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(54) **METAL-ORGANIC MATERIALS (MOMS)
FOR CO₂ ABSORPTION AND METHODS OF
USING MOMS**

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B01J 20/22 (2006.01)
B01J 20/28 (2006.01)

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(58) **Field of Classification Search**
CPC B01D 2253/204; B01D 2256/10; B01D
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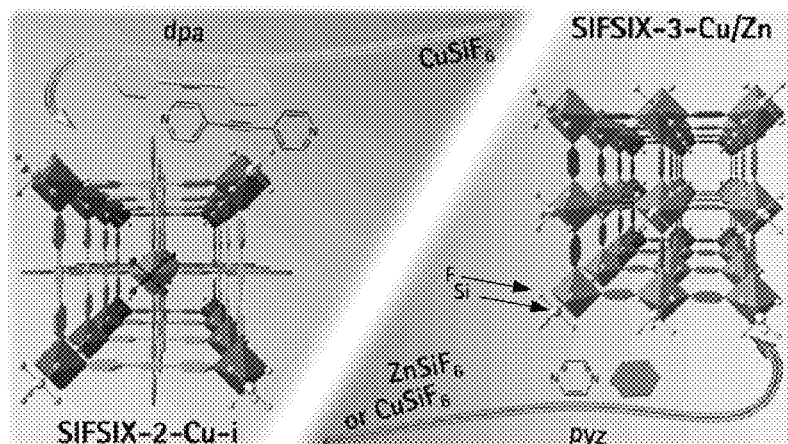
Primary Examiner — Christopher P Jones

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LLP

(57) **ABSTRACT**

Embodiments of the present disclosure provide for metal-
organic materials (MOMs), systems that exhibit permanent
porosity and using hydrophobic MOMs to separate compo-
nents in a gas, methods of separating CO₂ from a gas, and
the like.

8 Claims, 10 Drawing Sheets



Related U.S. Application Data

- continuation-in-part of application No. 13/800,690, filed on Mar. 13, 2013, now Pat. No. 9,138,719.
- (60) Provisional application No. 61/941,151, filed on Feb. 18, 2014, provisional application No. 61/682,017, filed on Aug. 10, 2012, provisional application No. 61/723,533, filed on Nov. 7, 2012.

(52) **U.S. CL.**

CPC *B01D 2253/204* (2013.01); *B01D 2256/10* (2013.01); *B01D 2256/16* (2013.01); *B01D 2256/245* (2013.01); *B01D 2257/504* (2013.01); *Y02C 10/08* (2013.01)

(58) **Field of Classification Search**

CPC .. *B01D 2257/504*; *B01D 53/02*; *B01J 20/226*; *B01J 20/28083*; *C07D 277/42*; *C07D 277/56*; *Y02C 10/08*

See application file for complete search history.

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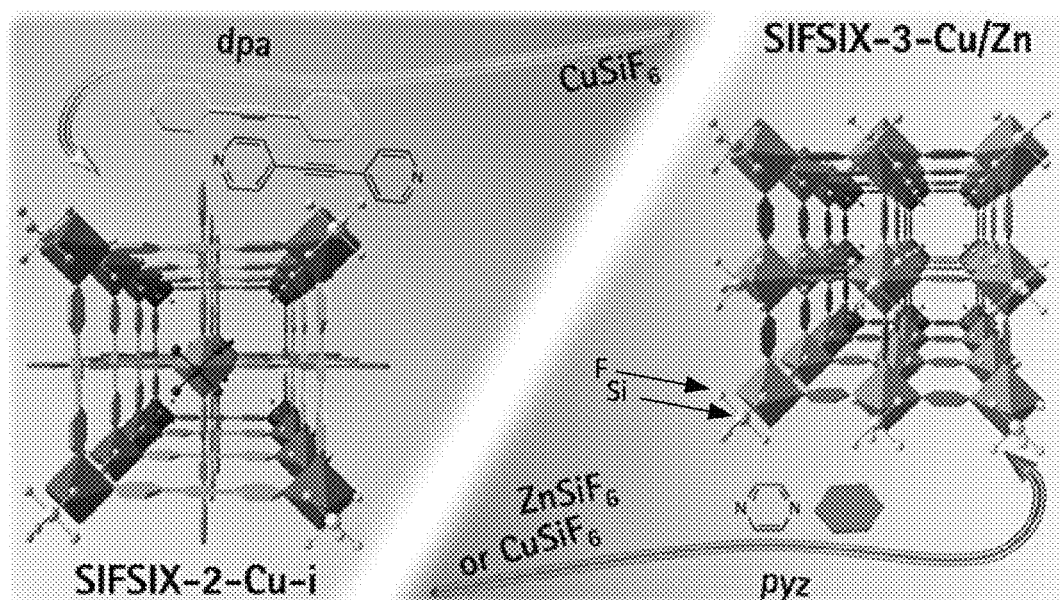


