



- (51) International Patent Classification:  
*B01D 53/02* (2006.01)    *B01J 20/22* (2006.01)
- (21) International Application Number:  
PCT/IB2016/051987
- (22) International Filing Date:  
7 April 2016 (07.04.2016)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
62/144,175    7 April 2015 (07.04.2015)    US
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- (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, 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).

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(54) Title: METAL ORGANIC FRAMEWORK ABSORBENT PLATFORMS FOR REMOVAL OF CO<sub>2</sub> AND H<sub>2</sub>S FROM NATURAL GAS

(57) Abstract: Provided herein are metal organic frameworks comprising metal nodes and N-donor organic ligands which have high selectivity and stability in the present of gases and vapors including H<sub>2</sub>S, H<sub>2</sub>O, and CO<sub>2</sub>. Methods include capturing one or more of H<sub>2</sub>S, H<sub>2</sub>O, and CO<sub>2</sub> from fluid compositions, such as natural gas.

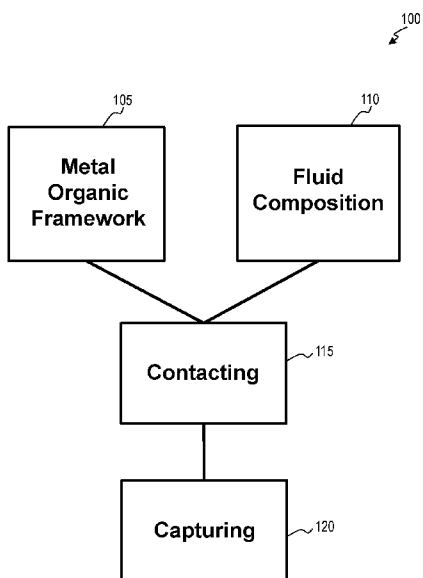


FIG 1A



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— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

**Published:**

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

## METAL ORGANIC FRAMEWORK ABSORBENT PLATFORMS FOR REMOVAL OF CO<sub>2</sub> AND H<sub>2</sub>S FROM NATURAL GAS

### 5 CROSS-REFERENCE TO RELATED APPLICATIONS

**[0001]** This application claims priority to U.S. Provisional Application No. 62/144,175, filed 7 April 2015, which application is incorporated herein by reference.

### BACKGROUND

10 **[0002]** Today there is an increasing global desire to reduce greenhouse gas emissions and develop clean alternative vehicle fuels. Methane (CH<sub>4</sub>), the primary component of natural gas (NG), is of particular interest as it is abundant and has lower carbon dioxide (CO<sub>2</sub>) emission and more efficient combustion than other hydrocarbons due its high H/C ratio. Biogases, including landfill gas, are also seen as promising renewable energy  
15 resources, but, like NG, they contain significant amounts of water, CO<sub>2</sub>, and hydrogen sulfide (H<sub>2</sub>S) which must be removed before being transported, stored, and burned as a fuel. For example, NG must contain less than 1-2% CO<sub>2</sub> and 4 ppm H<sub>2</sub>S to meet fuel gas specifications for pipeline transportation. Within many industries, gas dehydration and removal of CO<sub>2</sub> and H<sub>2</sub>S remain some of the most intensive and challenging separations, in part due to the  
20 intolerance of many technologies to water.

**[0003]** Available technologies for refining NG and other biogases are often costly, multi-stage processes. Amine scrubbing is a common liquid phase system used to remove acid gases such as CO<sub>2</sub> and H<sub>2</sub>S from NG. However, stagnant historical operating efficiencies, and the excessive oxidative degradation, evaporation, and the corrosive nature of  
25 the alkanolamine aqueous solutions create a myriad of performance, safety, and environmental concerns. Solid, porous material systems, such as zeolite and metal organic frameworks (MOFs), offer more environmentally friendly alternatives for CO<sub>2</sub> capture, but require cumbersome, multi-stage processes. For example, zeolite has single-species selectivity for CO<sub>2</sub> and cyclic adsorption performance in the presence of moisture that require  
30 prior dehydration and H<sub>2</sub>S removal stages. MOFs, similarly, can be designed for CO<sub>2</sub> capture but exhibit prohibitively low selectivity for acid gases such as H<sub>2</sub>S. Further, MOFs exhibit low selectivity and capture at low CO<sub>2</sub> partial pressures.

**[0004]** MOFs generally include porous crystals which are assembled from modular molecular building blocks, and provide a wide array of advantageous material properties,

including high surface area, porosity, stability, and sorption potential. While the available building block options, and combinations thereof, are virtually limitless, such potential highlights the statistical difficulty in identifying and assembling MOFs with desired and particularized material properties and multi-faceted functionality. For example, many MOFs exhibit high selectivity towards a particular molecular species, but are highly intolerant to water and H<sub>2</sub>S.

#### SUMMARY

**[0005]** 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.

**[0006]** In one embodiment, a method of capturing chemical species from a fluid composition comprises contacting a first 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 one or more of carbon dioxide, water, and hydrogen sulfide and capturing one or more of carbon dioxide, water, and hydrogen sulfide from the fluid composition.

**[0007]** 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

**[0008]** The accompanying drawings illustrate non-limiting example embodiments of the invention.

**[0009]** **FIG. 1A** illustrates a method for capturing one or more chemical species from a fluid composition via a metal organic framework, according to one or more embodiments of this disclosure.

**[0010]** **FIG. 1B** illustrates a multicolumn pressure-temperature swing adsorption (PTSA) method for capturing one or more chemical species from a fluid composition via a metal organic framework, according to one or more embodiments of this disclosure.

**[0011]** **FIG. 2** illustrates a method of fabricating a metal organic framework, according to one or more embodiments of the disclosure.

- [0012] FIG. 3A illustrates a schematic of an inorganic chain, according to one or more embodiments of this disclosure.
- [0013] FIG. 3B illustrates a schematic view of a metal organic framework, according to one or more embodiments of this disclosure.
- 5 [0014] FIG. 4A illustrates powder X-ray diffraction data of a metal organic framework, according to one or more embodiments of this disclosure.
- [0015] FIG. 4B illustrates powder X-ray diffraction data of a metal organic framework, according to one or more embodiments of this disclosure.
- [0016] FIG. 5A illustrates isotherm data for various metal organic frameworks,  
10 according to one or more embodiments of this disclosure.
- [0017] FIG. 5B illustrates isotherm data for various metal organic frameworks, according to one or more embodiments of this disclosure.
- [0018] FIG. 5C illustrates isotherm data for a metal organic framework, according to one or more embodiments of this disclosure.
- 15 [0019] FIG. 6 illustrates a block flow diagram of sequence of tests for adsorption column breakthrough studies to evaluate the performances of the materials in temperature swing cyclic (TSR) and vacuum swing regeneration (VSR) modes using CO<sub>2</sub>/H<sub>2</sub>S/CH<sub>4</sub>:5/5/90 mixture, according to one or more embodiments of this disclosure.
- [0020] FIG. 7 illustrates a graphical view of column breakthrough test of  
20 CO<sub>2</sub>/H<sub>2</sub>S/CH<sub>4</sub> with 10 cm<sup>3</sup>/min flow rate on NiAlF<sub>5</sub>O(pyrazine)<sub>2</sub> at 25°C (1 bar) using TSR mode, according to one or more embodiments of this disclosure.
- [0021] FIG. 8 illustrates a graphical view of column breakthrough tests of CO<sub>2</sub>/H<sub>2</sub>S/CH<sub>4</sub> with 10 cm<sup>3</sup>/min flow rate on NiAlF<sub>5</sub>O(pyrazine)<sub>2</sub> at 25°C and 50 °C (1 bar) respectively (effect of adsorption temperature on retention time), according to one or more  
25 embodiments of this disclosure.
- [0022] FIG. 9 illustrates a graphical view of column breakthrough tests of CO<sub>2</sub>/H<sub>2</sub>S/CH<sub>4</sub> with 10 cm<sup>3</sup>/min flow rate on NiAlF<sub>5</sub>O(pyrazine)<sub>2</sub> at 50°C (1 bar) after activation at different temperatures (effect of adsorption temperature on retention time of different gases), confirming the recyclability of the material, according to one or more  
30 embodiments of this disclosure.
- [0023] FIG. 10 illustrates a graphical view of comparison of retention time of CO<sub>2</sub> and H<sub>2</sub>S for studied materials during column breakthrough tests at 25°C (1 bar) after optimal

activation of the samples (gas mixture CO<sub>2</sub>/H<sub>2</sub>S/CH<sub>4</sub> (5/5/90) with 10 cm<sup>3</sup>/min flow rate was used for the experiments), according to one or more embodiments of this disclosure.

**[0024]** FIG. 11 illustrates a graphical view of comparison of retention time of CO<sub>2</sub> and H<sub>2</sub>S for studied materials during column breakthrough tests at 50°C (1 bar) after optimal activation of the samples (gas mixture CO<sub>2</sub>/H<sub>2</sub>S/CH<sub>4</sub> (5/5/90) with 10 cm<sup>3</sup>/min flow rate was used for the experiments), according to one or more embodiments of this disclosure.

**[0025]** FIG. 12 illustrates a graphical view of comparison of retention time of CO<sub>2</sub> and H<sub>2</sub>S for studied materials during column breakthrough tests at 25°C and 50°C (1 bar) respectively after optimal activation of the samples (gas mixture CO<sub>2</sub>/H<sub>2</sub>S/CH<sub>4</sub> (5/5/90) with 10 cm<sup>3</sup>/min flow rate was used for the experiments), according to one or more embodiments of this disclosure.

**[0026]** FIG. 13 illustrates a graphical view of comparison of retention time of CO<sub>2</sub> and H<sub>2</sub>S for studied materials during column breakthrough tests at 25°C after optimal activation and 25°C activation of the samples respectively (gas mixture CO<sub>2</sub>/H<sub>2</sub>S/CH<sub>4</sub> (5/5/90) with 10 cm<sup>3</sup>/min flow rate was used for the experiments) and comparison describes compatibility of the studied materials for Vacuum Swing Regeneration (VSR) at 25 °C., according to one or more embodiments of this disclosure.

**[0027]** FIG. 14 illustrates a graphical view of comparison of retention time of CO<sub>2</sub> and H<sub>2</sub>S for studied materials during column breakthrough tests at 50°C after optimal activation and 50°C activation of the samples respectively (gas mixture CO<sub>2</sub>/H<sub>2</sub>S/CH<sub>4</sub> (5/5/90) with 10 cm<sup>3</sup>/min flow rate was used for the experiments) and comparison describes compatibility of the studied materials for Vacuum Swing Regeneration (VSR) at 50°C., according to one or more embodiments of this disclosure.

**[0028]** FIG. 15 illustrates a graphical view of comparison of retention time of CO<sub>2</sub> and H<sub>2</sub>S for studied materials during column breakthrough tests at 25°C with fresh samples and samples after five breakthrough cycles respectively after optimal activation (gas mixture CO<sub>2</sub>/H<sub>2</sub>S/CH<sub>4</sub> (5/5/90) with 10 cm<sup>3</sup>/min flow rate was used for the experiments) and comparison describes recyclability of the studied materials., according to one or more embodiments of this disclosure.

#### DETAILED DESCRIPTION

**[0029]** Provided herein are a series of highly stable and highly tunable MOFs with high affinity and stability to water and H<sub>2</sub>S. 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 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 capture chemical species from fluid compositions under conditions and in the presence of chemical species which render known gas capture technologies inefficient, impracticable, or inoperable. In particular, the MOFs provided herein can capture one or more of H<sub>2</sub>O, CO<sub>2</sub> and H<sub>2</sub>S from a fluid composition, such as natural gas, while maintaining high structural integrity during both adsorption and desorption.

10 **[0030]** 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.

25 **[0031]** 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 CO<sub>2</sub>, H<sub>2</sub>S and water vapor.

**[0032]** As used herein, “refining” refers to removing one or more unwanted components or separating one or more components from remaining components of a composition, such as a fluid. For example, refining can include removing a fraction of H<sub>2</sub>S from a fluid, such as natural gas.

30 **[0033]** 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.

[0034] 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.

[0035] 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 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 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 H<sub>2</sub>S stable which consequently preclude their use in gas separation.

[0036] As disclosed in co-owned U.S. Application No.: 62/044,928, a series of isorecticular MOFs with periodically arrayed hexafluorosilicate (SiF<sub>6</sub>) pillars, called **SIFSIX-2-Cu-i** and **SIFSIX-3-Zn**, **SIFSIX-3-Cu** and **SIFSIX-3-Ni** showed particularly high CO<sub>2</sub> selectivity and capture. These properties in **SIFSIX-3-M** materials suggest broad applications from ppm level CO<sub>2</sub> removal to bulk CO<sub>2</sub> separation. However, with the exception of **SIFSIX-3-Ni**, the **SIFSIX-3-M** materials were not tolerant to H<sub>2</sub>S. And although these materials exhibit high structural stability in the presence of CO<sub>2</sub>, 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 CO<sub>2</sub> uptake. This indicates that the **SIFSIX-3-M** materials series is not sufficiently robust to handle CO<sub>2</sub> and H<sub>2</sub>S capture in most critical applications



throughout the oil and gas and renewable fuels industries, especially in applications which bring the materials into contact with moisture.

