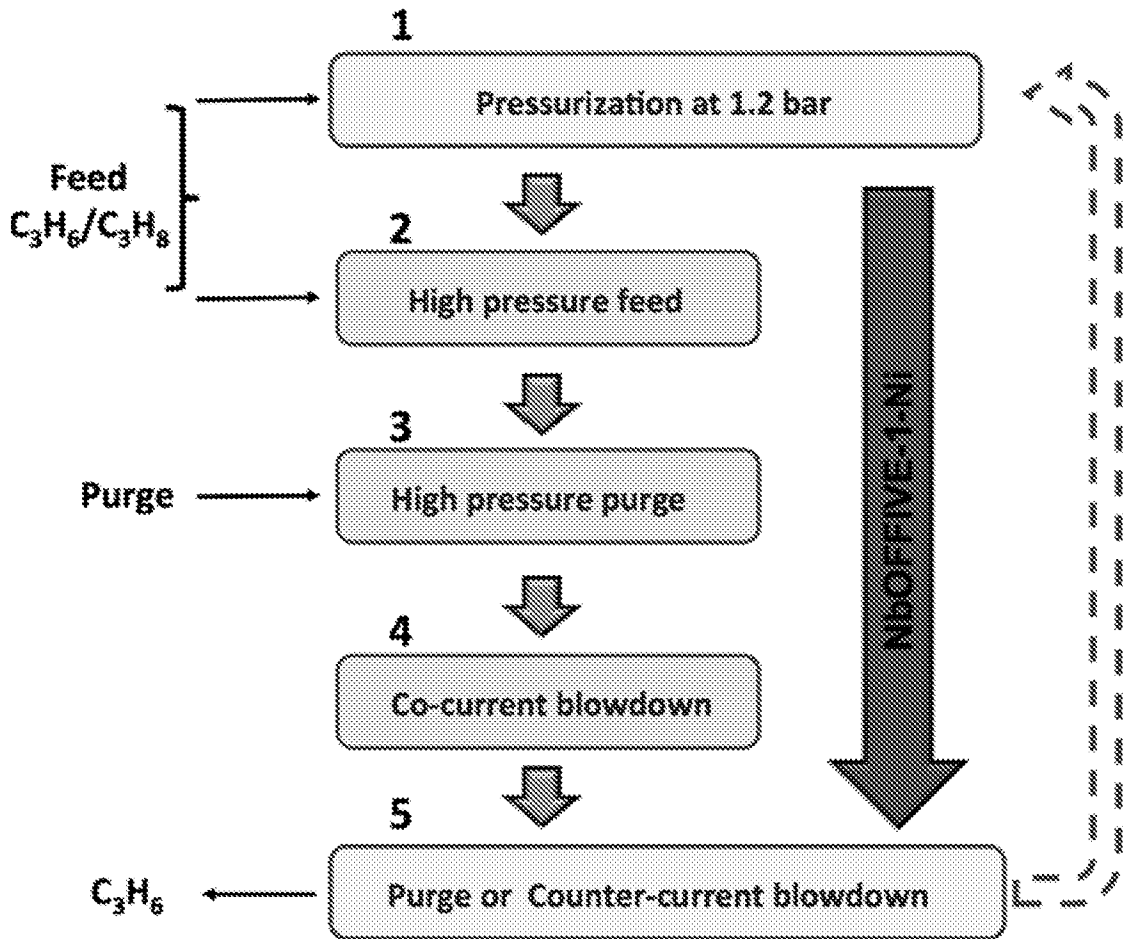


FIG 5B

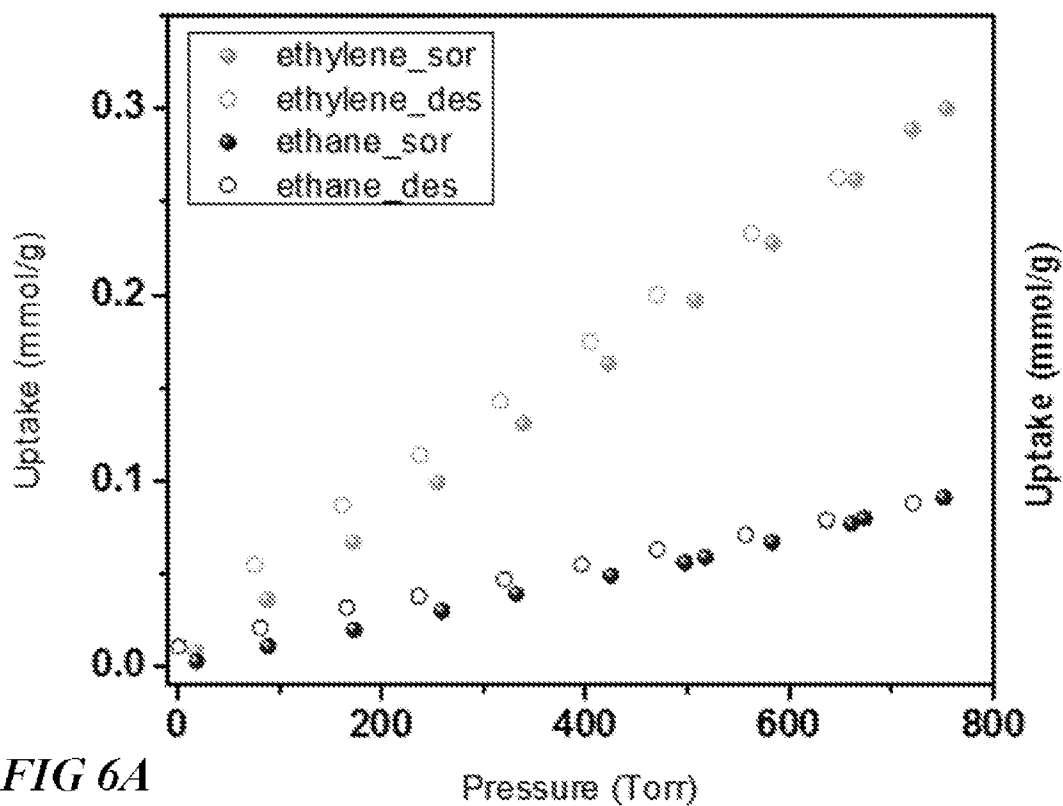


FIG 6A

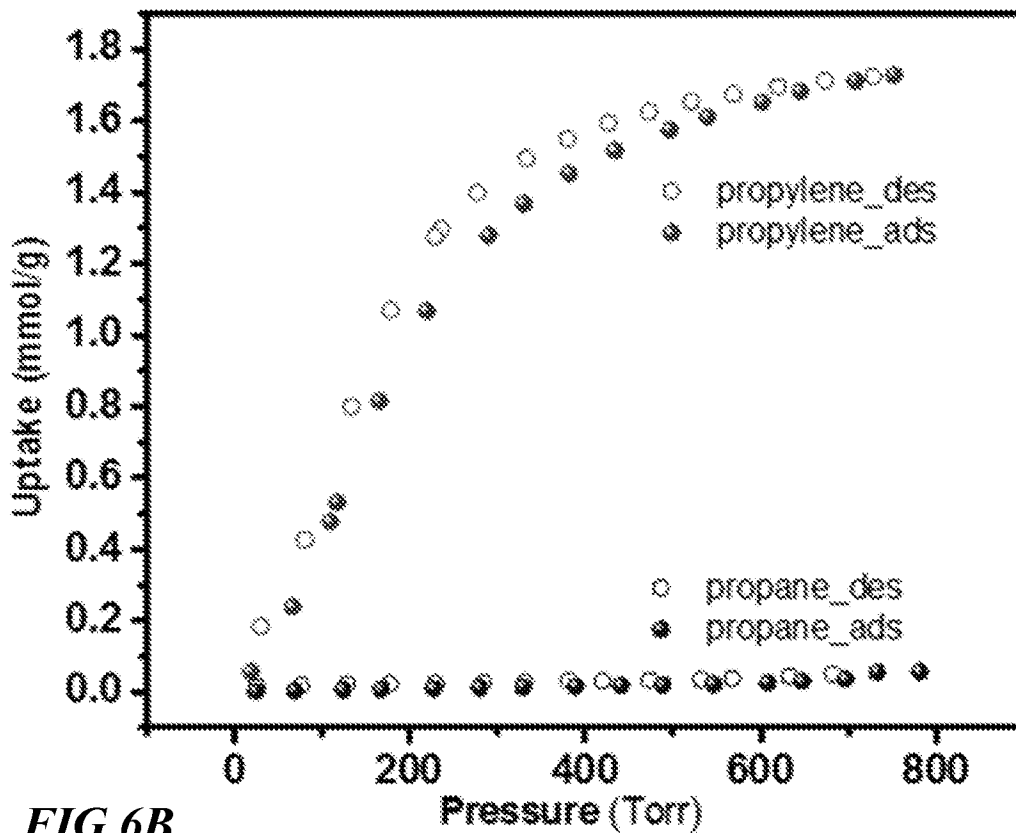


