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March 11, 2011

Kathleen McCowin, MS JD
Office of Technology Licensing
University of California, Berkeley
2150 Shattuck Drive, Suite 510
Berkeley, CA 94704-1347

VIA E-MAIL ONLY

Re: U.S. Provisional Patent Application

Title:	METAL-ORGANIC FRAMEWORKS AS MATERIALS FOR H2/CO2 SEPARATION
Inventor(s):	Jeffrey R. Long et al.
Filing Date:	March 7, 2011
Ser. No.:	61/450,048
Our File:	B11-087-1

Dear Kathleen:

Enclosed for your records, please find a copy of the U.S. provisional patent application that we filed in connection with this invention.

NOTICE REGARDING CRITICAL DEADLINES

Please keep in mind that a provisional application automatically expires one year from its filing date. If you do not file a regular (nonprovisional) U.S. patent application prior to that time, you will lose the benefit of the filing date of this provisional application and may lose the ability to obtain patent protection altogether. This deadline also applies to filing foreign patent applications.

If you elect to continue the patent process beyond this stage and file a regular (nonprovisional) patent application, please contact us at least three (3) months in advance of the deadline. ***Because of the lead times involved, unless we receive your written instructions at least three (3) months prior to the deadline we cannot guarantee that U.S. nonprovisional and/or foreign filings can be timely made or that rush charges will not be incurred. No filings will be made unless we receive your written instructions.***

NOTICE CONCERNING U.S. FILINGS

The deadline for filing a U.S. nonprovisional application assumes that:

1. there was no public disclosure, public use of, sale of, or offer to sell the invention described in the provisional application more than one year prior to the date on which the provisional application was filed; and

2. for subject matter to be described for the first time in the nonprovisional application, there was no public disclosure, public use of, sale of, or offer to sell the new technology more than one year prior to the deadline in the first sentence of this letter.

If there was a public disclosure, public use of, sale of, or offer to sell that invention more than one year prior to filing the U.S. provisional application (item 1) or prior to the deadline for filing the nonprovisional application (item 2), please urgently contact our office to discuss that event.

NOTICE CONCERNING FUTURE FOREIGN FILINGS

The deadline for filing a PCT international patent application or an application directly in a country of interest assumes that:

1. there was no public disclosure, public use of, sale of, or offer to sell the invention described in the provisional application prior to the date on which the provisional application was filed; and

2. for subject matter to be described for the first time in the PCT or direct foreign application, there was no public disclosure, public use of, sale of, or offer to sell the new technology prior to the deadline in the first sentence of this letter.

If there was a public disclosure, public use of, sale of, or offer to sell that invention prior to filing the U.S. provisional application (item 1) or prior to the deadline for filing the PCT or direct foreign application (item 2), please urgently contact our office to discuss that event.

Also, while it may be possible to file a PCT application or a direct foreign application in some countries after this deadline if your invention has not yet been publicly disclosed, we cannot safely rely on that possibility. Therefore, the deadline above should be considered your foreign filing deadline for all countries.

Furthermore, with regard to foreign patent applications, please keep in mind that a PCT international patent application covers over 100 countries, ***but not all countries are members of the PCT***. Therefore, it will be necessary to file directly in non-PCT countries in addition to filing a PCT application. It will also be necessary to obtain a foreign filing license from the United States Patent and Trademark Office (USPTO) in order to file in non-PCT countries.

Examples of non-PCT countries are:

☐ AR Argentina	☐ IR Iran	☐ PE Peru	☐ TW Taiwan
☐ BL Bolivia	☐ MY Malaysia	☐ SA Saudi Arabia	☐ UY Uruguay
☐ CL Chile	☐ PY Paraguay	☐ TH Thailand	☐ VE Venezuela

NOTE: THIS LIST MAY NOT INCLUDE ALL NON-PCT COUNTRIES. DO NOT ASSUME THAT IF A COUNTRY IS NOT ON THIS LIST THAT IT IS A PCT MEMBER COUNTRY. IF YOU DO NOT KNOW IF A PARTICULAR COUNTRY IS A PCT MEMBER, PLEASE CONTACT OUR OFFICE.

Please contact our office if you have any questions concerning PCT or non-PCT countries.

Additionally, ***please note that you will eventually have to file applications directly in PCT member countries even if you file a PCT application***. The advantages of the PCT route are lower initial costs and simplicity of filing, but the overall cost of obtaining foreign patent protection will be higher. In other words, the PCT international process extends the deadline for filing applications directly in member countries. However, you may also file applications in those countries at any time prior to the deadline.

As a reminder, the cost of preparing and filing a U.S. application is typically on the order of $8,000 to $10,000 plus drawing costs and government filing fees, the cost of preparing and filing a PCT international application is on the order of $3,500 including government filing fees, and the cost of preparing and filing foreign applications directly various countries/regions is on the order of $5,000 to $10,000 per region or country (including associate charges, official fees and translation costs in some cases). However, the total cost of your applications could be higher or lower. Therefore, please contact our office if you have any questions concerning costs.

NOTICE CONCERNING PRIOR ART SEARCH

If you have not already conducted a prior art search, or if you have conducted a prior art search and would like to update that search, please let us know. Unless we specifically requested to do so, our firm will not conduct a search prior to filing the nonprovisional and/or foreign applications.

GENERAL INFORMATION

Now that the application has been filed, you may disclose this invention ***only to the extent that it is described in the provisional patent application***. Do not disclose any aspect of the invention that is not described in the provisional application without first filing another patent application covering that additional material.

Also, you may now indicate that the invention is "patent pending." The fact that the invention is patent pending will often deter others from copying an invention, although you have no legal recourse until a patent is issued.

We also recommend that you do not show the patent application or any of the application documents to anyone. Furthermore, we also recommend that you keep the serial number of the application confidential. Otherwise, you risk someone figuring out a way to get around the protection which you are seeking or possibly protesting your patent application.