FIG. 1

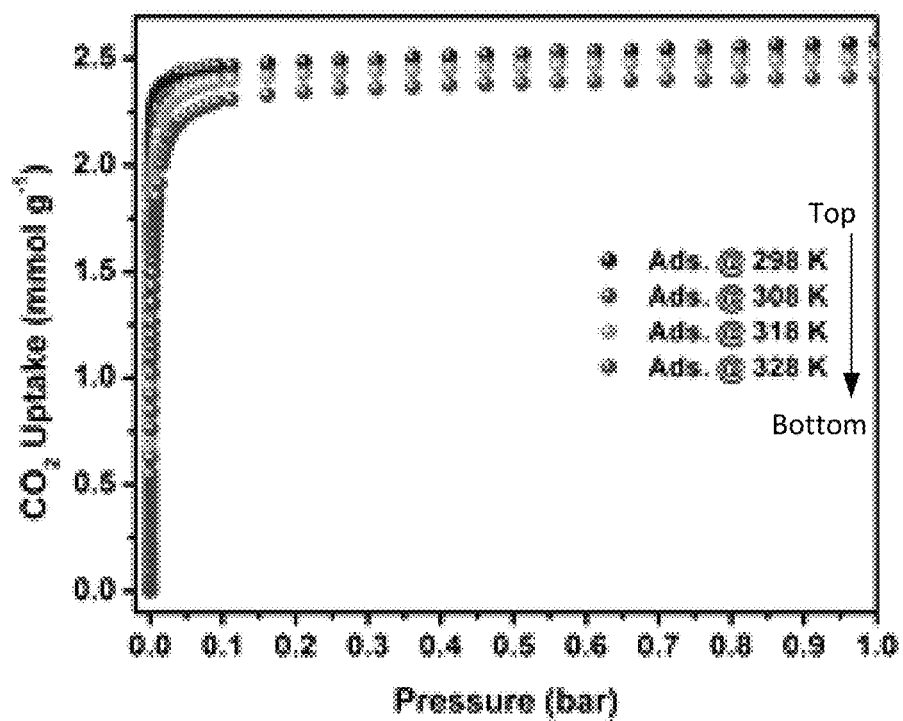


FIG. 2A

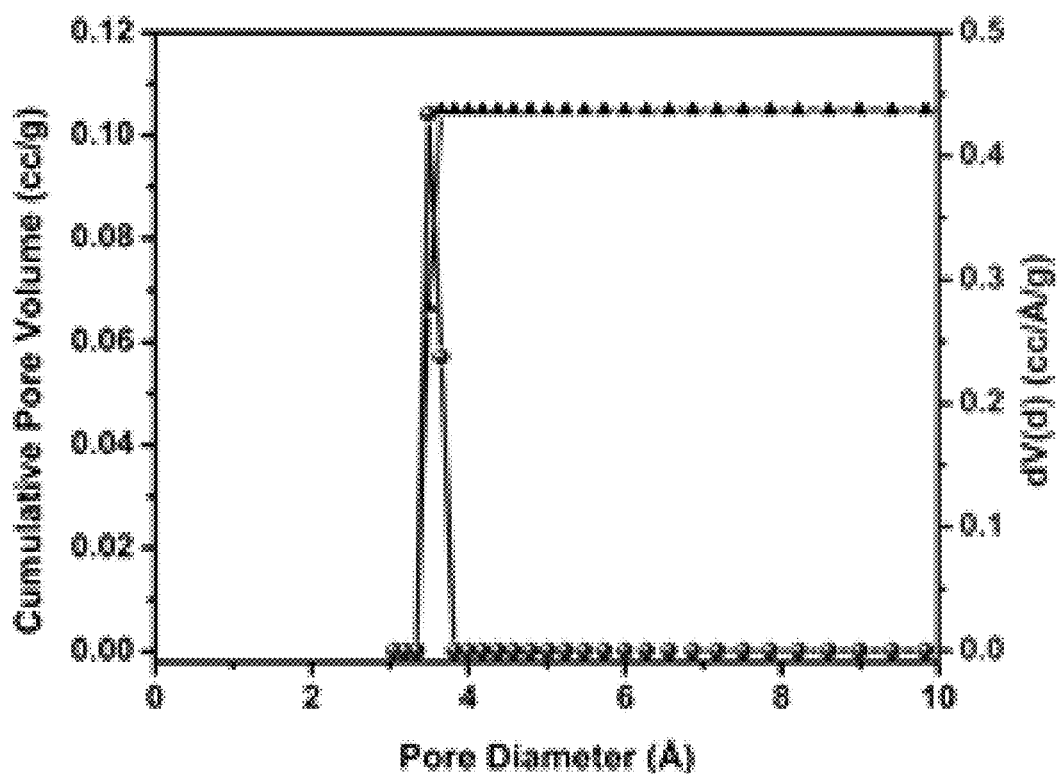


FIG. 2B

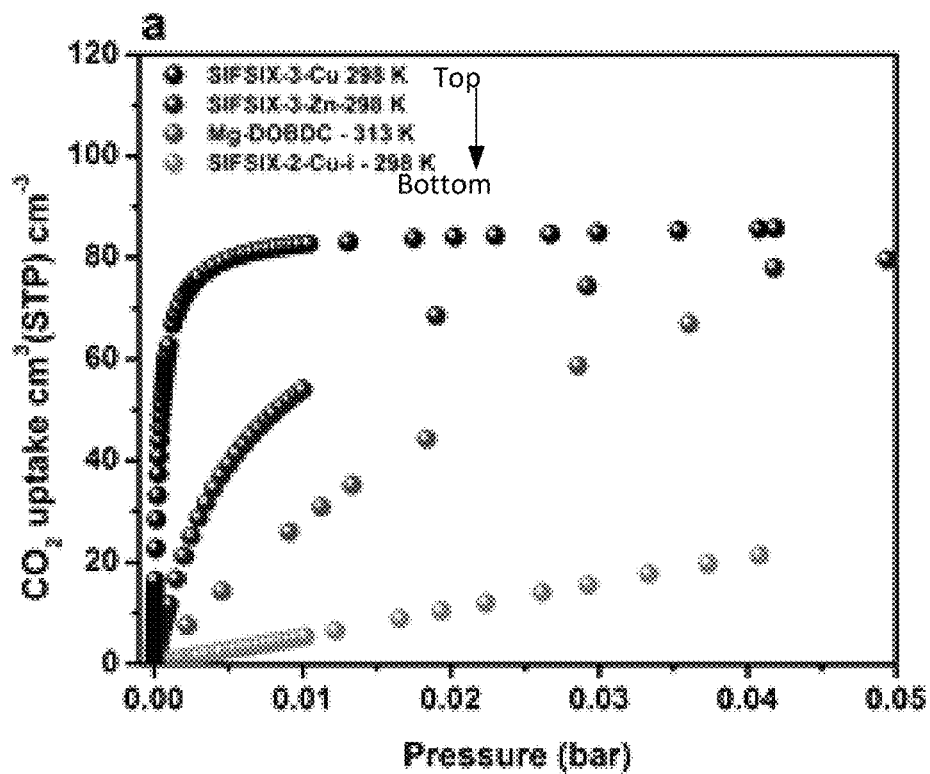


FIG. 3A

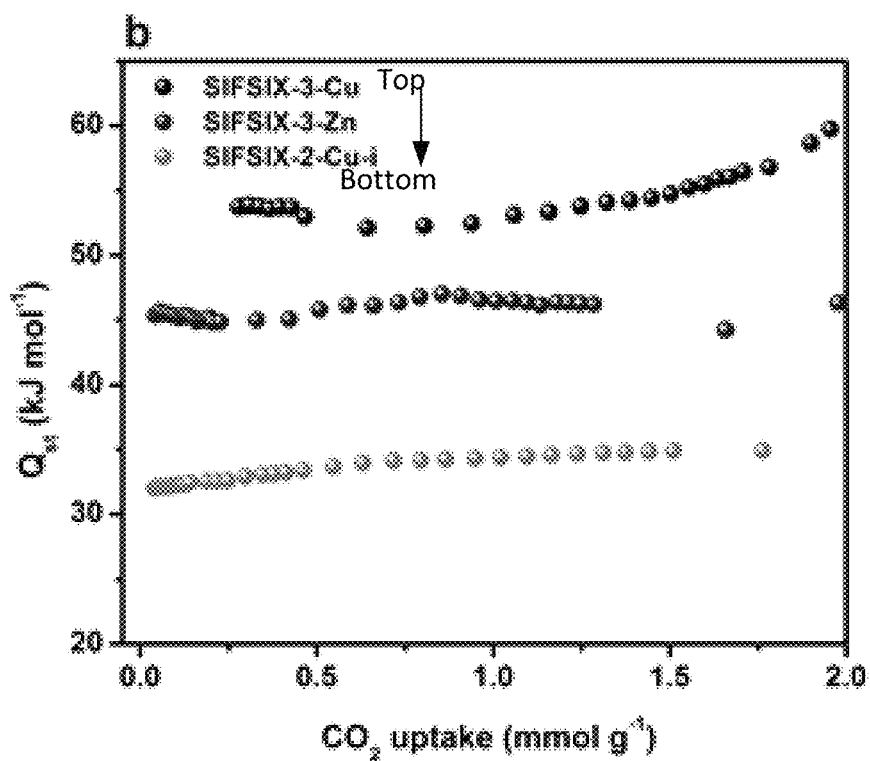


FIG. 3B

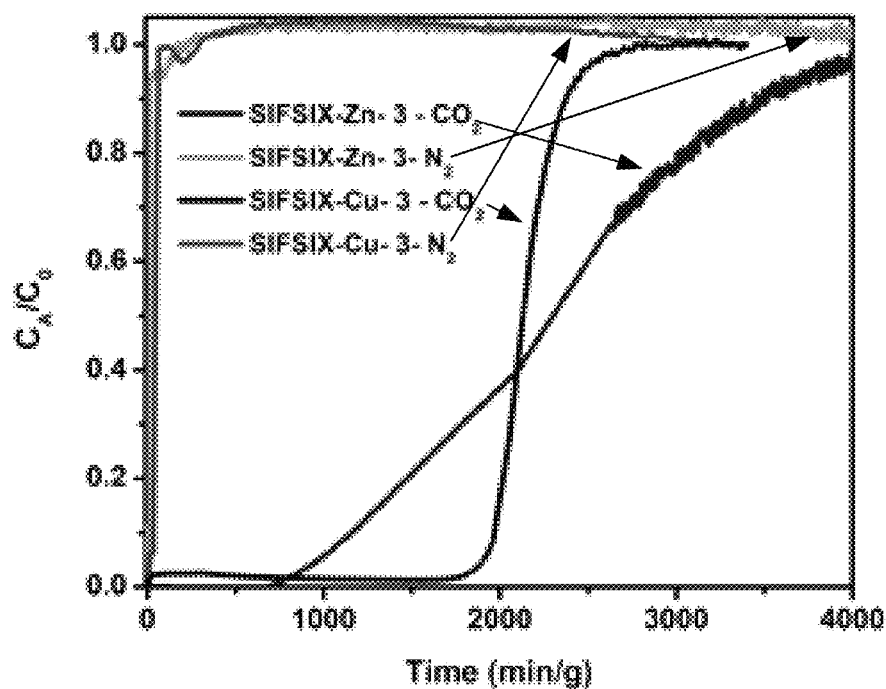


FIG. 4A

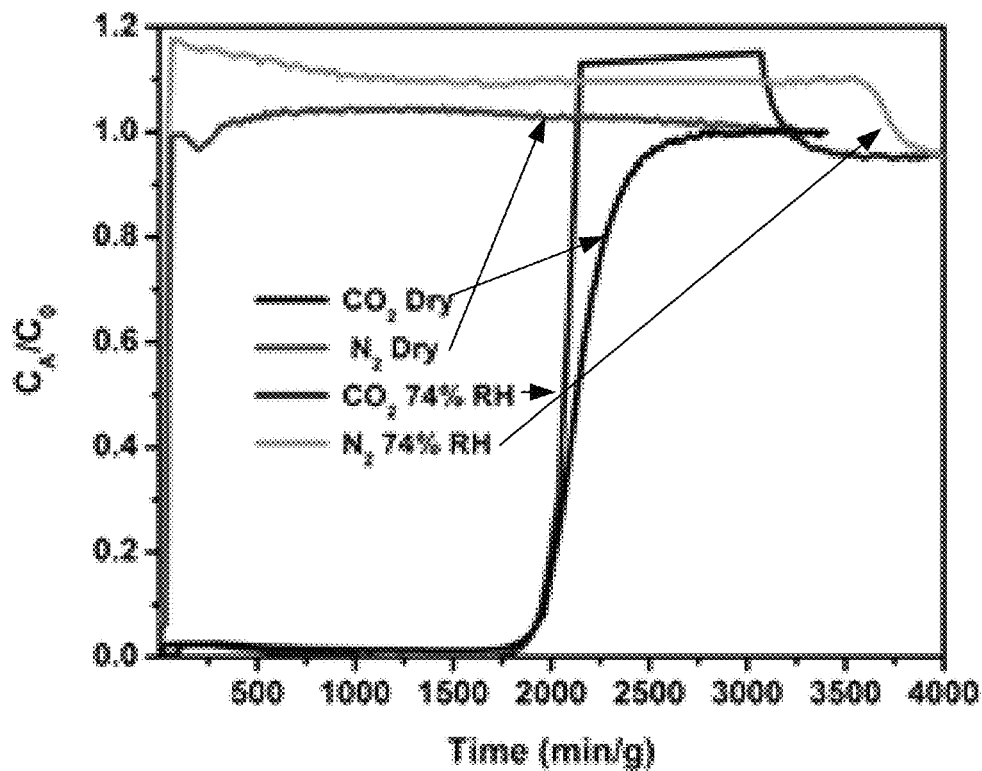


FIG. 4B

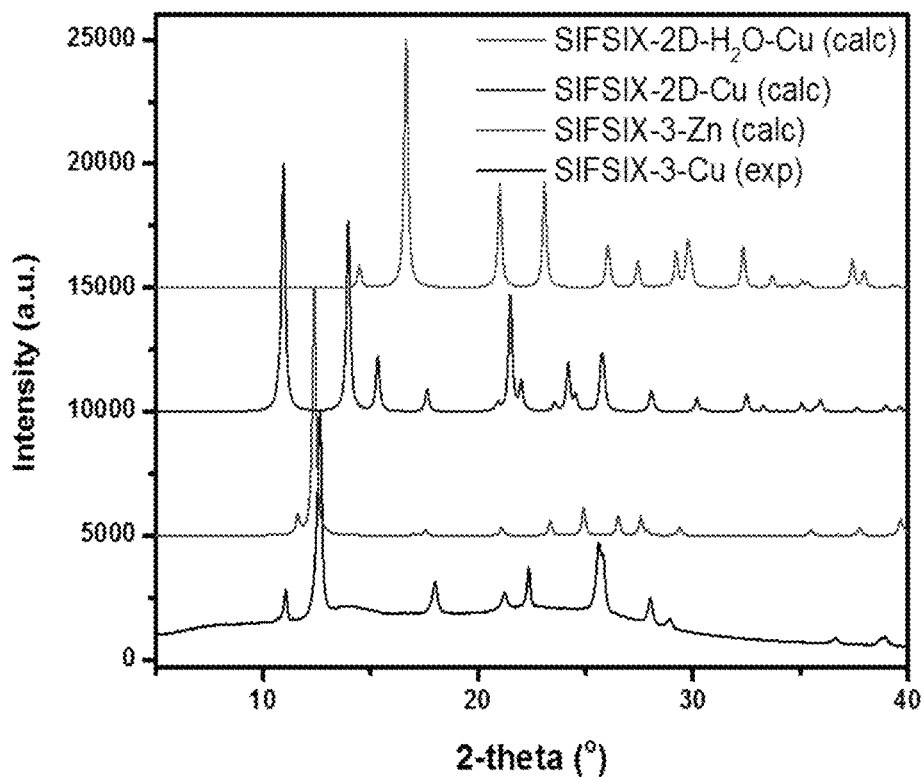


FIG. 5

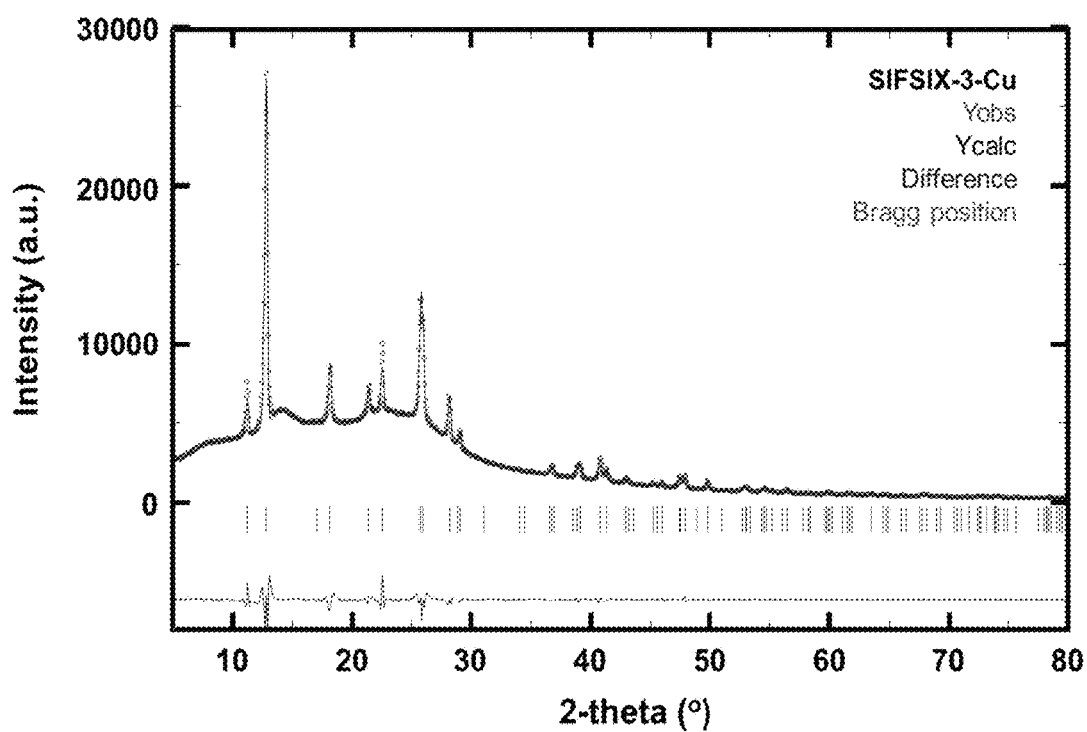


FIG. 6

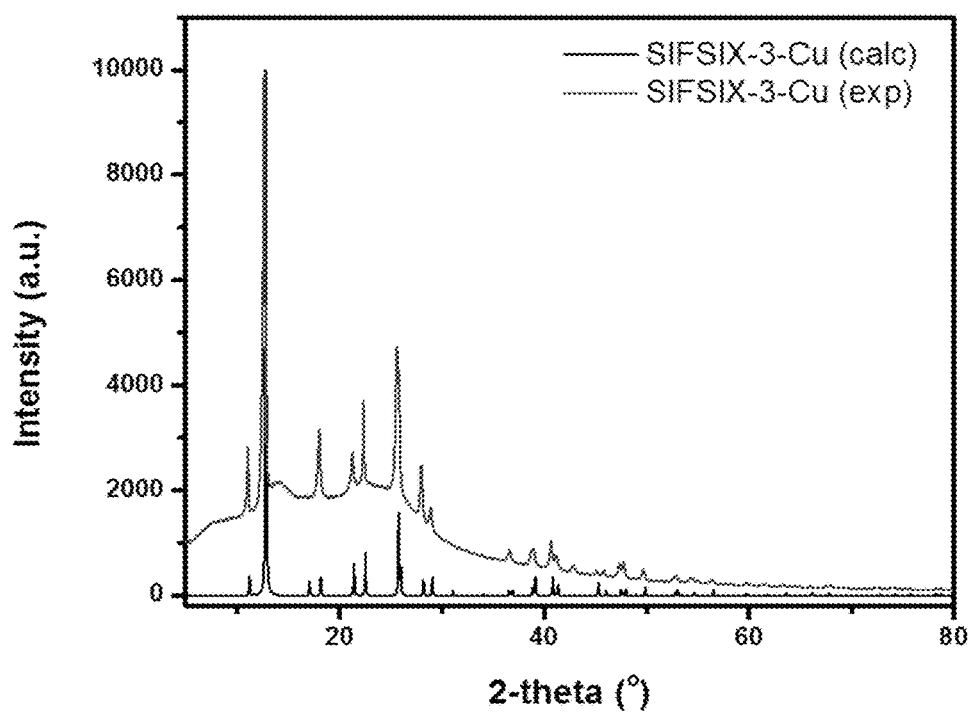


FIG. 7

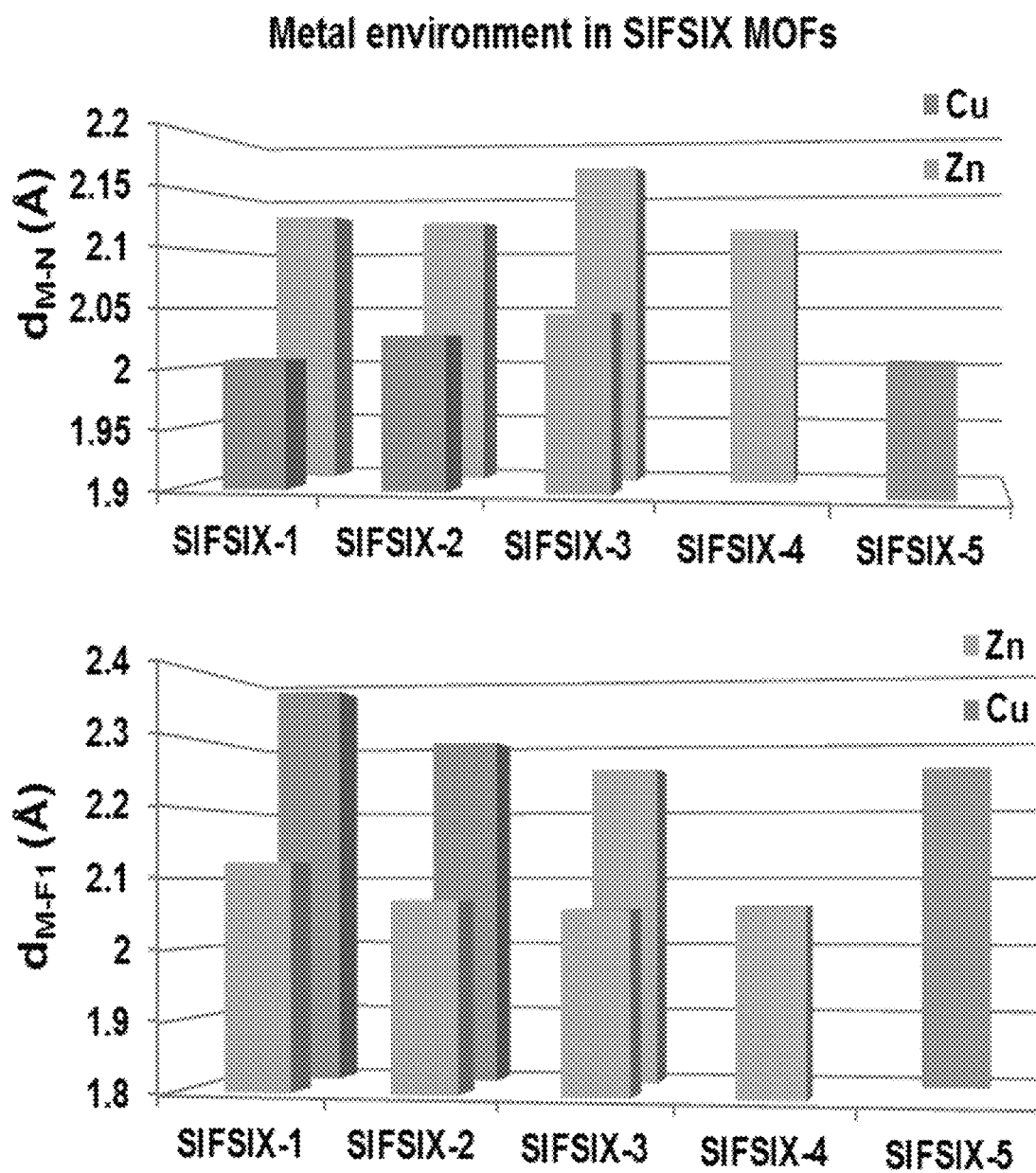


FIG. 8

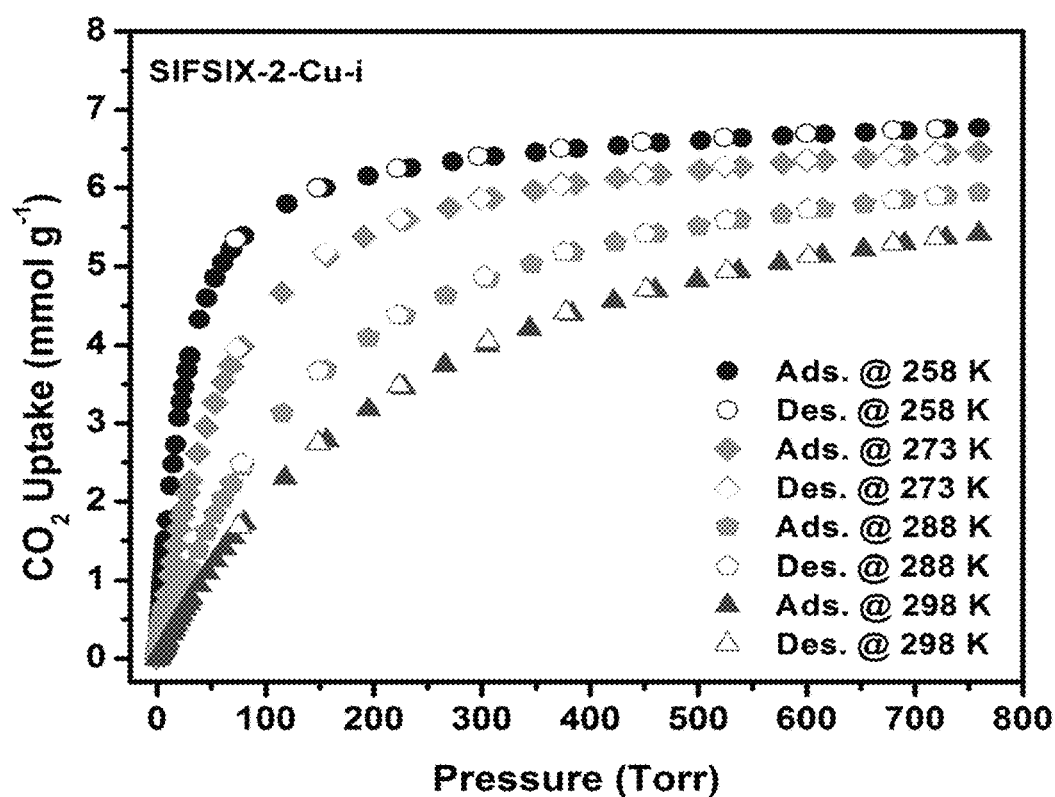


FIG. 9

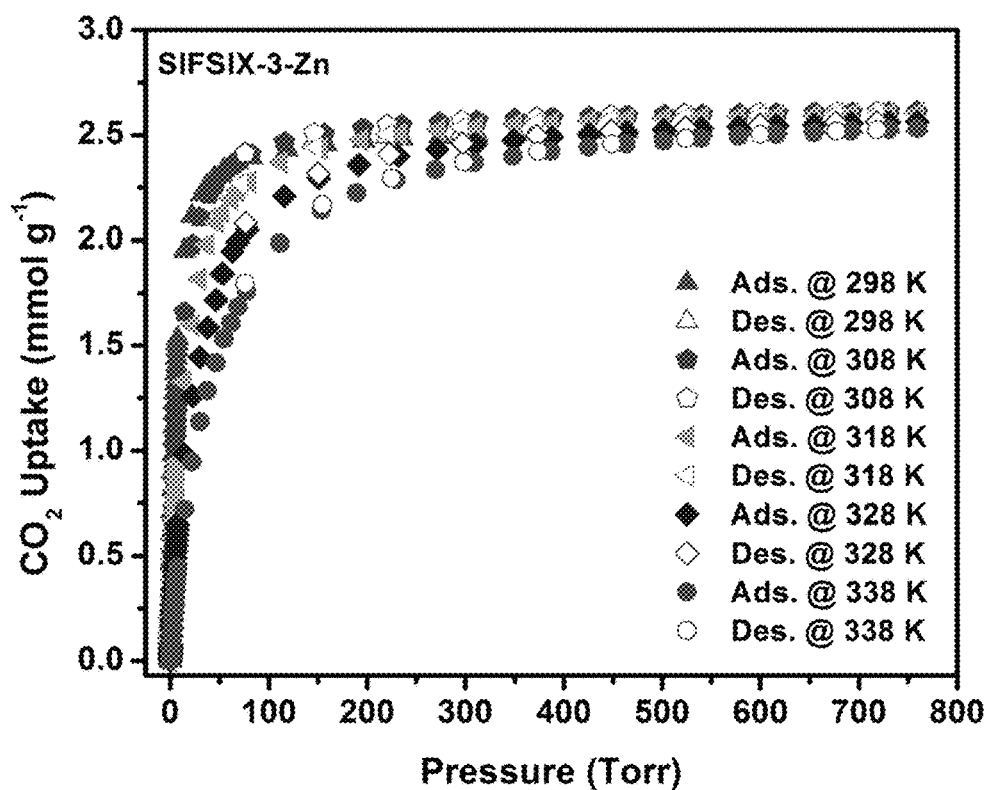


FIG. 10

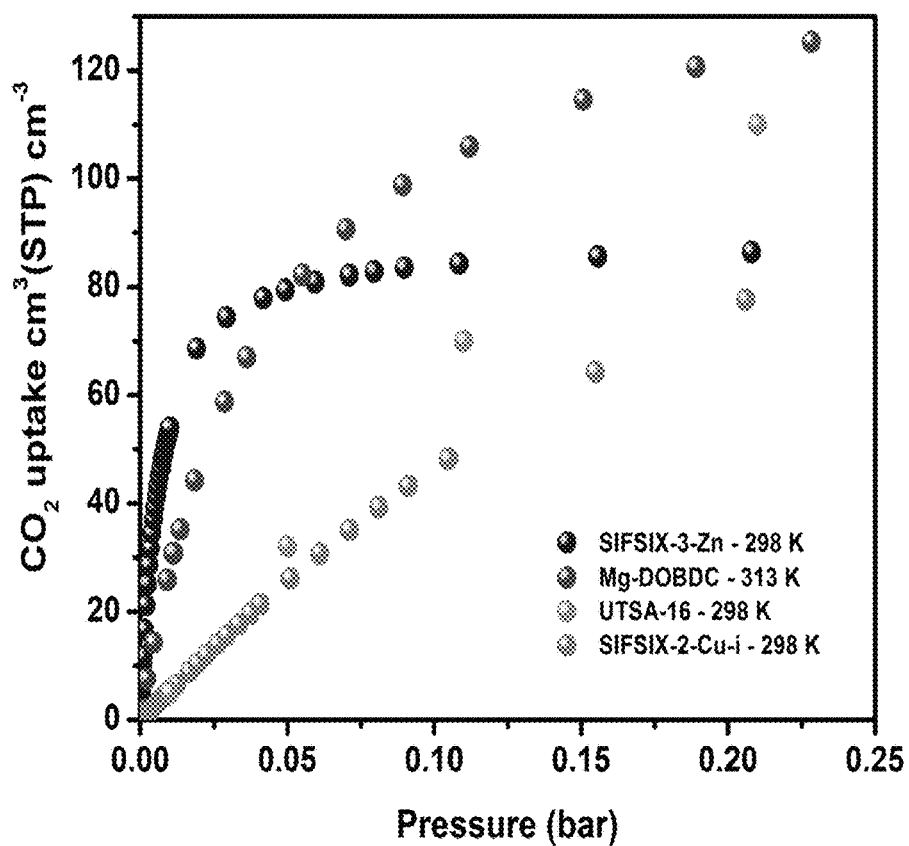


FIG. 11

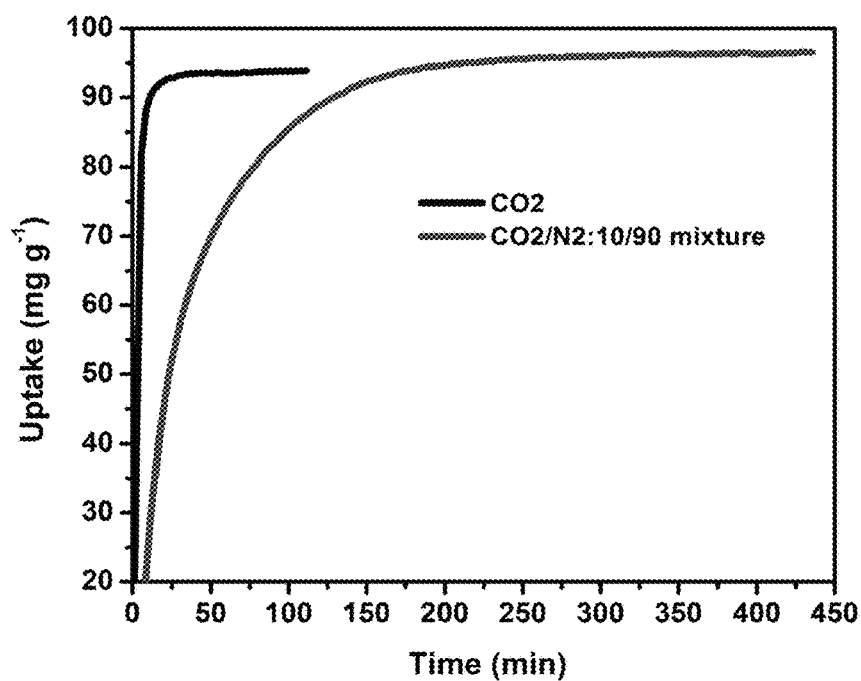


FIG. 12

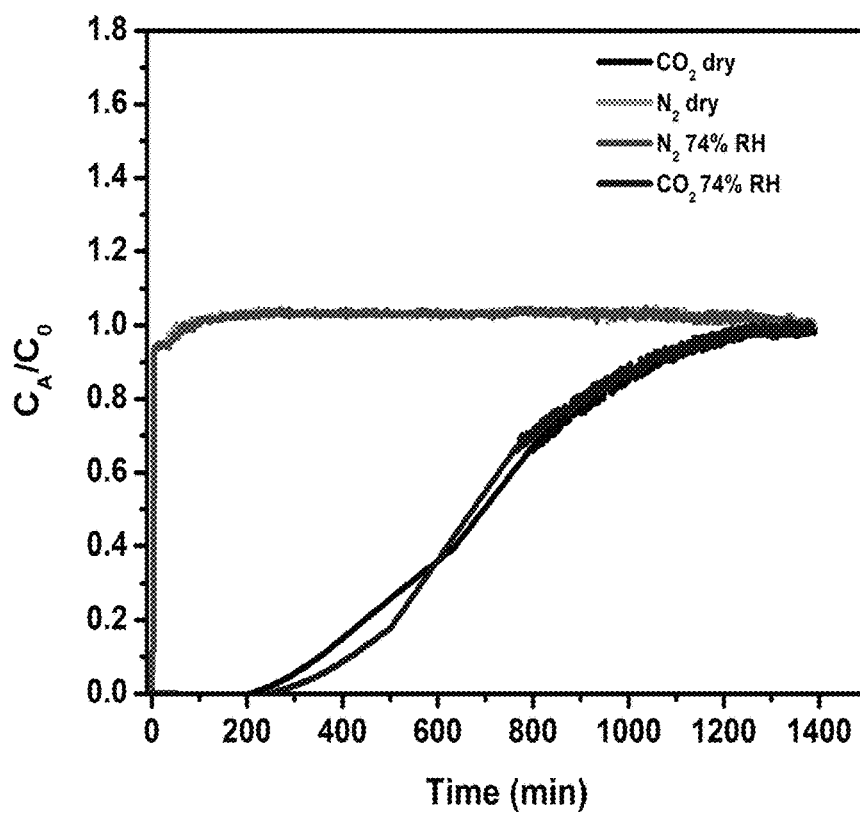


FIG. 13

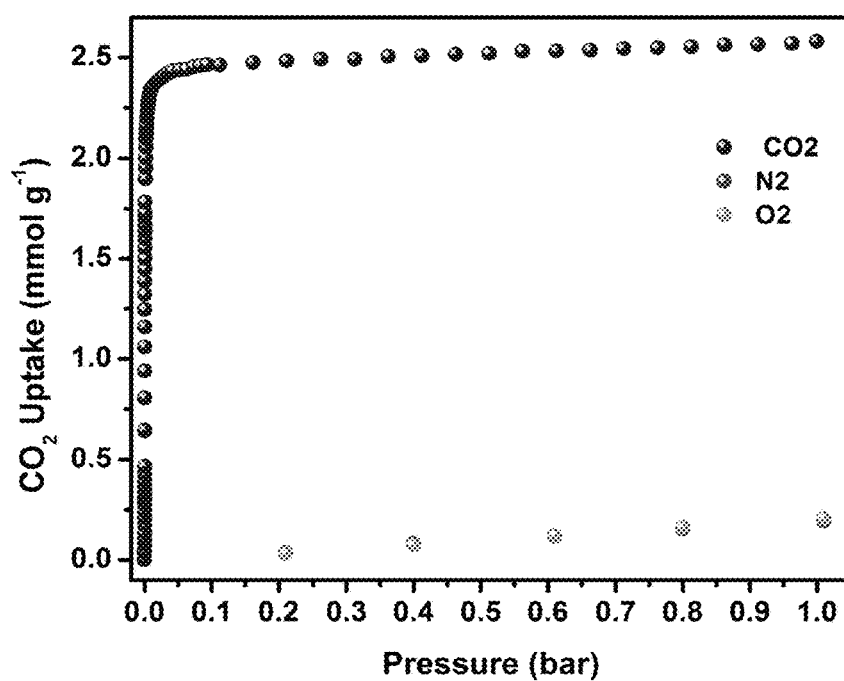


FIG. 14

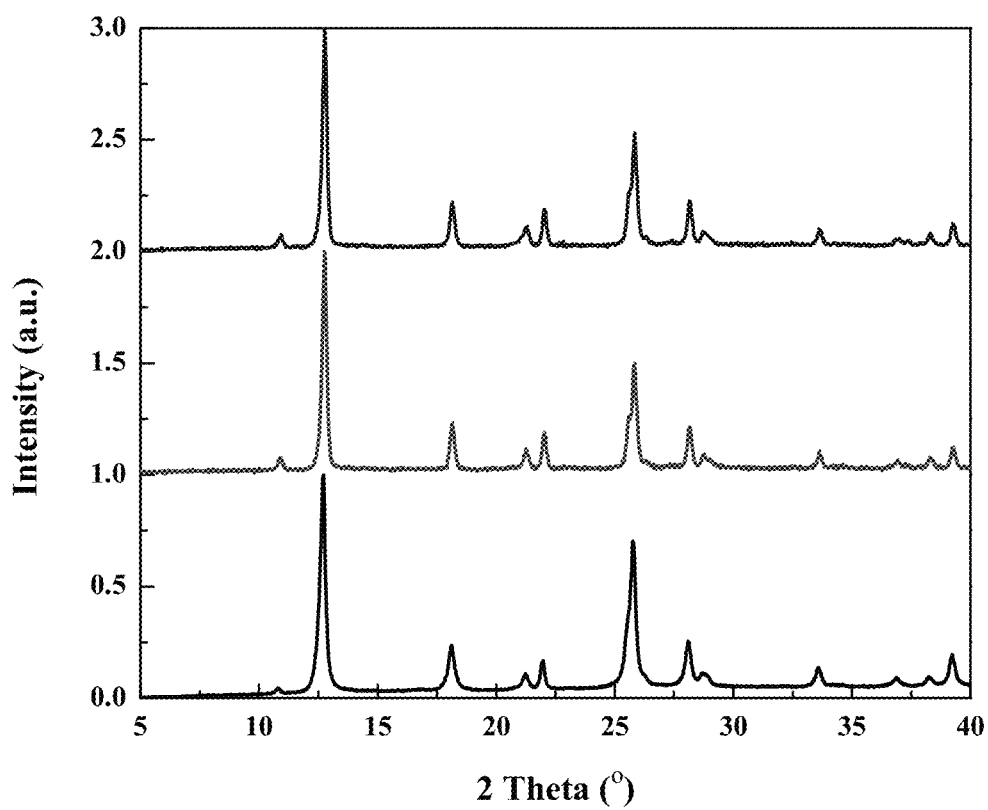


FIG. 15

METAL-ORGANIC MATERIALS (MOMS) FOR CO₂ ADSORPTION AND METHODS OF USING MOMS

CROSS-REFERENCE TO RELATED APPLICATION

This application is a divisional application and claims priority to U.S. Utility Application entitled "METAL-ORGANIC MATERIALS (MOMS) FOR CO₂ ADSORPTION AND METHODS OF USING MOMS" and having Ser. No. 14/624,763, filed on Feb. 18, 2015, now issued as U.S. Pat. No. 9,604,195, where