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(54) **TRACE AND LOW CONCENTRATION CO₂ REMOVAL METHODS AND APPARATUS UTILIZING METAL ORGANIC FRAMEWORKS**

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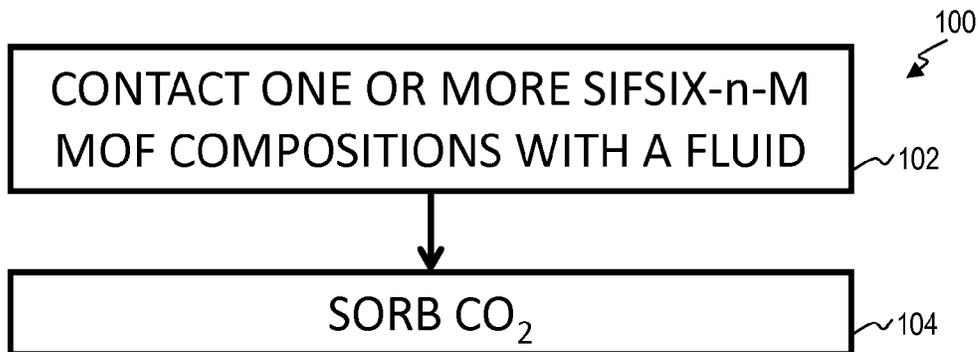
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(57) **ABSTRACT**

In general, this disclosure describes techniques for removing trace and low concentration CO₂ from fluids using SIFSIX-n-M MOFs, wherein n is at least two and M is a metal. In some embodiments, the metal is zinc or copper. Embodiments include devices comprising SIFSIX-n-M MOFs for removing CO₂ from fluids. In particular, embodiments relate to devices and methods utilizing SIFSIX-n-M MOFs for removing CO₂ from fluids, wherein CO₂ concentration is trace. Methods utilizing SIFSIX-n-M MOFs for removing CO₂ from fluids can occur in confined spaces. SIFSIX-n-M MOFs can comprise bidentate organic ligands. In a specific embodiment, SIFSIX-n-M MOFs comprise pyrazine or dipyrildiacetylene ligands.