Lastly, we have advised you of a number of critical deadlines above. Please keep track of those deadlines so that you do not inadvertently allow any of your patent rights to lapse. While we will endeavor to provide you with at least one reminder prior to a deadline as a backup, it is the client's responsibility for tracking these deadlines and providing timely instructions to our firm.

Thank you again for the opportunity of assisting you with this application. We will let you know as soon as we have additional information. In the meantime, please contact us if you have any questions.

Best regards.

Sincerely,

O'BANION & RITCHEY LLP

John P. O'Banion

Enclosure
JPO:bcs
cc: Richard Harris
Jeffrey R. Long, Ph.D.

Acknowledgement Receipt

The USPTO has received your submission at **19:05:04** Eastern Time on **07-MAR-2011** by Deposit Account: 071137.

$ **110** fee paid by e-Filer via *RAM* with Confirmation Number: 6738.

eFiled Application Information

EFS ID	9604833
Application Number	61450048
Confirmation Number	6607
Title	METAL-ORGANIC FRAMEWORKS AS MATERIALS FOR H2/CO2 SEPARATION
First Named Inventor	Jeffrey R. Long
Customer Number or Correspondence Address	08156
Filed By	John P. Obanion
Attorney Docket Number	B11-087-1
Filing Date	
Receipt Date	07-MAR-2011
Application Type	Provisional

Application Details

Submitted Files	Page Count	Document Description	File Size	Warnings
B11_087_1_prov_cover.pdf	4	Provisional Cover Sheet (SB16)	1060416 bytes	PASS
B11_087_1_prov_appln.pdf	32		301035 bytes	PASS

Document Description	Page Start	Page End
Specification	1	18
Claims	19	22
Abstract	23	23
Drawings-only black and white line drawings	24	32

fee-info.pdf	2	Fee Worksheet (PTO-875)	29569 bytes	PASS

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

If you need help:

- *Call the Patent Electronic Business Center at (866) 217-9197 (toll free) or e-mail EBC@uspto.gov for specific questions about Patent e-Filing.*
- *Send general questions about USPTO programs to the USPTO Contact Center (UCC) .*
- *If you experience technical difficulties or problems with this application, please report them via e-mail to Electronic Business Support or call 1 800-786-9199.*

Document Description: Provisional Cover Sheet (SB16)

PTO/SB/16 (11-08)
Approved for use through 09/30/2010 OMB 0651-0032
U.S. Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE
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Provisional Application for Patent Cover Sheet

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c)

Inventor(s)

Inventor 1 — Remove

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All Inventors Must Be Listed – Additional Inventor Information blocks may be generated within this form by selecting the **Add** button. Add

Title of Invention	METAL-ORGANIC FRAMEWORKS AS MATERIALS FOR H2/CO2 SEPARATION
Attorney Docket Number (if applicable)	B11-087-1

Correspondence Address

Direct all correspondence to (select one):

◉ The address corresponding to Customer Number	○ Firm or Individual Name
Customer Number	08156

PTO/SB/16 (11-08)
Approved for use through 09/30/2010 OMB 0651-0032
U.S. Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.
○ No.
◉ Yes, the name of the U.S. Government agency and the Government contract number are:
DOE No. DE-SC0001015

Document Description: Provisional Cover Sheet (SB16)

PTO/SB/16 (11-08)
Approved for use through 09/30/2010 OMB 0651-0032
U.S. Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE

Entity Status

Applicant claims small entity status under 37 CFR 1.27

(●) Yes, applicant qualifies for small entity status under 37 CFR 1.27

( ) No

Warning

Petitioner/applicant is cautioned to avoid submitting personal information in documents filed in a patent application that may contribute to identity theft. Personal information such as social security numbers, bank account numbers, or credit card numbers (other than a check or credit card authorization form PTO-2038 submitted for payment purposes) is never required by the USPTO to support a petition or an application. If this type of personal information is included in documents submitted to the USPTO, petitioners/applicants should consider redacting such personal information from the documents before submitting them to USPTO. Petitioner/applicant is advised that the record of a patent application is available to the public after publication of the application (unless a non-publication request in compliance with 37 CFR 1.213(a) is made in the application) or issuance of a patent. Furthermore, the record from an abandoned application may also be available to the public if the application is referenced in a published application or an issued patent (see 37 CFR1.14). Checks and credit card authorization forms PTO-2038 submitted for payment purposes are not retained in the application file and therefore are not publicly available.

Signature

Please see 37 CFR 1.4(d) for the form of the signature.

Signature	/John P. O'Banion/			Date (YYYY-MM-DD)	2011-03-07
First Name	John	Last Name	O'Banion	Registration Number (If appropriate)	33201

This collection of information is required by 37 CFR 1.51. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **This form can only be used when in conjunction with EFS-Web. If this form is mailed to the USPTO, it may cause delays in handling the provisional application.**

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or paten. Accordingly, pursuant to the requirements of the Act, please be advised that : (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, t o a n other federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

METAL-ORGANIC FRAMEWORKS AS MATERIALS FOR H_2/CO_2 SEPARATION

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] Not Applicable

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] This invention was made with Government support under Grant No. DE-SC0001015 awarded by the Department of Energy. The Government has certain rights in this invention.

INCORPORATION-BY-REFERENCE OF MATERIAL SUBMITTED ON A COMPACT DISC

[0003] Not Applicable

NOTICE OF MATERIAL SUBJECT TO COPYRIGHT PROTECTION

BACKGROUND OF THE INVENTION

[0005] 1. Field of Invention

[0006] This invention pertains to the use of metal-organic frameworks as adsorbents for hydrogen purification, and more particularly to the separation of

CO_2 from H_2 gases from a stream of combined gases.

[0007] 2. Background

[0008] Carbonaceous materials such as agricultural, forest and municipal waste as well as natural gas, coal, oil shale and oil sands can be converted into combustible gases through thermochemical processing. Rather than burning biomass or fossil resources directly, gasification can be used to produce a mixture of carbon monoxide, hydrogen and methane known as synthesis gas (syngas). These thermochemical processes utilize conversion technologies such as gasification, reforming, pyrolysis, catalysis and other relevant processes for the conversion of fossil fuels (natural gas, coal, oil, oil shale, etc) and renewable biomass to syngas.