U.S. Utility Application having Ser. No. 14/624,763 is a continuation in-part application of U.S. Utility Application entitled "METAL-ORGANIC MATERIALS (MOMS) FOR CO₂ ADSORPTION AND METHODS OF USING MOMS" and Ser. No. 13/800,690, filed Mar. 13, 2013, now U.S. Pat. No. 9,138,719; where the continuation-in-part having Ser. No. 13/800,690 claims priority to and the benefit of U.S. Provisional Application entitled "METAL ORGANIC COMPOSITION, FOR CARBON DIOXIDE SEPARATION AND CAPTURE," having Ser. No. 61/682,017, filed on Aug. 10, 2012, and also claims priority to U.S. provisional application entitled "METAL ORGANIC COMPOSITION, FOR CARBON DIOXIDE SEPARATION AND CAPTURE," having Ser. No. 61/723,533, filed on Nov. 7, 2012, each of which are entirely incorporated herein by reference.

U.S. Utility Application entitled "METAL-ORGANIC MATERIALS (MOMS) FOR CO₂ ADSORPTION AND METHODS OF USING MOMS" and having Ser. No. 14/624,763, filed on Feb. 18, 2015 also claims priority to U.S. provisional application entitled "AIR CAPTURE, TRACES AND LOW CONCENTRATION CO₂ REMOVAL IN CONFINED SPACES AND CLOSED BREATHING LOOPS USING PHYSICAL ABSORBENTS FROM THE CLASS METAL ORGANIC FRAMEWORK (MOFS)," having Ser. No. 61/941,151, filed on Feb. 18, 2014, which is entirely incorporated herein by reference.

BACKGROUND

Metal-organic framework (MOF) materials that exhibit permanent porosity have received extensive interest due to their potential applications for gas storage or capture. However, many of the currently used MOFs have limitations, and thus, other types of MOFs having desired characteristics are needed to be used in certain applications.

SUMMARY

Embodiments of the present disclosure provide for metal-organic materials (MOMS), systems using MOMs to separate components in a gas, methods of separating CO₂ from a gas, and the like.

An embodiment of the method of capturing CO₂ in a gas, among others, includes: exposing the gas to a metal-organic material (MOM), wherein the gas includes CO₂ at a concentration in the gas of about 5% or less; and capturing the CO₂ in the MOM.

An embodiment of the system for capturing CO₂ in a gas mixture, among others, includes: a first structure including a metal-organic material (MOM), wherein the gas includes CO₂ at a concentration in the gas of about 5% or less; and a second structure for introducing the gas to the first structure, wherein CO₂ is removed from the gas after the expo-

sure to the MOM to form a modified gas (CO₂ free), wherein the second structure flows the modified gas away from the first structure.