FIG 6B

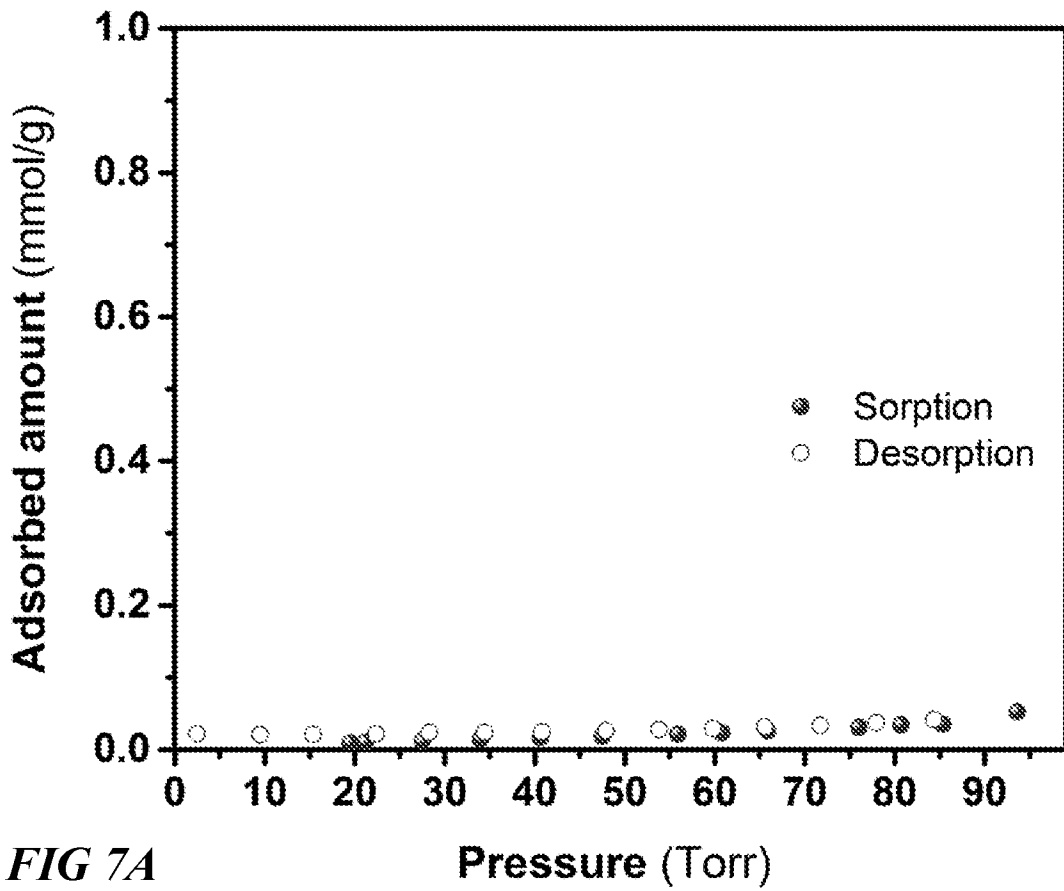


FIG 7A

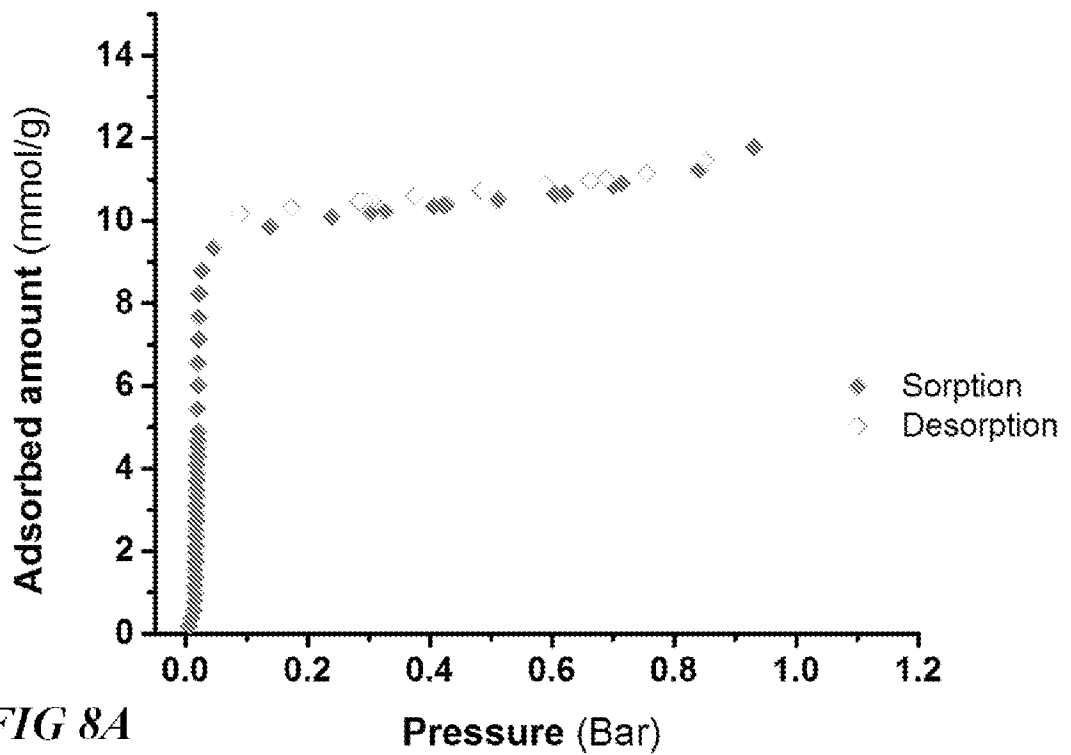


FIG 8A

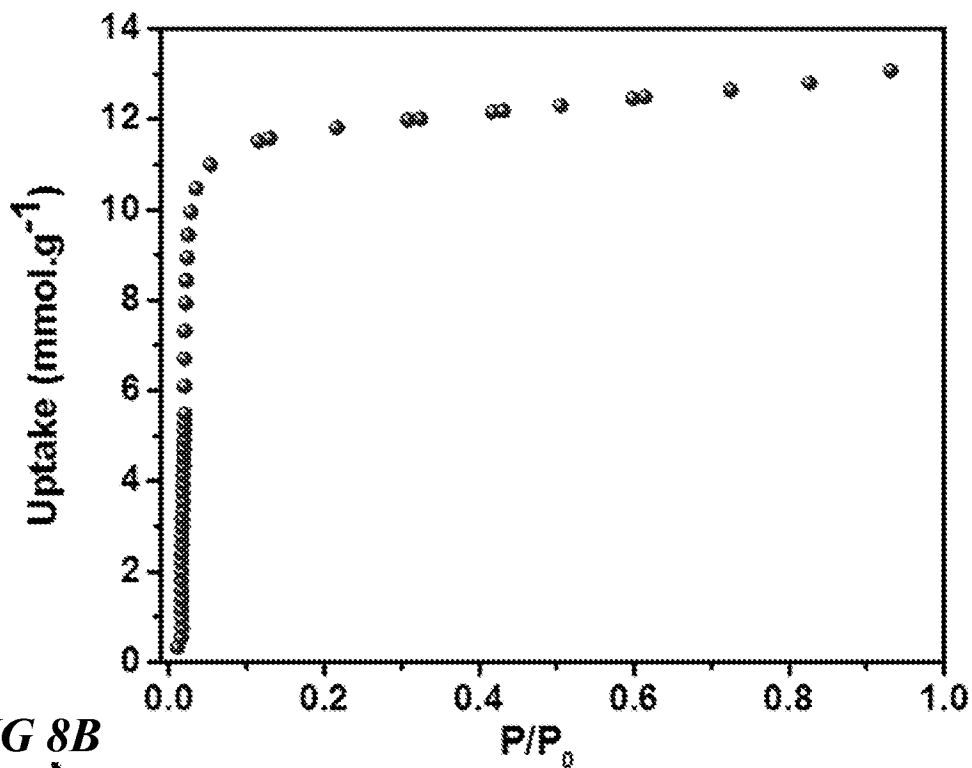