[0009] Synthesis gas comprises primarily carbon monoxide (CO) and hydrogen (H_2) and can come from many sources. Typical synthesis gas from gasified coal includes carbon monoxide, hydrogen and lesser amounts of carbon dioxide (CO_2) and other useful gases such as methane (CH_4) as well as small amounts of light paraffins, such as ethane and propane. Syngas may also contain gases such as nitrogen, argon, helium, oxygen-containing compounds and water in a gaseous state. Syngas can subsequently undergo the water-gas shift reaction to produce primarily hydrogen and carbon dioxide.

$$\text{Steam-Methane Reformation: } H_2O + CH_4 \rightarrow 3\,H_2 + CO$$

$$\text{Water-gas shift: } H_2O + CO \rightarrow H_2 + CO_2$$

[0010] The separation of CO_2 from H_2 is highly significant in the context of two distinct applications: (i) the capture of CO_2 emissions like those produced from coal gasification power plants, and (ii) the purification of hydrogen gas, which is synthesized on megaton scales annually. For example, CO_2/H_2 separation can be used to capture CO_2 from power plants in the context of coal gasification, where coal is converted into syngas (CO and H_2) which subsequently undergoes the water-gas shift reaction to generate CO_2 and H_2. The hydrogen is used to generate electricity after it is separated from CO_2, which can then be prevented from release into the atmosphere. This strategy, called pre-combustion CO_2

capture, is advantageous in comparison to other CO_2 capture technologies that require separation of CO_2 from N_2, O_2, or CH_4 because of the stark difference in size and polarizability between CO_2 and H_2.

[0011] As mentioned above, CO_2/H_2 separation is also relevant to hydrogen syntheses, which is primarily achieved by reforming natural gas to generate syngas and again utilizing the water-gas shift reaction to generate hydrogen.

[0012] Approximately 50 million tons of H_2 are synthesized each year using this pair of reactions, and the separation of H_2 and CO_2 is most commonly accomplished using pressure-swing adsorption (PSA), where the gas product mixture is exposed under high pressure to solid adsorbents (a mixture of zeolites and activated carbons) that selectively adsorb CO_2, and then release CO_2 upon a pressure decrease or purge with hydrogen. PSA is advantageous in comparison to other separations techniques such as liquid absorbents, membrane or cryogenic separation due to the high purity and yield of hydrogen that can be produced.

[0013] Much of the energy input for a PSA system is used in the mass transport of the gas and regeneration of the adsorbents, and as a result improving adsorbent selectivity and capacity for CO_2 would increase efficiency. Extensive experimental and theoretical investigations suggest that further optimization of zeolites and activated carbons will yield only modest improvements in CO_2/H_2 separation performance. Thus, there is a need for new types of adsorbents with the potential for displaying significantly improved CO_2 capacity and selectivity.

[0014] 3. Related Patent Documents

[0015] The following U.S. patents and published U.S. patent applications provide additional background information and are incorporated herein by reference in their entireties:

[0016] (a) U.S. Patents:

[0017] 3,176,444; 3,252,268; 3,323,288; 3,430,418; 3,564,816; 3,986,849; 4,077,779; 4,077,780; 4,553,981; 4,696,680; 4,726,815; 4,853,004; 4,957,514; 4,964,888; 5,152,975; 5,538,706; 5,674,311; 5,753,010; 5,912,422; 6,007,606;

6,027,548; 6,027,549; 6,152,991; 6,197092; 6,302,943; 6,340,382; 6,402,813; 6,514,317; 7,537,742; 4,810,266; 7,819,932; 6,929,679.

[0018] (b) U.S. Patent Application Publications:

[0019] 2006/0112696; 2007/0212295; 2007/0068389; 2010/0069234; 2006/0252641; 2006/0112696; 2007/0130832.

SUMMARY OF THE INVENTION

[0020] A novel group of adsorbents for pressure swing adsorption (PSA) separation of CO_2 from H_2 or other gases is provided that offers significant capacity and selectivity over zeolites and activated carbons. Metal-organic frameworks are a group of porous crystalline materials formed of metal cations or clusters joined by multitopic organic linkers. The high surface area and low bulk densities of these materials provide large gravimetric and volumetric capacities for CO_2.

[0021] Five selected metal-organic frameworks exhibiting representative properties, namely high surface area, structural flexibility, or the presence of open metal cation sites, were tested for utility in the separation of CO_2 from H_2 via pressure swing adsorption. Single-component CO_2 and H_2 adsorption isotherms were measured at 313 K and pressures up to 40 bar for (i) $Zn_4O(BTB)_2$ (MOF-177, BTB^{3-} = 1,3,5-benzenetribenzoate); (ii) $Be_{12}(OH)_{12}(BTB)_4$ (Be-BTB); (iii) Co(BDP) (BDP^{2-} = 1,4-benzenedipyrazolate); (iv) $H_3[(Cu_4Cl)_3(BTTri)_8]$ (Cu-BTTri, $BTTri^{3-}$ = 1,3,5-benzenetristriazolate), and (v) $Mg_2(dobdc)$ ($dobdc^{4-}$ = 1,4-dioxido-2,5-benzenedicarboxylate).

[0022] These materials exhibit record internal surface areas and, as a result, a tremendous CO_2 storage capacity at the pressures relevant for a CO_2/H_2 separation (i.e. 5-40 bar). Further, the high adsorbent surface area enhances the selectivity for adsorption of CO_2 over H_2, since H_2 packs more efficiently than CO_2 due to its smaller size. Moreover, the ability to adjust the nature of the surfaces within these materials can be exploited to increase the strength of the interaction with CO_2.

