



- (51) International Patent Classification:
B01J 20/22 (2006.01) *B01D 53/04* (2006.01)
B01J 20/28 (2006.01)
- (21) International Application Number: PCT/US2015/046756
- (22) International Filing Date: 25 August 2015 (25.08.2015)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 62/041,516 25 August 2014 (25.08.2014) 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).
- Published:
— with international search report (Art. 21(3))

(54) Title: METAL ORGANIC FRAMEWORKS FOR REMOVAL OF COMPOUNDS FROM A FLUID

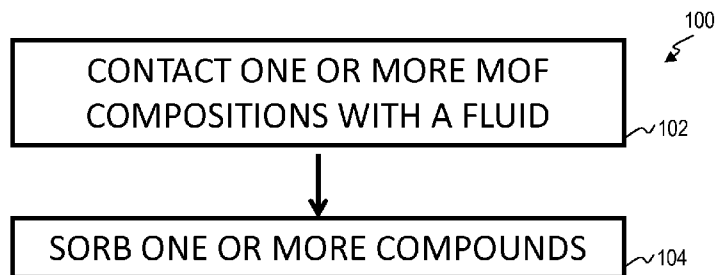


FIG 1

(57) Abstract: Embodiments provide a method of compound removal from a fluid. The method includes contacting one or more metal organic framework (MOF) compositions with a fluid and sorbing one or more compounds, such as CO₂, H₂S and condensable hydrocarbons. One or more of CO₂, H₂S and condensable hydrocarbons can be sorbed simultaneously or in series. The metal organic framework can be an M-soc-MOF.



METAL ORGANIC FRAMEWORKS FOR REMOVAL OF COMPOUNDS FROM A FLUID

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims benefit of US Provisional Application No. 62/041,516, filed on 25 August 2014 and which application is incorporated herein by reference. A claim of priority is made.

BACKGROUND

[0002] As society continues to deplete fossil fuel reserves, alternate energy solutions are constantly sought after to supplant fossil fuel sources, such as biogas and natural gas with cleaner and more abundant energy sources. Although natural gas is a fossil fuel, it is acknowledged as an excellent alternative before a transition to cleaner energy solutions. However, natural gas often contains significant amounts of CO₂ and H₂S that have to be removed or reduced to less than 1% for CO₂ and 4 ppm for H₂S to meet the specifications for pipeline transportation. Particularly, wells in Saudi Arabia and Russia can contain up to 20 % H₂S.

[0003] Biogas generally consists of methane (approx. 65% in volume), carbon dioxide (approx. 35% in volume) and traces of hydrogen sulfide (<2%) and ammonia (<1%). The high content of carbon dioxide and the presence of hydrogen sulfide and ammonia make it unsuitable to be used in place of natural gas in gas distribution networks. Absence of hydrogen sulfide is a must to avoid corrosion in compressors, gas storage tanks, pipes and engines.

[0004] Current technologies for natural gas upgrading (e.g., removing one or more of H₂S, CO₂, and condensable hydrocarbons) are often multi-stage processes, thus costly. In order to reduce costs and efficiency, industry desires selective adsorbents for the removal of CO₂, H₂S and condensable hydrocarbons which exhibit high structure stability over multiple sorption cycles.

SUMMARY

[0005] In general, embodiments of the present invention provide a method of removing compounds from a fluid. The method includes contacting one or more metal organic framework (MOF) compositions with one or more fluids, such as natural gas and biogas, and sorbing one or more compounds, such as of CO₂, H₂S and condensable hydrocarbons. In some embodiments, the one or more of CO₂, H₂S and/or condensable hydrocarbons can be sorbed simultaneously or in series.

[0006] In some embodiments, the MOF is an M-soc-MOF, wherein M is a trivalent metal. The trivalent metal can comprise gallium, indium, iron, scandium, or aluminum, in some embodiments. The M-soc-MOF can comprise a plurality of 6-connected trimer molecular building blocks (TMBBs) networked by tetradentate organic ligands, wherein each of the TMBBs can comprise three metal carboxylate octahedra.

[0007] In some embodiments, the tetradentate organic ligands are rectangular planar. In some embodiments, the tetradentate organic ligands comprise tetracarboxylate ligands. In some embodiments, the tetradentate organic ligands comprise amidetetracarboxylate or 3,3',5,5'-azobenzene-tetracarboxylate.

[0008] 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

[0009] **Figure 1** illustrates a block flow diagram of a method of removing one or more compounds from a fluid, according to an embodiment.

[0010] **Figure 2A** illustrates a ball-and-stick structure and a polyhedral representation of a trimer molecular building block, according to one or more embodiments.

[0011] **Figure 2B** illustrates a ball-and-stick structure and a polyhedral representation of a suitable organic ligand, according to one or more embodiments.

[0012] **Figure 2C** illustrates a ball-and-stick structure and a polyhedral representation of a M-soc-MOF, according to one or more embodiments.

[0013] **Figure 3** illustrates the results of a N₂ adsorption/desorption study for a M-soc-MOF, according to one or more embodiments.

[0014] **Figure 4A** illustrates a H₂S/CO₂/N₂/CH₄:1/30/10/59 mixture adsorption data for a Ga-soc-MOF, according to one or more embodiments.

[0015] **Figure 4B** illustrates CO₂, H₂S, and CH₄ adsorption isotherms at 25 °C for the Ga-soc-MOF, according to one or more embodiments.

DETAILED DESCRIPTION

[0016] Embodiments of the present invention provide the use of stable MOFs and MOF compositions, particularly M-soc-MOFs, for the subsequent (i.e., in series) or simultaneous removal of CO₂, H₂S, and condensable hydrocarbons. Embodiments as described have the potential to reduce the number of processes in the natural gas or biogas overall treatment scheme. It is expected that the regeneration of M-soc-MOF compositions will be cost effective in comparison to conventional amine scrubbing. M-soc-MOF compositions also exhibit high affinity for condensable hydrocarbons (C₂H₆, C₃H₈,...) at the inverse of zeolites and activated carbons.