FIG 8B

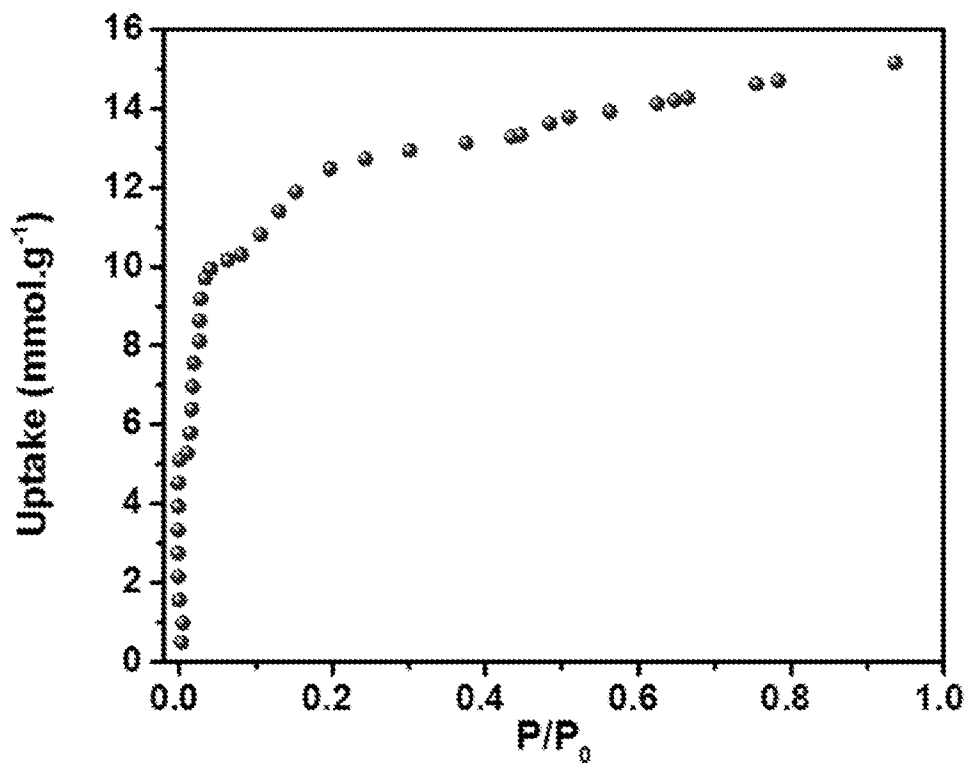


FIG 8C

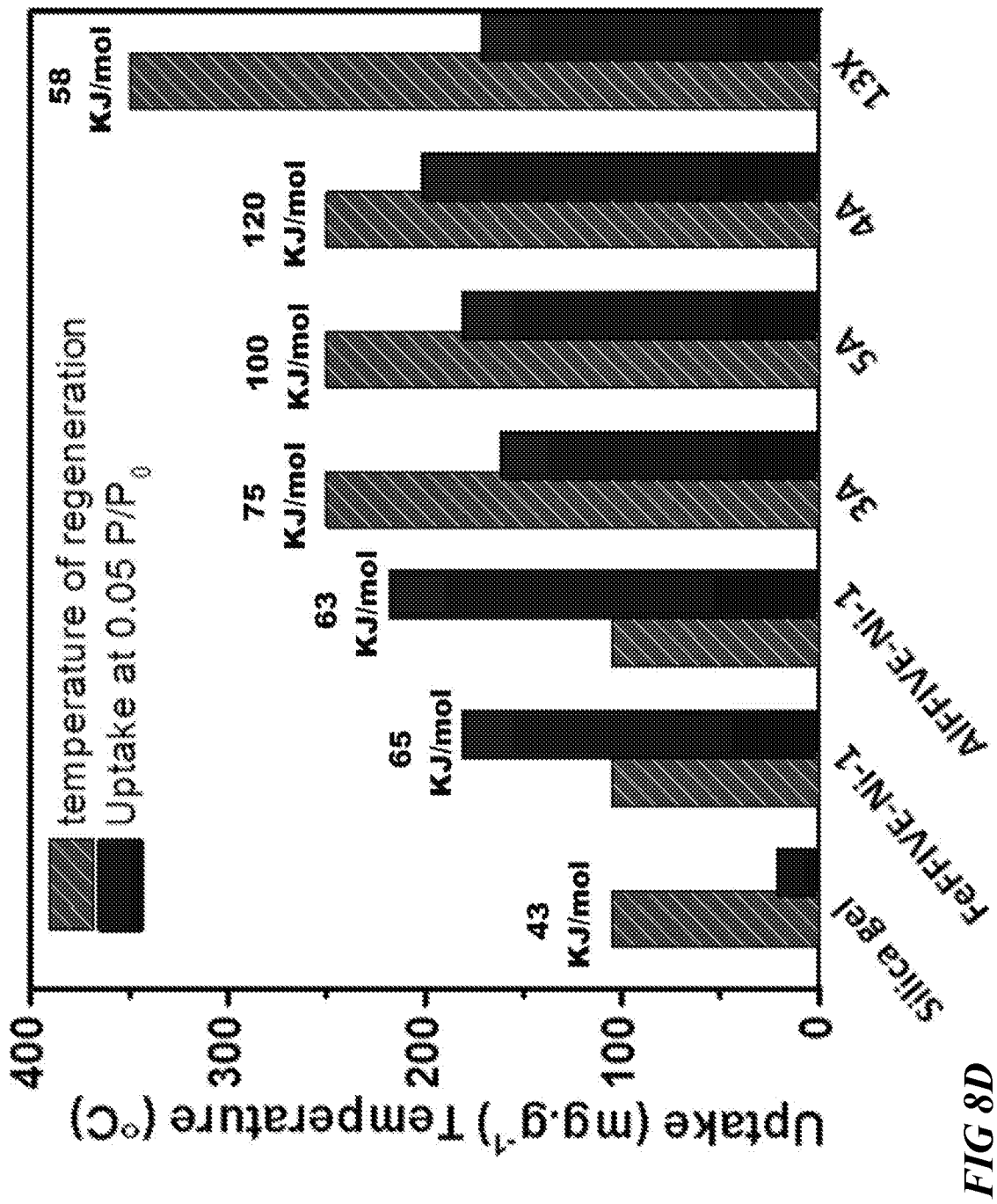


FIG 8D

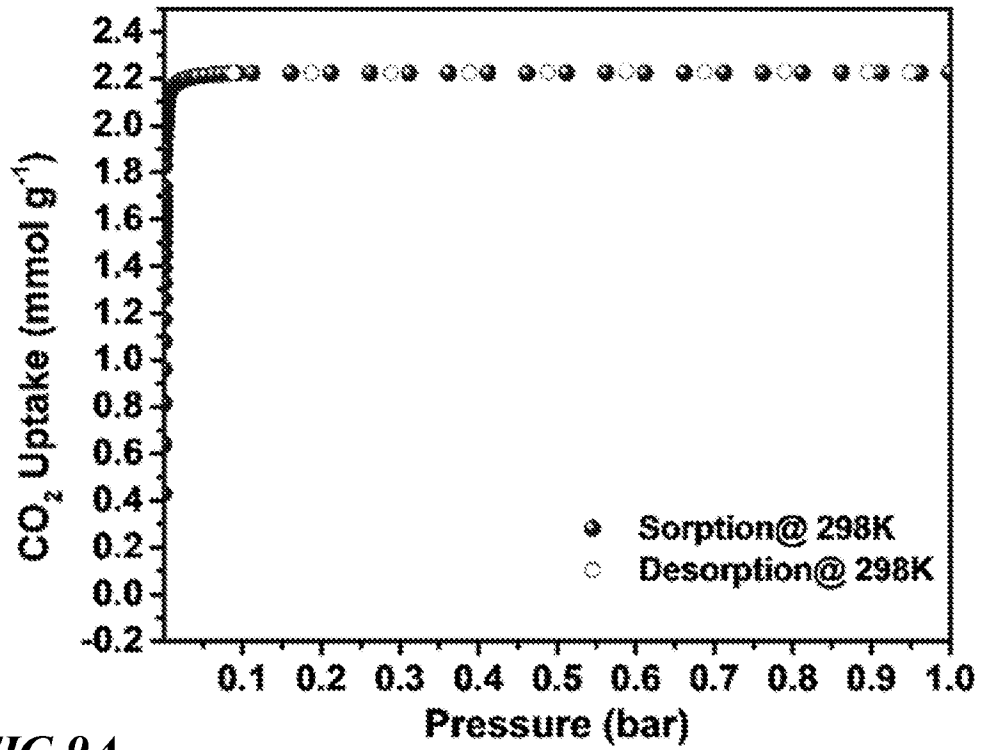