[0023] The Ideal Adsorbed Solution Theory was also used to estimate realistic

isotherms for the 80:20 and 60:40 H_2:CO_2 gas mixtures relevant to H_2 purification and pre-combustion CO_2 capture, respectively. In the former case, the results afford CO_2/H_2 selectivities between 5 and 450, and mixed-gas working capacities, assuming a 1 bar purge pressure, as high as 8.2 mol/kg and 7.5 mol/L. In particular it was discovered that, Mg_2(dobdc), a framework bearing surfaces with a high concentration of exposed Mg^{2+} cation sites, offers significant improvements over commonly used adsorbents.

[0024] Further aspects of the invention will be brought out in the following portions of the specification, wherein the detailed description is for the purpose of fully disclosing preferred embodiments of the invention without placing limitations thereon.

BRIEF DESCRIPTION OF THE DRAWINGS

[0025] Further aspects of the invention will be brought out in the following portions of the specification, wherein the detailed description is for the purpose of fully disclosing preferred embodiments of the invention without placing limitations thereon.

[0026] FIG. 1 depicts plots of adsorbed amounts of pure CO_2 (triangles) and H_2 (circles) as a function of bulk gas pressure on MOF-177, Be-BTB, Co(BDP), Cu-BTTri and Mg_2(dobdc).

[0027] FIG. 2A and FIG. 2B depict the adsorption selectivity of CO_2 over H_2 as a function of bulk gas pressure on MOF-177, Be-BTB, Co(BDP), Cu-BTTri and Mg_2(dobdc) for an 80:20 and 60:40 H_2:CO_2 gas mixture, respectively.

[0028] FIG. 3A and FIG. 3B depict the gravimetric working capacity of CO_2 as a function of bulk gas pressure on MOF-177, Be-BTB, Co(BDP), Cu-BTTri and Mg_2(dobdc) for an 80:20 and 60:40 H_2:CO_2 gas mixture, respectively. These represent a purge pressure of 1 bar.

[0029] FIG. 4A and FIG. 4B depict the volumetric working capacity of CO_2 as a function of bulk gas pressure on MOF-177, Be-BTB, Co(BDP), Cu-BTTri and Mg_2(dobdc) for an 80:20 and 60:40 H_2:CO_2 gas mixture, respectively. These represent a purge pressure of 1 bar.

[0030] FIG. 5A and FIG. 5B depict Configurational-Bias Monte Carlo simulations. FIG. 5A shows absolute pure-component adsorption isotherms for CO_2 (triangles) and H_2 (circles) at 313 K in MOF-177. The lines are the dual-Langmuir-Freundlich fits of the pure component isotherms for CO_2 (solid) and H_2 (dashed). FIG. 5B shows the component loadings in an 80:20 H_2:CO_2 mixture for CO_2 (triangles) and H_2 (circles) at 313 K in MOF-177 determined using CBMC simulations. The lines are the IAST estimations of the same mixture using the dual-Langmuir-Freundlich fits of the pure component isotherms for CO_2 (solid) and H_2 (dashed).

DESCRIPTION OF THE INVENTION

[0031] The present invention provides a method and metal-organic framework materials that act as adsorbents for hydrogen purification and pre-combustion carbon dioxide capture from a pressurized stream of mixed gases by pressure swing adsorption. The metal organic framework materials selectively adsorb carbon dioxide at high pressures in the presence of hydrogen and desorb carbon dioxide upon a decrease of carbon dioxide pressure.

[0032] Due to their high surface areas and low bulk densities, these materials demonstrate remarkable working capacities for sequestering carbon dioxide, making them ideal for use in large scale processing plants and a great improvement over current adsorbents. The successful implementation of these new adsorbents could both reduce the substantial energy cost of hydrogen purification and reduce or eliminate CO_2 emissions in the generation of electricity from coal or syngas.

[0033] Pure component H_2 and CO_2 isotherms up to 40 bar at 313 K were recorded on a representative variety of metal-organic frameworks using a volumetric Sieverts-type gas sorption analyzer. The compounds $Zn_4O(BTB)_2$ (MOF-177, BTB^{3-} = 1,3,5-benzenetribenzoate) and $Be_{12}(OH)_{12}(BTB)_4$ (Be-BTB) were chosen as representative of metal-organic frameworks exhibiting a high surface area and a rigid framework structure. As a flexible framework, Co(BDP) (BDP^{2-} = 1,4-benzenedipyrazolate) was selected owing to its high surface area

relative to most compounds of this type. Finally, $H_3[(Cu_4Cl)_3(BTTri)_8]$ (Cu-BTTri, $BTTri^{3-}$ = 1,3,5-benzenetristriazolate) and $Mg_2(dobdc)$ ($dobdc^{4-}$ = 1,4-dioxido-2,5-benzenedicarboxylate) were chosen as prototypical of two broad classes of metal-organic frameworks that possess surfaces coated with exposed metal cations. All five compounds were synthesized and activated, and their Langmuir surface areas (see FIG. 1) were determined from N_2 adsorption isotherms collected at 77 K.

[0034] FIG. 1 shows CO_2 and H_2 isotherms for MOF-177, Be-BTB, Co(BDP), Cu-BTTri, and $Mg_2(dobdc)$, where triangles represent CO_2 adsorption and circles represent H_2 adsorption. As can be seen, the CO_2 adsorption capacity scales roughly with surface area, and is much higher than the corresponding adsorption capacity for H_2 due to the higher polarizability and quadrupole moment of the CO_2 molecule. Notably, Cu-BTTri and $Mg_2(dobdc)$ exhibit high CO_2 adsorption (particularly at low pressures) relative to their surface areas due to the additional polarizing influence of the open metal cation sites decorating the framework surfaces. Contrasting with these results, the step-like features in the CO_2 isotherm for Co(BDP) are likely associated with a gate-opening phenomenon arising from the flexibility of the framework structure.

[0035] Ideal adsorbed solution theory (IAST) was applied to these data in order to estimate realistic adsorption isotherms for the 80:20 and 60:40 H_2:CO_2 gas mixtures relevant to H_2 purification and pre-combustion CO_2 capture, respectively. Evidence of the validity of its use for estimation of CO_2/H_2 equilibria in MOF's is presented in FIG. 5A and FIG. 5B. FIG. 2A and FIG. 2B, respectively, show the selectivity values obtained for 80:20 and 60:40 H_2:CO_2 mixtures for the five metal-organic frameworks studied along with two common activated carbons and zeolites 13X and 5A, both exceptionally selective with a high CO_2 capacity as well.