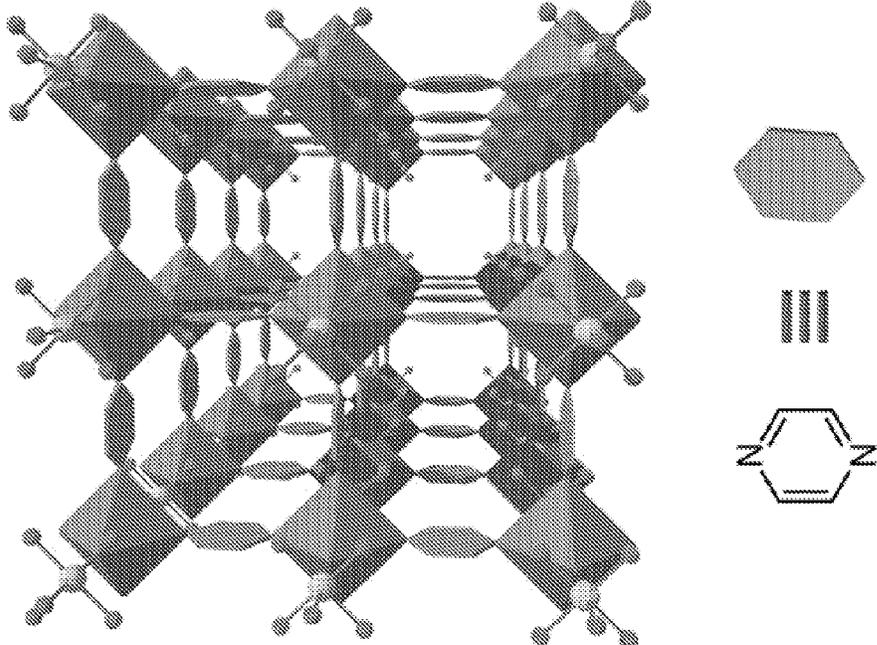


FIG 1A

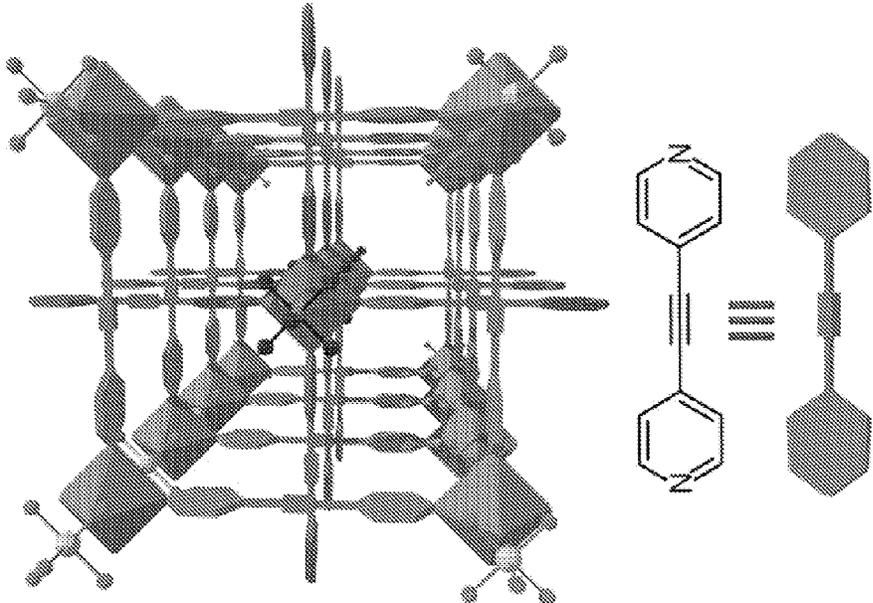


FIG 1B

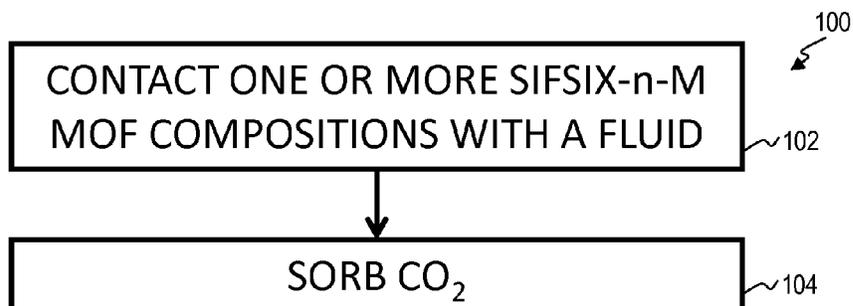


FIG 1C

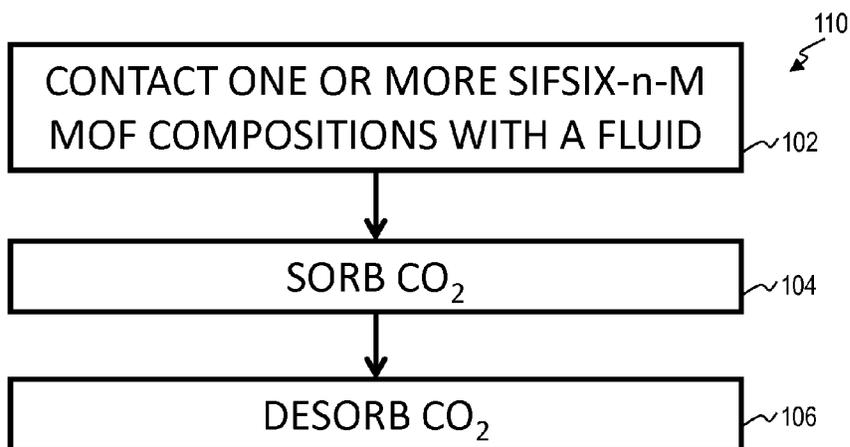


FIG 1D

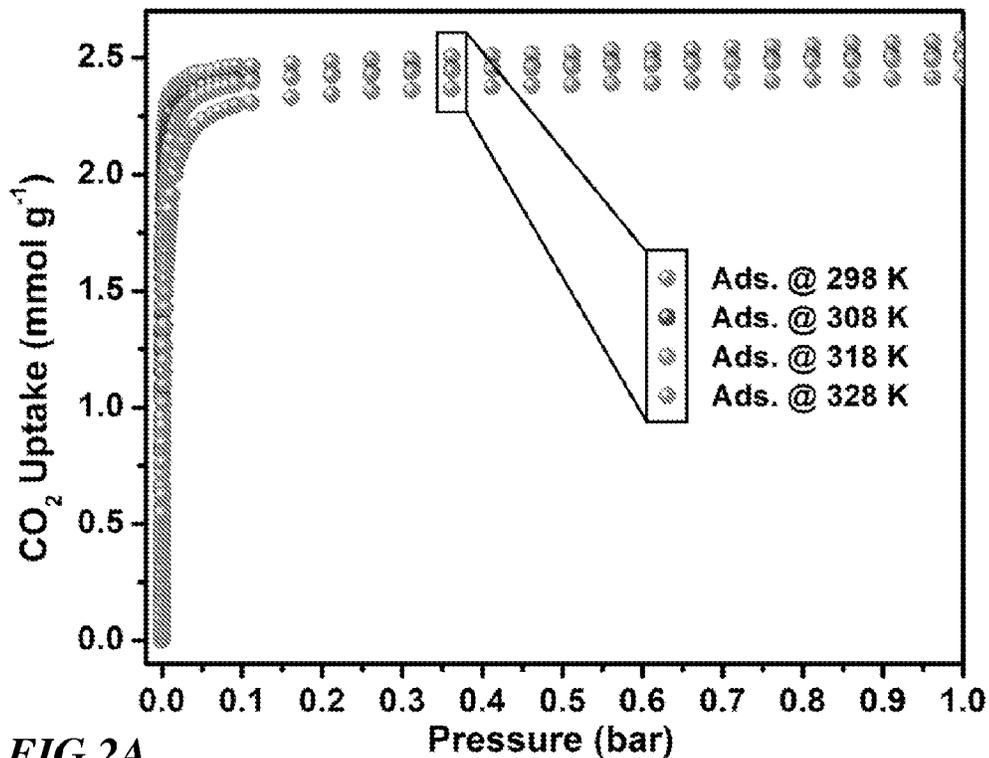


FIG 2A

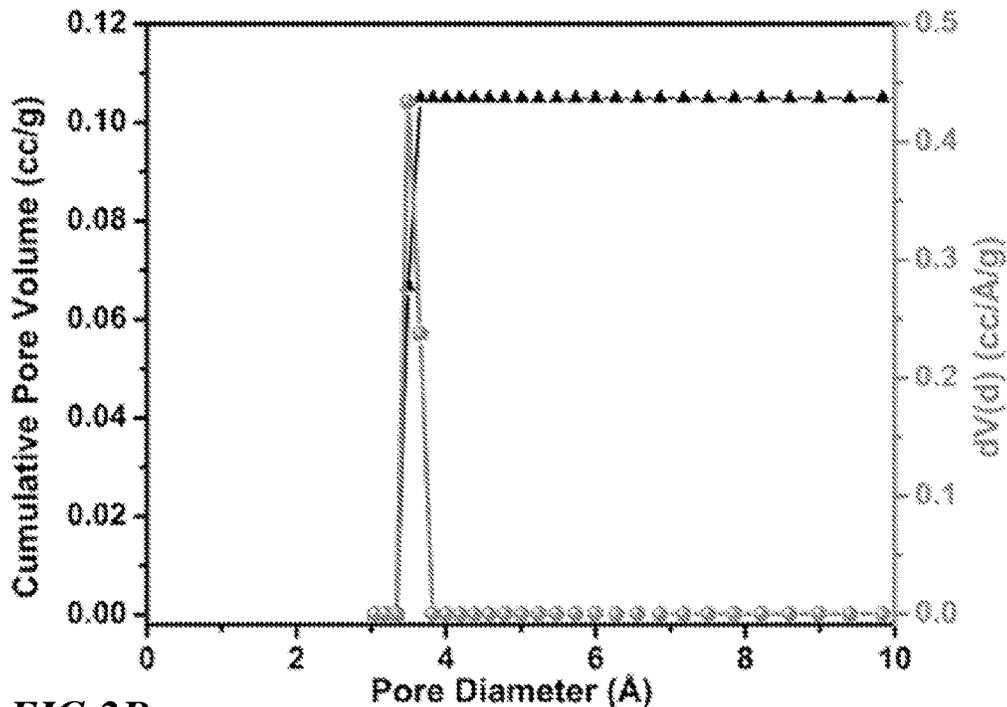


FIG 2B

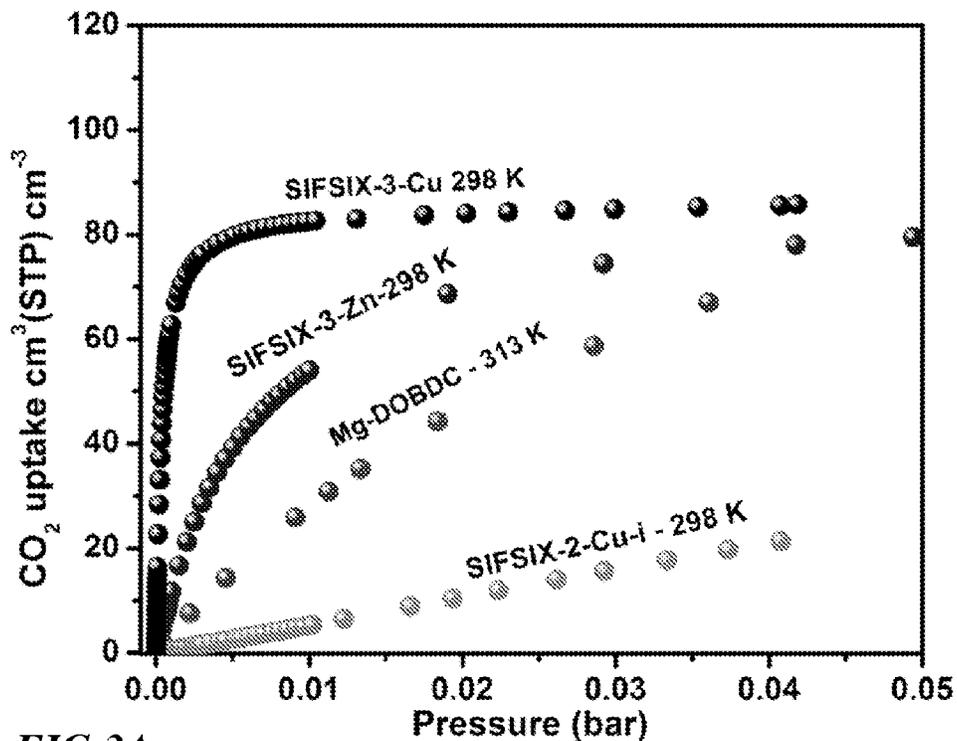


FIG 3A

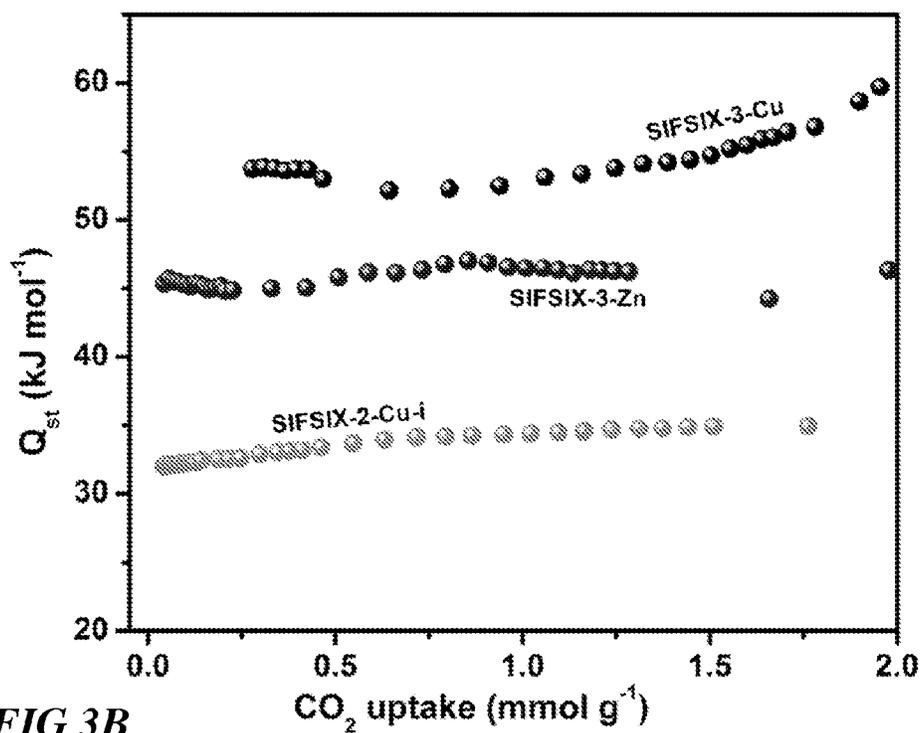


FIG 3B

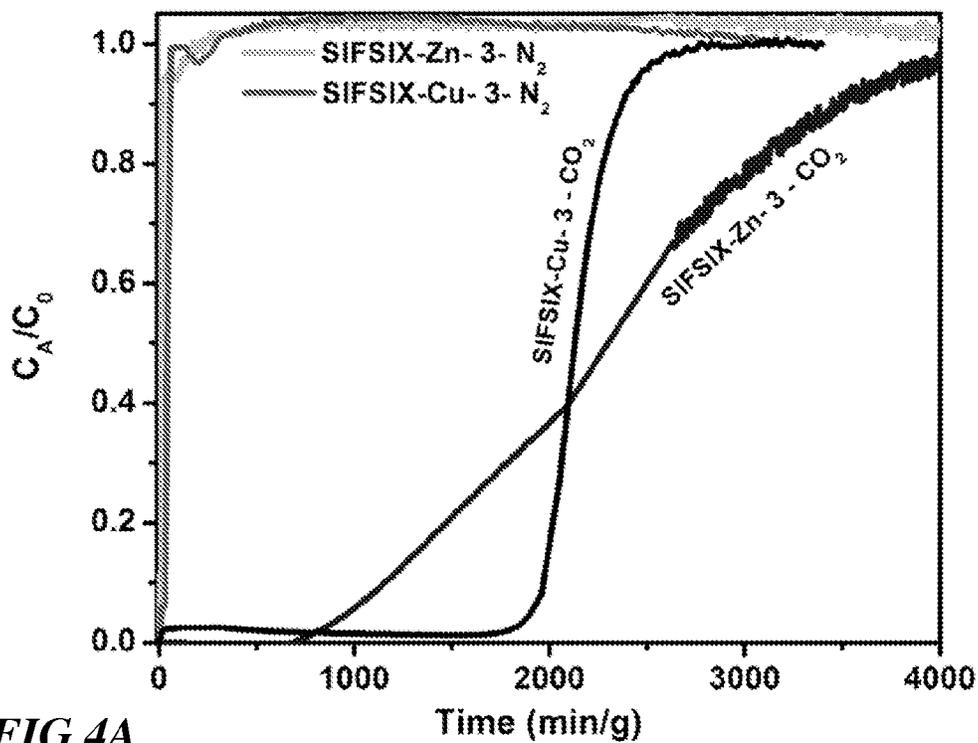


FIG 4A

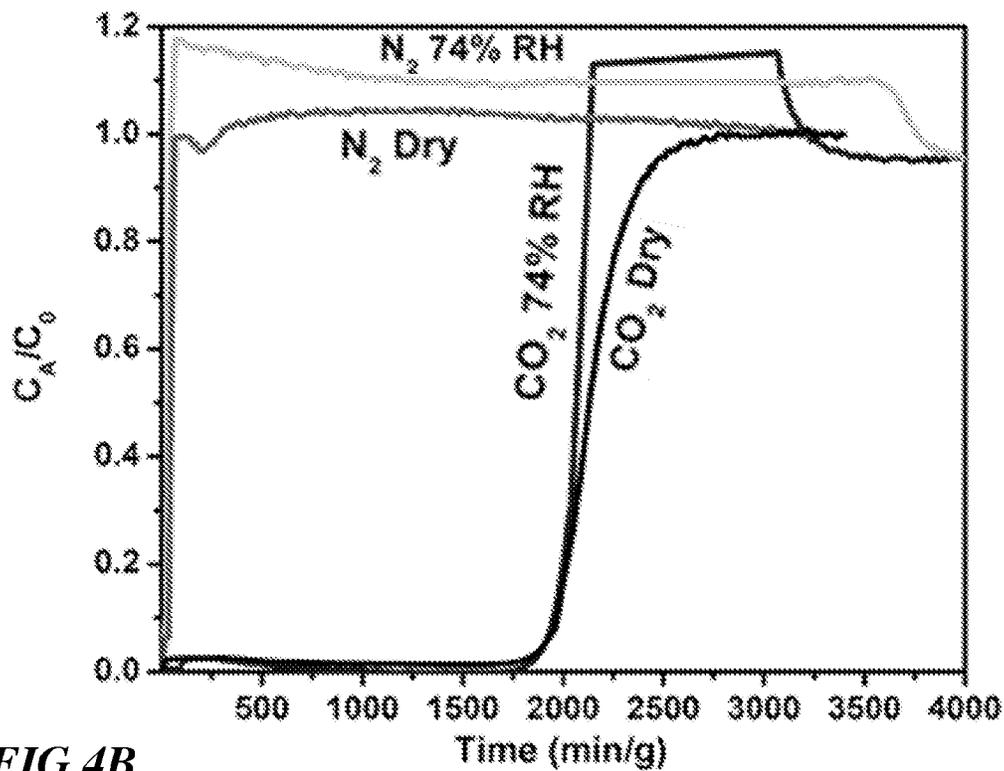


FIG 4B

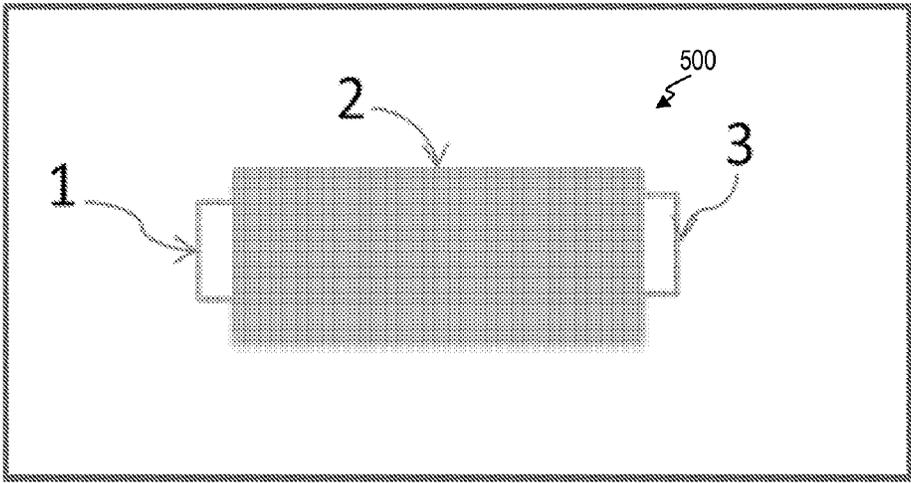


FIG 5

**TRACE AND LOW CONCENTRATION CO₂
REMOVAL METHODS AND APPARATUS
UTILIZING METAL ORGANIC
FRAMEWORKS**

BACKGROUND

[0001] Direct air capture can mitigate the increasing CO₂ emissions associated with the carbon polluting sources. Efficient and cost-effective removal of trace CO₂ is important in various key industrial applications pertaining to energy, environment and health. From an industry prospective, the removal of trace CO₂ from air is a growing area of research and development due to its substantial importance for pre-purification of air and particularly when atmospheric air is used during the separation of nitrogen and oxygen.

[0002] The amount of CO₂ in the atmosphere continues to rise rather rapidly due to unparalleled cumulative CO₂ emissions, provoking the undesirable greenhouse gas effect. Certainly, it is becoming critical to develop economical and practical pathways to reduce CO₂ emissions. Appropriately prospective routes to address this enduring challenge have been considered: (i) CO₂ emission reduction from post-combustion stationary and mobile sources where CO₂ concentration is in the range of 10-15% and (ii) CO₂ removal from air, called direct air capture (DAC), which is another alternative option to reduce greenhouse gases emissions in a uniform way globally. Although DAC is relatively more challenging than post-combustion capture, it is recognized that it might be practical, provided that suitable adsorbent combining optimum uptake, kinetics, energetics and CO₂ selectivity is available at trace CO₂ concentrations.

[0003] In an example, prior to air separation using cryogenic distillation or pressure swing adsorption (PSA), air must be CO₂ free to avoid (i) blockage of heat-exchange equipment as a result of frozen CO₂ during the liquefaction process and (ii) adsorbents (e.g., zeolites) contamination used for oxygen production by pressure swing adsorption (PSA).