An embodiment of the method of separating components in a gas mixture, among others, includes: exposing a gas including a CO₂ and a second component to a metal-organic material (MOM), wherein the MOM has a greater relative affinity (kinetic and thermodynamic) for the CO₂ over a second component, wherein the CO₂ is at a concentration in the gas of about 5% or less; and capturing the first component in the MOM.

An embodiment of the system for separating components in a gas, among others, includes: a first structure including a metal-organic material (MOM), wherein the gas includes CO₂ and a second component, wherein the MOM has a greater relative affinity for CO₂ over the second component, wherein the CO₂ is at a concentration in the gas of about 5% or less; and a second structure for introducing the gas to the first structure, wherein CO₂ is removed from the gas after the exposure to the MOM to form a modified gas, wherein the second structure flows the modified gas away from the first structure.

An embodiment of the composition, among others, includes: a MOM comprising [Cu(pyr)₂(SiF₆)_n], wherein n is 1 to 100,000,000, and wherein the MOM has a pore size of about 3.5 Å.

BRIEF DESCRIPTION OF THE DRAWINGS

Many aspects of the disclosed devices and methods can be better understood with reference to the following drawings. The components in the drawings are not necessarily to scale, emphasis instead being placed upon clearly illustrating the relevant principles. Moreover, in the drawings, like reference numerals designate corresponding parts throughout the several views.

FIG. 1 is a schematic that illustrates the ability of pore size tuning in the channel structures of SIFSIX-2-Cu-i, SIFSIX-3-Zn or/and SIFSIX-3-Cu. In particular, a) SIFSIX-2-Cu-i; pores size 5.15 Å, BET apparent surface area (N₂ adsorption) 735 m² g⁻¹; b) SIFSIX-3-Zn; pores size 3.84 Å, BET apparent surface area (determined from CO₂ adsorption isotherm) 250 m² g⁻¹; and c) SIFSIX-3-Cu; pores size 3.3.5 Å, BET apparent surface area (determined from CO₂ adsorption isotherm) 300 m² g⁻¹. Color code: Dipyrilidacetylene (dpa, thick light grey polyhedral), pyrazine (pyz, medium grey polyhedral), Zn, Cu (darker grey polyhedral), Si (light grey spheres), F (light grey spheres). All guest molecules are omitted for clarity. Note that the grey net represents the interpenetrated net in SIFSIX-Cu-2-i.

FIG. 2A illustrates the variable temperature adsorption isotherms of CO₂ for SIFSIX-Cu-3). FIG. 2B illustrates the pore size distribution from CO₂ sorption isotherms at 77 K for SIFSIX-Cu-3.

FIG. 3A illustrates the CO₂ volumetric uptake on SIFSIX-Cu-3, SIFSIX-Zn-3 and SIFSIX-Cu-2-i as compared to Mg-MOF-74. FIG. 3B illustrates the isosteric heats of adsorption at low coverage for SIFSIX-Cu-3, SIFSIX-Zn-3 and SIFSIX-Cu-2-i.

FIG. 4A illustrates the column breakthrough test of CO₂/N₂:1000 ppm/99.99% for SIFSIX-Cu-3, SIFSIX-Zn-3 in dry condition. FIG. 4B illustrates the column breakthrough test of CO₂/N₂:1000 ppm/99.99% for SIFSIX-Cu-3 in dry as well as at 74% RH.

FIG. 5 illustrates a comparison of PXRD diagrams of SIFSIX-3-Cu with other SIFSIX-pyz MOFs (λ_{Cu} =1.5406 nm).

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FIG. 6 illustrates a Lebail fit for SIFSIX-3-Cu ($\lambda_{Cu}=1.5406$ nm).

FIG. 7 illustrates a comparison of calculated and experimental PXRD diagrams for SIFSIX-3-Cu ($\lambda_{Cu}=1.5406$ nm).

FIG. 8 illustrates a comparison of the metal environment in SIF SIX based MOFs through the metal-nitrogen (top) and metal-fluorine (bottom) distances.

FIG. 9 illustrates variable temperature adsorption isotherms for SIFSIX-2-Cu-i.

FIG. 10 illustrates variable temperature adsorption isotherms for SIFSIX-3-Zn.

FIG. 11 illustrates a CO₂ adsorption isotherms at very low pressures up to 0.25 bar (250 mbar) for SIFSIX-Cu-3, SIFSIX-Zn-3 and SIFSIX-Cu-2-i as compared to Mg-MOF-74 [*J. Am. Chem. Soc.* 130, 10870-10871 (2008)] and UTSA-16 [*Nat. Commun.* 3:954 doi: 10.1038/ncomms1956 (2012)].

FIG. 12 illustrates competitive adsorption kinetics of CO₂/N₂:10/90 gas mixture as compared to the kinetics of adsorption of pure CO₂ at 1 bar and 298 K.

FIG. 13 illustrates a column breakthrough test of CO₂/N₂:1000 ppm/99.99% for SIFSIX-Zn-3 in dry as well as at 74% RH.

FIG. 14 illustrates adsorption isotherms of CO₂, N₂ and O₂ on Sif6-3-cu at 298 K.

FIG. 15 illustrates a comparison of experimental PXRD diagrams for SIFSIX-3-Cu ($\lambda_{Cu}=1.5406$ nm) as prepared (bottom curve), after high pressure experiments and exposed to air (middle curve) and after break-through experiments under dry and humid conditions (top curve).

DISCUSSION

Before the present disclosure is described in greater detail, it is to be understood that this disclosure is not limited to particular embodiments described, as such may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting, since the scope of the present disclosure will be limited only by the appended claims.

Where a range of values is provided, it is understood that each intervening value, to the tenth of the unit of the lower limit (unless the context clearly dictates otherwise), between the upper and lower limit of that range, and any other stated or intervening value in that stated range, is encompassed within the disclosure. The upper and lower limits of these smaller ranges may independently be included in the smaller ranges and are also encompassed within the disclosure, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included in the disclosure.

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure belongs. Although any methods and materials similar or equivalent to those described herein can also be used in the practice or testing of the present disclosure, the preferred methods and materials are now described.

As will be apparent to those of skill in the art upon reading this disclosure, each of the individual embodiments described and illustrated herein has discrete components and features which may be readily separated from or combined with the features of any of the other several embodiments without departing from the scope or spirit of the present

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disclosure. Any recited method can be carried out in the order of events recited or in any other order that is logically possible.

Embodiments of the present disclosure will employ, unless otherwise indicated, techniques of chemistry, organic chemistry, organometallic chemistry, coordination chemistry and the like, which are within the skill of the art. Such techniques are explained fully in the literature.

The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how to perform the methods and use the compositions and compounds disclosed and claimed herein. Efforts have been made to ensure accuracy with respect to numbers (e.g., amounts, temperature, etc.), but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight, temperature is in ° C., and pressure is at or near atmospheric. Standard temperature and pressure are defined as 25° C. and 1 atmosphere.

Before the embodiments of the present disclosure are described in detail, it is to be understood that, unless otherwise indicated, the present disclosure is not limited to particular materials, reagents, reaction materials, manufacturing processes, or the like, as such can vary. It is also to be understood that the terminology used herein is for purposes of describing particular embodiments only, and is not intended to be limiting. It is also possible in the present disclosure that steps can be executed in different sequence where this is logically possible.

It must be noted that, as used in the specification and the appended claims, the singular forms “a,” “an,” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a support” includes a plurality of supports. In this specification and in the claims that follow, reference will be made to a number of terms that shall be defined to have the following meanings unless a contrary intention is apparent.

General Discussion:

Embodiments of the present disclosure provide for metal-organic materials (MOMs), systems using MOMs to separate components in a gas, methods of separating CO₂ from a gas, and the like. In an embodiment, the MOM can be used to remove or separate CO₂ in a gas at a variety of concentrations. In a particular embodiment, the MOM can be used to remove or separate trace levels of CO₂ in a gas (e.g., CO₂ at a concentration of about 5% or less in a gas) with high specificity and removal capacity, which can be advantageous in a number of industries.

The growing interest in combating the greenhouse gas effect triggered a rising interest in the Direct Air Capture (CAD) as a viable option to reduce greenhouse gases emissions in uniform way. Although more challenging than post-combustion capture, embodiments of the present disclosure can be used in CAD since embodiments of the MOM have suitable uptake, kinetics, energetics and CO₂ selectivity, which enables removal or separation of trace levels of CO₂ concentration.

Removal of trace amounts of CO₂ from air for industrial purposes is important particularly for pre-purification of air when atmospheric air is used during the separation of nitrogen and oxygen. In a particular system, 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 due to frozen CO₂ during the liquefaction process and (ii) adsorbents (e.g., zeolites) contamination used for oxygen production by PSA. MOMs of the present disclosure can be used to remove CO₂ for air separation using cryogenic distillation or PSA.

In another application, alkaline Fuel Cells (AFCs) require the oxygen and hydrogen used as feedstock to be CO₂ free as trace amounts of CO₂ (300 ppm) degrade the electrolyte in AFCs. In this regard, MOMs of the present disclosure can be used in AFCs to remove CO₂.

Efficient removal of CO₂ at low concentrations is also vital for the proper operation of breathing systems in confined spaces such as submarines, planes, aerospace shuttles, and the like. In particular, in long-term space flight and submarine missions, CO₂ must be removed from the air and recycled because resupply opportunities are less frequent or non-existent. Humans require oxygen, and in return emit carbon dioxide. An average crew member requires approximately 0.84 kg of oxygen and emits approximately 1 kg of carbon dioxide. As a result, the ability to continuously purify the exhaled air (with a CO₂ concentration of 5% or less) can lead to an optimal recycling and considerable reduction in fresh air supply in closed, confined spaces such as space shuttles, planes and submarines. In this regard, embodiments of the MOMs can be used in breathing systems to manage CO₂ concentration.

Efficient CO₂ removal is also of importance in mining and rescue missions and diving. Thus, embodiments of the MOMs can be used to manage CO₂ concentration.

CO₂ removal is also a concern in medical applications such as anesthesia machines. The use of anesthesia machines is a growing clinical trend throughout the world, driven by the need to reduce cost and improve patient care. CO₂ removal in anesthesia machines is particularly important in semi- or closed rebreathing systems in which the rebreathing fraction is at least 50% of the exhaled gas volume is directed back to the patient after proper carbon dioxide removal in the next exhalation. Current solutions are costly, have limited recyclability, and have large disposal costs associated with them, while MOMs of the present disclosure can be used to remove and manage CO₂ concentration levels in anesthesia machines and in some situations can have a lifetime that is 10,000 times greater than current standards.

In an embodiment, the MOM can be porous and can be a three dimensional net so that molecules can be disposed (e.g., captured) within (e.g., pores or cavities) the MOM to the exclusion of other molecules. In an embodiment, the MOM combines sorption thermodynamics and kinetics to achieve advantageous results. Embodiments of the present disclosure describe MOMs that have no unsaturated metal centers and the pore walls have no hydrogen bonding donors or acceptors, while having strong electrostatics for inducing dipoles in polarizable molecules such as CO₂. For example, a gas such as CO₂ is absorbed faster and stronger than other gases in the gas mixture, so that CO₂ can be captured in the MOMs to the substantial exclusion of the other gases. In particular, the MOM can be used to remove or separate CO₂ in a gas, where the gas includes CO₂ at a concentration of about 5% or less. In an embodiment of the present disclosure have enhanced CO₂ interactions at the same time have reduced interactions with water vapor.

In an embodiment, the MOM can be a hydrophobic MOM. In an embodiment, the hydrophobic MOM can be used to separate CO₂ from one or more other gases, where the gas includes water vapor. Due to its hydrophobic characteristic, hydrophobic MOMs can be used in methods and systems that use gases that include water vapor, which was not previously possible in porous materials that exhibit strong physisorption towards CO₂. This is advantageous because other systems and methods that use other MOMs or other porous materials must separate water vapor from the gas prior to the gas being introduced to the other MOMs or

porous materials since the other MOMs or porous materials have a higher affinity for the water vapor than CO₂. If the water vapor is not removed, the other MOMs are not effective at removing CO₂. In addition, MOMs of the present disclosure can remove trace levels of CO₂. Embodiments of the systems and methods can be simplified and result in reduced expenditure since the water vapor does not have to be removed prior to introduction to the hydrophobic MOMs. Even in the presence of water vapor, hydrophobic MOMs used in embodiments of the present disclosure are still effective at removing CO₂ and are highly selective in separating CO₂ from other gases such as N₂, H₂, and/or CH₄, even at trace levels of CO₂.