FIG 9A

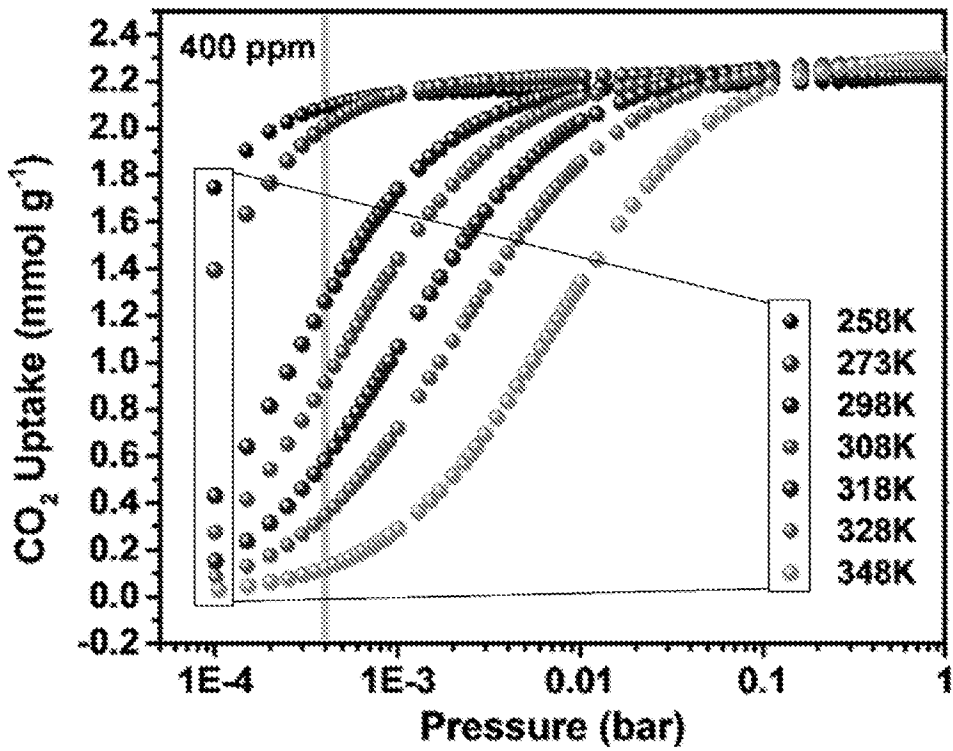


FIG 9B

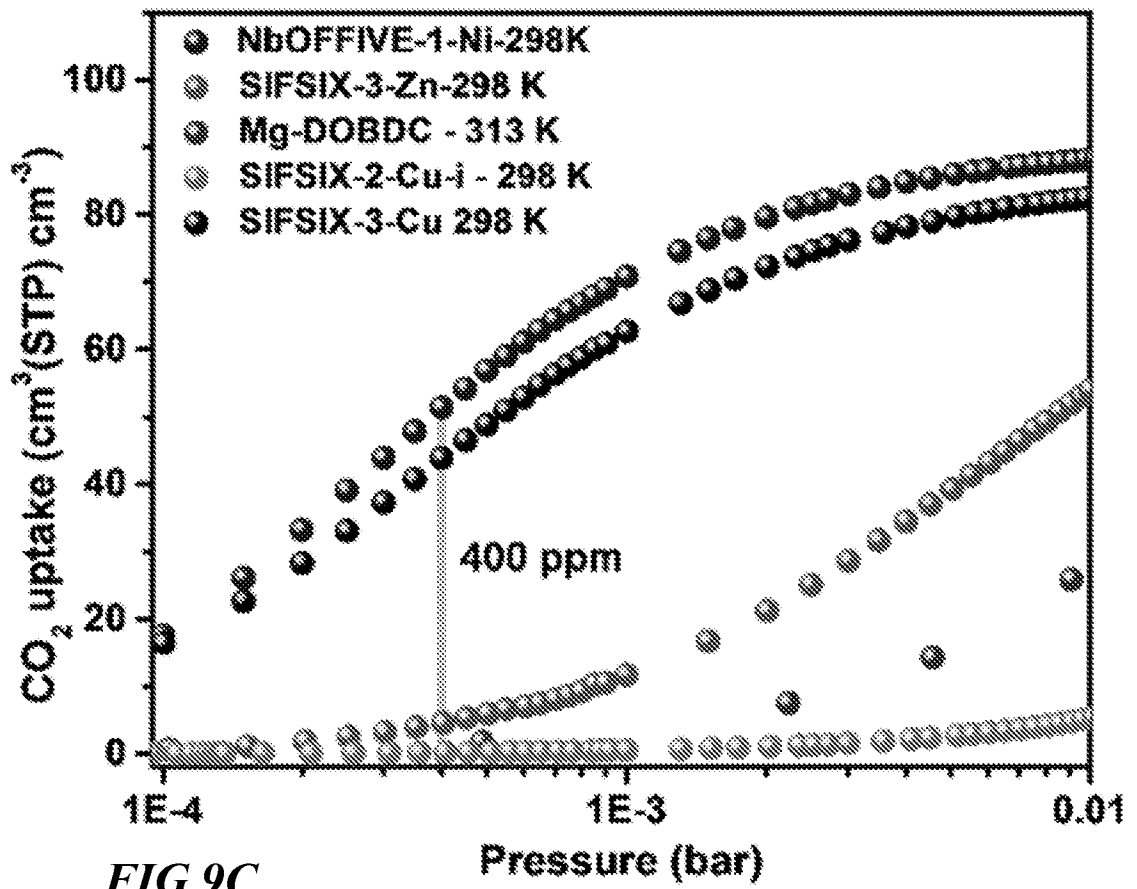


FIG 9C