**[0037]** Provided herein are novel functionalized MOFs suitable for the removal of acid gases, particularly CO<sub>2</sub> and H<sub>2</sub>S, which additionally exhibit high water vapor tolerance and stability over thousands of cycles. These MOFs eliminate the safety, efficiency, and environmental concerns associated with amine scrubbing techniques while providing high selectivity toward acid gases and negligible uptake of other components, including CH<sub>4</sub>. The proposed class of materials will permit NG and biofuels refining approaches based on simultaneous removal of CO<sub>2</sub>, H<sub>2</sub>S and water vapor. The benefits of this innovative approach include the following: (i) no environmental and safety hazards germane to amine scrubbing (ii) no preliminary separate desulfurization is necessary (iii) no separate gas drying is needed, and (iv) no compression-decompression/cooling of NG is required. Further, the MOFs provided herein offer exceptional thermal and mechanical stability, particularly during adsorption/desorption.

**[0038]** MOFs as provided herein comprise one or more MBBs. Generally, a MBB, or a network of MBBs, can be represented by the formula [(node)<sub>a</sub>(ligand)<sub>b</sub>(solvent)<sub>c</sub>]<sub>n</sub>, wherein 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 H<sub>2</sub>S. 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)<sub>a</sub>(ligand)<sub>b</sub>]<sub>n</sub>, without reference to a solvent or guest molecule component.

**[0039]** In some embodiments herein, MOFs can be characterized by the formula [(node)<sub>a</sub>(ligand)<sub>b</sub>(solvent)<sub>c</sub>]<sub>n</sub>. A non-limiting list of solvents can include one or more of H<sub>2</sub>O, DMF, and DEF. In some embodiments, solvent can include a chemical species present after fabrication of the MOF. In some embodiments, solvent can include a functionalizing guest molecule, such as water, DMF, and DEF. Some embodiments herein comprise a porous, uninhabited MOF characterized by the formula [(node)<sub>a</sub>(ligand)<sub>b</sub>]<sub>n</sub>, wherein node comprises, generally, M<sub>a</sub>M<sub>b</sub>F<sub>x</sub>O<sub>y</sub>(H<sub>2</sub>O)<sub>z</sub>. In some embodiments, M<sub>a</sub> 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  
 5 IIIA, IIIB, IVB, VB, VIB, or VIII. In some embodiments,  $M_a$  can comprise 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  $Co^3$ . In some embodiments,  $M_b$  can be one of the following  $Al^{+3}$ ,  $Fe^{+2}$ ,  $Fe^{+3}$ ,  $Cr^{2+}$ ,  $Cr^{3+}$ ,  $Ti^{3+}$ ,  $V^{3+}$ ,  $V^{5+}$ ,  $Sc^{3+}$ ,  $In^{3+}$ ,  $Nb^{5+}$ ,  $Y^{3+}$ . In some embodiments,  $M_a$  can comprise one of the following cations:  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  
 10  $Mn^{2+}$ ,  $Zr^{2+}$ ,  $Fe^{2+}$ ,  $Ca^{2+}$ ,  $Ba^{2+}$ ,  $Pb^{2+}$ ,  $Pt^{2+}$ ,  $Pd^{2+}$ ,  $Ru^{2+}$ ,  $Rh^{2+}$ ,  $Cd^{2+}$ ,  $Mg^{+2}$ ,  $Al^{+3}$ ,  $Fe^{+2}$ ,  $Fe^{+3}$ ,  $Cr^{2+}$ ,  $Cr^{3+}$ ,  $Ru^{2+}$ ,  $Ru^{3+}$  and  $Co^3$ ;  $M_b$  can be one of the following  $Al^{+3}$ ,  $Fe^{+2}$ ,  $Fe^{+3}$ ,  $Cr^{2+}$ ,  $Cr^{3+}$ ,  $Ti^{3+}$ ,  $V^{3+}$ ,  $V^{5+}$ ,  $Sc^{3+}$ ,  $In^{3+}$ ,  $Nb^{5+}$ ,  $Y^{3+}$ . In such embodiments, the ligand can be any bi-functional N-donor linkers based on monocyclic or polycyclic group (aromatic or not).

**[0040]** In some embodiments, a ligand can comprise a polydentate, or poly-functional  
 15 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  
 20 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.

**[0041]** Some embodiments of suitable MOFs can be represented by the following general formula:  $[M_a M_b F_x (O/H_2O)_z (Ligand)_2]_n$  wherein  $M_a$  can be one of the following cations:  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Mn^{2+}$ ,  $Zr^{2+}$ ,  $Fe^{2+}$ ,  $Ca^{2+}$ ,  $Ba^{2+}$ ,  $Pb^{2+}$ ,  $Pt^{2+}$ ,  $Pd^{2+}$ ,  $Ru^{2+}$ ,  $Rh^{2+}$ ,  
 25  $Cd^{2+}$ ,  $Mg^{+2}$ ,  $Al^{+3}$ ,  $Fe^{+2}$ ,  $Fe^{+3}$ ,  $Cr^{2+}$ ,  $Cr^{3+}$ ,  $Ru^{2+}$ ,  $Ru^{3+}$  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-  
 30 functional N-donor linkers based on monocyclic or polycyclic group (aromatic or not).

**[0042]** 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  $\text{Al}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{V}^{3+}$ ,  $\text{V}^{4+}$ ,  $\text{V}^{5+}$ ,  $\text{Nb}^{5+}$ , to afford highly stable materials with or without open metals sites. In some embodiments, the use of specific cations, such as  $\text{Al}^{+3}$ ,  $\text{Fe}^{+2}$ ,  $\text{Fe}^{+3}$ ,  $\text{Cr}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Ti}^{3+}$ ,  $\text{V}^{3+}$ ,  $\text{V}^{5+}$ ,  $\text{Sc}^{3+}$ ,  $\text{In}^{3+}$ ,  $\text{Y}^{3+}$ , in  $M_b$  site positions can introduce open-metal sites within the channels that enhance properties of gas capture.

10 **[0043]** These, and other features, collaborate to achieve MOFs with high affinity and stability to water and  $\text{H}_2\text{S}$ . 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  $\text{CO}_2$  and/or  $\text{H}_2\text{S}$ . 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  $\text{CO}_2$  and  $\text{H}_2\text{S}$ .

20 **[0044]** In some embodiments, a representative  $M_aM_bF_wO_x(\text{H}_2\text{O})_y(\text{Ligand})_z$  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, wherein x can vary from 0 to 10. All such embodiments offer high affinity and stability to water vapor and  $\text{H}_2\text{S}$ , unlike the Cu and Zn-based analogues of SIFSIX-3-M materials made with Si. In some embodiments a MOF characterized by the formula  $[M_aM_bF_{6-n}(\text{O}/\text{H}_2\text{O})_n(\text{Ligand})_2(\text{solvent})_x]_n$  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 3.8Å. 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  $\text{m}^2/\text{g}$  to about 500  $\text{m}^2/\text{g}$ . In either of the same MOFs or in an alternative embodiment, a MOF can have a pore volume of about 0.1  $\text{cm}^3/\text{g}$  to about 0.25  $\text{cm}^3/\text{g}$ . In a different embodiment, a more elongated ligand can provide an analogous MOF with much higher porosity.

**[0045]** Figure 1A illustrates a method 100 for capturing 120 one or more chemical species from a fluid composition 110 via a first MOF 105. A method 100 for capturing 120

one or more chemical species from a fluid composition 110 can comprise contacting 115 a metal organic framework 105 characterized by the formula  $[M_aM_bF_6-n(O/H_2O)_w(Ligand)_x(solvent)_y]_z$  with a fluid composition 110. Fluid composition 310 can comprise two or more chemical species. Fluid composition 310 can comprise natural gas. In one embodiment, fluid composition 110 comprises one or more of carbon dioxide, water, and hydrogen sulfide. In such an embodiment, fluid composition 110 can further comprise methane.

**[0046]** Method 100 can further comprise capturing 120 one or more chemical species from the fluid composition 110. Capturing 120 can comprise capturing one or more of carbon dioxide, water, and hydrogen sulfide. Capturing 120 can comprise capturing two or more of carbon dioxide, water, and hydrogen sulfide. In some embodiments, capturing 120 comprises physical adsorption of the one or more captured chemical species by the first MOF 105. In some embodiments, capturing 120 comprises chemisorption of the one or more captured chemical species by the first MOF 105. Chemisorption can occur by one or more captured chemical species chemically interacting with one or more open metal sites of the first MOF 105. In other embodiments, capturing 120 comprises physical adsorption and chemisorption of the one or more captured chemical species by the metal organic framework. Capturing 120 can comprise wholly or partially containing a chemical species within a pore of a MOF. In some embodiments, capturing 120 consists of chemisorption. In some embodiments, capturing 120 consists of physical adsorption. Capturing 120 can occur in a capturing environment. A capturing environment can comprise one or more of ambient temperature or pressure. A capturing environment can comprise a pressurize-controlled vessel. A capturing environment can comprise a temperature-controlled vessel. A capturing environment can comprise a pressure and temperature-controlled vessel. A capturing environment can comprise the first MOF 105 in the form of a fixed bed, a packed column, or combinations thereof.

**[0047]** Capturing 120 can further comprise changing the temperature of the capture environment to alter the affinity of one or more chemical species for the MOF. Similarly, capturing 120 can further comprise changing the pressure of the capture environment to alter the affinity of one or more chemical species for the MOF. Additionally, capturing 120 can further comprise changing the temperature and pressure of the capture environment to alter the affinity of one or more chemical species for the MOF. In such embodiments, the chemical species can particularly include carbon dioxide, water, and hydrogen sulfide.

**[0048]** Method 100 can further comprise desorbing one or more of carbon dioxide, water, and hydrogen sulfide from the MOF. Method 100 can further comprise desorbing two or more of carbon dioxide, water, and hydrogen sulfide from the MOF. Desorbing can occur in a desorbing environment. A desorbing environment can comprise one or more of ambient  
5 temperature or pressure. A desorbing environment can comprise a pressurize-controlled vessel. A desorbing environment can comprise a temperature-controlled vessel. A desorbing environment can comprise a pressure and temperature-controlled vessel. While a MOF can capably capture a number of gaseous or vapor phase species, a relative affinity hierarchy will, in principle, exist among those species. In embodiments where method 100 comprises  
10 desorbing two or more of carbon dioxide, water, and hydrogen sulfide from the MOF, carbon dioxide, water, and hydrogen sulfide can be sequentially desorbed in descending order of affinity. In a particular embodiment, H<sub>2</sub>S is desorbed first, CO<sub>2</sub> is desorbed second, and H<sub>2</sub>O is desorbed last.

**[0049]** In some embodiments, the relative affinity hierarchy of chemical species can  
15 be manipulated. Accordingly, desorbing can further comprise changing the temperature of the desorbing environment to alter the affinity of one or more chemical species for the MOF. Similarly, desorbing can further comprise changing the pressure of the desorbing environment to alter the affinity of one or more chemical species for the MOF. Additionally, desorbing can further comprise changing the temperature and pressure of the desorbing  
20 environment to alter the affinity of one or more chemical species for the MOF. In such embodiments, the chemical species can particularly include carbon dioxide, water, and hydrogen sulfide. In some embodiments, one or more of capturing and desorbing is effected by multicolumn pressure-temperature swing adsorption. Multicolumn pressure-temperature swing adsorption is known in the art.

**[0050]** Method 100 can further comprise contacting 115 the fluid composition 110  
25 with a second MOF, characterized by the formula  $[M_cM_dF_{6-n}(O/H_2O)_w(Ligand)_x(solvent)_y]_z$ . In some embodiments, the second MOF is different from the first MOF 105. In some embodiments, contacting 115 the fluid composition with the first MOF 105 and the second MOF occurs separately. In some embodiments, contacting 115 the fluid composition with  
30 the first MOF 105 and the second MOF occurs sequentially. In some embodiments, contacting 115 the fluid composition with the first MOF 105 and the second MOF occurs simultaneously. Method 100 can further comprise contacting 115 the fluid composition 110 with three or more MOFs.

**[0051]** In some embodiments, the first MOF comprises one or more MOFs as provided herein. For example, the first MOF can comprise an MOF characterized by the formula  $[\text{NiNbF}_{6-n}(\text{O}/\text{H}_2\text{O})_w(\text{Ligand})_x(\text{solvent})_y]_z$ . In some embodiments the second MOF comprises one or more MOFs as provided herein. For example, the second MOF can  
 5 comprise an MOF characterized by the formula  $[\text{NiM}_d\text{F}_{6-n}(\text{O}/\text{H}_2\text{O})_w(\text{Ligand})_x(\text{solvent})_y]_z$  wherein  $\text{M}_d$  comprises  $\text{Al}^{+3}$ ,  $\text{Fe}^{+2}$ , or  $\text{Fe}^{+3}$ . In some embodiments, the MOF is characterized by the formula  $[\text{NiNbF}_{6-n}(\text{O}/\text{H}_2\text{O})_w(\text{Ligand})_x(\text{solvent})_y]_z$  and the second MOF is characterized by the formula  $[\text{NiM}_d\text{F}_{6-n}(\text{O}/\text{H}_2\text{O})_w(\text{Ligand})_x(\text{solvent})_y]_z$  wherein  $\text{M}_d$  comprises  $\text{Al}^{+3}$ ,  $\text{Fe}^{+2}$ , or  $\text{Fe}^{+3}$ .