In particular, embodiments of the present disclosure can be used in CO₂ capture systems where the gas has trace levels of CO₂, and these can include direct air capture systems, pre-purification systems (e.g., PSA and cryogenic distillation), AFCs, breathing systems, mining and rescue missions, diving, and in medical applications. In addition, embodiments of the present disclosure can be used in post-combustion systems (e.g., flue gas to separate CO₂ and N₂), pre-combustion systems (e.g., shifted synthesis gas stream to separate CO₂ and H₂), and/or natural gas upgrading (e.g., natural gas cleanup to separate CO₂ and CH₄). In an embodiment, the hydrophobic MOMs can be used to separate other gases and can be used in processes such as He separation from natural gas, Ar separation, Kr separation, and H₂/D₂ separation.

Embodiments of the present disclosure provide for MOMs that are three dimensional nets that have a primitive cubic topology (See FIG. 1) that can be used in methods and systems of the present disclosure. In an embodiment, the MOM (e.g., [Cu(pyr)₂(SiF₆)]_n) can be designed and synthesized using two dimensional square grids (or nets) (e.g., Cu (4,4'-dipyridylacetylene)₂) that are linked via metal nodes using a pillar (e.g., SiF₆²⁻). In an embodiment, the two dimensional square grids include metal cations, metal cluster molecular building blocks (MBBs), or metal-organic polyhedral supermolecular building blocks (SBBs). The MBBs or SBBs serve the geometric role of the node in a network and they are connected by organic molecules, inorganic anions and/or metal complexes, which serve as linkers. The two dimensional square grids are connected to one another using other linkers or pillars that connect the metal nodes. In an embodiment, the components of the MOM (the two dimensional square grids, and its components, and pillars) can be selected to design a MOM that can be used in a system or method that includes trace levels of CO₂ and/or water vapor and is highly effective at separating gases due to the MOM having a higher relative affinity for one component of the gas (e.g., CO₂) over one or more other components (e.g., N₂, H₂, and CH₄) in the gas. In this way not only is the MOM able to operate in methods and systems having high water vapor conditions, but the MOM is highly selective between or among CO₂ and other components, even where the CO₂ concentration is at trace levels.

In an embodiment, a method of the present disclosure includes exposing a gas to a MOM (e.g., [Cu(pyr)₂(SiF₆)]_n). As noted above, the MOM has a greater relative affinity for a first component (e.g., trace levels of CO₂) of the gas over a second component of the gas. The phrase "greater relative affinity" or similar phrases mean that a MOM can interact with a first component much more strongly than a second component so that the MOM and the first component interact to the substantial exclusion of the second component. Thus, the first component can be captured (e.g., separated) from the gas mixture to form a modified gas,

where the modified gas includes the second component and a substantially reduced amount (e.g., greater than about 80% or more, about 90% or more, about 95% or more, about 99% or more, about 99.9% or more, removal of the first component from the gas) of the first component.

In an embodiment, the selectivity for CO₂/N₂ can be about 100 or more, about 500 or more, about 1000 or more, or about 2000 or more, based on column breakthrough experiments and at conditions of 25° C. and 1 bar total pressure using gas stream with CO₂ in the range 400 ppm to 50%. The column breakthrough tests were run by passing the non-treated gas stream through a column containing the MOFs. The gas downstream the column is monitored by a gas analyzer to determine the change in composition of each gas.

In an embodiment, the MOM has a removal capacity of about 1.2-2 mmol/g (44-71 cm³ (STP)/cm³) at 400 ppm or about 2.2-2.5 mmol/g (80-88 cm³ (STP)/cm³) at 5000 ppm.

In an embodiment, the system for capturing CO₂ in a gas mixture can include pressure (vacuum) swing adsorption, temperature swing adsorption, and combination thereof. In an embodiment, the method of separating components in a gas mixture can include removal of high CO₂ concentrations, removal of intermediate CO₂ concentrations, and very low CO₂ concentration. In an embodiment, the method of capturing CO₂ in a gas can include bulk CO₂ separation (50% CO₂>), CO₂ purification (<5%) and CO₂ ultra-purification (<1%).

As described herein, a substantial advantage of some embodiments of the present disclosure is that methods and systems using the MOMs can be conducted using a gas having water vapor, which is a completely unexpected result since most of other MOMs and related inorganic porous materials are typically hydrophilic and have a strong affinity for water so that the water vapor needs to be substantially or completely removed from the gas for the MOM to be commercially viable. In an embodiment, the water vapor in the gas can be at a concentration of about 1% to 10% at a temperature of about 273K to 340K.

In an embodiment, the gas can include two or more components and can include water vapor. In an embodiment, gas does not include water vapor. It should be noted that in many situations, the gas may primarily include a few components or only a few components that are important to the desired separation. In an embodiment, the component can include one or more of the following: CO₂ (e.g., trace levels), N₂, H₂, CH₄, He, hydrocarbons having 2 or more carbons (saturated or unsaturated and/or linear or branched), and a combination thereof. In an embodiment, CO₂ can be in the gas in an amount of about 400 ppm to 50% or in an amount of about 5% or less. In an embodiment, N₂ can be in the gas in an amount of about 50% to 99.99%. In an embodiment, H₂ can be in the gas in an amount of about 50% to 99.99%. In an embodiment, CH₄ can be in the gas in an amount of about 50% to 99.99%. In an embodiment, He can be in the gas in an amount of about 50% to 99.99%.

In an embodiment, the components in a gas can be separated using a system to introduce the gas to the MOM and remove the modified gas. In an embodiment, a first structure or device including the MOM can be interfaced with a second structure or device to introduce a gas to the first structure so that the gas and the MOM can interact so that the MOM can capture the first component (e.g., trace levels of CO₂). After a sufficient period of time and under appropriate temperature conditions, the remaining gas or modified gas can be removed from the first structure. This process can be repeated as appropriate for the particular system. After a period of time, the first component can be

removed from the MOM and the MOM can be reused and/or recycled using an appropriate gas handling system.

In an embodiment, the first structure and the second structure can include those used in systems such as direct air capture systems, pre-purification systems (e.g., PSA and cryogenic distillation), AFCs, breathing systems, mining and rescue missions, diving, medical applications, post-combustion systems, pre-combustion systems, natural gas upgrading systems, and He separation systems. In particular, the first structure can include structures such as those used in typical systems mentioned above. In an embodiment, the second structure can include standard gas handling systems, valves, pumps, flow meters, and the like.

As noted above, MOMs can be three dimensional nets that can have a primitive cubic topology but they could also exhibit a different topology (See FIG. 1). In an embodiment, the MOM can be designed and synthesized using two dimensional square nets that are linked via metal nodes using a molecule or ion that serves the role of a pillar. In an embodiment, the two dimensional square nets can include metal cations, MBBs, or SBBs, and linkers can be used to bond the metal ions and the MBB and the SBB.

In an embodiment, MOMs can have one of the following generic structure: (M(L)_a(P)_n), where M is the metal ion, L is the linker, and P is the pillar, a is 2 and n is 1. In an embodiment, the MOM has a pore size of about 3.3 Å to 3.9 Å or about 3.5 Å. L and P can be difunctional ligands that are capable of linking the metal clusters or ions such as pyrazine, 4,4'-bipyridine, 1,4-benzenedicarboxylate, hexafluorosilicate, and hexafluorotitanate. In an embodiment, these types of MOMs are described in references 13-15 below in the Example, which are incorporated herein by reference for how to describe MOMs and MOFs and the components of each.

In an embodiment, the metal cations can include M¹⁺ (e.g., Na, K, Li, Ag, etc.); M²⁺ (e.g., Cu, Zn, Co, Mn, Mo, Cr, Fe, Ca, Ba, Cs, Pb, Pt, Pd, Ru, Rh, Cd, etc.); M³⁺ (e.g., In, Fe, Y, Ln (Yb, Tb, etc.)); M⁴⁺ (e.g., Zr, Ti, V, etc.); or other higher oxidative state metals such as +4, +5, +6, +7, and +8. In an embodiment, the MBBs and SBBs can include these metal cations as well.

In an embodiment, the linkers in the two dimensional square grid can include organic molecules, inorganic anions and/or metal complexes. In an embodiment, the linkers can include pyrazine (substituted and unsubstituted) and derivatives thereof, bipyridine (substituted and unsubstituted) and derivatives thereof, and the like.

In an embodiment, the pillars can include organic molecules, inorganic anions and/or metal complexes. In an embodiment, the pillars can include SiF₆²⁻, GeF₆²⁻, TiF₆²⁻, SnF₆²⁻, PF₆⁻, and NO₃⁻.

In an embodiment, MOMs of the present disclosure can be designed consistent with the description of (M(L)_a(P)_n) so that the MOM has a pore size of about 3.3 Å to 3.9 Å or about 3.5 Å. As described in the Example, MOMs having pore sizes in this range and having a high charge density are effective at trapping CO₂ at concentrations of about 5% or less, about 4% or less, about 0.1 to 5%, or about 0.1 to 4%. In an embodiment, the MOM can include: [Cu(pyr)₂(SiF₆)]_n, wherein n is 1 to 100,000,000.

EXAMPLE

Now having described the embodiments of the present disclosure, in general, the Examples describe some additional embodiments of the present disclosure. While embodiments of present disclosure are described in connec-

tion with the Examples and the corresponding text and figures, there is no intent to limit embodiments of the present disclosure to these descriptions. On the contrary, the intent is to cover all alternatives, modifications, and equivalents included within the spirit and scope of embodiments of the present disclosure.

Example 1

Brief Introduction:

Direct air capture (DAC) is another alternative approach to mitigate the increasing CO₂ emissions while accounting for both carbon emissions from various sources such as transportation sector and stationary power plants sources. We previously reported how a material design and engineering approaches to pore size control, in combination with suitable sorption energetics of favourable electrostatics from an array of inorganic anions, affords MOFs with unprecedented CO₂ uptake and selectivity in the context of bulk (5% and higher) CO₂ capture. Herein, we report how this same approach can be used to develop isostructural materials rather suitable to air capture and traces CO₂ removal. In contrast to amine scrubbing systems, amine supported materials, and sodalime sorbents, these materials exhibit also very high but non-reactive and uniformly distributed CO₂ energetics, pushing the borders in enhancement of physical interactions in MOFs, in addition to fully reversible physical driven adsorption-desorption operations at very mild condition. This work shows that due to their ability for rational pore size modification and inorganic-organics moieties substitution, MOFs with periodically arrayed hexafluorosilicate (SIFSIX) pillars offers for the first time remarkable CO₂ adsorption, uptake and selectivity in highly diluted gas streams that other plain class of materials are unable to achieve.

Introduction/Discussion:

The growing interest in combating the greenhouse gas effect¹ triggered a rising interest in the direct air capture (DAC) as a viable option to reduce greenhouse gases emissions in a uniform way.²⁻⁵ Although more challenging than post-combustion capture, it is recognized that DAC might be feasible, provided that suitable adsorbent combining optimum uptake, kinetics, energetics and CO₂ selectivity is available at traces CO₂ concentration.⁶

Particularly the removal of traces of CO₂ from air for industrial purposes is a growing area of research and development, owing to its substantial importance particularly for pre-purification of air, when atmospheric air is used during the separation of nitrogen and oxygen. In fact, 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^{7, 8} and (ii) adsorbents (e.g., zeolites) contamination used for oxygen production by PSA.⁹

At the same level of importance, alkaline fuel cells (AFCs) require oxygen and hydrogen used as feedstock to be CO₂ free. Indeed, trace amounts of CO₂ (300 ppm) degrade the electrolyte in AFCs.¹⁰⁻¹² In addition, humans require oxygen, and in return emit carbon dioxide. Therefore, 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.¹³⁻¹⁵ In fact, in long-term space flight and submarine missions, CO₂ must be removed from the air and recycled because resupply opportunities are less frequent or non-existent. An average crew member requires approximately 0.84 kg of oxygen and emits approximately 1 kg of carbon dioxide.¹⁵

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 closed, confined spaces.