[0036] As can be seen in FIG. 2A and FIG. 2B, the two frameworks with exposed metal cation sites, Cu-BTTri and $Mg_2(dobdc)$, display by far the highest selectivities, presumably owing to the greater polarizability of CO_2 versus H_2.

With a greater concentration of cationic sites exposed on its surface, Mg_2(dobdc) shows the best performance, exhibiting a selectivity that gradually decreases from 538 at 5 bar to 244 at 40 bar.

[0037] Due to the nature of PSA purification, the working capacity, that is the difference between the capacity at the high intake pressure and at the lower purge pressure, is one metric for evaluating adsorbent candidates. The CO_2 working capacities for the metal-organic frameworks under an 80:20 H_2:CO_2 mixture and assuming a purge pressure of 1 bar were calculated using IAST and compared to the values obtained for the zeolites and activated carbons. While gravimetric capacities (moles of CO_2 adsorbed per kg of adsorbent) are normally reported when evaluating materials for a CO_2/H_2 separation, the volumetric working capacities (moles of CO_2 adsorbed per L of adsorbent) were also calculated, since both factors are critical in designing a PSA separation process. Here, the true advantage of utilizing metal-organic frameworks comes to the fore. Gravimetric working capacities are shown in FIG. 3A and FIG. 3B and volumetric working capacities are shown in FIG. 4A and FIG. 4B, where FIG. 3A and FIG. 4A represent an 80:20 H_2:CO_2 mixture and FIG. 3B and FIG. 4B represent a 60:40 H_2:CO_2 mixture. Owing to its greater specific surface area and larger pore sizes, Mg_2(dobdc) outperforms the zeolites by a considerable margin, with working capacities climbing to values of 7.8 mol/kg and 7.1 mol/L at 40 bar. Thus, at higher pressures, use of Mg_2(dobdc) in place of zeolite 13X could reduce the mass of adsorbent needed by a factor of 2.4 and the volume needed by a factor of 3.2. For a 60:40 H_2:CO_2 mixture, the working capacities of metal-organic frameworks offer similar benefits. Here, however, due to the higher partial pressure of CO_2, the relative steepness of the CO_2 isotherm for Mg_2(dobdc) is less of an advantage, resulting in working capacities that are very comparable to those of Cu-BTTri.

[0038] In concert, the selectivity and working capacity demonstrate that Mg_2(dobdc) outperforms all materials studied in terms of capacity while still maintaining the selectivity similar to zeolite 13X, as the 313 K data for

Mg_2(dobdc) falls between 323 K and 303 K selectivities for zeolite 13X. In a similar comparison, Cu-BTTri exhibited selectivity values comparable to an activated carbon but demonstrated a much higher working capacity that carbon.

[0039] The stability of the proposed metal-organic frameworks under PSA H_2/CO_2 separation conditions, the regenerability by H_2 purge as opposed to pressure drop, and the cost of these materials when synthesized on industrial scales will improve with further investigation. Generally, the regeneration of these metal-organic framework adsorbents is not expected to prevent their use because Mg_2(dobdc) has a similar heat of adsorption to zeolite 5A, a material regularly used in this process.

[0040] While one of the most productive applications of this technology is in pressure-swing adsorption columns using metal-organic frameworks as adsorbents, many other opportunities exist for the use of these materials in H_2/CO_2 separations as well. For example, mixtures of metal-organic frameworks and activated carbons could prove economically ideal, such as seen with mixtures of zeolites and activated carbons are used currently in PSA beds. Additionally, the incorporation of metal-organic frameworks into either H_2- or CO_2-selective membranes is considered feasible. Finally, the use of thermally-stable and hydrolytically-stable metal-organic frameworks in high temperature sorption-enhanced water-gas shift reactions could make use of the advantages of PSA while also increasing the efficiency and decreasing the temperature of the water-gas shift reaction itself.

[0041] Compound Synthesis

[0042] The synthesis and characterization of the five illustrative compounds studied for CO_2/H_2 separation are detailed below. In these syntheses, dichloromethane was received from Aldrich and dried over activated 4 Å sieves prior to use. Ethanol was refluxed for 24 hours over Mg turnings and I_2. All other reagents were obtained from commercial vendors and used without further purification. Powder X-ray diffraction patterns were obtained on a Bruker D8 Advance diffractometer with a Cu anode (λ = 1.5406 Å). Infrared spectra were

obtained on a Perkin-Elmer Spectrum 100 Optica FTIR spectrometer furnished with an attenuated total reflectance accessory (ATR).

[0043] **Low-Pressure Gas Sorption Measurements**. These were used to confirm that the samples maintained a surface area in agreement with (or higher than) those previously reported. Glass sample tubes of a known weight were loaded with approximately 200 mg of sample, and sealed using a TranSeal. Samples were degassed at 100 °C for 24 hours on a Micromeritics ASAP 2020 analyzer until the outgas rate was no more than 1 mTorr/min. The degassed sample and sample tube were weighed precisely and then transferred back to the analyzer (with the TranSeal preventing exposure of the sample to the air after degassing). The outgas rate was again confirmed to be less than 1 mTorr/min. Adsorption isotherms were measured at 77 K in a liquid nitrogen bath for H_2 and N_2, and at 87 K in a liquid argon bath for H_2.

[0044] **High-Pressure Gas Sorption Measurements**. In a typical measurement, at least 200 mg of sample was loaded in a sample holder in a glove box under an argon atmosphere. The sample was evacuated at 100 °C for 10 hours under a pressure of less than 10^{-5} torr. Hydrogen and carbon dioxide excess adsorption measurements were performed on an automated Sieverts' apparatus (PCTPro-2000 from Hy-Energy Scientific Instruments LLC) over a pressure range of 0-50 bar. UHP-grade hydrogen, carbon dioxide and helium (99.999% purity) were used for all measurements. Total adsorption was calculated using NIST Thermochemical Properties of Fluid Systems: CO_2 and H_2 densities between 0 and 50 bar were fit using a sixth-order polynomial, then multiplied by the pore volume of each material.