**[0052]** Figure 1B illustrates a method 101 for removing one or more of carbon dioxide, water, and hydrogen sulfide from natural gas via a MOF. Removing one or more of carbon dioxide, water, and hydrogen sulfide from natural gas can occur simultaneously. Removing one or more of carbon dioxide, water, and hydrogen sulfide from natural gas can occur separately. Removing can occur in a multicolumn pressure-  
 15 temperature swing adsorption (PTSA) system. In one embodiment, the MOF comprises one of  $\text{Ni}(\text{Al}/\text{Fe}/\text{V}/\text{Nb})\text{F}_5(\text{O}/\text{H}_2\text{O})_x(\text{pyrazine})_2(\text{solvent})_x$ . In another embodiment, the MOF comprises two or more of  $\text{Ni}(\text{Al}/\text{Fe}/\text{V}/\text{Nb})\text{F}_5(\text{O}/\text{H}_2\text{O})_x(\text{pyrazine})_2(\text{solvent})_x$ .

**[0053]** MOFs as provided herein can be fabricated using a solvo(hydro)thermal synthetic procedure. As shown in Figure 2, a method for fabricating 200 a MOF 230 can  
 20 include combining 205 reactants. Reactants can include one or more of a fluorhydric acid solution 206 with a  $\text{Ni}^{2+}$  source 207, a second metal source 208, and a solvent 209 to form a mixture 210. A  $\text{Ni}^{2+}$  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  $\text{Al}^{+3}$   
 25 source, an  $\text{Fe}^{+2}$  source, an  $\text{Fe}^{+3}$  source, a  $\text{Cr}^{2+}$  source, a  $\text{Cr}^{3+}$  source, a  $\text{Ti}^{3+}$  source, a  $\text{V}^{3+}$  source, a  $\text{V}^{5+}$  source, a  $\text{Sc}^{3+}$  source, an  $\text{In}^{3+}$  source, a  $\text{Nb}^{5+}$  source, or a  $\text{Y}^{3+}$  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  $\text{H}_2\text{O}$ , dimethylformamide (DMF), and  
 30 diethylformamide (DEF).

**[0054]** 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  $\text{Ni}^{2+}$  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.

**[0055]** 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  $M_aN_4F_2$  and  $M_bF_4(H_2O)_2$  octahedra or between  $M_aN_4F_2$  and  $M_bF_5(H_2O)$  octahedra or between  $M_aN_4F_2$  octahedra and  $M_bF_5(O)$  octahedra. Figure 3A illustrates an example of an inorganic chain, built up from  $M_aN_4F_2$  and  $M_bF_5(H_2O)$  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 3B illustrates a schematic view of one embodiment of a MOF comprising a  $NiNbF_5O(pyrazine)_2$  structure, viewed along the c-axis.

**[0056]** 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 this MOF, characterized by the formula  $NiNbF_5O(pyrazine)_2(solvent)_x$ , confirming the high stability of the MOF in the presence of water. Figure 4B illustrates powder X-ray diffraction data of this MOF, confirming the high stability of the MOF in the presence of  $H_2S$ .

**[0057]** Figures.5A-C illustrates the broad potential for MOFs characterized by the formula  $Ni(Al/Fe/V/Nb)F_5(O/H_2O)_x(pyrazine)_2(solvent)_x$ , and variants thereof. Figure 5A illustrates  $CO_2$  isotherms at 298 K for each of these four MOFs, which show extremely high sorption of  $CO_2$  across all test pressures (0-1 bar), Figure 5B illustrates  $H_2S$  isotherms at 298K for three MOFs characterized by the formula  $Ni(Al/Fe/V)F_5(O/H_2O)_x(pyrazine)_2(solvent)_z$ , which shows across all test pressures (0-1, wherein 1 corresponds to a 0.1  $H_2S$  partial pressure).

**[0058]** Figure 5C Illustrates  $H_2O$  sorption isotherms at 298K for  $Ni(Al)F_5(O/H_2O)_x(pyrazine)_2(solvent)_z$ , indicating the high suitability of this MOF for gas dehydration applications, among others. These results demonstrate the value of the MOF embodiment characterized by the formula  $Ni(Al/Fe/V/Nb)F_5(O/H_2O)_x(pyrazine)_2(solvent)_x$  as

a platform for refining a number of valuable hydrocarbon gases and fluids, including methane, natural gas, and biogas. The exemplary performance and properties of the Nb<sup>5+</sup> 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<sub>b</sub>F<sub>5</sub>O(pyrazine)<sub>2</sub>, wherein M<sub>b</sub> can be one of the following Al<sup>+3</sup>, Fe<sup>+2</sup>, Fe<sup>+3</sup>, Cr<sup>+2</sup>, Cr<sup>+3</sup>, Ti<sup>+3</sup>, V<sup>+3</sup>, V<sup>+5</sup>, Sc<sup>+3</sup>, In<sup>+3</sup>, Nb<sup>+5</sup>, Y<sup>+3</sup>. 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<sub>a</sub>NbF<sub>5</sub>O(pyrazine)<sub>2</sub>, wherein M<sub>a</sub> can be one of the following cations: Cu<sup>+2</sup>, Zn<sup>+2</sup>, Co<sup>+2</sup>, Ni<sup>+2</sup>, Mn<sup>+2</sup>, Zr<sup>+2</sup>, Fe<sup>+2</sup>, Ca<sup>+2</sup>, Ba<sup>+2</sup>, Pb<sup>+2</sup>, Pt<sup>+2</sup>, Pd<sup>+2</sup>, Ru<sup>+2</sup>, Rh<sup>+2</sup>, Cd<sup>+2</sup>, Mg<sup>+2</sup>, Al<sup>+3</sup>, Fe<sup>+2</sup>, Fe<sup>+3</sup>, Cr<sup>+2</sup>, Cr<sup>+3</sup>, Ru<sup>+2</sup>, Ru<sup>+3</sup>. These and other results can also be expected in similar other embodiments, with or without open metal sites, such as MOF structure characterized by the formula M<sub>a</sub>(Al/Fe/V)F<sub>5</sub>O(pyrazine)<sub>2</sub>, wherein M<sub>a</sub> can be one of the following cations: Cu<sup>+2</sup>, Zn<sup>+2</sup>, Co<sup>+2</sup>, Ni<sup>+2</sup>, Mn<sup>+2</sup>, Zr<sup>+2</sup>, Fe<sup>+2</sup>, Ca<sup>+2</sup>, Ba<sup>+2</sup>, Pb<sup>+2</sup>, Pt<sup>+2</sup>, Pd<sup>+2</sup>, Ru<sup>+2</sup>, Rh<sup>+2</sup>, Cd<sup>+2</sup>, Mg<sup>+2</sup>, Al<sup>+3</sup>, Fe<sup>+2</sup>, Fe<sup>+3</sup>, Cr<sup>+2</sup>, Cr<sup>+3</sup>, Ru<sup>+2</sup>, Ru<sup>+3</sup>.

### EXAMPLE 1

**[0059]** In order to study the performance of NiAlF<sub>5</sub>O(pyrazine)<sub>2</sub> for adsorption of CO<sub>2</sub> and H<sub>2</sub>S, a series of cyclables testing were carried out in a flow mode system using the sequence of tests described in Figure 6.

**[0060]** NiAlF<sub>5</sub>O(pyrazine)<sub>2</sub>, a material from a related SiF<sub>6</sub> platform which is known to be very selective to CO<sub>2</sub> was tested. Interestingly, the gas adsorption testings using CO<sub>2</sub>/H<sub>2</sub>S/CH<sub>4</sub>:5/5/90 at 25°C in TSR mode showed a retention time in the column of 27 min/g for H<sub>2</sub>S and CO<sub>2</sub>, respectively (Figure 7), indicative of similar affinity of the NiAlF<sub>5</sub>O(pyrazine)<sub>2</sub> framework to both CO<sub>2</sub> and H<sub>2</sub>S. These results showed that H<sub>2</sub>S and CO<sub>2</sub> could be removed simultaneously with the same affinity.

**[0061]** Most importantly, heating the adsorption column in a second TSR (temperature swing regeneration mode) cycle to 50°C for NiAlF<sub>5</sub>O(pyrazine)<sub>2</sub> did not significantly affect the retention time (25 vs 27 min/g) for both H<sub>2</sub>S and CO<sub>2</sub> respectively (Figure 8).

**[0062]** Figure 9 shows that TSR mode could be practiced for NiAlF<sub>5</sub>O(pyrazine)<sub>2</sub> using reactivation at 50°C and even VSR mode at 25°C with a minimum loss in the H<sub>2</sub>S retention time while keeping the same affinity for H<sub>2</sub>S and CO<sub>2</sub>. Figure 9 shows that for



NiAlF<sub>5</sub>O(pyrazine)<sub>2</sub>, the H<sub>2</sub>S and CO<sub>2</sub> uptakes were reduced by 20% between TSR and VSR (vacuum swing regeneration) mode when adsorption is carried at 50°C.

[0063] Finally, the reproducibility test (6th cycle) after 5 adsorption-desorption tests showed that NiAlF<sub>5</sub>O(pyrazine)<sub>2</sub> exhibit a reproducible H<sub>2</sub>S and CO<sub>2</sub> adsorption

5 performance. In this case, NiAlF<sub>5</sub>O(pyrazine)<sub>2</sub> can be utilized as a potential material for the simultaneous removal of H<sub>2</sub>S and CO<sub>2</sub>.

## EXAMPLE 2

[0064] With the exception of NiAlF<sub>5</sub>O(pyrazine)<sub>2</sub>, it was shown that other MOF  
10 materials studied exhibit higher selectivity and higher retention time for H<sub>2</sub>S than CO<sub>2</sub> at 25°C (Figure 10). Y-1,4-NDC-**fcu**-MOF is the best material from the studied materials for H<sub>2</sub>S removal with retention time of 70 min/gm (5% H<sub>2</sub>S, 10 cm<sup>3</sup>/min flowrate). Retention time for H<sub>2</sub>S decreases for almost 40 % when temperature is increased to 50°C (Figures 11, 12), with highest retention time of 41 min/g (5% H<sub>2</sub>S, 10cc/min flowrate) for Y-1,4-NDC-**fcu**-MOF. Retention time of H<sub>2</sub>S and CO<sub>2</sub> for Y-1,4-NDC-**fcu**-MOF and Y-fum-**fcu**-MOF  
15 does not change during VSR at 25°C (Figure 13), while retention time for all the samples does not change during VSR at 50 °C (Figure 14).

[0065] Unlike all other studied materials here, NiAlF<sub>5</sub>O(pyrazine)<sub>2</sub> has the same retention time of 28 min/gm (5% H<sub>2</sub>S, 5% CO<sub>2</sub> 10cm<sup>3</sup>/min flowrate) for both H<sub>2</sub>S and CO<sub>2</sub> at  
20 25°C (Figure 10). By increasing temperature to 50°C, the retention time for CO<sub>2</sub> and H<sub>2</sub>S only decrease slightly to 26 min/gm (5% H<sub>2</sub>S, 5% CO<sub>2</sub> 10cc/min flowrate) unlike other materials (Figures 11, 12). During VSR at 25°C for NiAlF<sub>5</sub>O(pyrazine)<sub>2</sub>, the retention time for H<sub>2</sub>S decreases slightly (Figure 13), however the retention time for H<sub>2</sub>S and CO<sub>2</sub> remains unchanged during VSR at 50°C (Figure 14). NiAlF<sub>5</sub>O(pyrazine)<sub>2</sub> is a good candidate for  
25 simultaneous removal of H<sub>2</sub>S and CO<sub>2</sub> over the wide temperature range, while other studied materials can be good candidates for removal of H<sub>2</sub>S first and then CO<sub>2</sub> in the presence of CH<sub>4</sub> containing gas streams at 25°C.

[0066] As shown in Figure 15, uptake for all the materials remains practically unchanged between 1<sup>st</sup> cycle and 6<sup>th</sup> cycle under the same condition showing that all these  
30 materials selected for mixed gas testing are very stable.

[0067] The CO<sub>2</sub> and H<sub>2</sub>S uptakes for all the MOFs studied in the course of this project, using TSR and VSR mode, are reported in Tables 1 and 2.

[0068] **Table 1.** Summary of H<sub>2</sub>S and CO<sub>2</sub> adsorption uptakes of the best MOFs in TSR mode using CO<sub>2</sub>/H<sub>2</sub>S/CH<sub>4</sub> (5/5/90) Gas mixture (1 bar).