Efficient CO₂ removal and resupply of fresh air is also of prime importance in mining and rescue missions,¹⁶ diving, and most importantly in medical applications such as anaesthesia machines.¹⁷ The use of anaesthesia machine was and still a growing clinical trend throughout the world, driven by the need to reduce cost and improve patient care via the use of efficient CO₂ sorbents. 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. 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.¹⁸ Nevertheless, a major drawback of this technology is that one sodalime cartridge can only be used for a single cycle and is non-regenerable, generating therefore a huge amount of waste that should be disposed properly. Recently, a growing interest to low CO₂ concentration removal applications,¹² was spotted and few materials were reported to adsorb efficiently traces of CO₂, particularly with regards to DAC using a variety of amine supported (silica based) materials.^{12,19} Recently, metal-organic frameworks (MOFs), which is a burgeoning class of porous materials, was intensively investigated for intermediate and high CO₂ concentration removal applications such as post-combustion, pre-combustion capture, natural gas and biogas upgrading.²⁰⁻²³ However, the capability of MOFs to remove traces and low CO₂ concentration from gas streams was rarely debated.²⁴⁻²⁷ The main reason for this lack of studies is that most of MOFs reported so far with or without unsaturated metal sites (UMC) or/and functionalized ligands exhibited relatively low selectivity and uptake particularly at low CO₂ partial pressure. With the aim to enhance the CO₂ adsorption energetics and uptake in MOFs and covalent organic frameworks (COFs), a few scientist,^{26,27} were inspired by the amine chemistry and the huge know how gained so far from amine-supported silica.²⁰⁻²² In fact, recently, Jones and co-workers studied for the first time the effect of ethylenediamine (ED) grafting with Mg-MOF-74 as a support for CO₂ adsorption from ultra-dilute gas streams such as ambient air.²⁸ Long and co-workers investigated the effect of N,N-dimethylethylenediamine grafting for DAC using an expanded version of Mg-MOF-74.²⁸ Thus, the few strategies reported so far targeting air capture using MOFs rely on the ability of grafted amines to form strong chemical bonding (at least 70 kJ/mol) with CO₂, affording high affinity toward CO₂ and therefore high CO₂ selectivity. Interestingly, there is no work reported so far on tuning pore size of plain MOFs with the optimal CO₂ energetics (strong, uniform and enough low to allow reversible physical adsorption-desorption) to target traces CO₂ removal in general and DAC application in particular.

Results and Discussion:

Recently, we reported a CO₂ study on a series of isorecticular MOFs with periodically arrayed hexafluorosilicate (SIF SIX) pillars, called SIFSIX-2-Cu-i and SIFSIX-3-Zn (FIG. 1). These porous MOFs having a combination of tunable pore size (rather than large surface area) coupled with requisite chemistry led to materials exhibiting fast and highly selective CO₂ behaviour over N₂, CH₄ and H₂ with

uniformly aligned strong CO₂ adsorption sites.²³ Particularly the denser isorecticular analogue of SIFSIX pillars; SIFSIX-3-Zn revealed very steeper variable CO₂ adsorption isotherms (FIG. 12) than SIFSIX-2-Cu-I (FIG. 11) suitable for post-combustion capture (at the CO₂ partial pressure of 100-mbar), but also excellent features suitable for natural and biogas upgrading, as well as pre-combustion capture^[20] (high CO₂ concentration and high pressure).

Because of the importance of this discovery and the unprecedented steep CO₂ adsorption isotherms over a wide range of temperature, particularly for this class of materials; MOFs, we found it compelling to explore the capability of these SIF SIX MOFs for CO₂ adsorption in trace concentration (diluted streams in vacuum or in mixture containing large fraction of N₂ up to 95%). In order to highlight the concealed capability of these MOFs for low CO₂ concentration related applications involving CO₂ concentration below 5% (below 50 mbar CO₂ partial pressure) such as anaesthesia machines, pre-purification before air separation and air capture, single gas CO₂ adsorption was investigated for SIFSIX-2-Cu-i and SIFSIX-3-Zn. Upon contraction the pore size from 5.15 Å (for SIFSIX-2-Cu-i) to 3.8 Å (for SIFSIX-3-Zn) the CO₂ uptake increased drastically (FIG. 13) resulting to the highest CO₂ uptake ever reported for MOFs in the range of below 5% CO₂. For example, SIFSIX-3-Zn showed an order of magnitude higher volumetric CO₂ uptake (55 cm³ (STP)/cm³) than Mg-MOF-74,²⁰ (28 cm³ (STP)/cm³) at 10 mbar (1% CO₂), while UTSA-16,²⁹ exhibited much lower CO₂ uptake similar to SIFSIX-2-Cu-I.

To further investigate the effect of tuning further the pore size on the adsorption properties of SIFSIX-3-M, and by studying other coordination polymers constructed from hexafluorosilicate ions with pyrazine, we found that the bonding of the Cu(II) with pyrazine leads to a slightly shorter M-N (nitrogen) bond than the zinc (see table S1 in SI),³⁰ which will lead to further decrease in the pore size of the constructed 3D MOF, if we could substitute Zn by Cu. In order to explore this prospect, we deliberately intended to prepare the SIFSIX-3-Cu analogue which was never reported before and it was successfully prepared by layering a methanol solution (5.0 mL) of pyrazine (pyz, 0.30 g, 3.0 mmol) in a glass tube onto a methanol solution (5.0 mL) of CuSiF₆·xH₂O (0.325 g, 0.6 mmol). Upon layering, an extremely fast formation of light violet powder was observed, and the powder was left for 24 hours in the mother solution. The powder was then collected and washed extensively with methanol then dried under vacuum and characterized using powder X-ray diffraction (PXRD).

The PXRD diagram was found not to match with any of the related reported structures, i.e. the Cu-2D structures or the 3D Zn analogue reported by Kita et al.³⁰ (FIG. 5). Despite extensive attempts, it was not possible to isolate synthetic conditions affording single crystals of sufficient size for single crystal diffraction (SCD), and the structure was then solved from PXRD using direct methods. The structural model was then energetically and geometrically refined, and the good agreement between experimental and calculated PXRD diagrams validates our model (FIGS. 6 and 7). Analysis of the structure revealed the formula of the Cu analogue; [Cu(SiF₆)(pyz)₂·solv]. As initially expected, it is in very good agreement with the 3D structure of the Zn analogue reported previously (FIG. 1),³⁰ but with a slightly smaller unit cell (375 vs. 388 Å³) attributed to the stronger bonding between the Cu(II) and the pyrazine (Table S1 in SI).³⁰ The smaller unit cell of the Cu analogue was in good agreement with the relatively sharp pore size distribution (PSD) analysis centred at 3.5 Å (average pore size), as

determined from the CO₂ isotherms, which shows smaller average pore size than the SIFSIX-3-Zn (3.5-4 Å) (FIG. 2(right)). The thermal gravimetric analysis (TGA) of the SIFSIX-3-Cu was tested in the temperature range 25-250° C. The thermogram (FIG. 8) shows a mass loss of about 10% for the dried sample in the range of 50-150 corresponding to guest molecules. Further gradual loss was observed above 150° C. due to the decomposition and loss of pyrazine and SiF₆ ions. The TGA for the SIFSIX-3-Cu is in a good agreement with the one reported for the SIFSIX-3-Zn.³⁰ Infra-red (IR) spectrum for the SIFSIX-3-Cu (FIG. 9), exhibits bands characteristic of the C—H aromatic bonds of the pyrazine at 3114 and 3073 cm⁻¹ and bands characteristic for the C—N bond at 1445, 1122 and 1070 cm⁻¹. In addition to that the characteristic bands for the octahedral SiF₆ were also observed at 743 and 833 cm⁻¹.³¹

It is logically expected that this new Cu analogue should at least show the same promising adsorption properties as the SIFSIX-3-Zn.²³ Surprisingly, the Cu analogue showed even steeper variable temperature adsorption isotherms (FIG. 2(left)) at very low pressure indicative of the stronger CO₂-SIFSIX-3-Cu interactions.

The mechanistic behind the unprecedented selective CO₂ adsorption involving the unique synergetic effect of thermodynamics and kinetics²³ was confirmed by the competitive kinetics of CO₂/N₂:10/90 gas mixture adsorption (FIG. 14). As was expected and based on the similar study carried out on the Zn analogue,²³ the uptake at equal times for variable CO₂ compositions mixtures follow the behaviour of pure CO₂ (FIG. 10). In addition at equilibrium, the total uptake of the CO₂ containing gas mixtures overlay perfectly with the equilibrium uptake for pure CO₂ (FIG. 10). These findings show that similarly to SIFSIX-3-Zn, when CO₂ containing mixtures are in contact with SIFSIX-3-Cu, CO₂ adsorbs more strongly and faster than N₂ (and by analogy also O₂, CH₄ and H₂ (FIG. 14, thus occupying all the available space and sorption sites and excluding other gases which is a desirable feature in many CO₂ separation and purification applications. Examination of the SIFSIX-3-M adsorption results in the spectra of low concentration applications (400 ppm-5%) showed that the Cu analogue exhibits even steeper adsorption isotherms at very low CO₂ concentration (FIG. 3a) translated into the highest uptake ever reported for MOFs without UMC or amino groups at low CO₂ pressure below 38 torr (0.05 bar). This unprecedented finding is even more interesting owing to its fully physical adsorption nature where complete desorption of CO₂ was established at only 323 K. At 7.6 torr (0.01 bar) SIFSIX-3-Cu exhibited 82.6 cm³ (STP)/cm³ vs. 55 and 28 cm³ (STP)/cm³ for SIFSIX-3-Zn and Mg-MOF-74, respectively. Interestingly, the gravimetric uptake of SIFSIX-3-Cu at 400 ppm and 298 K (1.24 mmol/g) is 10 and 15.5 times higher than the corresponding uptakes for SIFSIX-3-Zn (0.13 mmol/g) and Mg-MOF-74 (0.08 mmol/g) and even higher than the uptake of most of amine-supported silica materials (with optimal compromise of amine loading and kinetics)³² at 298 K (for example TRI-PE-MCM-4¹¹⁻²³ (1 mmol/g)). Table 1 shows a summary of the 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. It is to notice that SIFSIX-3-Cu showed even higher CO₂ uptake at 400 ppm and 328 K as compared to the corresponding uptake at 323 K for amine functionalized Mg-dobpdc-mmen (Table S3).

TABLE 1

((CO ₂ adsorption uptake at various traces CO ₂ concentration and at 298K in comparison to 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 Q _{st} (kJ/mol)
SIFSIX-2-Cu-i	0.0684 ^c /0.2 ^d	0.097 ^c /2.7 ^d	0.19 ^c /5.32 ^d	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	0.088 ^c /1.8 ^d	0.7 ^c /14.3 ^d	1.27 ^c /25.86 ^d	47
Mg-MOF-74-ED ^a	1.5 ^c	ND	ND	ND
Mg-dobpdc-mm ^b	2 ^c	2.5 ^c	2.75 ^c	70
TRI-PE-MCM-41 ^f	1 ^c	1.45 ^c	1.6 ^c	92
HAS ^f	1.7 ^c	ND	ND	ND

^a((Ethylenediamine functionalized²⁴);^b((N,N-dimethylethylenediamine functionalized²⁵);^cmmol/g;^dcm³ (STP)/cm³;^eat 328 K;^fAmine supported silica.

ND: non determined;

Interestingly, 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 case of the Cu analogue at very low pressure. This increase is mainly attributed to the small unit cell and the small pore size of the Cu analogue. The Q_{st} of CO₂ adsorption is an intrinsic property that dictates the affinity of the pore surface toward CO₂; this in turn plays a major role in determining the adsorption selectivity and the necessary energy to release CO₂ during the regeneration step. Although the Q_{st} for CO₂ was slightly above the range of fully reversible CO₂ adsorption (30-50 kJ mol⁻¹)²³, SIFSIX-3-Cu was fully evacuated at 50° C. in vacuum (or in N₂ environment). As in case of SIFSIX-3-Zn and SIFSIX-2-Cu-i, the Q_{st} for CO₂ adsorption was relatively constant up to high CO₂ loadings indicating homogenous binding sites over the full range of CO₂ loading (FIG. 3b).²³

The CO₂ selectivity of SIFSIX-3-Zn and SIFSIX-3-Cu was investigated experimentally using column breakthrough tests for binary CO₂/N₂:1000 ppm/99.99% mixture (FIG. 4 left) at 298 K in dry as well as in humid conditions. In dry condition, the first CO₂ signal downstream the column was observed only after ca. 798 and ca.1922 min/g for SIFSIX-3-Zn and SIFSIX-3-Cu, respectively after starting continuous CO₂/N₂ gas mixture flux (5 cm³ min⁻¹), while N₂ breakthrough occurred in a few seconds. Accordingly, at 1000 ppm CO₂ and breakthrough time, SIFSIX-3-Cu showed higher selectivity (ca. 10500) than SIFSIX-3-Zn (7259). We also note that the calculated and measured selectivity exceeding 1000-2000 are often subject to uncertainties associated with measurement of the gas uptake of weakly adsorbed gases (N₂) in the mixture, thus the reported selectivity is highly qualitative and aiming the comparison of the studied compounds only.