[0045] **Ideal Adsorbed Solution Theory Calculations**. The ideal adsorbed solution theory (IAST) of Prausnitz and Myers was used to estimate the composition of the adsorbed phase from pure component isotherm data. Experimental absolute isotherm data were fit to the dual-site Langmuir-Freundlich isotherm for CO_2 adsorption and the single-site Langmuir-Freundlich model for H_2. H_2 saturation capacities were allowed to refine between two and

three times the saturation capacity for CO_2, which was confirmed visually. These fits computed according to equation 1 are reported in Table 1. Table 1 details fit parameters used in this study for CO_2 and H_2 using equation 1, where *n* is gas uptake in mmol/g. The integrals were computed numerically and the adsorbed phase composition that minimized the difference between the integrals of the two spreading pressures was found using Mathematica®.

[0046] A sample calculation for determining the mole fraction of CO_2 adsorbed in an 80:20 H_2:CO_2 mixture in Mg_2(dobdc) is included below. Selectivities were then calculated according to equation 2 below, where x_i is the mole fraction of component i in the adsorbed phase and y_i is the mole fraction of component i in the bulk. Working capacities were calculated according to equation 3 where n_t is the total number of adsorbed moles of gas per unit mass of adsorbent and n_i^o is the number of moles of component i in the adsorbed phase per unit mass of adsorbent at the partial pressure of i in the gas phase divided by the mole fraction in the adsorbed phase.

$$n = \frac{a * b * p^{1/c}}{1 + b * p^{1/c}} + \frac{d * e * p^{1/f}}{1 + e * p^{1/f}} \quad (1)$$

$$S = \frac{x_i y_j}{x_j y_i} \quad (2)$$

$$\frac{1}{n_t} = \frac{x_i}{n_i^o} + \frac{x_j}{n_j^o} \quad (3)$$

[0047] Ideal Adsorbed Solution Theory Validation for CO_2/H_2 Mixtures in Metal-Organic Frameworks. The accuracy of the IAST for estimation of component loadings for adsorption of a wide variety of binary mixtures in zeolites has been established with the aid of Configurational-Bias Monte Carlo (CBMC) simulations. As illustration of the validity of the use of the IAST for estimation of CO_2/H_2 adsorption equilibrium in MOF's, CBMC results for adsorption of CO_2/H_2 mixtures in MOF-177 were obtained at 313 K, the temperature used in the experimental

work. The CBMC simulation methodology is similar to that described in published work. The symbols in FIG. 5A represent the pure component adsorption isotherms for CO_2 and H_2 in MOF-177 obtained from CBMC. The continuous solid lines in FIG. 5A are the dual-Langmuir-Freundlich fits of the isotherms.

[0048] The component loadings in an 80:20 H_2:CO_2 mixture at 313 K, determined using CBMC simulations, are presented FIG. 5B as filled symbols. The continuous solid lines are the IAST estimations using the dual-Langmuir-Freundlich fits of the pure component isotherms. It is to be noted that there is excellent agreement between the IAST predictions and the CBMC simulated component loadings in the mixture. This agreement is typical for adsorption of CO_2: H_2 mixtures in MOF's.

[0049] 1. Synthesis of MOF-177

[0050] **(a) Synthesis of 1,3,5-triphenylbenzene**. 1,3,5-triphenylbenzene was prepared according to literature procedure.

[0051] **(b) Synthesis of 4,4',4''-benzene-1,3,5-triyl-tribenzoic acid (H_3BTB)**. H_3BTB was synthesized from 1,3,5-triphenylbenzene and nitric acid according to literature procedure.

[0052] **(c) Synthesis of MOF-177**. MOF-177 was prepared according to literature procedure.

[0053] **(d) Activation of MOF-177**. Activation of the sample was performed by transferring the collected product into a nitrogen-filled glove bag, where the solid was soaked in N,N-Dimethylformamide (50 mL) for 24 hours. The supernatant was decanted and replenished a further two times over two days. The solid was then soaked in dichloromethane (50 mL) for 24 hours. The supernatant was decanted and replenished a further three times over three days, and after the final wash a gentle stream of nitrogen was passed over the sample so as to remove excess solvent. The product is hygroscopic and was therefore stored in a glove box under a dinitrogen atmosphere. The final degassing was performed on a vacuum manifold at 1 mTorr and 100 °C for 10 hours. Surface area was

determined by N_2 adsorption at 77 K and confirmed with literature data. Powder pattern was compared to the simulated pattern from the crystal structure.

[0054] 2. Synthesis of Be-BTB

[0055] **(a) Synthesis of $Be_{12}(OH)_{12}$(1,3,5-benzenetribenzoate)$_4$ (Be-BTB)**. The same sample characterized in Sumida *et al.* was used for this study.

[0056] **(b) Activation of BeBTB**. BeBTB was activated according to literature procedure.

[0057] 3. Synthesis of Co(BDP)

[0058] **(a) Synthesis of 1,4-benzenedi(4'-pyrazolyl) (H_2BDP)**. H_2BDP was synthesized according to literature procedure.

[0059] **(b) Synthesis of CoBDP**. CoBDP was synthesized according to literature procedure.

[0060] **(c) Activation of CoBDP**. CoBDP was evacuated at ambient temperature at 1000 mTorr for 24 hours and then transferred quickly to a Schlenk flask in a glovebag. The sample was then evacuated at 1 mTorr for two days and brought to 170 °C at a ramp rate of 5 °C per hour.

[0061] 4. Synthesis of Cu-BTTri

[0062] **(a) Synthesis of 1,3,5-tris(triazol-5-yl)benzene (H_3BTTri)**. H_3BTTri was synthesized according to literature procedure.

[0063] **Synthesis of CuBTTri**. CuBTTri was synthesized according to literature procedure.