[0004] Equally important, alkaline fuel cells (AFCs) require a CO₂ free feedstock of oxygen and hydrogen gases as it is widely recognized that trace amounts of CO₂ (i.e. 300 ppm) degrade the electrolyte in AFCs. Furthermore, efficient removal of CO₂ at low concentrations is also vital for the proper operation of breathing systems in confined spaces such as submarines and aerospace shuttles.

[0005] Efficient CO₂ removal and resupply of fresh air is also critical in mining and rescue missions, diving, and most importantly in medical applications such as anaesthesia machines. The use of anaesthesia machine is still a growing clinical trend worldwide, driven by the need to reduce cost and improve patient care via the use of efficient CO₂ sorbents. A CO₂ removal feature in anaesthesia machine is particularly important in semi-closed or closed rebreathing systems, as the rebreathing fraction is at least 50% of the exhaled gas volume, directed back to the patient after proper CO₂ removal in the next exhalation. Currently, common sorbents for this application are non-recyclable, and generate large amounts of unwanted medical waste.

[0006] There is a pressing need to develop novel porous materials that can adequately address the growing interest to low CO₂ concentration removal applications. Only a few materials were reported to adsorb efficiently traces of CO₂, particularly with regards to DAC using a variety of amine supported materials (e.g. porous silica). However, these

materials contain primary amines which require high energy for regeneration, such as about 80-120 kJ/mol, in part due to the materials' chemical adsorption mechanisms. Additionally, amine grafting is conducted in a step separate from the platform material synthesis, thus adding additional cost and time to manufacturing.

[0007] Modular and tunable porous materials, namely metal-organic frameworks (MOFs), can be used to tackle this ongoing challenge. Recently, MOFs were intensively investigated for intermediate and high CO₂ concentration removal applications such as post-combustion, pre-combustion capture, natural gas and biogas upgrading. Nevertheless, the potential of MOFs to remove traces and low CO₂ concentration from gas streams was rarely considered. The main reason for this lack of studies is that most MOFs reported so far, with or without unsaturated metal sites (UMC) or/and functionalized ligands, exhibit relatively low CO₂ selectivity and uptake particularly at relatively low CO₂ partial pressure. To overcome this downfall, various research groups have adopted the amine grafting chemistry and the acquired knowledge from amine-supported silica, as a prospective pathway to enhance the CO₂ adsorption energetics and uptake in MOFs and covalent organic frameworks (COFs). Markedly, the few reported strategies targeting air capture using MOFs are centred on the aptitude of grafted amines to form a strong chemical bond (at least 70 kJ.mol⁻¹) with CO₂, affording high affinity toward CO₂ and therefore high CO₂ selectivity. Particularly, ethylenediamine (ED) grafting on Mg-MOF-74 supports have been studied for CO₂ adsorption from ultra-dilute gas streams such as ambient air. Similarly, N,N-dimethylethylenediamine grafting for DAC using an expanded isostructure of Mg-MOF-74 has also been studied. All such materials suffer from the drawbacks of amine grafted materials as discussed above.

SUMMARY

[0008] In general, this disclosure describes techniques for removing CO₂ from fluids using SIFSIX-n-M MOFs, wherein n is at least two and M is a metal. In some embodiments, the metal is zinc or copper. Embodiments include devices comprising SIFSIX-n-M MOFs for removing CO₂ from fluids. In particular, embodiments relate to devices and methods utilizing SIFSIX-n-M MOFs for removing CO₂ from fluids, wherein CO₂ concentration is trace. Methods utilizing SIFSIX-n-M MOFs for removing CO₂ from fluids can occur in confined spaces. SIFSIX-n-M MOFs can comprise bidentate organic ligands. In a specific embodiment, SIFSIX-n-M MOFs comprise pyrazine or diprydilacetylene ligands.

[0009] 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

[0010] The accompanying drawings illustrate non-limiting example embodiments of the invention.

[0011] FIG. 1A illustrates a SIFSIX-n-M MOF coordinated by pyrazine ligands, according to one or more embodiments.

[0012] FIG. 1B illustrates a perspective view of a SIFSIX-n-M MOF coordinated by diprydilacetylene ligands, according to one or more embodiments.

[0013] FIG. 1C-D illustrate block flow diagrams of a methods for removing CO₂ from a fluid, according to one or more embodiments.

[0014] FIG. 2A illustrates CO₂ adsorption isotherms at variable temperatures for a SIFSIX-3-Cu MOF, according to one or more embodiments.

[0015] FIG. 2B illustrates a pore size distribution for a SIFSIX-3-Cu MOF, according to one or more embodiments.

[0016] FIG. 3A illustrates CO₂ volumetric uptake for various SIFSIX metal organic frameworks, according to one or more embodiments.

[0017] FIG. 3B illustrates isosteric heats of adsorption at low coverage for SIFSIX-3-Cu, SIFSIX-3-Zn and SIFSIX-2-Cu-I metal organic frameworks, according to one or more embodiments.

[0018] FIG. 4A illustrates a column breakthrough test of CO₂/N₂:1000 ppm/99.9% for SIFSIX-3-Cu and SIFSIX-3-Zn metal organic frameworks in dry conditions, according to one or more embodiments.