[0017] Metal organic frameworks (MOFs) are a versatile and promising class of crystalline solid state materials which allow porosity and functionality to be tailored towards various applications. For example, MOF materials exhibit exceptionally high specific surface area, in addition to tunable pore size and functionality (e.g., CO₂ and H₂S selectivity), which make them suitable for many applications including gas storage, gas separation, catalysis, drug delivery, light-emitting devices, and sensing.

[0018] Generally, MOFs comprise a network of nodes and ligands, wherein a node has a connectivity capability at two or more functional sites, and a ligand has a connectivity capability at two functional sites each of which connect to a node. Nodes are typically metal ions or metal containing clusters, and, in some instances, ligands with node connectivity capability at two or more functional sites can also be characterized as nodes. In some instances, ligands can include two functional sites capable of each connecting to a node, and optionally one or more additional functional sites which do not connect to nodes within a particular framework. In some embodiments, ligands can be poly-functional, or polytopic, and comprise two or more functional sites capable of each connecting to a node. In some embodiments, polytopic ligands can be heteropolytopic, wherein at least two of the two or more functional sites are different.

[0019] A MOF can comprise a metal-based node and an organic ligand which extrapolate to form a coordination network. Such coordination networks have advantageous crystalline and porous characteristics affecting structural integrity and interaction with foreign species (e.g., gases). The particular combination of nodes and ligands within a framework will dictate the framework topology and functionality.

Through ligand modification or functionalization, the environment in the internal pores can be modified to suit specific applications.

[0020] MOF can be represented by the formula $[(\text{node})_a(\text{ligand})_b(\text{solvent})_c]_n$, 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. Accordingly, the value of c can vary down to zero, without changing the definitional framework of the MOF. Therefore, in many instances, MOFs can be defined as $[(\text{node})_a(\text{ligand})_b]_n$, without reference to a solvent or guest molecule component.

[0021] Figure 1 illustrates a block flow diagram of a method 100 of removing one or more compounds from one a fluid, according to an embodiment. Method 100 includes contacting 102 one or more metal organic framework (MOF) compositions with a fluid and sorbing 104 one or more compounds from the fluid with the one or more MOF compositions. In particular, method 100 includes contacting 102 one or more M-soc-MOF compositions with a fluid and sorbing 104 one or more compounds from the fluid with the one or more M-soc-MOF compositions. Contacting 102 can include mixing, bringing in close proximity, chemically contacting, physically contacting or combinations thereof. Fluids can include general liquids and gases. In some embodiments, fluids include industrial process fluids. Examples of specific fluids include one or more of natural gas and biogas. Fluids can further comprise water, including water in a liquid form, a gaseous form, or combinations thereof.

[0022] In one embodiment, sorbing 104 comprises absorbing. In one embodiment, sorbing 104 comprises adsorbing. In one embodiment, sorbing 104 comprises a combination of adsorbing and absorbing. Sorbing 104 can include selective sorption (i.e., sorption of a single compound), or simultaneous sorption (e.g., sorption of a plurality of compounds). The M-soc-MOF compositions can sorb about 1% to about 99.9%, about 1% to about 90%, about 1% to about 50% or about 1% to about 30% of one or more compounds in a fluid. Sorbing 104 can occur at ambient temperature, at an elevated temperature, at a cooled temperature, or over a temperature range. In one embodiment, a temperature can be selectively changed to manipulate sorption and/or desorption of different compounds. Sorbing 104 can occur at ambient pressure, at an elevated pressure, at a cooled pressure, or over a pressure range. In one embodiment, pressure can be selectively changed to manipulate sorption and/or desorption of different compounds. In addition to or in the alternative to, a concentration of one or more M-soc-MOF

compositions can be varied to affect a rate and/or magnitude of sorbing 104. One or more of temperature, pressure and M-soc-MOF concentration can be regulated to produce a simultaneous sorption of compounds, or a subsequent, step-wise sorption (i.e., in series) of compounds from a fluid. In series sorption generally includes sorbing a quantity of a first compound via a MOF, and subsequently sorbing a quantity of a second compound via the same MOF while at least a portion of the quantity of the first compound remains sorbed. Simultaneous sorption generally includes contacting a plurality of compounds with an MOF, and sorbing a quantity of each of the two compounds with the MOF.

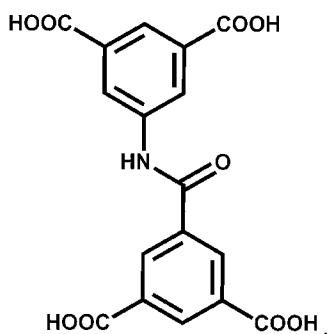
[0023] One compound which can be sorbed by an M-soc-MOF from a fluid is CO₂. CO₂ can be sorbed from a fluid comprising H₂O and/or CH₄ by an M-soc-MOF with selectivity over one or more of H₂O and CH₄. One compound which can be sorbed by an M-soc-MOF from a fluid is H₂S. H₂S can be sorbed from a fluid comprising H₂O and/or CH₄ by an M-soc-MOF with selectivity over one or more of H₂O and CH₄. CO₂ and H₂S can be simultaneously sorbed from a fluid comprising H₂O and/or CH₄ by an M-soc-MOF with selectivity over one or more of H₂O and CH₄. CO₂ and H₂S can be sorbed from a fluid comprising H₂O and/or CH₄ in series by an M-soc-MOF with selectivity over one or more of H₂O and CH₄. In a specific embodiment, CO₂ and H₂S can be simultaneously sorbed from natural gas and/or biogas by an M-soc-MOF with selectivity over other one or more of H₂O and CH₄. In a specific embodiment, CO₂ and H₂S can be sorbed from a fluid comprising H₂O and/or CH₄ in series by an M-soc-MOF with selectivity over other one or more of H₂O and CH₄. Generally, the above sorption abilities and stability in the presence of water of suitable M-soc-MOFs as disclosed herein is an advantageous aspect unavailable from other M-soc-MOFs and industrial materials such as zeolites and activated carbon.