[0064] **(b) Activation of CuBTTri**. CuBTTri was activated according to literature procedure.

[0065] 5. Synthesis of Mg_2 (dobdc)

[0066] **(a) Synthesis of Mg_2(dobdc)**. Mg_2(dobdc) was synthesized according to literature procedure.

[0067] **(b) Activation of Mg_2(dobdc)**. Mg_2(dobdc) was activated using a strategy adapted from the literature procedure. The yellow microcrystalline material was combined and washed repeatedly with DMF and soaked in DMF for 24 hours. The DMF was decanted, and freshly distilled methanol was added. The

solid was then transferred to a nitrogen-filled glovebox. The methanol was decanted and the solid was soaked in DMF on a hotplate set at 100 °C for 18 hours. The DMF was decanted and replaced, and the solid was soaked at 100 °C for 4 hours. The DMF was decanted and replaced by methanol, which was decanted and replenished 6 times with a minimum of 6 hours between washes.

[0068] From the discussion above it will be appreciated that the invention can be embodied in various ways, including the following:

[0069] 1.A method for separating carbon dioxide gas from a mixture of gases, comprising providing a stream of mixed gases containing carbon dioxide; pressurizing the stream of mixed gases to a pressure between approximately 5 bar and approximately 40 bar; bringing and maintaining gas stream temperature to a temperature between approximately 300 K and approximately 320 K; exposing the pressurized mixed gases to a contained bed of at least one metal-organic framework carbon dioxide adsorbent; and collecting gases from the pressurized mixed gas stream that are not adsorbed to the metal-organic carbon dioxide adsorbent.

[0070] 2. An method as recited in embodiment 1, further comprising: removing the bed of adsorbent from the pressurized mixed gas stream; lowering the pressure within the contained bed of adsorbents; and purging the contained bed of adsorbent of carbon dioxide with a purge gas; wherein the change in pressure in the contained bed and purge gas desorbs carbon dioxide from the adsorbent bed and expels the carbon dioxide from the contained bed.

[0071] 3. A method as recited in embodiment 2, wherein the purge gas comprises hydrogen gas.

[0072] 4. A method as recited in embodiment 2, wherein the purge gas is maintained at a pressure of approximately one bar and a temperature between approximately 300 K and approximately 320 K.

[0073] 5. A method as recited in embodiment 1, wherein the metal-organic framework adsorbent is an adsorbent selected from the group of adsorbents consisting essentially of MOF-177, Co(BDP), Cu-BTTri, Be-BTB and Mg_2(dobdc).

[0074] 6. A method as recited in embodiment 1, wherein the mixed gas is a gas selected from the group of mixed gases consisting essentially of synthesis gas, steam-methane water gas shift reaction products, contaminated hydrogen gas and gaseous carbon fuel combustion products.

[0075] 7. A method as recited in embodiment 1, wherein the temperature of the mixed gas is maintained at temperature of between approximately 310 K and approximately 315 K.

[0076] 8. A method as recited in embodiment1, wherein the temperature of the mixed gas is maintained at temperature of 313 K.

[0077] 9. A method as recited in embodiment 1, wherein the pressure of the mixed gas is maintained at between approximately 25 bar and approximately 35 bar.

[0078] 10. A method as recited in embodiment1, wherein the pressure of the mixed gas is maintained at pressure of 35 bar.

[0079] 11. A method for separating carbon dioxide gas from synthesis gas, comprising: converting biomass or fossil fuels to a stream of synthesis gases; pressurizing the stream of synthesis gases to a pressure between approximately 5 bar and approximately 40 bar; bringing and maintaining the gas stream temperature to a temperature between approximately 300 K and approximately 320 K; exposing the pressurized synthesis gases to a container with a bed of at least one metal-organic framework carbon dioxide adsorbent; collecting gases from the pressurized synthesis gas stream that are not adsorbed to the metal-organic carbon dioxide adsorbent; and releasing adsorbed carbon dioxide from said bed by reducing the partial pressure of carbon dioxide in the bed container.

[0080] 12. A method as recited in embodiment 11, further comprising: purging the bed of adsorbent of carbon dioxide with a purge gas; wherein the change in partial pressure of carbon dioxide in the bed and purge gas desorbs carbon dioxide from the adsorbent bed and expels the carbon dioxide from the container.

[0081] 13. A method as recited in embodiment 12, wherein the purge gas is a gas selected from the group of gases consisting essentially of hydrogen gas,

methane gas and synthesis gas.

[0082] 14. A method as recited in embodiment 12, wherein the purge gas is a gas introduced to said adsorbent bed container at a pressure of approximately 1 bar or greater.

[0083] 15. A method as recited in claim 11, further comprising: filtering the synthesis gas prior to pressurization to remove volatile liquids.

[0084] 16. A method for separating carbon dioxide gas from a mixture of gases, comprising: providing a stream of mixed gases containing carbon dioxide; pressurizing the stream of mixed gases to a pressure between approximately 5 bar and approximately 40 bar; bringing and maintaining gas stream temperature to a temperature between approximately 300 K and approximately 320 K; exposing the pressurized mixed gases to a contained bed of at least one metal-organic framework carbon dioxide adsorbent; collecting gases of the pressurized mixed gas stream that are not adsorbed to the metal-organic carbon dioxide adsorbent for a first period of time; closing the flow of pressurized mixed gas to the contained bed of adsorbents; reducing the pressure of the contained bed for a second period of time; purging said contained bed of adsorbed carbon dioxide sequestered in the adsorbent by opening the flow of pressurized mixed gas stream; and collecting purged gases from the contained bed.

[0085] 17. A metal-organic framework carbon dioxide adsorbent, comprising an adsorbent selected from the group of adsorbents consisting essentially of MOF, Co(BDP), Cu-BTTri, Be-BTB and Mg_2(dobdc).

[0086] 18. A metal-organic framework carbon dioxide adsorbent, comprising a combination of activated carbon and an adsorbent selected from the group of adsorbents consisting essentially of MOF, Co(BDP), Cu-BTTri, Be-BTB and Mg_2(dobdc).