[0019] FIG. 4B illustrates a column breakthrough test of CO₂/N₂:1000 ppm/99.9% for a SIFSIX-3-Cu metal organic framework in dry conditions as well as at 74% relative humidity (RH), according to one or more embodiments.

[0020] FIG. 5 illustrates a schematic view of a device for removing CO₂ from a gas, according to one or more embodiments.

DETAILED DESCRIPTION

[0021] 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.

[0022] The present disclosure provides SIFSIX-n-M MOFs for use in trace and low CO₂ concentration removal, and CO₂ sequestration in confined spaces. A particular advantage of SIFSIX-n-M MOFs is high CO₂ removal efficiency at very low CO₂ partial pressure without any post-functionalization (e.g., amine functionalization), thereby eliminating costly and inefficient processing steps as necessary with amine functionalized MOFs. A further advantage is the ability to regenerate and reuse SIFSIX-n-M MOFs after CO₂ capture. Generally, energy for regenerating SIFSIX-n-M MOFs as provided herein is only about 45-55 kJ/mol, as compared to 80-120 kJ/mol for amine functionalized materials.

[0023] As used herein, “trace” refers to species concentrations which are less than about 10%, less than about 7.5%, less than about 5%, less than about 2.5%, or less than about 1% of a system. “Trace” can additionally or alternatively

refer to a species having a partial pressure below about 125 mbar, below about 100 mbar, below about 75 mbar, below about 50 mbar, or below about 25 mbar. For example, CO₂ concentration can be deemed “trace” when the partial pressure of CO₂ in a system is less than 50 mbar. An example of a system having a trace CO₂ concentration is a system having at least 95% N₂. As used herein, “confined spaces” refer to areas which have limited or no supply of fresh air. Examples of confined spaces include aeronautical vessels such as an airplane or space, submarines, and industrial vessels such as those with small hatched openings.

[0024] Metal organic frameworks (MOFs) are a versatile and promising class of crystalline solid state materials which allow porosity and functionality to be tailored towards various applications. For example, MOF materials exhibit exceptionally high specific surface area, in addition to tunable pore size and functionality (e.g., CO₂ selectivity, and H₂O tolerance), which make them suitable for many applications including gas storage, gas separation, catalysis, drug delivery, light-emitting devices, and sensing.

[0025] 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 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.

[0026] 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.

[0027] A MOF can be represented by the formula [(node)_a(ligand)_b(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 as provided herein can be defined as [(node)_a(ligand)_b]_n, without reference to a solvent or guest molecule component.

[0028] An example of a class of MOFs is SIFSIX-n-M, wherein n is at least two, and M can comprise Cu, Zn, Co, Mn, Mo, Cr, Fe, Ca, Ba, Cs, Pb, Pt, Pd, Ru, Rh, and Cd. The SIFSIX-n-M MOF class is isoreticular across its metal analogues (i.e., each M analogue has the same framework topology) and is characterized by periodically arrayed hexafluorosilicate (SIFSIX) octahedral pillars. SIFSIX-n-M

MOFs have many desirable characteristics, including tunable pore sizes, which lend the various analogues well to a number of industrial applications. FIG. 1A-B show examples of SIFSIX-n-MOF analogues.

[0029] FIG. 1A illustrates a SIFSIX-n-M MOF coordinated by pyrazine ligands. Specific analogues of this MOF include SIFSIX-3-Cu and SIFSIX-3-Zn, among others. Such SIFSIX-3-M analogues are iso-structural, based on pyrazine/M(II) 2-D periodic 4^4 square grids pillared by $(\text{SiF}_6)^{2-}$ anions. SIFSIX-3-Zn MOFs comprising pyrazine ligands can have average pore sizes of about 3.84 Å and BET apparent surface areas of about $250 \text{ m}^2 \cdot \text{g}^{-1}$ (determined from the CO_2 adsorption isotherm at 298K). SIFSIX-3-Cu MOFs comprising pyrazine ligands can have average pore sizes of about 3.50 Å (NLDFT) and BET and Langmuir apparent surface areas of ca. $300 \text{ m}^2 \cdot \text{g}^{-1}$ (determined from the CO_2 adsorption isotherm at 298K). FIG. 1B illustrates a SIFSIX-n-M MOF coordinated by dipyrilidylacetylene (DPA) ligands. A specific analogue of this MOF is SIFSIX-2-Cu-i, among others. SIFSIX-2-Cu-I MOFs comprising DPA ligands can have average pore size of 5.15 Å and BET apparent surface areas (determined by N_2 adsorption) of about $735 \text{ m}^2 \cdot \text{g}^{-1}$. In FIG. 1A-B, guest molecules have been omitted for clarity.

[0030] SIFSIX-n-M MOFs can be coordinated by a variety of organic ligands. In some embodiments, the ligand can be any bidentate (i.e., bi-functional) N-donor linkers based on monocyclic or polycyclic group (aromatic or not). In some embodiments, a ligand can comprise a polydentate, or poly-functional ligand, such as a bi-functional ligand, a tri-functional ligand, or ligands with four or more functional sites. In some embodiments, a ligand can comprise an N-donor linker. In some embodiments a ligand can comprise a poly-functional ligand. In some embodiments, a ligand can comprise a plurality of N-donor functional groups. Pyrazine is an example of a ligand with two N-donor functional groups. In some embodiments, a ligand can comprise a monocyclic or polycyclic group structure, wherein the cyclic groups can be aromatic or nonaromatic. In some embodiments, a ligand can comprise a nitrogen-containing monocyclic or polycyclic group structure. In some embodiments, a ligand can comprise a nitrogen-containing heterocyclic ligand, including pyridine, 4,4'-Bipyridin, pyrazine, pyrimidine, pyridazine, triazine, thiazole, oxazole, pyrrole, imidazole, pyrazole, triazole, oxadiazole, thiadiazole, quinoline, benzoxazole, benzimidazole, 1,4-Diazabicyclo[2.2.2]octane (DABCO), 1,2-bis(4-pyridyl)acetylene (dpa), and tautomers thereof.

[0031] The SIFSIX-n-M MOFs presented herein provide uniformly distributed and non-reactive CO_2 adsorption energetics and remarkable CO_2 adsorption properties, uptake and selectivity in highly diluted gas streams. Such performance is currently unachievable with other class of porous materials. In particular, SIFSIX-n-M MOFs are suitable for trace CO_2 removal applications, due to their strong CO_2 adsorption sites. SIFSIX MOF materials exhibit very high (non-reactive) CO_2 energetics, but fully reversible physical driven adsorption-desorption operations at very mild conditions. The ideal combination of contracted pore size and the high charge density also provide unprecedented CO_2 uptake and selectivity over H_2 , CH_4 and N_2 at very low partial pressures.

[0032] SIFSIX-n-M MOFs are suitable for post-combustion capture (at CO_2 partial pressures of about 100 mbar), but also excellent features suitable for natural and biogas

upgrading as well as pre-combustion capture (high CO_2 concentration and high pressure).

[0033] FIG. 1C illustrates a block flow diagram of a method **100** for removing CO_2 from a fluid via a SIFSIX-n-M MOF. Method **100** includes contacting **102** one or more SIFSIX-n-M MOF compositions with a fluid and sorbing **104** CO_2 from the fluid with the one or more SIFSIX-n-M MOF compositions. In particular, method **100** can include contacting **102** one or more SIFSIX-n-Cu and SIFSIX-n-Zn MOF compositions with a fluid and sorbing **104** CO_2 from the fluid with the one or more SIFSIX-n-Cu and SIFSIX-n-Zn MOF compositions. In particular, method **100** can include contacting **102** one or more SIFSIX-n-M MOF compositions with a fluid and sorbing **104** CO_2 from the fluid with the one or more SIFSIX-n-M MOF compositions, wherein M can comprise Cu, Zn, Co, Mn, Mo, Cr, Fe, Ca, Ba, Cs, Pb, Pt, Pd, Ru, Rh, and Cd. SIFSIX-n-M MOFs can comprise bidentate organic ligands. SIFSIX-n-M MOFs can comprise bidentate N-donor organic ligands. The bidentate N-donor organic ligands can comprise a cyclic moiety. The bidentate N-donor organic ligands can include monocyclic or polycyclic moieties. Monocyclic and polycyclic bidentate N-donor organic ligands can be aromatic and non-aromatic. SIFSIX-n-M MOFs can comprise pyrazine or DPA ligands.