Materials	CO <sub>2</sub> uptake wt% TSR mode		H <sub>2</sub> S uptake wt% TSR mode	
	298 K	323 K	298 K	323 K
Ga-soc-MOF	0.58	0.39	3.11	1.74
Y-FTZB-fcu-MOF	0.98	0.78	3.30	2.04
Y-1,4-NDC-fcu-MOF	1.18	0.74	5.31	3.14
Y-fum-fcu-MOF	0.78	0.49	3.94	2.58
NiAlF <sub>5</sub> (H <sub>2</sub> O)(pyrazine) <sub>2</sub> (solvent)	2.75	2.55	2.12	1.97
NiSiF <sub>6</sub> DPA-i	1.57	1.32	3.94	2.27

[0069] \* CH<sub>4</sub> uptake not detected by the flow mode system and CO<sub>2</sub>/CH<sub>4</sub>, H<sub>2</sub>S/CH<sub>4</sub> selectivity is calculated assuming 0.1 mg as the lowest detectable uptake

5 [0070] **Table 2:** Summary of H<sub>2</sub>S and CO<sub>2</sub> adsorption uptakes of the best MOFs in VSR mode using CO<sub>2</sub>/H<sub>2</sub>S/CH<sub>4</sub> (5/5/90) at 1 bar Gas mixture (1 bar).

Materials	CO <sub>2</sub> uptake wt% VSR mode		H <sub>2</sub> S uptake wt% VSR mode	
	298 K	323 K	298 K	323 K
Ga-soc-MOF	0.49	0.34	2.35	1.63
Y-FTZB-fcu-MOF	0.88	0.78	2.95	2.04
Y-1,4-NDC-fcu-MOF	1.18	0.78	5.16	3.19
Y-fum-fcu-MOF	0.78	0.59	3.87	2.58
NiAlF <sub>5</sub> (H <sub>2</sub> O)(pyrazine) <sub>2</sub> (solvent)	2.45	2.55	1.78	1.97
NiSiF <sub>6</sub> DPA-i	1.76	1.32	3.49	2.28

[0071] Because of the low uptake of CH<sub>4</sub> vs H<sub>2</sub>S and CO<sub>2</sub> during the mixed gas tests, it was impossible to detect and quantify the CH<sub>4</sub> uptake for all the studied materials.

10 Accordingly, in order to determine the CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/H<sub>2</sub>S selectivity (Tables 3 and 4), it was assumed that the non-detectable uptake of CH<sub>4</sub> is equal to the accuracy of the set-up (0.1 mg).

[0072] **Table 3:** Summary of CO<sub>2</sub>/CH<sub>4</sub> and H<sub>2</sub>S/CH<sub>4</sub> adsorption selectivities determined for the best MOFs in TSR mode using CO<sub>2</sub>/H<sub>2</sub>S/CH<sub>4</sub> (5/5/90) at 1 bar Gas mixture (1 bar).

Materials	CO <sub>2</sub> /CH <sub>4</sub> Selectivity* TSR mode		H <sub>2</sub> S/CH <sub>4</sub> Selectivity* TSR mode	
	298 K	323 K	298 K	323 K
Ga-soc-MOF	385	257	2635	1478

Y-FTZB-fcu-MOF	642	514	2796	1735
Y-1,4-NDC-fcu-MOF	771	482	4500	2667
Y-fum-fcu-MOF	514	321	3342	2185
NiAlF <sub>5</sub> (H <sub>2</sub> O)(pyrazine) <sub>2</sub> (solvent)	1800	1671	1800	1671
NiSiF <sub>6</sub> DPA-i	1028	867	3342	1928

[0073] \* CH<sub>4</sub> uptake not detected by the flow mode system and CO<sub>2</sub>/CH<sub>4</sub>, H<sub>2</sub>S/CH<sub>4</sub> selectivities are calculated assuming the uptake of CH<sub>4</sub> is equal to 0.1 mg, which is the lowest detectable uptake by the set-up.

5 [0074] **Table 4:** Summary of CO<sub>2</sub>/CH<sub>4</sub> and H<sub>2</sub>S/CH<sub>4</sub> adsorption selectivities determined for the best MOFs in VSR mode using CO<sub>2</sub>/H<sub>2</sub>S/CH<sub>4</sub> (5/5/90) at 1 bar Gas mixture (1 bar).

Materials	CO <sub>2</sub> /CH <sub>4</sub> Selectivity* VSR mode		H <sub>2</sub> S/CH <sub>4</sub> Selectivity* VSR mode	
	298 K	323 K	298 K	323 K
Ga-soc-MOF	321	225	1992	1382
Y-FTZB-fcu-MOF	578	514	2507	1735
Y-1,4-NDC-fcu-MOF	771	514	4371	2700
Y-fum-fcu-MOF	514	385	3278	2185
NiAlF <sub>5</sub> (H <sub>2</sub> O)(pyrazine) <sub>2</sub> (solvent)	1607	1671	1510	1671
NiSiF <sub>6</sub> DPA-i	1028	867	3342	1928

[0075] \* CH<sub>4</sub> uptake not detected by the flow mode system and CO<sub>2</sub>/CH<sub>4</sub>, H<sub>2</sub>S/CH<sub>4</sub> selectivities are calculated assuming the uptake of CH<sub>4</sub> is equal to 0.1 mg, which is the lowest detectable uptake by the set-up.

[0076] Overall, all the materials selected exhibit very high selectivity for H<sub>2</sub>S vs CH<sub>4</sub>. As expected, the NiAlF<sub>5</sub>O(pyrazine)<sub>2</sub> exhibited the highest selectivity for CO<sub>2</sub>. It is noted that adsorption selectivity values higher than 700-1000 are often attached with elevated degree of inaccuracy, hence, this values should be considered as infinite. Accordingly, the high values for CO<sub>2</sub>/CH<sub>4</sub> and H<sub>2</sub>S/CH<sub>4</sub> selectivities reported in tables 3 and 4 are highly qualitative.

[0077] In summary, highly stable recyclable MOF materials for H<sub>2</sub>S and CO<sub>2</sub> removal from natural gas with a wide range of H<sub>2</sub>S /CO<sub>2</sub> selectivity are described that can be used for TSR and VSR at room and higher temperatures. Highly selective materials are shown for CO<sub>2</sub> having open metals sites (such as NiAlF<sub>5</sub>(H<sub>2</sub>O)(pyrazine)<sub>2</sub>(solvent)) that have the potential to remove CO<sub>2</sub> and H<sub>2</sub>S simultaneously with high selectivity.

**WHAT IS CLAIMED IS**

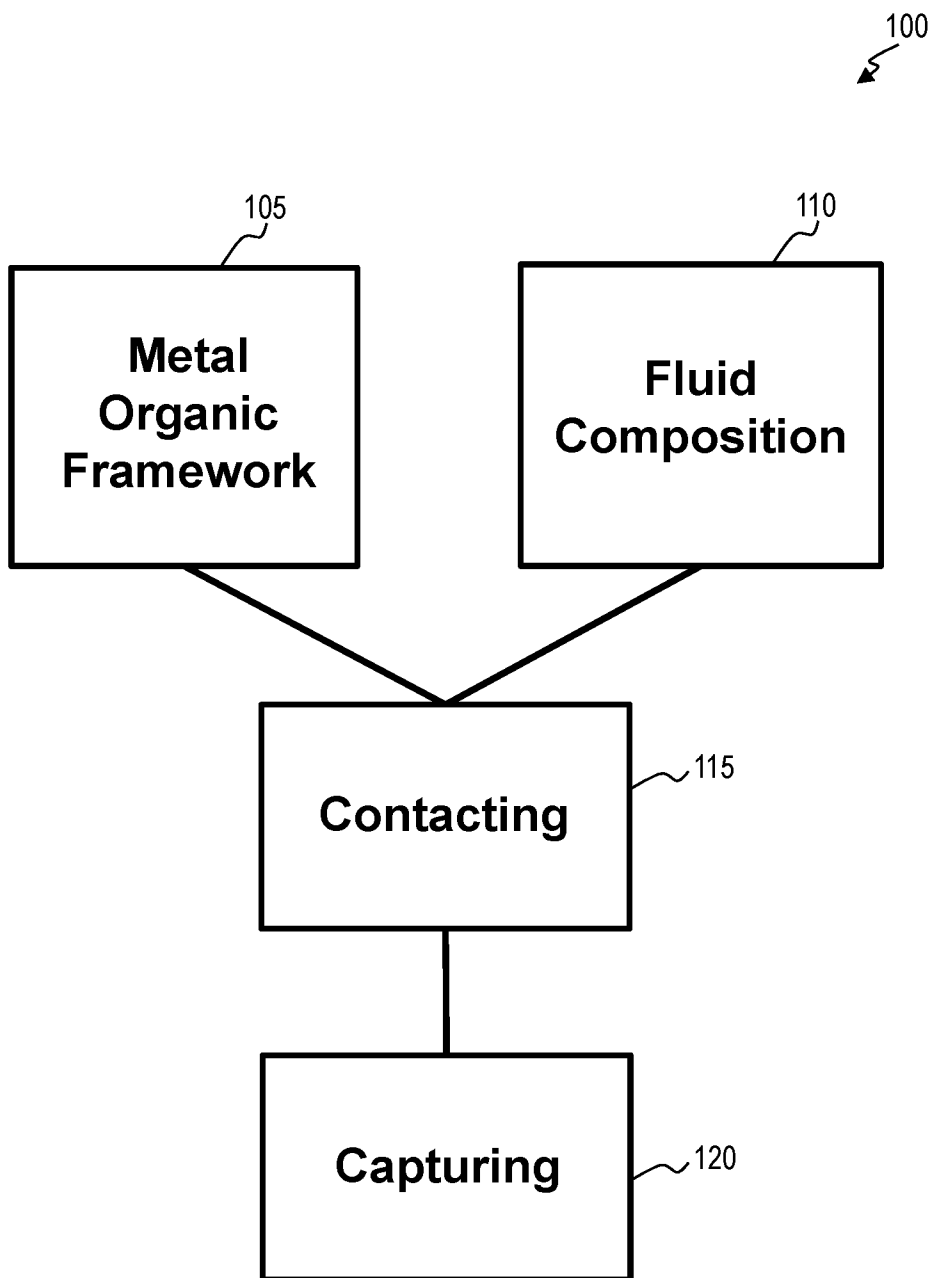
1. A method of capturing chemical species from a fluid composition, the method comprising contacting a first metal organic framework characterized by the formula  $[M_a M_b F_{6-n} (O/H_2O)_w (Ligand)_x (solvent)_y]_z$  with a fluid composition comprising one or more of carbon dioxide, water, and hydrogen sulfide; and capturing one or more of carbon dioxide, water, and hydrogen sulfide 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 further comprises methane.
10. The method of claim 1, further comprising capturing two or more of carbon dioxide, water, and hydrogen sulfide from the fluid composition.
11. The method of claim 10, further comprising desorbing two or more of carbon dioxide, water, and hydrogen sulfide.
12. The method of claim 11, wherein two or more of carbon dioxide, water, and hydrogen sulfide are sequentially desorbed in descending order of affinity.
13. The method of claim 1, further comprising changing the pressure of the capture environment to alter the affinity of one or more of carbon dioxide, water, and hydrogen sulfide for the metal organic framework adsorbent.
14. The method of claim 1, further comprising changing the temperature of the capture environment to alter the affinity of one or more of carbon dioxide, water, and hydrogen sulfide for the metal organic framework adsorbent.
15. The method of claim 14 further comprising changing the temperature of the capture environment to alter the affinity of one or more of carbon dioxide, water, and hydrogen sulfide for the metal organic framework adsorbent.
16. The method of claim 1, simultaneously or separately contacting the fluid composition with a second metal organic framework, characterized by the formula  $[M_c M_d F_{6-n} (O/H_2O)_w (Ligand)_x (solvent)_y]_z$ , wherein the second metal organic framework is different from the first metal organic framework.
17. The method of claim 16, wherein the first metal organic framework is characterized by the formula  $[NiNbF_{6-n} (O/H_2O)_w (Ligand)_x (solvent)_y]_z$ , and the second metal organic framework is characterized by the formula  $[M_c M_d F_{6-n} (O/H_2O)_w (Ligand)_x (solvent)_y]_z$ , wherein  $M_c$  comprises  $Ni^{+}$  and  $M_d$  comprises  $Al^{+3}$ ,  $Fe^{+2}$ , or  $Fe^{+3}$ .

18. The method of claim 1, wherein the metal organic framework adsorbent is in the form of a fixed bed, a packed column, or combinations thereof.