[0024] Condensable hydrocarbons can be sorbed by an M-soc-MOF from a fluid. Examples of condensable hydrocarbons include ethane, propane, butane, pentane, and hexane. In some embodiments, examples of condensable hydrocarbons include straight chained alkanes with 6 carbons or less. Condensable hydrocarbons and one or more of CO₂ and H₂S can be simultaneously sorbed from a fluid, with selectivity over other one or more of H₂O and CH₄. Condensable hydrocarbons and one or more of CO₂ and H₂S can be sorbed in series from a fluid, with selectivity over other one or more of H₂O and CH₄. The ability to sorb condensable hydrocarbons is one advantageous aspect of suitable M-soc-MOFs as disclosed herein over other materials such as zeolites and activated carbon.

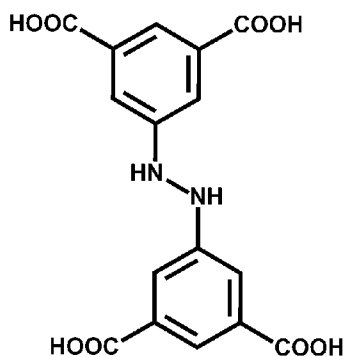
[0025] M-soc-MOFs suitable for method 100 include M-soc-MOFs 200 comprising one or more trimer molecular building blocks (TMBB) 201, as shown in Figure 2A, and one or more organic ligands 202, as shown in Figure 2B. Figure 2A illustrates a ball-and-stick structure 201' and a polyhedral representation 201'' of a TMBB 201. Figure 2B illustrates a ball-and-stick structure 202' and a polyhedral representation 202'' of one example of a suitable organic ligand 202. A TMBB 201 comprises three metal carboxylate octahedra, each octahedron generally described as $[\text{MO}_5(\text{H}_2\text{O})]$, wherein M = a metal. A TMBB 201 can be generally described as $\text{M}_3\text{O}_x(\text{CO}_2)_y$. One example of a TMBB 201 can be described as $[\text{Ga}_3\text{O}(\text{CO}_2)_6(\text{H}_2\text{O})_3]$. One example of a TMBB 201 can be described as $[\text{In}_3\text{O}(\text{CO}_2)_6]$. One example of a TMBB 201 can be described as $[\text{Al}_3\text{O}(\text{CO}_2)_6]$. The three metal octahedra are metal-centered, and all share one central μ_3 -oxo anion. In each octahedron, the apical position can be occupied by a terminal water molecule. The metal-carboxylate clusters generate a rigid node with fixed geometry involving multiple metal-oxygen coordination bonds which induce the stability of the node and subsequently enhance the thermal stability and overall rigidity of the framework.

[0026] Suitable metals (M) include trivalent metals (i.e., metals capable of exhibiting a +3 oxidation state). Trivalent metals include aluminum, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, gallium, germanium, arsenic, yttrium, zirconium, niobium, molybdenum, palladium, silver, indium, tin, antimony, lanthanum, cerium, praseodymium, samarium, europium, gadolinium, terbium, erbium, thulium, ytterbium, lutetium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold, lead, and bismuth. Particularly suitable trivalent metals include gallium, indium, iron, scandium, and aluminum. The three trivalent metals yield an overall cationic framework (+1 per formula unit) that is balanced by $[\text{NO}_3]^{-1}$ ions. The disordered $[\text{NO}_3]^{-1}$ ions occupy statistically two positions on the threefold axis with equal probability. A broad range of suitable trivalent metals advantageously allows for M-soc-MOFs to be customized for particular purposes. For example, lighter trivalent metals can provide an M-soc-MOF with increased sorption uptake per unit volume.

[0027] Each TMBB unit is linked by six separate organic ligands 202, as shown in Figure 2A, to produce a novel 3D structure 200 having an soc-topology, as shown in Figure 2C. Suitable ligands are tetradentate. Suitable tetradentate ligands include rectangular planar ligands. A generally suitable ligand is a tetracarboxylate ligand. One particular suitable ligand is amidetetracarboxylate:



One particular suitable ligand is 3,3',5,5'-azobenzene-2,2'-dicarboxylate:



[0028] Figure 2C illustrates a ball-and-stick structure 200' and a polyhedral representation 200'' of a suitable M-soc-MOF 200 comprised of a plurality of 6-connected TMBBs 201 networked by organic tetradentate planar ligands 202. In Figure 3C, hydrogen atoms, water molecules, and $[\text{NO}_3]^-$ ions are omitted for clarity. One example M-soc-MOF 200 can be described as $[\text{In}_3\text{O}(\text{C}_{16}\text{N}_2\text{O}_8\text{H}_6)_{1.5}(\text{H}_2\text{O})_3](\text{H}_2\text{O})_3(\text{NO}_3)$. All such M-soc-MOFs are characterized by an soc-topology, and can generally be denoted as M-soc-MOFs. The soc-topology of M-soc-MOF 200 provides unique structure features, including the presence of isolated nanometer-scale carcerand-like capsules, which anchor nitrate ions, and which are strictly accessible through the two main channels by very restricted windows. Such characteristics provide high, localized charge density advantageous for chemical and physical sorption of compounds.