[0034] Contacting **102** can include mixing, bringing in close proximity, chemically contacting, physically contacting or combinations thereof. Fluids can include general liquids and gases which include CO_2 . In particular, fluids can include general liquids and gases which include trace amounts of CO_2 . In some embodiments, fluids include industrial process fluids. In some embodiments, fluids include breathing air. Breathing can include any air which is inhaled by a living organism. Breathing air can include air in a confined space. Breathing air can include air provided by a breathing device such as a medical device and a SCUBA tank. Fluids can include one or more of water, N_2 , O_2 , and H_2 . In a specific embodiment, fluids can include CO_2 and one or more of water, N_2 , O_2 , and H_2 .

[0035] 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 of CO_2 over other species present within the fluid. For example, sorbing **104** can include selectively sorbing CO_2 over one or more of water, N_2 , O_2 , and H_2 . The SIFSIX-n-M 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 include reducing the CO_2 concentration in a fluid to less than about 1%, less than about 0.5%, less than about 0.1%, or less than about 0.01%.

[0036] 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 SIFSIX-n-M MOF compositions can be varied to affect a rate and/or magnitude of sorbing **104**. One or more of temperature, pressure and SIFSIX-n-M MOF concentration can be regu-

lated 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.

[0037] Sorbing **104** can be reversible. FIG. 1D illustrates a block flow diagram of a method **110** for removing CO₂ from a fluid via a SIFSIX-n-M MOF. Method **110** includes contacting **102** one or more SIFSIX-n-M MOF compositions with a fluid, sorbing **104** CO₂ from the fluid with the one or more SIFSIX-n-M MOF compositions, and desorbing **106** CO₂ from the one or more SIFSIX-n-M MOF compositions. Method **110** can constitute one sorbing cycle. SIFSIX-n-M MOFs can perform a plurality of sorbing cycles and maintain structural integrity. Optimal CO₂ energetics of SIFSIX-n-M MOF compositions which are strong, uniform, and relatively low enable reversible sorption.

[0038] Methods **100** and **110** can be utilized in the context of breathing systems. Specifically, sorbing **104** can be utilized within a breathing system. Efficient removal of CO₂ at low concentrations is vital for the proper operation of breathing systems in confined spaces such as submarines and aerospace shuttles. During long-term space flight and submarine missions, CO₂ must be removed from the air and recycled because resupply opportunities are scarce. An average crew member requires approximately 0.84 kg of oxygen and emits approximately 1 kg of carbon dioxide. Thus, the ability to continuously purify the exhaled air (with a maximum CO₂ concentration of 2-5%) will lead to an optimal recycling and considerable reduction in fresh air supply in remote confined spaces. The problem of the existing technologies is the capture capacity/day which is low due to mainly to the long temperature swing adsorption cycling mode (TSAM). The TSAM is mainly determined by the way the adsorbent is cleaned. In the case of low CO₂ concentration removal, chemical (amine supported) adsorbents are preferred with a Heat of adsorption of 70-100 kJ/mol, —a parameter indicative of the energy required to clean the material after each adsorption cycle. Implementing MOF-based physical adsorption (such as SIFSIX-Cu-3) in a process such as VTSA or VSA (with mild vacuum) will increase the CO₂ removal capacity/day and decrease the energy penalty needed for regeneration.

[0039] Methods **100** and **110** can be utilized in the context of anaesthesia. Specifically, sorbing **104** can be utilized within an anesthetic system. The use of anaesthesia machines is a growing clinical trend worldwide, driven by the need to reduce costs and improve patient care via the use of efficient CO₂ sorbents. CO₂ removal features in anaesthesia machines are particularly important in semi-closed or closed rebreathing systems, as the rebreathing fraction is at least 50% of the exhaled gas volume. Exhaled gas volume is directed back to the patient after proper CO₂ removal. Sodalime is currently the sorbent of choice in most commercially available anaesthesia machines. This sorbent exhibits a high CO₂ removal efficiency from exhaled air, with an average continuous operation of about 24 hours using a pre-packed commercial cartridge. Nevertheless, a major drawback of this technology is that one sodalime

cartridge can only be used for a single cycle and is non-recyclable, generating therefore undesirable waste that should be disposed properly.

[0040] In case of anaesthesia machines, the use of recyclable SIFSIX-n-M MOFs allow the same regenerable cartridge much longer durations than 24 hours. A single SIFSIX-n-M MOF cartridge can be in operation while two of the same are in regeneration, for example. Assuming the CO₂ uptake of MOF is 10 times lower than sodalime but its life time is 10000 higher than the commercial adsorbents, this can lead to an increase in the overall capacity by 1000 times. SIFSIX-n-M MOF cartridges can be replace existing cartridges, such as sodalime cartridges, to without any major changes in the existing anaesthesia machines. The main change in case of the recyclable MOF can be the addition of small devices (desorber) for re-activation of the MOF cartridges or in-situ continuous temperature-pressure adsorption system.

[0041] Methods **100** and **110** can be utilized in the context of alkaline fuel cells (AFCs). Specifically, sorbing **104** can be utilized within an AFC. AFCs require a CO₂-free feedstock of oxygen and hydrogenfuel, as even trace amounts of CO₂ (i.e. 300 ppm) can degrade AFC electrolytes through progressive carbonation. During typical AFC operation, air is transmitted through the gas diffusion layer of the cathode to the catalyst layer which can include a KOH solution. Any CO₂ present in the air can react with the KOH to form K₂CO₃ in the catalyst layer, thereby reducing fuel oxidation and oxygen reduction kinetics and AFC power output, inducing precipitation of carbonate salts in porous AFC electrodes, and reducing AFC electrolyte conductivity. SIFSIX-n-M MOFs can capably remove trace amounts of CO₂ from any air contacting AFC catalyst layers. The ability of SIFSIX-n-M MOFs to regenerate (i.e., desorb CO₂ while retaining structural integrity) after CO₂ sorption lends further benefits to fuel cell applications such as military vehicles, which can lack access to fresh CO₂ sorbents while in combat.

EXAMPLE 1

Synthesis of SIFSIX-3-Cu MOF

[0042] A methanol solution (5.0 mL) of pyrazine (pyz, 0.30 g, 3.0 mmol) was layered in a glass tube onto a methanol solution (5.0 mL) of CuSiF₆·xH₂O (0.325 g, 0.6 mmol). Upon layering, a fast formation of light violet powder was observed, and the powder was left for 24 hours in the mother solution. The SIFSIX-3-Cu powder was then collected and washed extensively with methanol then dried under vacuum. The thermal gravimetric analysis (TGA) of the SIFSIX-3-Cu showed a weight loss of about 10% for the dried sample in the range of 50-150° C. attributed to guest molecules. From PXRD measurements, the cell parameters, a=b=6.919(1) Å, c=7.906(1) Å, were refined by a whole powder pattern fit using the Le Bail method, implemented in FULLPROF software. The final Rietveld refinement yielded: R_{Bragg}=0.051 and R_{Factor}=0.056.