19. The method of claim 1, further comprising desorbing one or more of carbon dioxide, water, and hydrogen sulfide.

20. The method of claim 19, wherein one or more of capturing and desorbing is effected by multicolumn pressure-temperature swing adsorption



**FIG 1A**

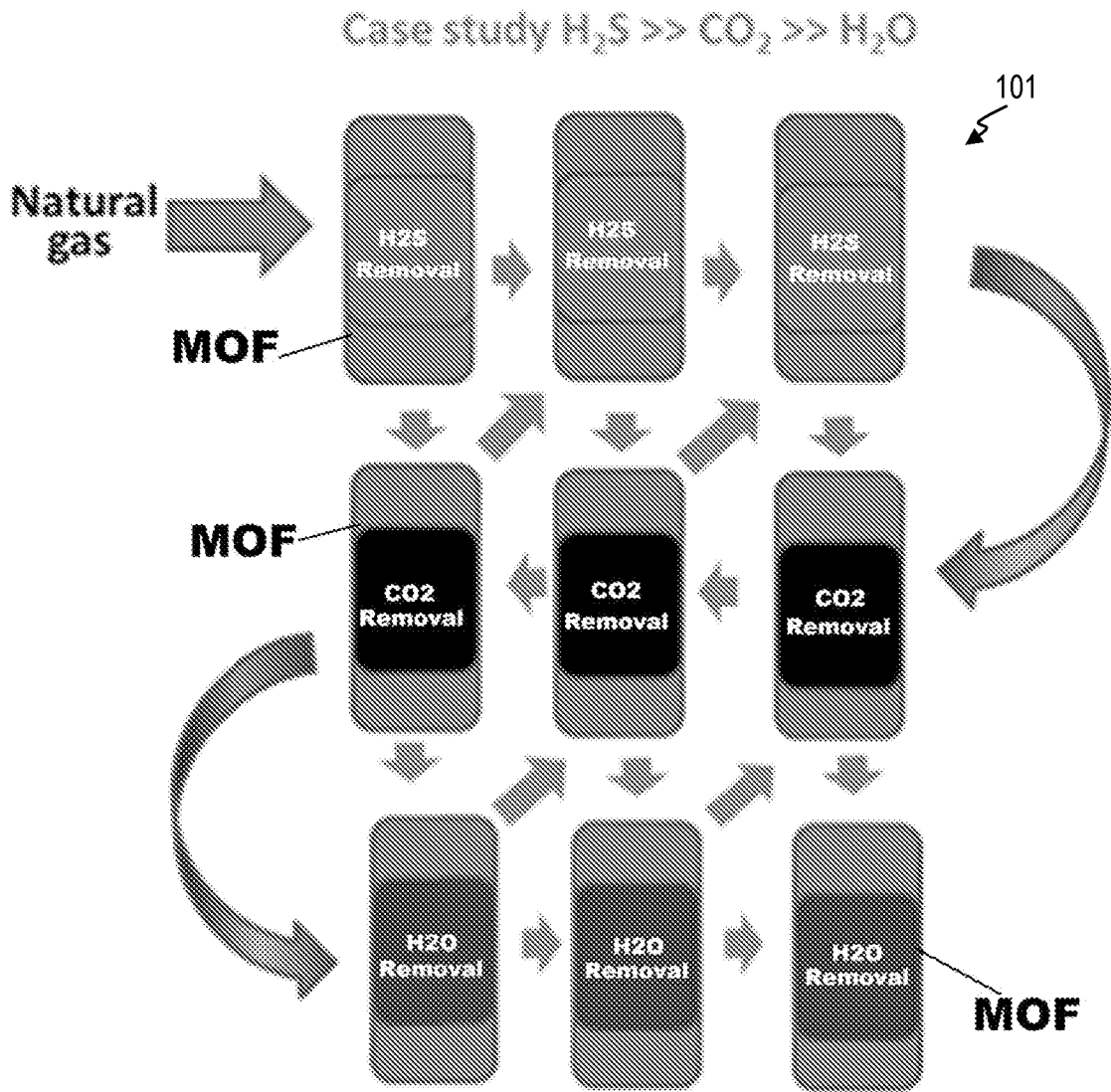
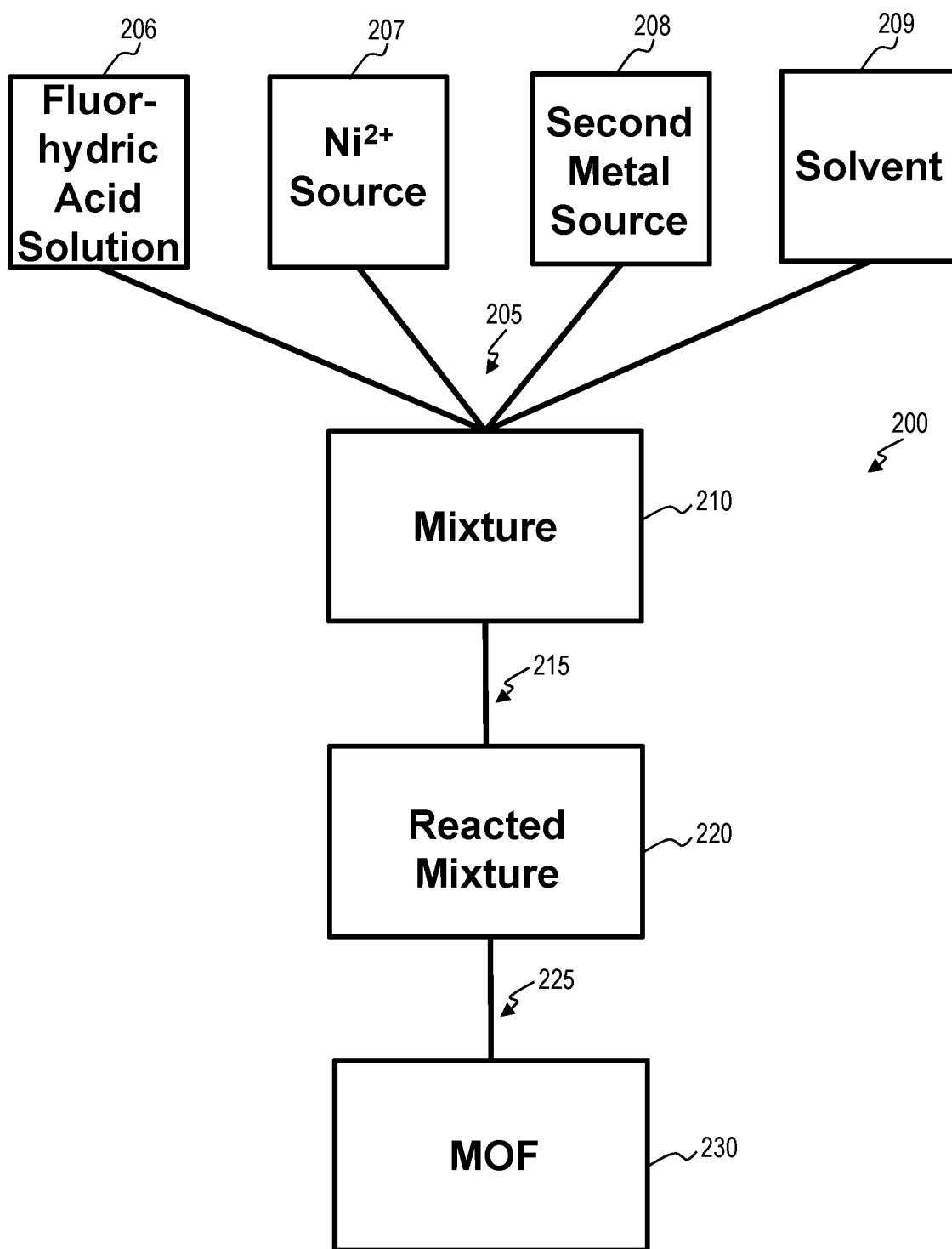
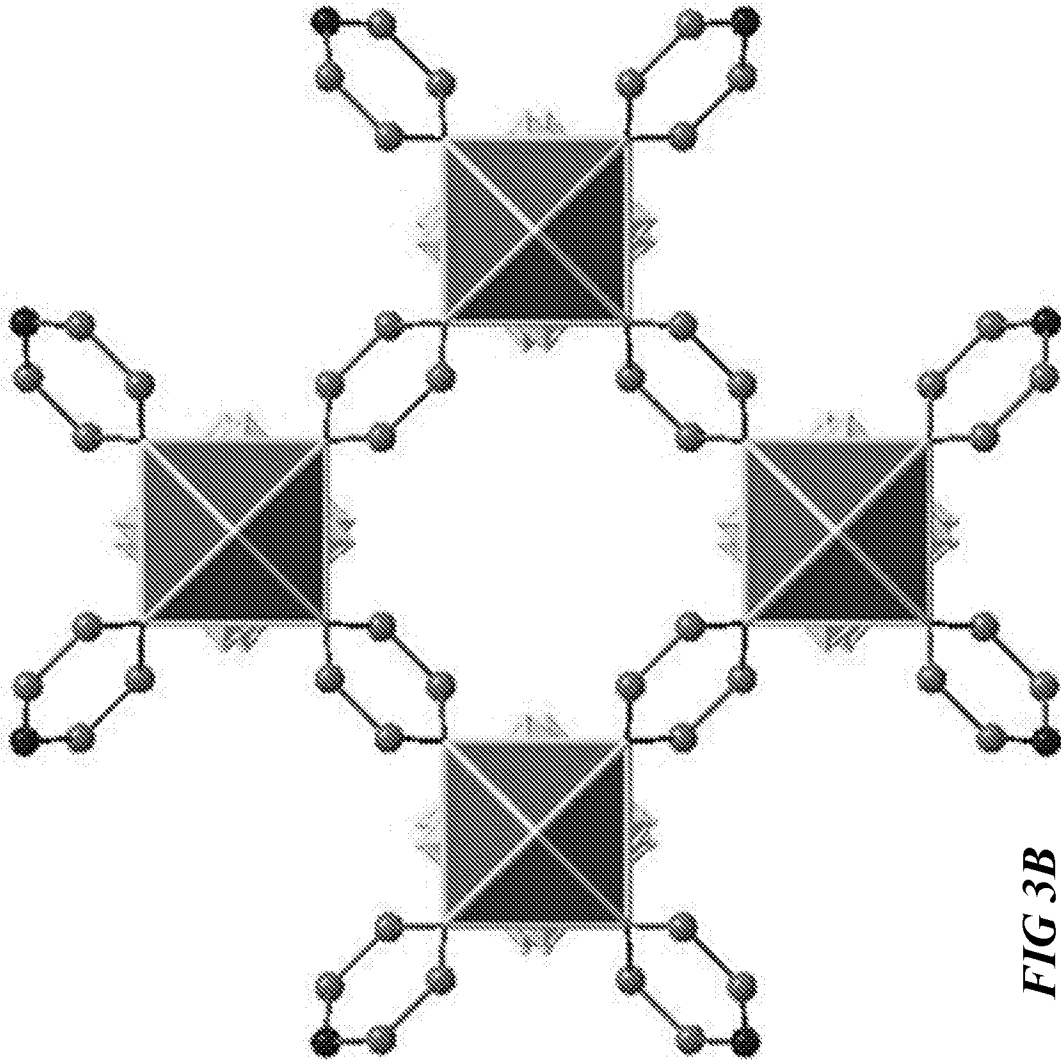