[0029] Other interesting structural features of the crystalline structure are its two types of infinite channels. The first type is hydrophilic, due to the water molecules coordinated to the indium centers which are pointed inside these channels. Guest water molecules occupy the remaining free volume in these channels and form hydrogen bonds with coordinated water molecules. The second type of channels can be guest free, and have an approximately 1 nm diameter.

[0030] M-soc-MOFs can have a BET surface area of at least about $800 \text{ m}^2/\text{g}$, at least about $900 \text{ m}^2/\text{g}$, at least about $1,000 \text{ m}^2/\text{g}$, at least about $1,200 \text{ m}^2/\text{g}$, at least about $1,400$

m²/g, or at least about 1,600 m²/g. In a specific embodiment, an M-soc-MOF has a BET surface area of at least about 800 m²/g. In a specific embodiment, an M-soc-MOF has a BET surface area of about 1,000 m²/g. In a specific embodiment, an M-soc-MOF has a BET surface area of about 1,000 m²/g to about 1,600 m²/g.

[0031] M-soc-MOFs can have an average pore volume of at least about 0.2 cm³/g, at least about 0.25 cm³/g, at least about 0.3 cm³/g, at least about 0.45 cm³/g, at least about 0.6 cm³/g, or at least about 0.65 cm³/g. In a specific embodiment, an M-soc-MOF has an average pore volume of at least about 0.2 cm³/g. In a specific embodiment, an M-soc-MOF has an average pore volume of about 0.3 cm³/g. In a specific embodiment, an M-soc-MOF has an average pore volume of about 0.3 cm³/g to about 0.65 cm³/g.

EXAMPLE 1: Synthesis of Indium-soc-MOF

[0032] In this example, an In-soc-MOF formulated as $[\text{In}_3\text{O}(\text{C}_{16}\text{N}_2\text{O}_8\text{H}_6)_{1.5}(\text{H}_2\text{O})_3](\text{H}_2\text{O})_3(\text{NO}_3)$ was synthesized by reacting 3,3',5,5'-azobenzenetetracarboxylic acid and $\text{In}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ in a N,N-dimethylformamide (DMF)/CH₃CN solution in the presence of piperazine. The resulting In-soc-MOF consisted of orange polyhedral crystals. Its structure included indium trimer building blocks, each trimer containing three $\{\text{InO}_5(\text{H}_2\text{O})\}$ octahedra sharing one central m³-oxo anions, and networked by six separate 3,3',5,5'-azobenzenetetracarboxylate ligands. The total solvent-accessible volume for the In-soc-MOF was determined to be 57.2% by summing voxels more than 1.2 Å away from the framework using PLATON software. Figure 3 illustrates the results of a N₂ adsorption/desorption study, which revealed a reversible type I isotherm with no hysteresis. Such results are characteristic of a microporous material with homogeneous pores. The estimated Langmuir surface area and pore volume for In-soc-MOF are 1417 m² g⁻¹ and 0.50 cm³ g⁻¹, respectively.

[0033] Other interesting structural features of the crystalline In-soc-MOF structure are the two types of infinite channels. The first type is hydrophilic, because the water molecules coordinated to the indium centers are pointed inside these channels. Guest water molecules occupy the remaining free volume in these channels and form hydrogen bonds with coordinated water molecules. The second type of channels have a diameter of approximately 1 nm diameter, and are guest-free as-synthesized.

[0034] The synthesis methods of this study are generally applicable to similar M-soc-MOFs, including those with lighter trivalent metals.

EXAMPLE 2 : CO₂ and H₂ Sorption by Gallium-soc-MOF

[0035] This example utilizes use of metal organic frameworks as sorbents for use in simultaneous or subsequent removal of CO₂ and H₂S. The Ga-soc-MOF in question is constructed based on the assembly of Gallium–carboxylate trimer molecular building block (TMBB) and 3,3',5,5'-azobenzenetetracarboxylate. The oxygen-centered gallium–carboxylate TMBB, [Ga₃O(CO₂)₆(H₂O)₃] comprises a 6-connected node having trigonal-prismatic geometry networked by 3,3',5,5'-azobenzenetetracarboxylate tetradentate ligands.

[0036] Figure 4A illustrates H₂S/CO₂/N₂/CH₄:1/30/10/59 mixture adsorption experiments performed in a column breakthrough set-up. The Ga-soc-MOF adsorbed H₂S and CO₂ from CH₄ with high selectivity. The 1% (of 15 ml/min) H₂S was retained for 40 min, while 30% CO₂ (of 15 ml/min) was retained for about 15 minutes, indicative of the potential of selective removal of H₂S and CO₂ from CH₄ containing gas streams. Figure 4B illustrates CO₂, H₂S, and CH₄ adsorption isotherms at 25 °C for the Ga-soc-MOF, indicating selectivity for CO₂ and H₂S over CH₄.

WHAT IS CLAIMED IS:

1. A method of removing one or more compounds from a fluid, the method comprising:
 contacting one or more metal organic framework (MOF) compositions with a fluid; and
 sorbing one or more compounds from a fluid,
wherein the one or more compounds comprise CO₂, H₂S and condensable hydrocarbons, and the MOF is an M-soc-MOF.
2. The method of claim 1, wherein the metal comprises gallium, indium, iron, scandium, or aluminum.
3. The method of claim 1, wherein the M-soc-MOF comprises tetradentate organic ligands.
4. The method of claim 3, wherein the tetradentate organic ligands comprise tetracarboxylate ligands.
5. The method of claim 1, wherein the M-soc-MOF comprises rectangular planar organic ligands.
6. The method of claim 1, wherein the M-soc-MOF comprises amidetetracarboxylate or 3,3',5,5'-azobenzene-tetracarboxylate organic ligands.
7. The method of claim 1, wherein the M-soc-MOF comprises two distinct types of channels.
8. The method of claim 7, wherein one of the two types of channels is hydrophilic.
9. The method of claim 1, wherein the M-soc-MOF comprises a plurality of 6-connected trimer molecular building blocks networked by organic ligands.
10. The method of claim 9, wherein each of the trimer molecular building blocks comprises three metal carboxylate octahedra.