The CO₂ removal selectivity at 1000 ppm CO₂ on SIFSIX-3-Cu 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% (FIG. 4(right)). This unprecedented finding was also valid in case of SIFSIX-3-Zn for the removal of low (FIG. 15) and higher CO₂ concentration.²³

In conclusion, we showed herein how a material design and engineering approaches to pore size control in combination with suitable energetics of favourable electrostatics from an array of inorganic anions affords MOFs with unprecedented CO₂ uptake and selectivity in the context of air capture and traces CO₂ removal. These materials exhibit

very high (non-reactive) CO₂ energetics but fully reversible physical driven adsorption-desorption operations at very mild conditions, without the well documented drawbacks associated with amine reactive chemistry.

5 This work shows for the first time that thanks to their ability for rational pore size modification and inorganic-organics moieties substitution, MOFs offers remarkable CO₂ adsorption attributes in highly diluted gas streams that other plain class of materials are unable to achieve. Further works will be dedicated to study the effect of substituting other metals such as cadmium, cobalt, chromium etc., on the CO₂ separation properties in diluted CO₂-containing gases.

Methods: SIFSIX-3-Cu:

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 powder was then collected and washed extensively with methanol then dried under vacuum Characterization:

The powder PXRD patterns were recorded on a Panalytical X'pert PRO MPD X-ray Diffractometer with Cu Kα radiation (λ=0.15418 nm, 45 kV, 40 mA).

Low pressure gas sorption measurements were performed on a fully automated micropore gas analyzer Autosorb-1C (Quantachrome Instruments) at relative pressures up to 1 atm. The cryogenic temperatures were controlled using a liquid nitrogen bath at 77 K. Pore size analyses were performed using a cylindrical NLDFT pore model system by assuming an oxidic (zeolitic) surface.

High Pressure Adsorption:

Adsorption equilibrium measurements of pure gases were performed using a Rubotherm gravimetric-densimetric apparatus (Bochum, Germany) (Scheme S1), composed mainly of a magnetic suspension balance (MSB) and a network of valves, mass flowmeters and temperature and pressure sensors. The MSB overcomes the disadvantages of other commercially available gravimetric instruments by separating the sensitive microbalance from the sample and the measuring atmosphere and is able to perform adsorption measurements across a wide pressure range, i.e. from 0 to 20 MPa. The adsorption temperature may also be controlled within the range of 77 K to 423 K. In a typical adsorption experiment, the adsorbent is precisely weighed and placed in a basket suspended by a permanent magnet through an electromagnet. The cell in which the basket is housed is then closed and vacuum or high pressure is applied. The gravimetric method allows the direct measurement of the reduced gas adsorbed amount Ω. Correction for the buoyancy effect is required to determine the excess and absolute adsorbed amount using equation 1 and 2, where V_{adsorbent} and V_{ss} and V_{adsorbed phase} refer to the volume of the adsorbent, the volume of the suspension system and the volume of the adsorbed phase, respectively.

$$\Omega = m_{\text{absolute}} - \rho_{\text{gas}}(V_{\text{adsorbent}} + V_{\text{ss}} + V_{\text{adsorbed phase}}) \quad (1)$$

$$\Omega = m_{\text{excess}} - \rho_{\text{gas}}(V_{\text{adsorbent}} + V_{\text{ss}}) \quad (2)$$

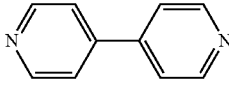
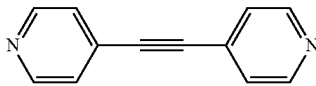

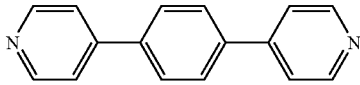
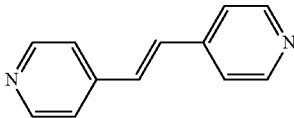
The buoyancy effect resulted from the adsorbed phase maybe taken into account via correlation with the pore volume or with the theoretical density of the sample.

60 Structure Determination

DICVOLO6 was used for pattern indexing of SIFSIX-3-Cu; the cell refinement was carried out by a structureless whole pattern profile refinement using the FullProf software and its graphical interface WinPlotr. (*J. Epdic 7: European Powder Diffraction, Pts 1 and 2 Vol. 378-3 Materials Science Forum* (eds R. Delhez & E. J. Mittemeijer) 118-123 (2001)) The structure of SIFSIX-3-Cu was solved ab initio

on the as-synthesized solid using powder X-Ray diffraction (PXRD) data by direct method using Expo2009. (*J. Appl. Crystallogr.* 42, 1197-1202, (2009)). All framework atoms were found directly and their coordinates geometrically and energetically refined through Forcite in Materials Studio 6.0.0.

TABLE S1

Comparison of characteristic interatomic distances in SIFSIX based MOFs.						
MOF	d_{M-N} (Å)	d_{M-F1} (Å)	D_{Si-F1} (Å)	D_{Si-F2} (Å)†	reference	Ligand
SIFSIX-1-Zn	2.157	2.082	1.757	1.600	3	
	2.131	2.122	1.720	1.650	4	
SIFSIX-1-Cu	2.007	2.379	1.703	1.672	5	
	2.009	2.357	1.698	1.609	6	
	1.966	2.336	1.692	1.685	7	
SIFSIX-2-Zn	2.125	2.069	1.698	1.668	4	
SIFSIX-2-Cu	2.027	2.300	1.684	1.684	8	
SIFSIX-2i-Cu	2.015	2.353	1.693	1.679	8	
SIFSIX-3-Zn	2.172	2.057	1.747	1.657	9	
SIFSIX-3-Cu	2.046	2.259	1.684	1.686	this work	
SIFSIX-2D-Cu	2.061*	2.402	1.727	1.688	9	
SIFSIX-2D-H ₂ O—Cu	2.031	2.412	1.695	1.675	7	
SIFSIX-4-Zn	2.117	2.062	1.712	1.653	4	
SIFSIX-5-Cu	2.012	2.258	1.727	1.681	5	

†Average distance, due to disorder of F atoms.

* Average distance, due to lower symmetry, SIFSIX-2D contains two independent N atoms bonded to Cu

³Subramanian, S. & Zaworotko, M. J. Porous Solids by Design—[Zn(4,4'-Bpy)(2)(SiF₆)](N) Center-Dot-Xdmf, a Single Framework Octahedral Coordination Polymer with Large Square Channels (Vol 34, Pg 2127, 1995). *Angew. Chem. Int. Ed.* 34, 2127-2129, (1995).

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⁸Nugent, P. et al. Porous materials with optimal adsorption thermodynamics and kinetics for CO₂ separation. *Nature* 495, 80-84, (2013).

⁹Uemura, K., Maeda, A., Maji, T. K., Kanoo, P. & Kita, H. Syntheses, Crystal Structures and Adsorption Properties of Ultramicroporous Coordination Polymers Constructed from Hexafluorosilicate Ions and Pyrazine. *Eur. J. Inorg. Chem.*, 2329-2337, (2009).

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from Hexafluorosilicate Ions and Pyrazine. *Eur. J. Inorg. Chem.*, 2329-2337, (2009).

TABLE S2

Crystallographic data of SIFSIX-3-Cu.	
Compound	SIFSIX-3-Cu
Formula (dried solid)	C ₈ N ₄ H ₈ CuSiF ₆
Molar weight (g · mol ⁻¹)	365.80
Calculated density (g · cm ⁻³) (dried solid)	1.62
Symmetry	Tetragonal
Space group	P 4/m m m (n° 123)
a (Å)	6.901(1)
b (Å)	6.901(1)
c (Å)	7.886(1)
V (Å ³)	375.5
Z	1
Wavelength λ(Cu Kα)	1.5406
Temperature (K)	298
Angular range 2-theta (°)	3-80
Number of independent atoms (dried solid)	8

65

TABLE S3

Gravimetric CO ₂ uptake at 400 ppm and 328 K for SiF ₆ -Cu-3, SiF ₆ -Zn-3 and SiF ₆ -Cu-2-i in comparison to Mg-dobpdc-mmen	
Adsorbent	Uptake at 400 ppm (0.4 mbar) mmHg/g
SiF ₆ -2-Cu-i	negligible
SiF ₆ -3-Zn	0.0287
SiF ₆ -3-CU	0.242
Mg-dobpdc-mmen ^b	≈0.12

^bat 323 K

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porous coordination polymers constructed from hexafluorosilicate ions and pyrazine. *Eur. J. inorg. Chem.*, 2329-2337 (2009).

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32 It is important to notice that hyperbranched aminosilica material (HAS)25 was reported to exhibit higher gravimetric uptake (1.7 mmol/g) at 390 ppm and 298 K, however the kinetics of adsorption was much slower due to the diffusion limitation caused by the high amine loading. To overcome this issue, The strategy of use of highly porous materials as MOFs as support for amine grafting is a clever pathway to develop highly CO₂ selective MOFs with high uptake and optimal CO₂ adsorption kinetics as reported recently^{27,28}. ED amine grafted Mg-dobdc²⁷ and N,N-dimethylethylenediamine Mg-dobdc²⁸ were reported recently to exhibit 1.5 and 2 mmol/g uptake at 390 ppm, respectively. Nevertheless reactive air capture of CO₂ using amines may have relatively larger energy input in term of desorption and regeneration options is yet to be studied.

In regard to the discussion herein including the Examples above and the claims, it should be noted that ratios, concentrations, amounts, and other numerical data may be expressed herein in a range format. It is to be understood that such a range format is used for convenience and brevity, and thus, should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. To illustrate, a concentration range of "about 0.1% to about 5%" should be interpreted to include not only the explicitly recited concentration of about 0.1 wt % to about 5 wt %, but also include individual concentrations (e.g., 1%, 2%, 3%,

and 4%) and the sub-ranges (e.g., 0.5%, 1.1%, 2.2%, 3.3%, and 4.4%) within the indicated range. In an embodiment, the term "about" can include traditional rounding according to measurement techniques and the units of the numerical value. In addition, the phrase "about 'x' to 'y'" includes "about 'x' to about 'y'".

Many variations and modifications may be made to the above-described embodiments. All such modifications and variations are intended to be included herein within the scope of this disclosure and protected by the following claims.

We claim:

1. A method of capturing CO₂ in a gas, comprising: exposing the gas to a metal-organic material (MOM), wherein the MOM includes at least one of an inorganic linker or an inorganic pillar, wherein the gas includes CO₂ at a concentration in the gas of about 5% or less; and capturing the CO₂ in the MOM.
2. The method of claim 1, wherein the gas includes at least one of the following gases: N₂, H₂, or CH₄, wherein the MOM has a greater relative affinity for CO₂ over each one of N₂, H₂, and CH₄.
3. The method of claim 1, wherein the MOM is [Cu(pyr)₂(SiF₆)]_n, wherein n is 1 to 100,000,000.
4. The method of claim 1, wherein the MOM has a pore size of about 3.35 Å.
5. The method of claim 1, wherein the gas includes N₂.
6. The method of claim 1, wherein the gas includes H₂.
7. The method of claim 1, wherein the gas includes CH₄.
8. The method of claim 1, wherein capturing the CO₂ in the MOM is performed in the presence of at least one of N₂, H₂, and CH₄ so that the CO₂ is captured by the MOM to the exclusion of N₂, H₂, CH₄, or a combination thereof.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 10,112,175 B2
APPLICATION NO. : 15/427147
DATED : October 30, 2018
INVENTOR(S) : Eddaoudi et al.

Page 1 of 1

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

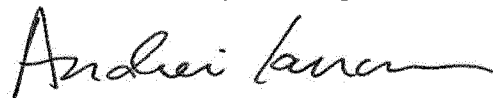
On the Title Page

Item (71), should read:

Assignee 1: University of South Florida Tampa, Florida

Assignee 2: King Adbullah University of Science and Technology Thuwal, Saudi Arabia

Signed and Sealed this
Thirteenth Day of August, 2019



Andrei Iancu
Director of the United States Patent and Trademark Office