FIG 1B

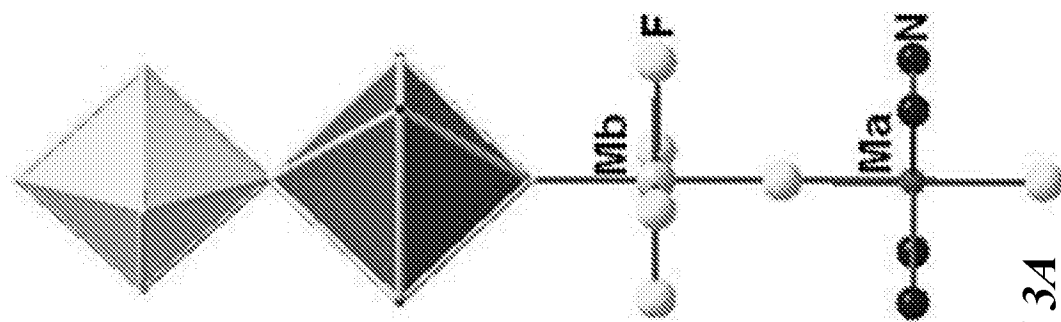




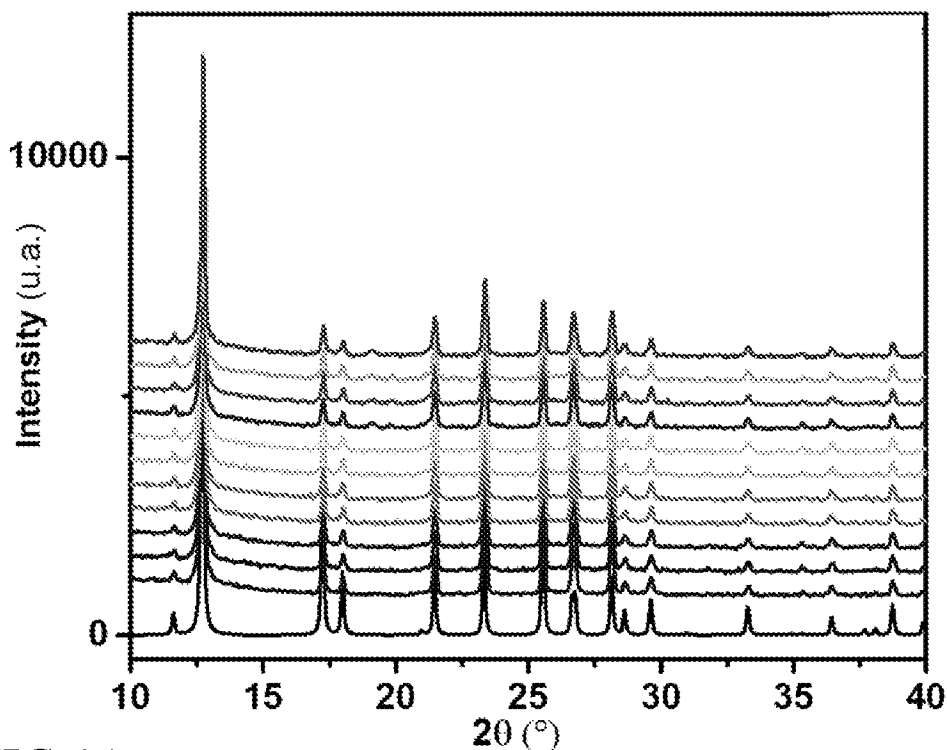
**FIG 2**



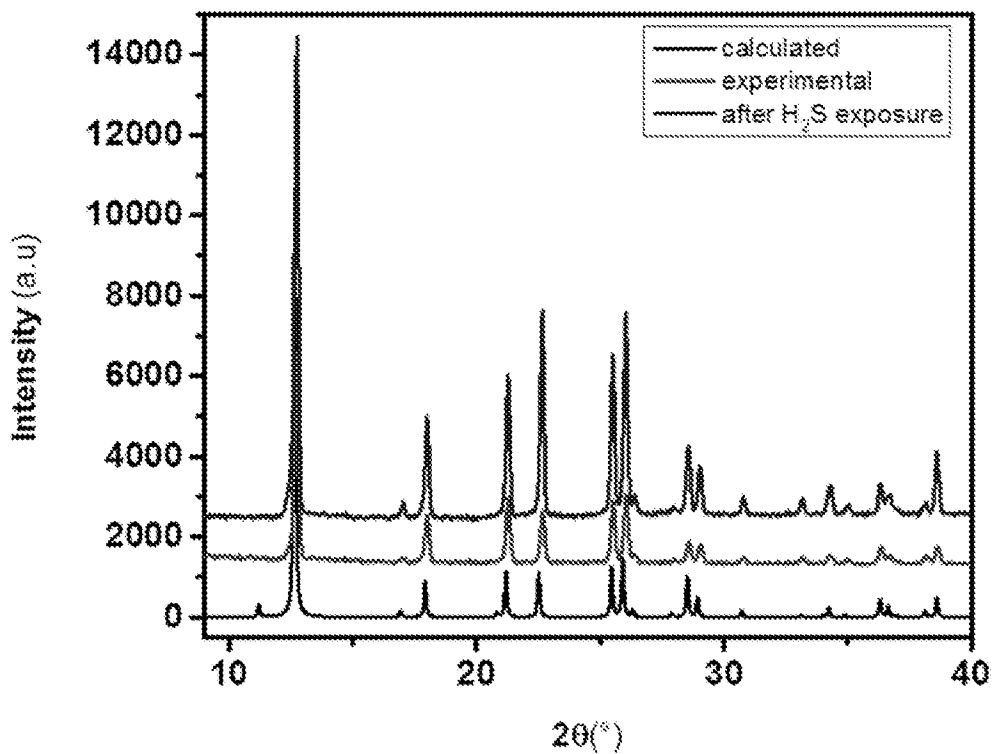
**FIG 3B**



**FIG 3A**



**FIG 4A**



**FIG 4B**

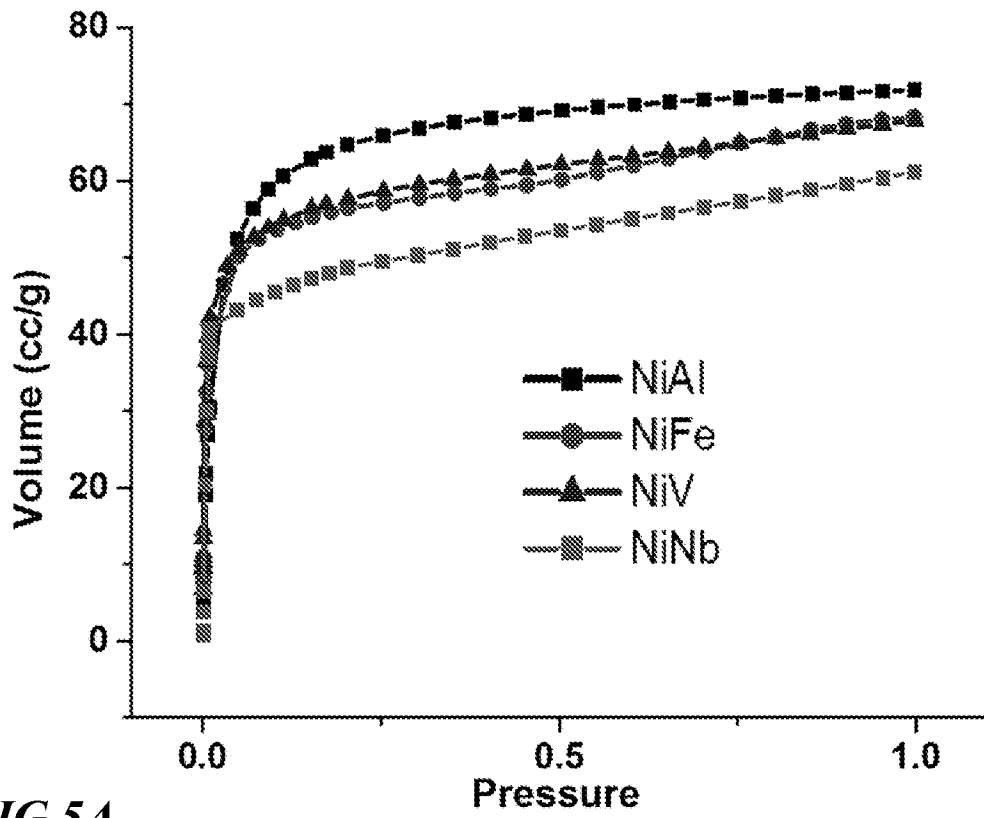


FIG 5A

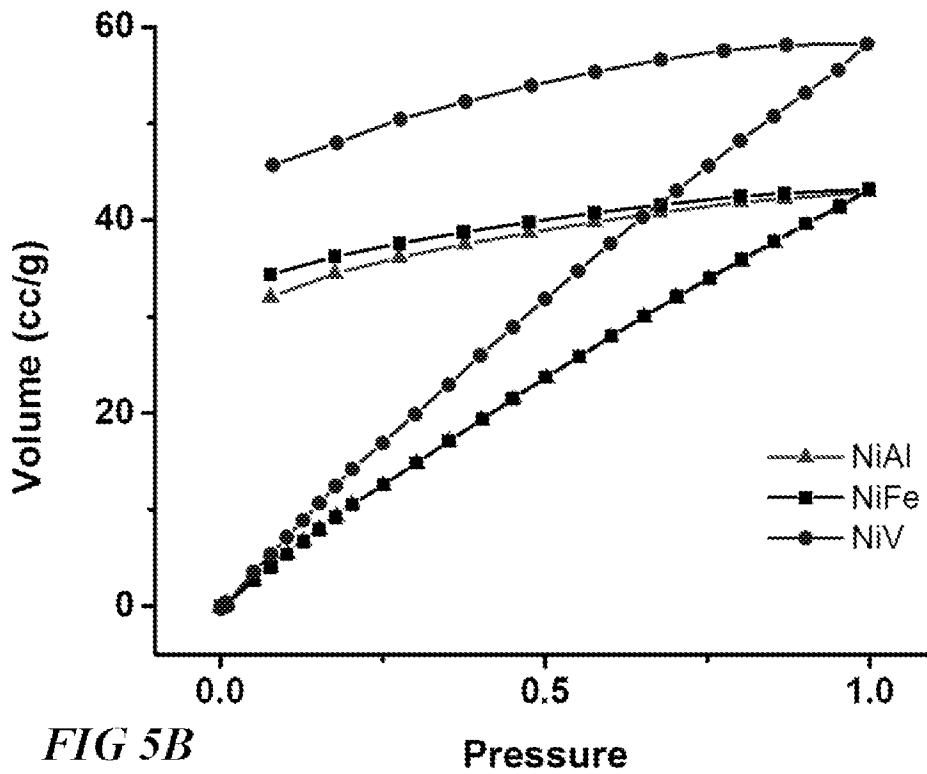
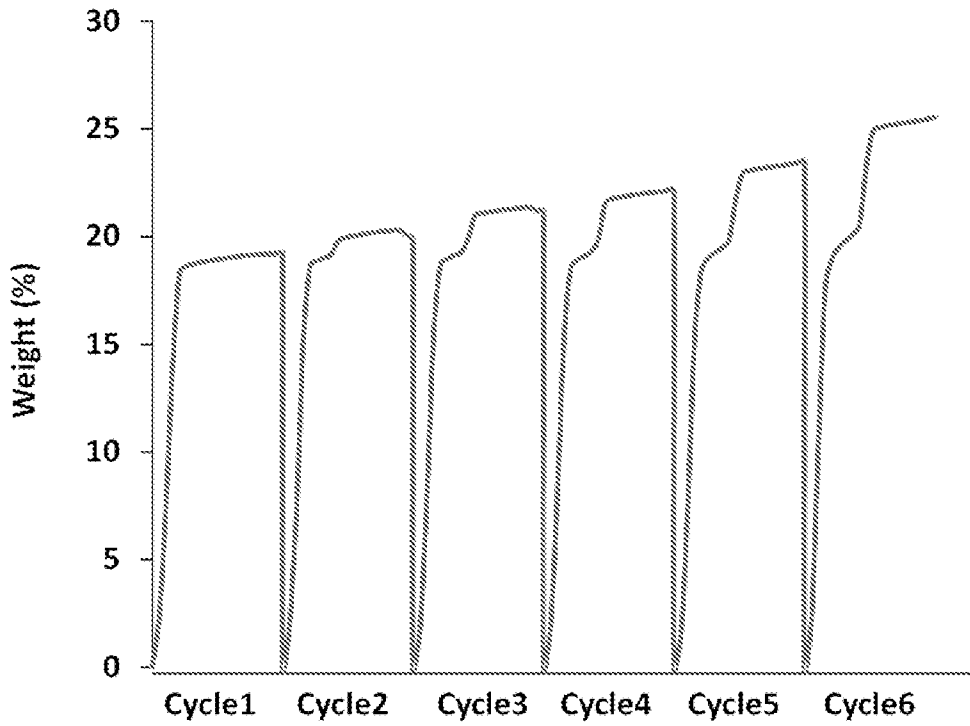
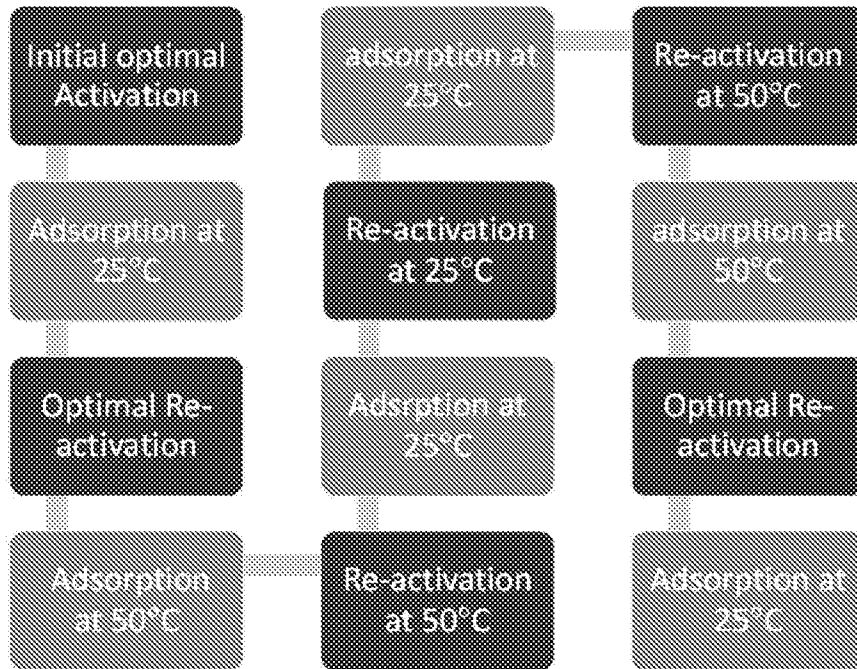