11. The method of claim 10, wherein each of the metal carboxylate octahedral of a trimer molecular building block are metal-centered and share one central μ_3 -oxo anion.
12. The method of claim 10, wherein the apical position of each metal carboxylate octahedral is occupied by a terminal water molecule.
13. The method of claim 1, wherein the M-soc-MOF has a BET surface area of at least $800 \text{ m}^2/\text{g}$.
14. The method of claim 1, wherein the M-soc-MOF has an average pore volume of at least $0.2 \text{ cm}^3/\text{g}$.
15. The method of claim 1, wherein contacting comprises mixing, bringing in close proximity, chemically contacting, physically contacting or combinations thereof.
16. The method of claim 1, wherein one or more of CO_2 , H_2S and condensable hydrocarbons are sorbed in series.
17. The method of claim 1, wherein one or more of CO_2 , H_2S and condensable hydrocarbons are sorbed simultaneously.
18. The method of claim 1, wherein sorbing comprises adsorbing.
19. The method of claim 1, wherein sorbing comprises absorbing.
20. The method of claim 1, wherein the fluid comprises one or more of natural gas and biogas.

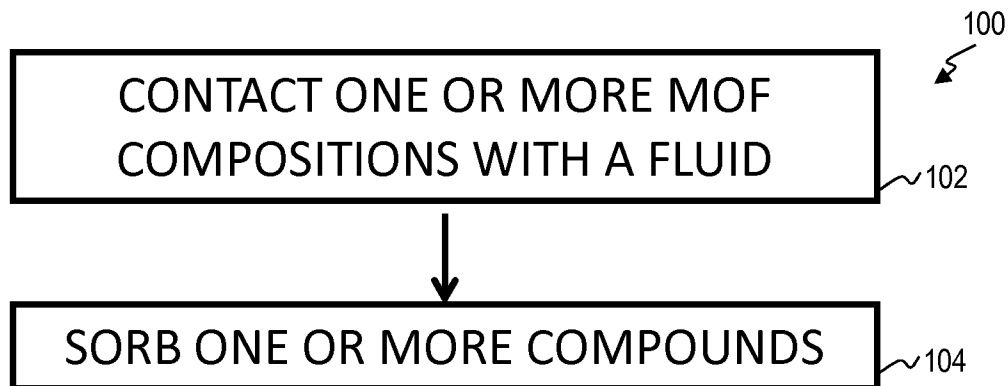


FIG 1

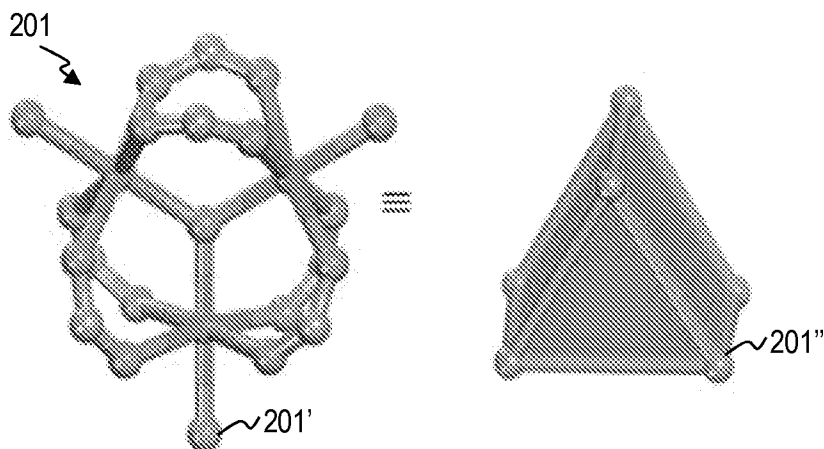


FIG 2A

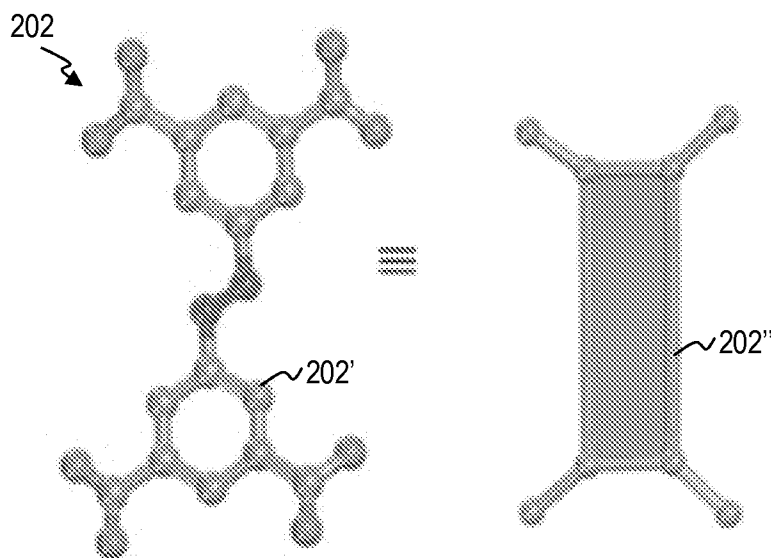


FIG 2B

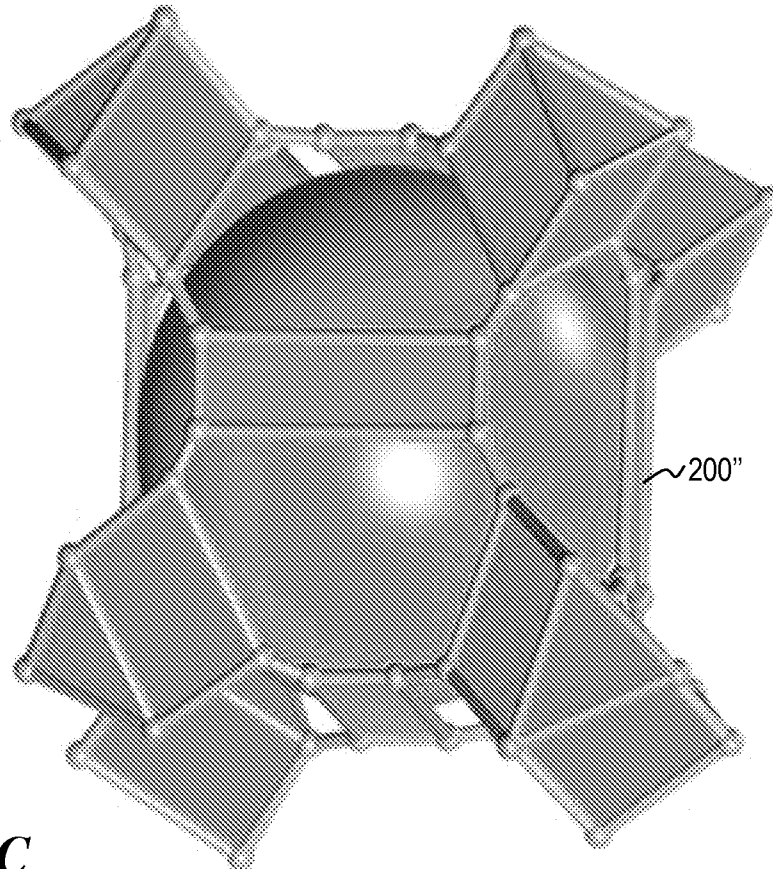
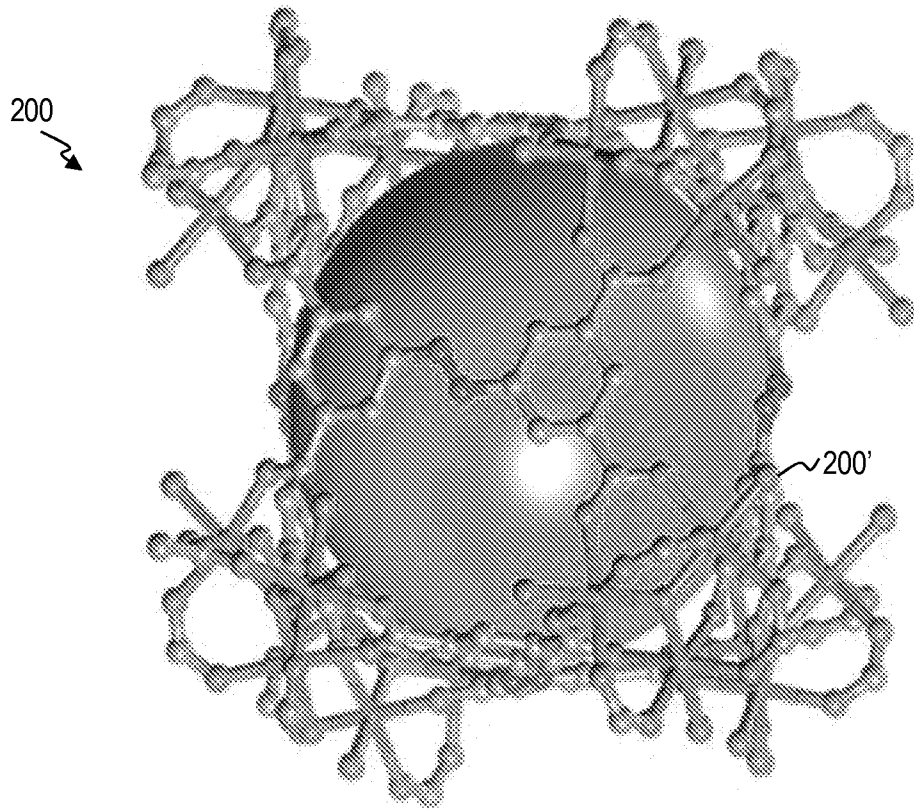
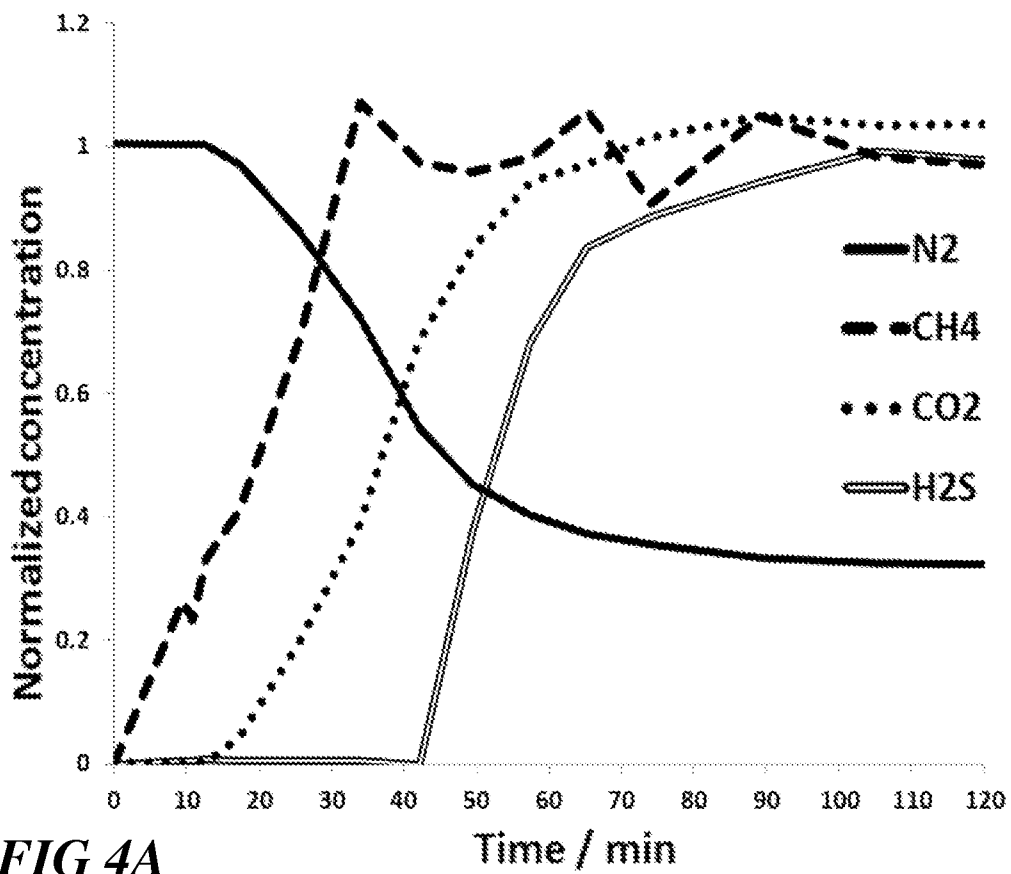
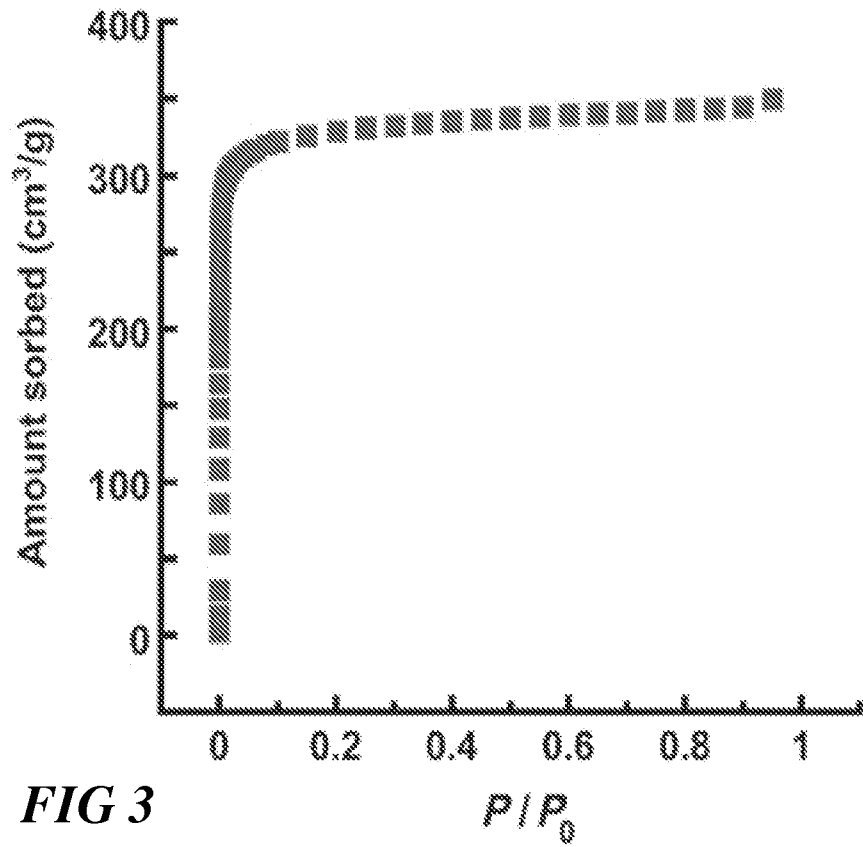