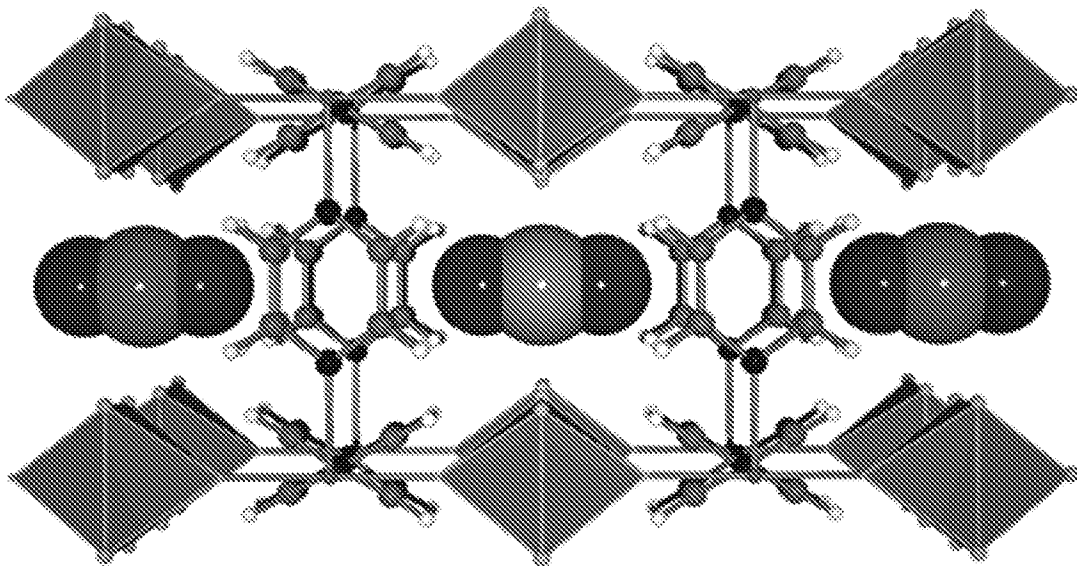


FIG 9D

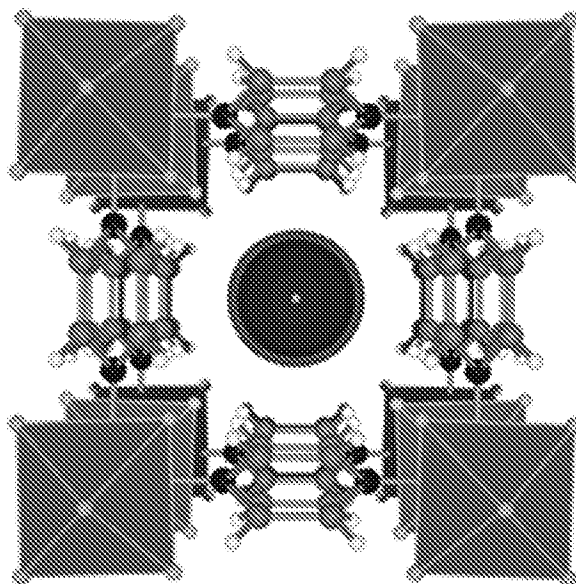


FIG 9E

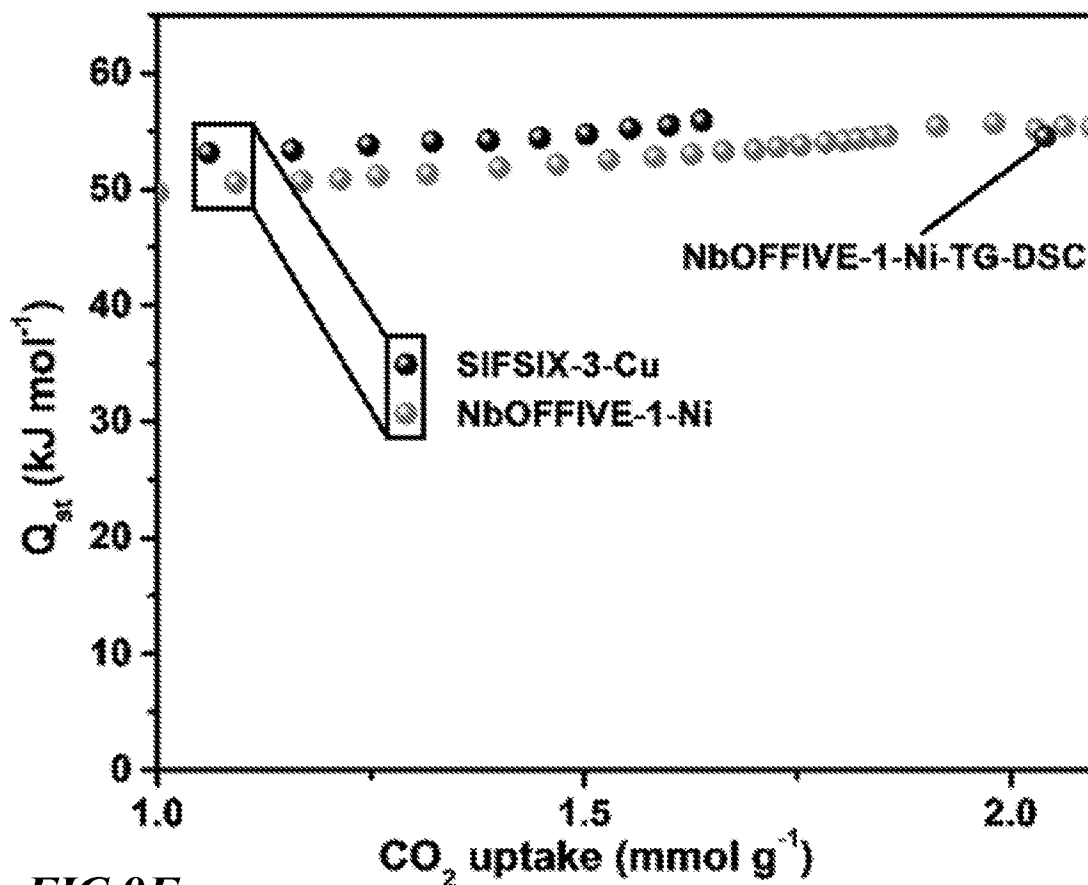


FIG 9F