FIG 5B



**FIG 5C**



**FIG 6**

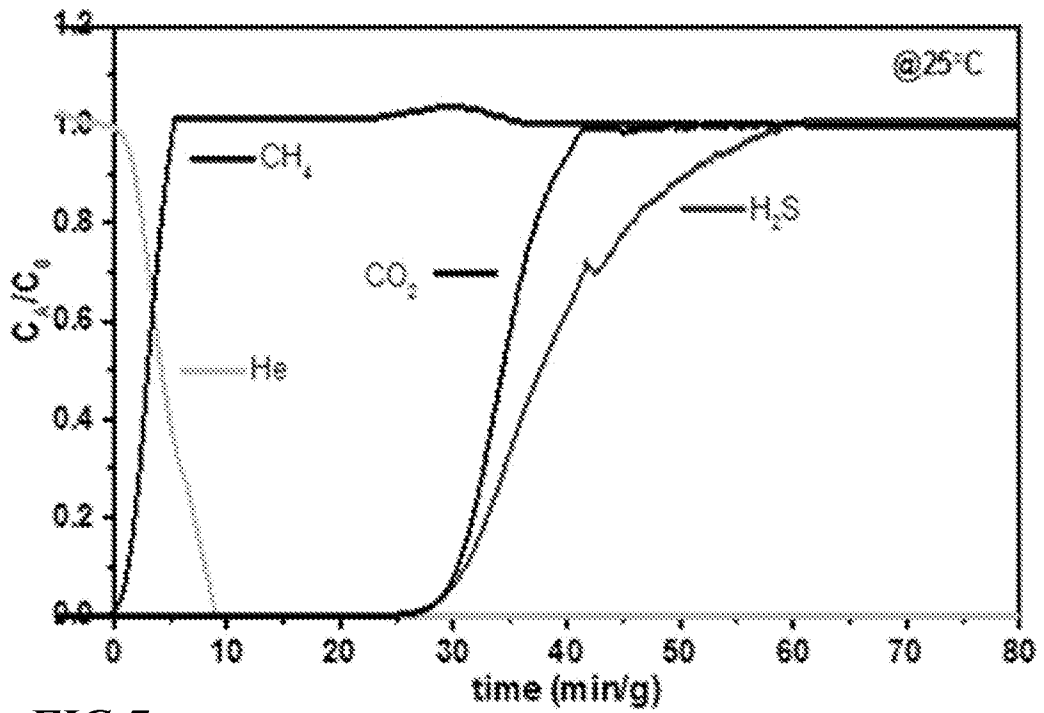


FIG 7

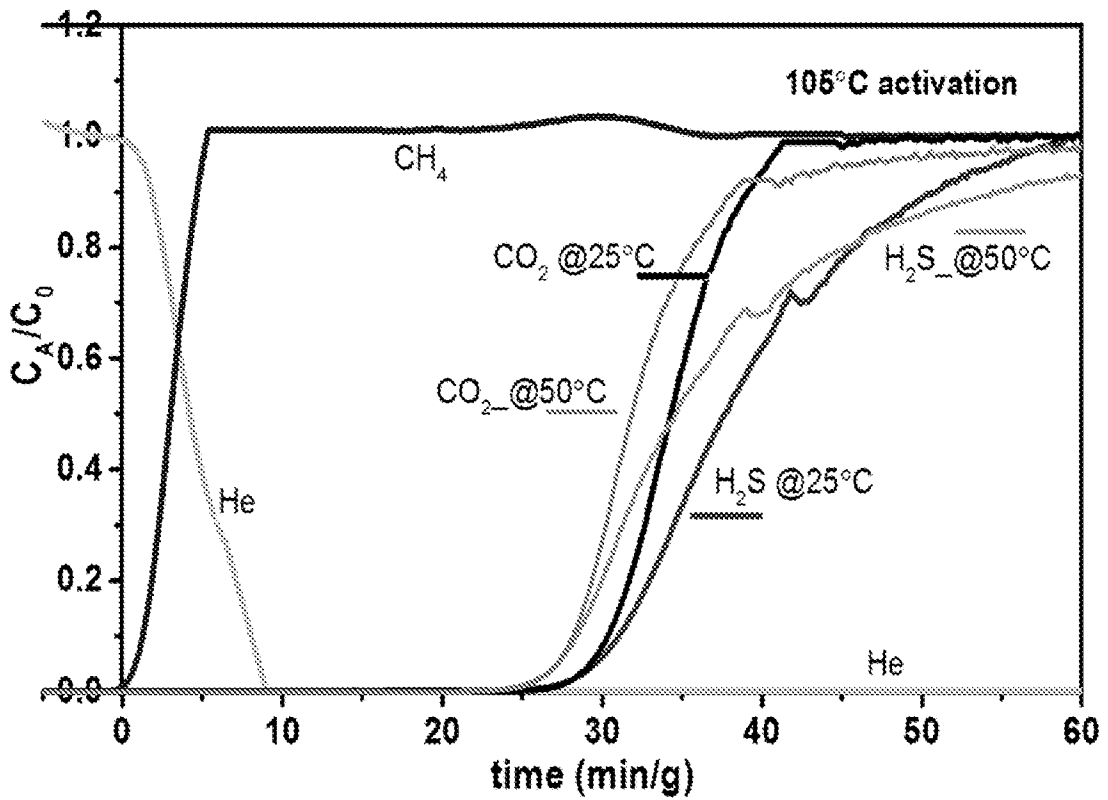


FIG 8

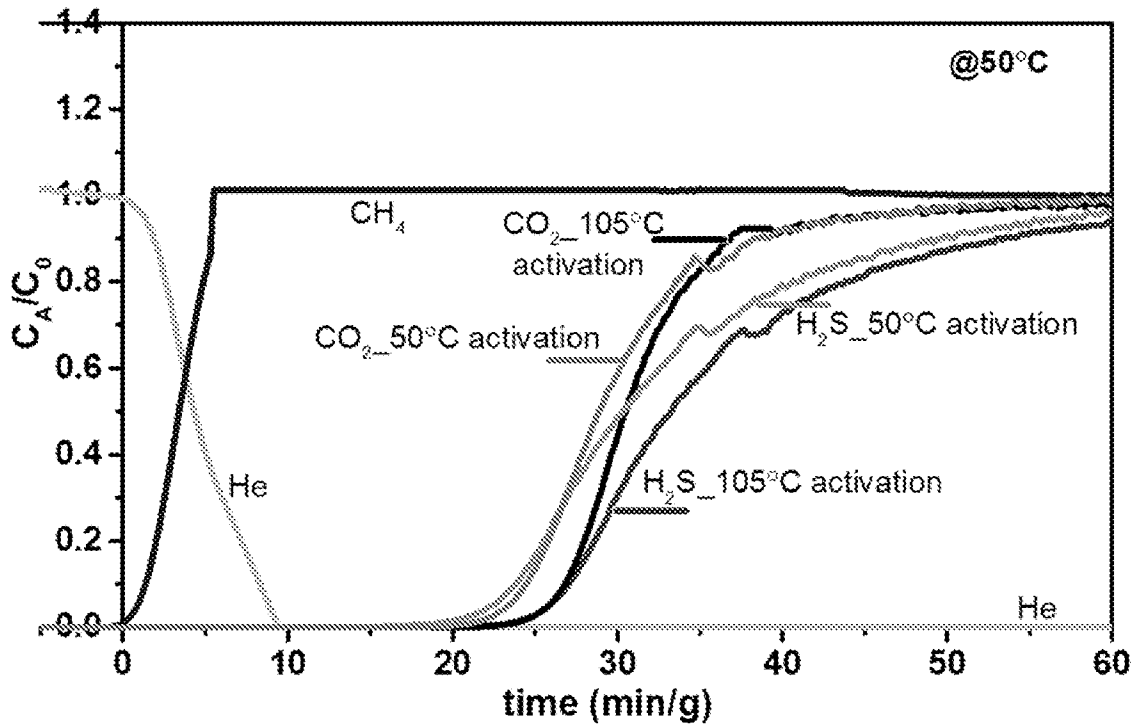


FIG 9

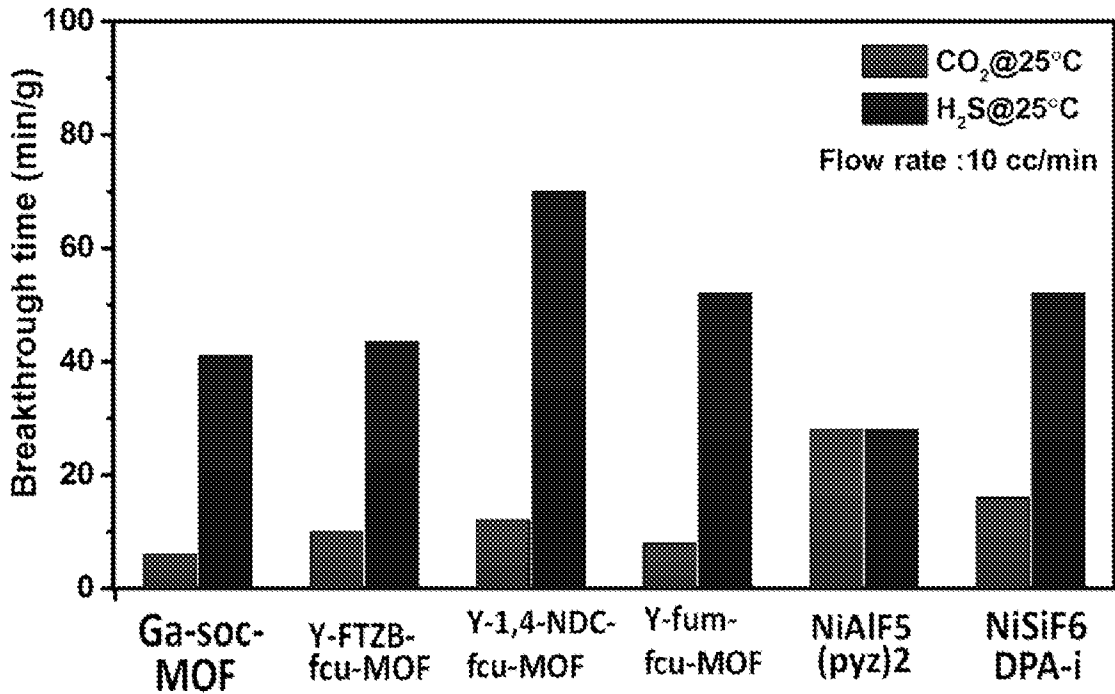


FIG 10

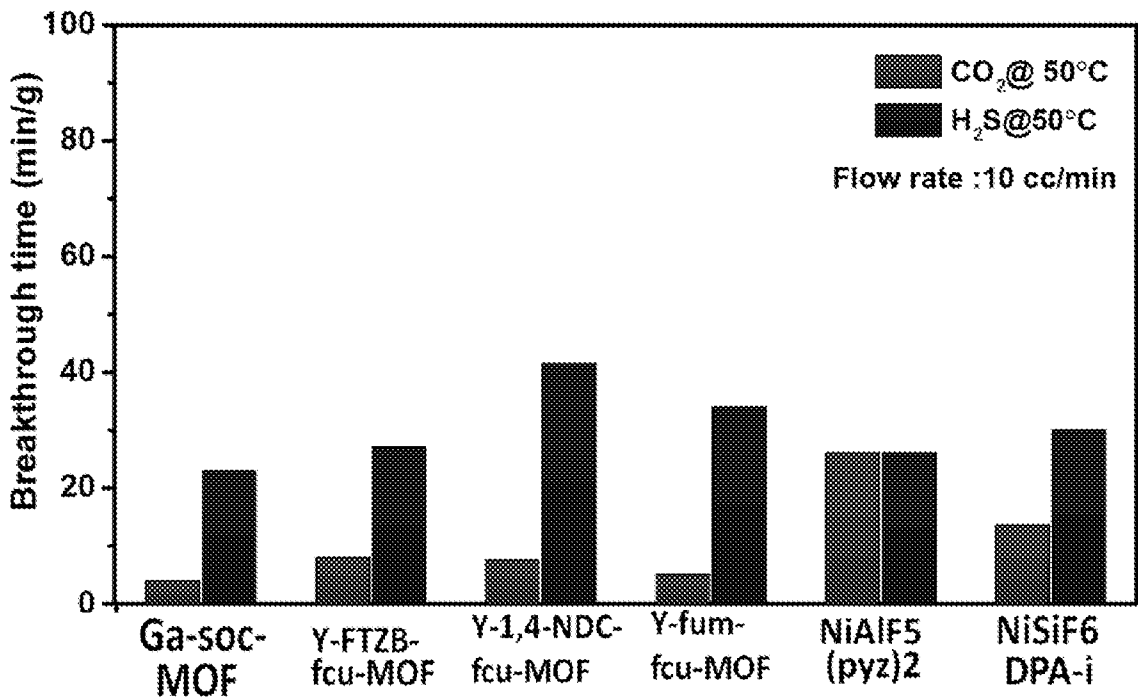


FIG 11

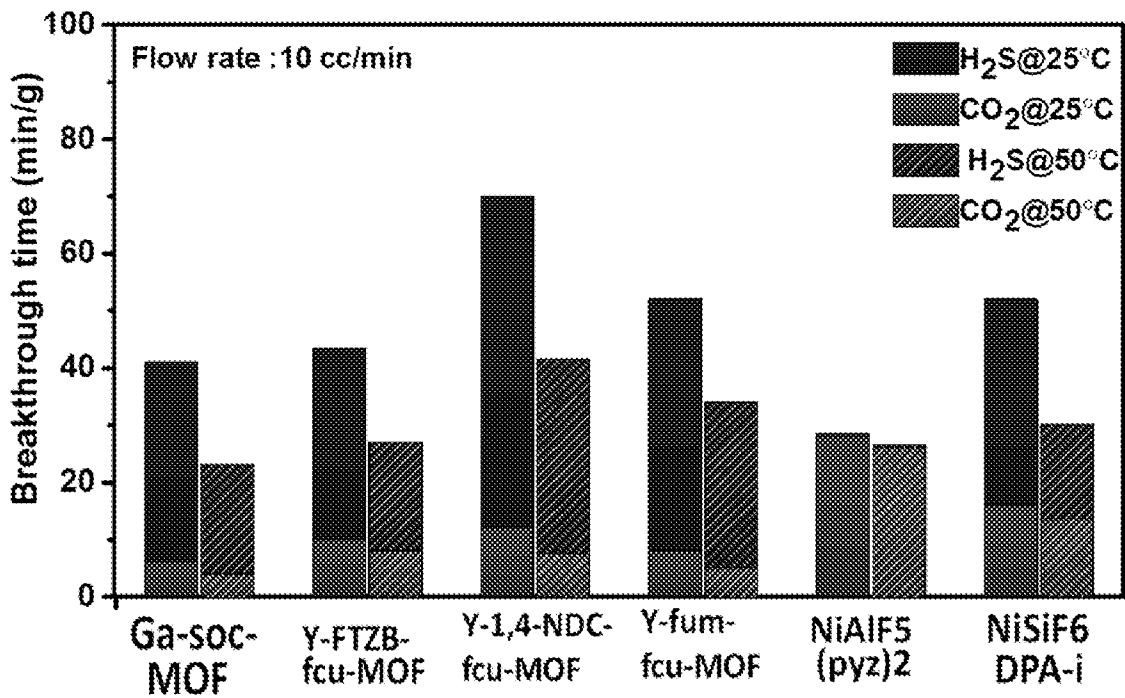


FIG 12



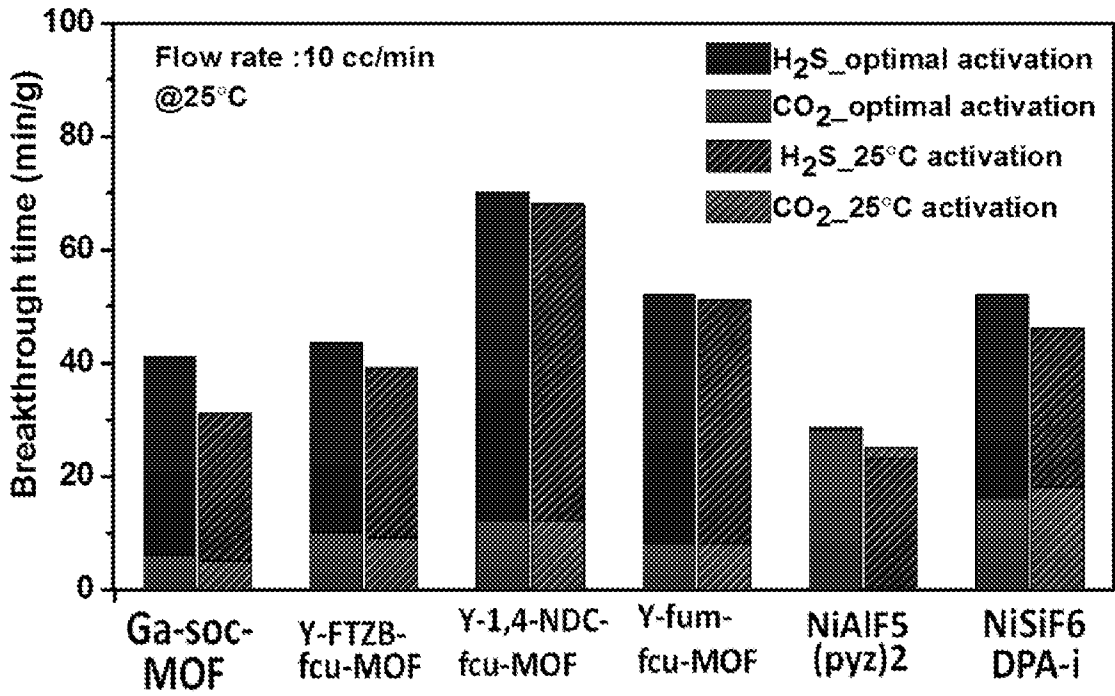


FIG 13

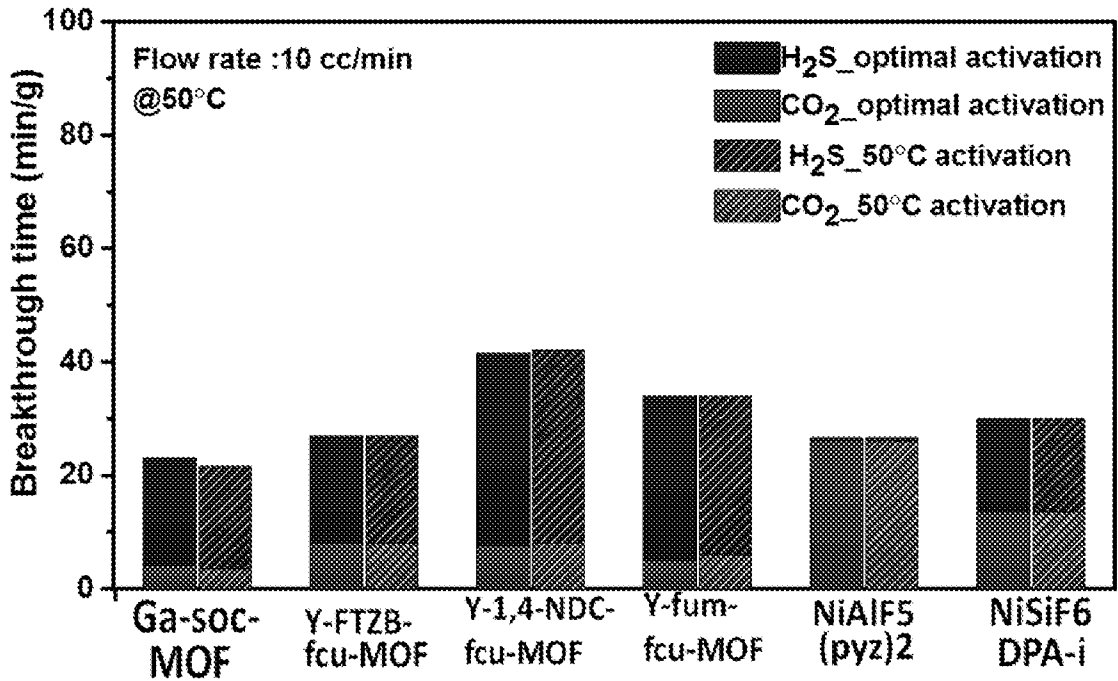
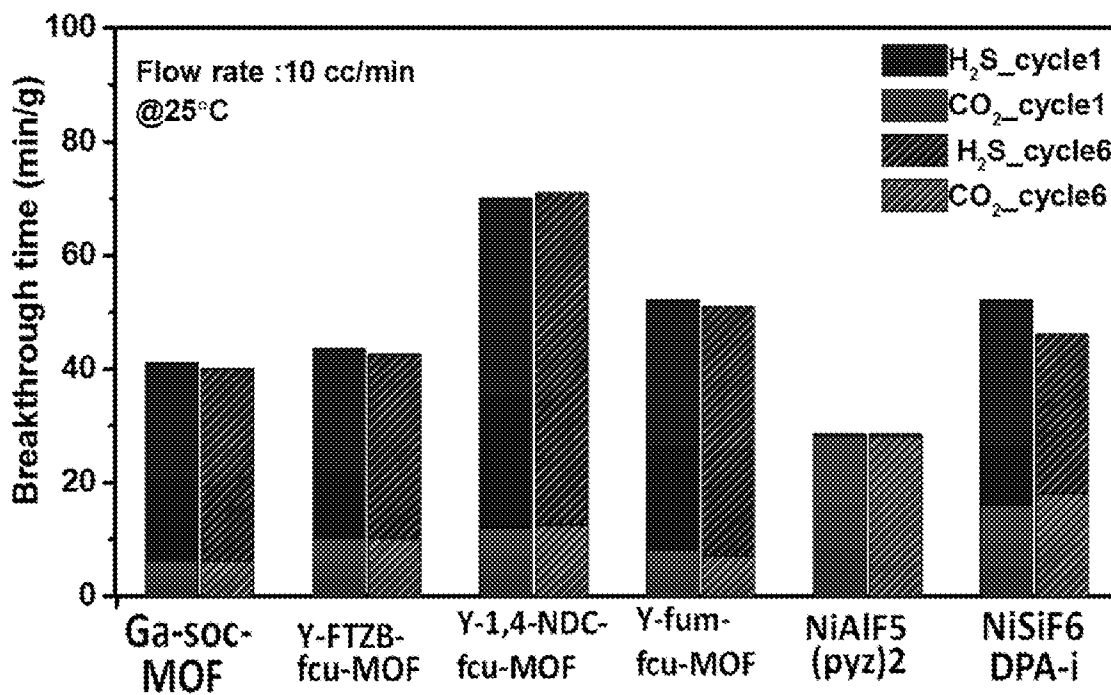


FIG 14



**FIG 15**

INTERNATIONAL SEARCH REPORT

International application No  
PCT/IB2016/051987

A. 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) page 14, line 2 - page 16, line 28 -----	1-20
A	ROMAIN GAUTIER ET AL: "On the Origin of the Differences in Structure Directing Properties of Polar Metal Oxyfluoride [MO <sub>x</sub> F <sub>6-x</sub> ] <sub>2</sub> - (x = 1, 2) Building Units", INORG. CHEM., 22 January 2015 (2015-01-22), pages 1712-1719, XP055282145, DOI: 10.1021/ic5026735 the whole document ----- -/--	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  29 June 2016	Date of mailing of the international search report  07/09/2016
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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
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## INTERNATIONAL SEARCH REPORT

International application No  
PCT/IB2016/051987

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>AMANDINE CADIAU ET AL: "ZnAlF5.[TAZ]: an Al fluorinated MOF of MIL-53(A1) topology with cationic {Zn(1,2,4 triazole)}<sup>2+</sup> 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 -----</p>	1-20

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/IB2016/051987

## 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.: 1-20(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.:  
1-20(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: 1-20(partially)

NiAlF50(pyrazine)2 for capturing one or more of CO<sub>2</sub>, H<sub>2</sub>O and H<sub>2</sub>S from a fluid composition.

---

2. claims: 1-20(partially)

NiNbF50(pyrazine)2 for capturing one or more of CO<sub>2</sub>, H<sub>2</sub>O and H<sub>2</sub>S from a fluid composition.

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## FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 1-20(partially)

1 Claims 120 were only partially searched for the following reasons:

1.1 Present claims 1-3 and 16 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 [0059]ff, Examples 1-2, Tables 1-4: only NiAlF50(pyrazine)2 is explicitly tested in terms of its CO2 and H2S adsorption capabilities.