[0043] FIG. 2A illustrates CO₂ adsorption isotherms at variable temperatures for the SIFSIX-3-Cu MOF. The Cu analogue shows the same promising adsorption properties as SIFSIX-3-Zn analogues. Moreover, the Cu analogue shows even steeper variable temperature adsorption isotherms at very low pressures, indicative of relatively stronger CO₂—

SIFSIX-3-Cu interactions. These results emphasize the potential of SIFSIX-3-Cu for CO₂ capture applications.

[0044] The SIFSIX-3-Cu MOF exhibited a slightly smaller unit cell as compared to its Zn analogue (378 vs. 388 Å³). The attributed to the relatively stronger bonding between the Cu(II) and the pyrazine. FIG. 2B illustrates a pore size distribution for the SIFSIX-3-Cu MOF, as determined from the CO₂ adsorption isotherms, using a CO₂ at 273 K NLDFT model. The relatively sharp pore size distribution (PSD) analysis centred at 3.5 Å yields a smaller average pore size than the SIFSIX-3-Zn analogue average pore size of 3.84 Å, which is in good agreement with the determined unit cell sizes. These determinations are supported by a rational based on conventional coordination chemistry which suggests that replacement of Zn(II) by Cu(II) to form an iso-structural SIFSIX-3-Cu will potentially induce an additional pore contraction due to Jahn-Teller distortions of the octahedral coordination geometry of Cu(II), CuN₂F₂. The Cu(II) has an open shell valence electron configuration 3d⁹, in contrast to Zn(II) with a close shell 3d¹⁰, and thus will experience a distorted octahedral coordination geometry with potentially elongated Cu—F (fluorine) bonds and relatively shorter Cu—N (nitrogen) bonds.

EXAMPLE 2

CO₂ Sorption by Various MOFs

[0045] FIG. 3A illustrates CO₂ volumetric uptake for SIFSIX-3-Cu at 298 K compared to SIFSIX-3-Zn, SIFSIX-2-Cu-I and Mg-MOF-74. FIG. 3B illustrates isosteric heats of adsorption at low coverage for SIFSIX-3-Cu, SIFSIX-3-Zn and SIFSIX-2-Cu-I. Upon the substitution of Zn by Cu, the Q_{st} of CO₂ adsorption in the contracted structure increased by 20%, from 45 to 54 kJ mol⁻¹ (FIG. 3b), in perfect agreement with the relatively steeper CO₂ adsorption isotherms in the case of the Cu analogue at very low pressure. This increase is mainly attributed to the small unit cell and the contracted pore size of the Cu analogue which in turn tend to increase the electron density surrounding the adsorbed CO₂ molecules. The Q_{st} of CO₂ adsorption is an intrinsic property that dictates the affinity of the pore surface toward CO₂, which in turn plays a major role in determining the adsorption selectivity and the necessary energy to release CO₂ during the regeneration step.

[0046] Although the Q_{st} for CO₂ was slightly above the typical range of fully reversible CO₂ adsorption (30-50 kJ mol⁻¹),²² SIFSIX-3-Cu was fully and quickly evacuated at 323 K in vacuum (or under N₂ flow environment). As in case of SIFSIX-3-Zn and SIFSIX-2-Cu-i, the Q_{st} for CO₂ adsorption was mostly constant up to relatively high CO₂ loadings indicating homogenous binding sites over the full range of CO₂ loading. The further increase of CO₂ Qst for SIFSIX-3-Cu at the average loading of 1.5 mmol.g⁻¹ can be explained by the spark of the CO₂—CO₂ interactions or possible experimental errors close to the saturation (plateau) of adsorption isotherm.

EXAMPLE 3A

Trace CO₂ Uptake of Various MOFs

[0047] The steep CO₂ adsorption isotherms over a wide range of temperatures exhibited by SIFSIX-n-M MOFs suggest potential for the same for trace CO₂ adsorption

applications (e.g., diluted streams in vacuum or in mixtures containing a large fraction of N₂ up to 95%). In order to highlight the concealed potential of these MOFs for low CO₂ concentration applications (i.e. involving CO₂ concentration below 5%, below 50 mbar CO₂ partial pressure, such as anaesthesia machines and pre-purification before air separation and air capture), single gas CO₂ adsorption properties were evaluated for SIFSIX-2-Cu-i and SIFSIX-3-Zn. Table 1 summarizes the CO₂ adsorption uptake at variable low CO₂ concentration (partial pressures) for SIFSIX compounds as compared to Mg-MOF-74 and amine supported materials (including MOFs), relevant to different traces CO₂ removal applications. The SIFSIX-3-Cu MOF also showed even higher CO₂ uptake at 400 ppm and 328 K than the corresponding uptake at 323 K for amine functionalized Mg-dobpdc-mmen (data not included).

TABLE 1

CO ₂ adsorption uptake at various traces CO ₂ concentration and at 298 K in comparison to the most promising MOFs and other various amine supported materials.				
Adsorbent	uptake at 400 ppm (0.4 mbar)	Uptake at 5000 ppm (5 mbar)	Uptake at 10000 ppm (10 mbar)	CO ₂ Qst (kJ · mol ⁻¹)
SIFSIX-2-Cu-i	0.0684 ^c /0.2 ^d	0.097 ^c /2.7 ^d	0.19 ^c /5.32 ^c	32
SIFSIX-3-Zn	0.13 ^c /5.6 ^d	1.12 ^c /39.26 ^d	1.53 ^c /53.97 ^d	45
SIFSIX-3-Cu	1.24 ^c /43.9 ^d	2.26 ^c /79.8 ^d	2.34 ^c /82.5 ^d	54
Mg-MOF-74	—	—	—	47
Mg-MOF-74-ED ^{a,g}	0.088 ^c /1.8 ^d	0.7 ^c /14.3 ^d	1.27 ^c /25.86 ^d	ND
Mg-MOF-74-ED ^{a,g}	1.5 ^c	ND	ND	70
Mg-dobpdc-mmen ^{b,g}	2 ^c	2.5 ^c	2.75 ^c	92
TRI-PE-MCM-41 ^{f,g}	1 ^c	1.45 ^c	1.6 ^c	ND
HAS ^{f,g}	1.7 ^c	ND	ND	ND

^aEthylenediamine functionalized;

^bN,N-dimethylethylenediamine functionalized;

^cmmol · g⁻¹;

^dcm³ (STP)/cm³;

^eat 328 K;

^fAmine supported silica;

ND: non determined.

^gChemical adsorbent

[0048] The contraction of the pore size from 5.15 Å (for SIFSIX-2-Cu-i) to 3.8 Å (for SIFSIX-3-Zn) has prompted a drastic increase in CO₂ uptake and consequently a recorded highest CO₂ uptake ever reported for a given MOF in the range under 5% CO₂. Specifically, SIFSIX-3-Zn showed an order of magnitude higher volumetric CO₂ uptake (55 cm³ (STP)/cm³) than other materials such as Mg-MOF-74, (28 cm³ (STP)/cm³) at 10 mbar (1% CO₂), while UTSA-16, exhibits much lower CO₂ uptake similar to SIFSIX-2-Cu-i.