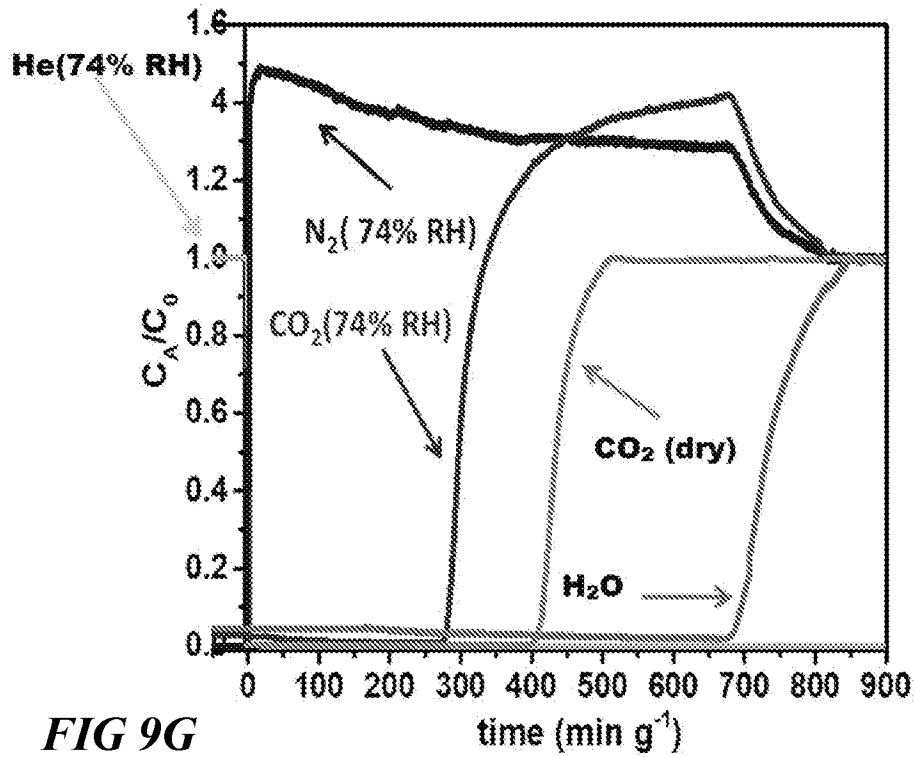


FIG 9G

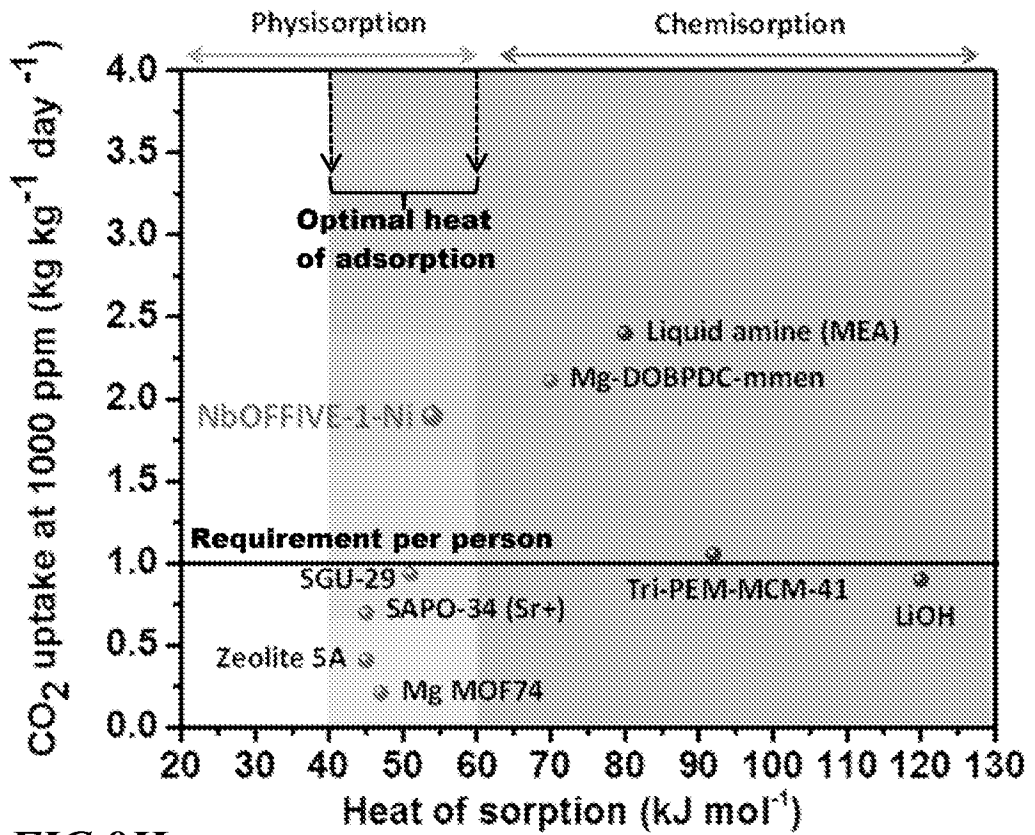


FIG 9H

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2016/051991A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/02 B01J20/22
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