Furthermore, the stability NiNbF50(pyrazine)2 in the presence of water is also tested ([0056; Fig. 4A, 4B) in the presence of water and H2S respectively.

Additionally, CO2 isotherms are disclosed for Ni(Al/Fe/V/Nb)F5(O/H2O)x(pyrazine)2(solvent)(x) ([0057]; Fig. 5A), H2S isotherms for Ni(Al/Fe/V)F5(pyrazine)2(solvent)z ([0057; Fig. 5B) and H2O isotherms for NiAlF5(O/H2O)x(pyrazine)2(solvent)z) ([0058]; Fig. 5C) are disclosed.

1.2 Claims 1 and 16 essentially disclose any possible fluorinated (and even unfluorinated for n=6) nodes with any metal combinations (Ma+Mb) 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)F5(O/H2O)x(pyrazine)2(solvent)z as listed above.

1.3 In that light, also the generalisations as in claims 4 and 17 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 Any generalization beyond the clearly disclosed 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

## FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

suitable as adsorbent (see p. 3950, left column of: AMANDINE CADIAU ET AL: "ZnAlF<sub>5</sub>.[TAZ]: an Al fluorinated MOF of MIL-53(Al) topology with cationic {Zn(1,2,4 triazole)}<sub>2+</sub> 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)F<sub>3</sub> compounds are known to heavily react with water. In the absence of evidence, that MOFs with MaTi(III)F<sub>5</sub> nodes are stable adsorbents in the presence of water, these compounds are also considered not suitable for the desired method.

1.6 It is neither explicitly nor implicitly disclosed which formula may apply for Ni(Fe/V)F<sub>5</sub>(O/H<sub>2</sub>O)<sub>x</sub>(pyrazine)<sub>2</sub>(solvent)<sub>z</sub> and which characteristics may arise therefrom. It is considered to make a big difference, whether Fe(II) or Fe(III) and V(III) or V(V) may be present, and whether O and/or H<sub>2</sub>O are present in the respective framework. It is not at all clear, which of these possible frameworks was tested and shown in the illustrated results.

Consequently, the generalization (as in claim 4) Ma=Ni and Mb= Al<sup>3+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, V<sup>3+</sup>, V<sup>5+</sup> or Nb<sup>5+</sup> 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 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, 16, 17, as well as any claims depending on these claims (PCT Guidelines 9.19, 9.23 and 9.24).

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

NiAlF<sub>5</sub>(pyrazine)<sub>2</sub> and  
NiNbF<sub>5</sub>(pyrazine)<sub>2</sub>

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/IB2016/051987

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
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