[0049] In the context low concentration applications (400 ppm-5%), the exhibits steep adsorption isotherms at very low CO₂ concentration of the SIFSIX-3-Cu analogue, as shown in FIG. 3A, translate into the highest uptake ever reported for MOFs without unsaturated metal centers (UMCs) or exposed amino functionality at low CO₂ pressures below 38 ton (0.05 bar). This can be even more appealing owing to its fully physical adsorption nature where complete and fast desorption of CO₂ was established

under vacuum at only 323 K. At 7.6 torr (0.01 bar) SIFSIX-3-Cu uptakes $82.6 \text{ cm}^3(\text{STP})\cdot\text{cm}^{-3}$ vs. 55 and $28 \text{ cm}^3(\text{STP})\cdot\text{cm}^{-3}$ for SIFSIX-3-Zn and Mg-MOF-74, respectively. The gravimetric uptake of SIFSIX-3-Cu at 400 ppm and 298 K ($1.24 \text{ mmol}\cdot\text{g}^{-1}$) is ca. 10 and 15 times higher than the corresponding uptakes for SIFSIX-3-Zn ($0.13 \text{ mmol}\cdot\text{g}^{-1}$) and Mg-MOF-74 ($0.08 \text{ mmol}\cdot\text{g}^{-1}$) and even higher than the observed uptakes for most amine-supported silica materials (with optimal compromise of amine loading and kinetics) at 298 K (for example TRI-PE-MCM-4 ($1 \text{ mmol}\cdot\text{g}^{-1}$)^{10,22}).

EXAMPLE 3B

Column Breakthrough Tests of SIFSIX MOFs

[0050] The CO_2 selectivity exhibited by SIFSIX-3-Zn and SIFSIX-3-Cu MOFs was investigated experimentally at trace CO_2 concentrations using column breakthrough tests for binary CO_2/N_2 :1000 ppm/99.9% mixtures at 298 K in dry conditions, as well as in humid conditions. FIG. 4A illustrates a column breakthrough test of CO_2/N_2 :1000 ppm/99.9% for SIFSIX-3-Cu and SIFSIX-3-Zn MOFs in dry conditions. FIG. 4B illustrates a column breakthrough test of CO_2/N_2 :1000 ppm/99.9% for SIFSIX-3-Cu in dry conditions as well as at 74% relative humidity (RH). In dry conditions, the first CO_2 signal downstream the column was observed only after ca. 798 and ca. 1922 $\text{min}\cdot\text{g}^{-1}$ for SIFSIX-3-Zn and SIFSIX-3-Cu, respectively after starting continuous CO_2/N_2 gas mixture flux ($5 \text{ cm}^3\cdot\text{min}^{-1}$), while N_2 breakthrough occurred immediately within a few seconds. Accordingly, at 1000 ppm CO_2 and breakthrough time, SIFSIX-3-Cu shows higher selectivity (ca. 10500) than SIFSIX-3-Zn (7259). It should be noted that calculated and measured selectivity exceeding 1000-2000 are often subject to uncertainties associated with measurement of the gas uptake of weakly adsorbed gases (N_2) in the mixture, thus the reported selectivity is highly qualitative and aimed mainly for relative comparison of the studied compounds in this work. The steeper CO_2 signal after breakthrough for SIFSIX-3-Cu as compared to the Zn analogue is a direct indication of the steeper CO_2 adsorption for the Cu analogue as shown in FIG. 3A.

[0051] The CO_2 removal selectivity at 1000 ppm CO_2 for SIFSIX-3-Cu MOFs was not affected by the presence of humidity as shown from the column breakthrough tests performed on both compounds at the relative humidity (RH) of 74%. This unprecedented finding was also valid in case of SIFSIX-3-Zn for the removal of low and higher CO_2 concentration. Finally, as was demonstrated for SIFSIX-3-Zn, SIFSIX-3-Cu is a recyclable and moisture stable MOFs.

EXAMPLE 4

CO_2 Uptake Kinetic Study for SIFSIX-3-Cu MOFs

[0052] Kinetic studies of CO_2 and CO_2/N_2 :10/90 adsorption on SIFSIX-3-Cu were carried out using the Rubotherm gravimetric apparatus operating in dynamic regime. Initially, the SIFSIX-3-Cu MOF was properly evacuated at 323 K in vacuum. In order to achieve an immediate constancy of pressure (0.5 bar) during kinetics tests and avoid the often noisy uptake during the rapid introduction of the studied gas, an initial baseline was set-up using helium gas at 0.5 bar for single gases and 1 bar for mixture, then the studied single gas or mixture is flushed with a flow of 300 ml/min to avoid any dependence of the kinetics on the mass flow controller.

[0053] The mechanistic behind the unprecedented selective CO_2 adsorption involving the unique synergetic effect of thermodynamics and kinetics was confirmed by the competitive kinetics of CO_2/N_2 :10/90 gas mixture adsorption. As anticipated, the uptake at equal times for variable CO_2 compositions mixtures follows the behaviour of pure CO_2 . Further, the total uptake of the CO_2 containing gas mixtures at equilibrium overlay perfectly with the equilibrium uptake for pure CO_2 . These findings show that similarly to SIFSIX-3-Zn, when CO_2 containing mixtures are in contact with SIFSIX-3-Cu, CO_2 adsorbs stronger and faster than N_2 , and, by analogy, also O_2 , CH_4 and H_2 . Adsorbed CO_2 thus occupies all available physical space and adsorption sites and subsequently exclude other gases, a desirable feature in many CO_2 separation and purification applications.

EXAMPLE 5

Devices for CO_2 Removal

[0054] FIG. 5 illustrates a schematic view of a device 500 for removing CO_2 from a gas, comprising a gas flow inlet, a housing for containing one or more SIFSIX-n-M MOF compositions (not pictured) for sorbing CO_2 , and a gas flow outlet 3. Sorbing can comprise absorbing, adsorbing, or a combination of absorbing and adsorbing. Gas can pass through gas flow inlet 1 and out gas flow outlet 3. Gas can include a mixture of gases having a CO_2 concentration of less than 5%.

What is claimed is:

1. A method of removing CO_2 from a fluid, the method comprising:
 - a) contacting one or more SIFSIX-n-M compositions with a fluid; and
 - b) sorbing CO_2 from a fluid;
 wherein n is at least 2, and M is a metal.
2. The method of claim 1, wherein the metal comprises zinc or copper.
3. The method of claim 1, wherein the metal comprises Cu, Zn, Co, Mn, Mo, Cr, Fe, Ca, Ba, Cs, Pb, Pt, Pd, Ru, Rh, or Cd
4. The method of claim 2, wherein n is 3.
5. The method of claim 1, wherein the SIFSIX-n-M composition comprises bidentate organic ligands.
6. The method of claim 1, wherein the SIFSIX-n-M composition comprises bidentate N-donor organic ligands.
7. The method of claim 6, wherein the bidentate N-donor organic ligands each comprise a cyclic moiety.
8. The method of claim 1, wherein the SIFSIX-n-M composition comprises pyrazine or dipryridilacetylene ligands.
9. The method of claim 1, wherein the SIFSIX-n-M composition comprises a SIFSIX-3-Cu metal organic framework.
10. The method of claim 1, wherein the SIFSIX-n-M composition comprises a SIFSIX-3-Zn metal organic framework.
11. The method of claim 1, wherein the method further comprises desorbing CO_2 .
12. The method of claim 1, wherein the concentration of CO_2 in the fluid is less than 10%.
13. The method of claim 1, wherein sorbing comprises reducing the CO_2 concentration in the fluid to less than about 1%.

14. The method of claim 1, wherein sorbing occurs in a confined space.

15. The method of claim 1, wherein sorbing occurs in connection with one or more of an anesthetic system or an alkaline fuel cell.

16. The method of claim 1, wherein the fluid further comprises one or more of water, N₂, O₂, and H₂.

17. The method of claim 16, wherein sorbing CO₂ occurs selectively over one or more of water, N₂, O₂, and H₂.

18. The method of claim 17, wherein sorbing CO₂ occurs in the presence of humidity and selectivity for CO₂ is not affected.

19. The method of claim 1, wherein the fluid is breathing air.

20. The method of claim 1, wherein the CO₂ in the fluid has a partial pressure less than 100 mbar.

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