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.
A	WO 2014/074679 A1 (UNIV SOUTH FLORIDA [US]) 15 May 2014 (2014-05-15) the whole document	1-21
A	AMANDINE CADIAU ET AL: "ZnAlF5.[TAZ]: an Al fluorinated MOF of MIL-53(A1) topology with cationic {Zn(1,2,4 triazole)} ₂₊ linkers", JOURNAL OF MATERIALS CHEMISTRY, vol. 21, no. 11, 31 January 2011 (2011-01-31), page 3949, XP055283861, GB ISSN: 0959-9428, DOI: 10.1039/c0jm03559a the whole document	1-21



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 June 2016

Date of mailing of the international search report

07/09/2016

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

Bergt, Thomas

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2016/051991

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.: **1-21(partially)**
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-21(partially)

Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-21(partially)

NiAlF5(H2O)(pyrazine)2.2H2O for capturing chemical species from a fluid composition.

2. claims: 1-21(partially)

NiFeF5(H2O)(pyrazine)2.2H2O for capturing chemical species from a fluid composition.

3. claims: 1-21(partially)

NiNbOF5(H2O)(pyrazine)2.2H2O for capturing chemical species from a fluid composition.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 1-21(partially)

1 Claims 1-21 were only partially searched for the following reasons:

1.1 Present claims 1-3 relate to an extremely large number of possible compounds (Marcush formula with essentially no or low limitations concerning metals and ligands). Support and disclosure in the sense of Article 6 and 5 PCT is to be found however for only a very small proportion of the compounds (see [0040], [0044], [0045]: NiNbOF₅(pyrazine)₂, NiAlF₅(H₂O)(pyrazine)₂.2H₂O, NiFeF₅(H₂O)(pyrazine)₂.4H₂O are explicitly listed and tested ([0058]-[0064]; Figs. 4A-9H) in terms of their CO₂, H₂O and H₂S adsorption capabilities and stability.

For NiNbOF₅(pyrazine)₂ it could not be derived from the description whether or not solvent (H₂O) forms part of the structure.

1.2 Claim 1 essentially disclose any possible fluorinated (and even unfluorinated for n=6) nodes with any metal combinations (Ma+Mb) and any ligands. Claim 2 restricts this to an almost unlimited combination of groups from the periodic system with any N-donor ligand, and claim 3 restricts the metals to a combination of 24 with 12 specific ions (288 combinations of ions) with an unlimited number of ligands. Even in combination with claim 5, disclosing a list of 16 ligands, claim 1 still amounts to an essentially unlimited amount of compounds. None of these limitations is considered to fulfil the requirements of conciseness, nor is any generalization as in these claims considered justified by the mere examples of Ni(Al/Fe/V/Nb)F₅O_x(pyrazine)₂ as listed above.

1.3 In that light, also the generalisations as in claim 4 are also not considered justified: any ligand, without any limitations, is disclosed for the given compositions. The resulting structure, physical and chemical properties are consequently not defined. Compounds within the scope of these claims, which are not suitable adsorbents are thus not only likely but inevitable.

1.4 The same applies mutatis mutandis to the generalization of ligands in claim 5 in combination with the almost unlimited number of nodes as disclosed in claim 1.

1.5 Further reasoning:

Any generalization beyond these compounds is not considered justified for the following reasons: it is neither obvious, nor clearly derivable from the description, that such changes in the formula do neither influence the structure, nor the chemical and/or physical characteristics of the resulting MOF to such a low extent that further testing would not be necessary, and the characteristics would be essentially the same.

For example, ZnAlF₅(triazole), falling within the scope of claims 1-3 and 5, is not even porous and consequently not suitable as adsorbent (see p. 3950, left column of: AMANDINE CADIAU ET AL: "ZnAlF₅.[TAZ]: an Al fluorinated MOF of MIL-53(Al) topology with

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

cationic {Zn(1,2,4 triazole)}₂+ linkers", JOURNAL OF MATERIALS CHEMISTRY, vol. 21, no. 11, 1 January 2011 (2011-01-01), page 3949, XP055283861, GB ISSN: 0959-9428, DOI: 10.1039/c0jm03559a).

Furthermore, Ti(III)F₃ compounds are known to heavily react with water. In the absence of evidence, that MOFs with MaTi(III)F₅ nodes are stable adsorbents, these compounds are also considered not suitable for the desired method.

1.6 Also the generalization (as in claim 4) Ma=Ni and Mb= Al³⁺, Fe²⁺, Fe³⁺, V³⁺, V⁵⁺ or Nb⁵⁺ is not considered justified under these circumstances, as not even all the resulting formulas are listed in the application, let alone the possible impact on structure, physical and chemical characteristics of the additional possible MOFs.

1.7 Consequently, the non-compliance with the substantive provisions is to such an extent, that the search was performed taking into consideration the non-compliance in determining the extent of the search of claims 1-5, as well as any claims depending on these claims (PCT Guidelines 9.19 and 9.24).

1.8 The search of all claims was consequently restricted to the supported, disclosed and tested compounds:

NiNbOF₅(pyrazine)₂,
NiAlF₅(H₂O)(pyrazine)₂.2H₂O, NiFeF₅(H₂O)(pyrazine)₂.4H₂O

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guidelines C-IV, 7.2), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2016/051991

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2014074679	A1	EP 2916931 A1	16-09-2015
		WO 2014074679 A1	15-05-2014