FIG 2C



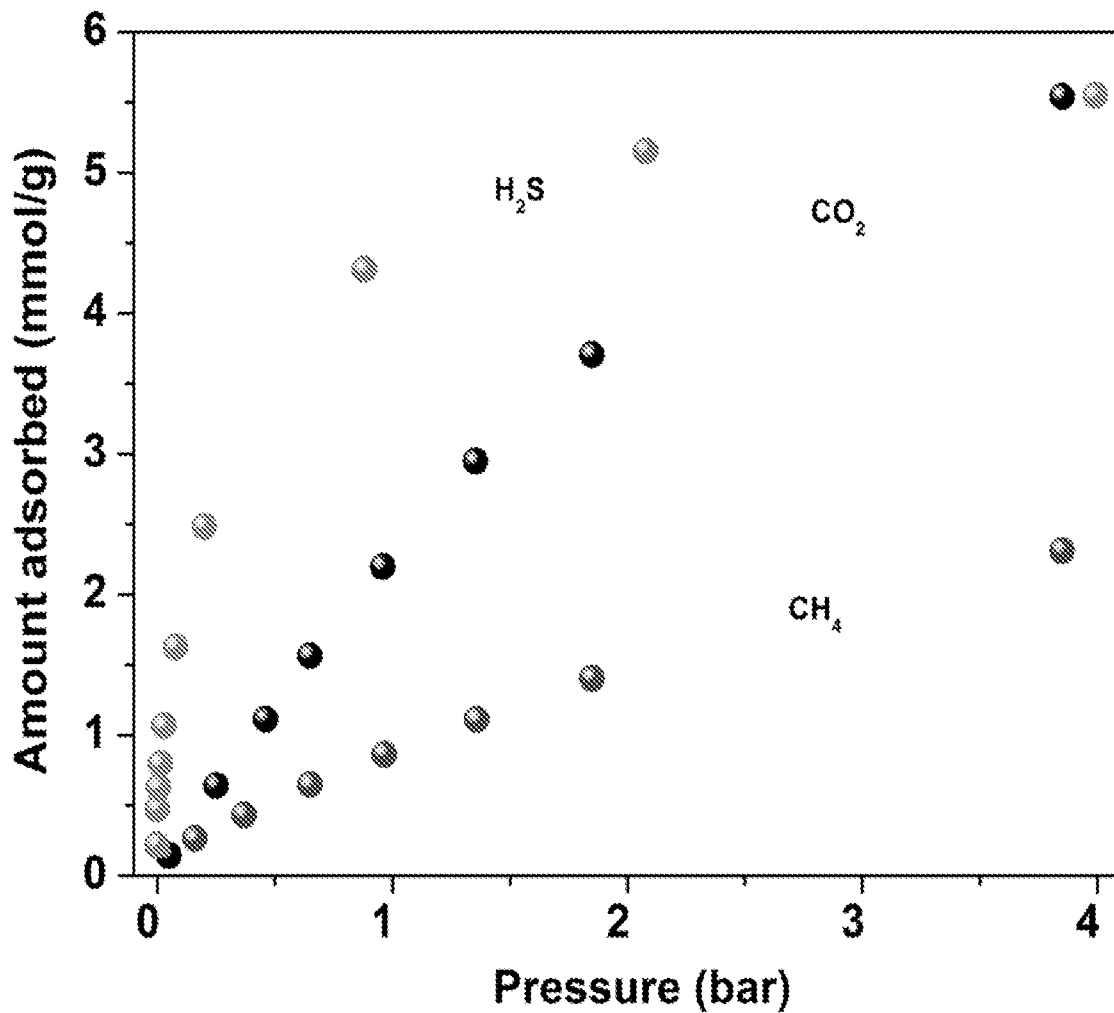


FIG 4B

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2015/046756

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J20/22 B01J20/28 B01D53/04
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
B01J B01D
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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MOELLMER J ET AL: "Insights on Adsorption Characterization of Metal-Organic Frameworks: A Benchmark Study on the Novel soc-MOF", MICROPOROUS AND MESOPOROUS MATERIALS, ELSEVIER SCIENCE PUBLISHING, NEW YORK, US, vol. 129, no. 3, 15 April 2010 (2010-04-15), pages 345-353, XP026834584, ISSN: 1387-1811 [retrieved on 2009-06-17] 2.materials and experimental 2.1. Synthesis of soc MOF; page 345 - page 346 figures 1,2,4-11 3.2. Adsorption properties of socMOF; page 349, right-hand column - page 353, right-hand column ----- -/--	1-20

Further documents are listed in the continuation of Box C.

See patent family annex.

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Date of the actual completion of the international search

22 October 2015

Date of mailing of the international search report

02/11/2015

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Kaluza, Nicoleta

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2015/046756

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>JOHN P S MOWAT ET AL: "Synthesis, characterisation and adsorption properties of microporous scandium carboxylates with rigid and flexible frameworks", MICROPOROUS AND MESOPOROUS MATERIALS, ELSEVIER SCIENCE PUBLISHING, NEW YORK, US, vol. 142, no. 1, 11 December 2010 (2010-12-11), pages 322-333, XP028163823, ISSN: 1387-1811, DOI: 10.1016/J.MICROMESO.2010.12.016 [retrieved on 2010-12-17] abstract tables 2,5 page 328 - page 329 page 332 4.7.1. Rigid frameworks; page 330, left-hand column</p>	1-20
X	<p>RAVICHANDAR BABARAO ET AL: "Molecular Simulations for Adsorptive Separation of CO₂ /CH₄ Mixture in Metal-Exposed, Catenated, and Charged Metal-Organic Frameworks", LANGMUIR, vol. 25, no. 9, 5 May 2009 (2009-05-05), pages 5239-5247, XP055222779, NEW YORK, NY; US ISSN: 0743-7463, DOI: 10.1021/la803074g abstract figures 1(g),8,9 table 1 page 5241, left-hand column page 5246, left-hand column</p>	1-20
X	<p>XUAN PENG ET AL: "Computational screening of porous carbons, zeolites, and metal organic frameworks for desulfurization and decarburization of biogas, natural gas, and flue gas", AICHE JOURNAL, vol. 59, no. 8, 27 February 2013 (2013-02-27), pages 2928-2942, XP055222784, US ISSN: 0001-1541, DOI: 10.1002/aic.14046 figures 1(q),2,4,5 table 1 page 2929, left-hand column page 2931, left-hand column Screening adsorbents for removal of sulfide only; page 2935, right-hand column</p>	1-20

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2015/046756

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>Maolin Pang ET AL: "Highly monodisperse M III-based soc -MOFs (M = in and Ga) with cubic and truncated cubic morphologies", 15 August 2012 (2012-08-15), XP055222783, DOI: 10.1021/ja3049282 Retrieved from the Internet: URL:http://pubs.acs.org/doi/pdf/10.1021/ja3049282 [retrieved on 2015-10-21] the whole document</p> <p style="text-align: center;">-----</p>	1-20
A	<p>YUNLING LIU ET AL: "Assembly of Metal-Organic Frameworks (MOFs) Based on Indium-Trimer Building Blocks: A Porous MOF with soc Topology and High Hydrogen Storage", ANGEWANDTE CHEMIE INTERNATIONAL EDITION, vol. 46, no. 18, 27 April 2007 (2007-04-27), pages 3278-3283, XP055222777, DE ISSN: 1433-7851, DOI: 10.1002/anie.200604306 the whole document</p> <p style="text-align: center;">-----</p>	1-20