[0087] 19. A carbon dioxide adsorbent and gas separation system as disclosed and described herein.

[0088] Although the description above contains many details, these should not be construed as limiting the scope of the invention but as merely providing

illustrations of some of the presently preferred embodiments of this invention. Therefore, it will be appreciated that the scope of the present invention fully encompasses other embodiments which may become obvious to those skilled in the art, and that the scope of the present invention is accordingly to be limited by nothing other than the appended claims, in which reference to an element in the singular is not intended to mean "one and only one" unless explicitly so stated, but rather "one or more." All structural, chemical, and functional equivalents to the elements of the above-described preferred embodiment that are known to those of ordinary skill in the art are expressly incorporated herein by reference and are intended to be encompassed by the present claims. Moreover, it is not necessary for a device or method to address each and every problem sought to be solved by the present invention, for it to be encompassed by the present claims. Furthermore, no element, component, or method step in the present disclosure is intended to be dedicated to the public regardless of whether the element, component, or method step is explicitly recited in the claims. No claim element herein is to be construed under the provisions of 35 U.S.C. 112, sixth paragraph, unless the element is expressly recited using the phrase "means for."

Table 1

		a	b	c	d	e	f
BPL Carbon	CO_2	13.64863	0.09936	1.11448	1.15061	1.43805	1.2677
	H_2	44	0.00118	.9443			
Activated Carbon JX101	CO_2	7.09833	0.07527	0.98214	4.52688	0.29105	1.3196
	H_2	23	0.00137	1.078			
Zeolite 5A	CO_2	1	0.17293	2.03809	6	1.26959	5.04918
	H_2	21	0.00126	0.9551			
Zeolite 13X 303 K	CO_2	3.95656	1.0857	1.15515	2.64889	1097.22264	0.33342
	H_2	12	0.00798	1.333			
Zeolite 13X 323 K	CO_2	1.84393	0.13012	0.70246	4.22215	6.73101	0.86914
	H_2	12.07927	0.00515	1.129			
Mg_2(dobdc)	CO_2	6.38772	0.03797	0.57124	9.05573	5.176	1.05626
	H_2	30	0.003	1.170			
MOF-177	CO_2	34.47581	$3.16502*10^{-4}$	0.37141	4.73161	0.11846	0.56647
	H_2	120	$7.89134*10^{-4}$	1.074			
Be-BTB	CO_2	33.6845	0.00262	0.51675	4.84087	0.19147	0.81552
	H_2	65	0.00155	0.8533			
Co(BDP)	CO_2	10.79363	0.00172	0.26894	5.89547	$2.61295*10^{-8}$	0.17522
	H_2	39.5	$6.9614*10^{-4}$	0.7460			
Cu-BTTri	CO_2	20.74633	0.09711	0.98401	1.09309	$1.89857*10^{-19}$	0.0864
	H_2	63	$5.13767*10^{-4}$	0.8573			

CLAIMS

We claim:

1. A method for separating carbon dioxide gas from a mixture of gases, comprising:

providing a stream of mixed gases containing carbon dioxide;

pressurizing said stream of mixed gases to a pressure between approximately 5 bar and approximately 40 bar;

bringing and maintaining gas stream temperature to a temperature between approximately 300 K and approximately 320 K;

exposing said pressurized mixed gases to a contained bed of at least one metal-organic framework carbon dioxide adsorbent; and

collecting gases of said pressurized mixed gas stream that are not adsorbed to the metal-organic carbon dioxide adsorbent.

2. A method as recited in claim 1, further comprising:

removing the bed of adsorbent from the pressurized mixed gas stream;

lowering the pressure within the contained bed of adsorbents; and

purging the contained bed of adsorbent of carbon dioxide with a purge gas;

wherein the change in partial pressure of carbon dioxide in said contained bed and purge gas desorbs carbon dioxide from the adsorbent bed and expels the carbon dioxide from the contained bed.

3. A method as recited in claim 2, wherein said purge gas comprises hydrogen gas.

4. A method as recited in claim 2, wherein said purge gas is maintained at a pressure of approximately one bar and a temperature between approximately 300 K and approximately 320 K.

5. A method as recited in claim 1, wherein said metal-organic framework adsorbent is an adsorbent selected from the group of adsorbents consisting essentially of an MOF, Co(BDP), Cu-BTTri, Be-BTB and Mg_2(dobdc).

6. A method as recited in claim 1, wherein said mixed gas is a gas selected from the group of mixed gases consisting essentially of reacted synthesis gas, steam-methane water gas shift reaction products, contaminated hydrogen gas and gaseous carbon fuel combustion products.

7. A method as recited in claim 1, wherein said temperature of said mixed gas is maintained at temperature of between approximately 310 K and approximately 315 K.

8. A method as recited in claim 1, wherein said temperature of said mixed gas is maintained at temperature of 313 K.

9. A method as recited in claim 1, wherein said pressure of said mixed gas is maintained at between approximately 25 bar and approximately 35 bar.

10. A method as recited in claim 1, wherein said pressure of said mixed gas is maintained at pressure of 35 bar.

11. A method for separating carbon dioxide gas from synthesis gas, comprising:

converting biomass or fossil fuels to a stream of synthesis gases;

pressurizing said stream of synthesis gases to a pressure between approximately 5 bar and approximately 40 bar;

bringing and maintaining the gas stream temperature to a temperature between approximately 300 K and approximately 320 K;

exposing said pressurized synthesis gases to a container with a bed of at least

one metal-organic framework carbon dioxide adsorbent;

collecting gases from said pressurized synthesis gas stream that are not adsorbed to the metal-organic carbon dioxide adsorbent; and

releasing adsorbed carbon dioxide from said bed by reducing the pressure in the bed container.

12. A method as recited in claim 11, further comprising:

purging the bed of adsorbent of carbon dioxide with a purge gas;

wherein the change in pressure in said bed and purge gas desorbs carbon dioxide from the adsorbent bed and expels the carbon dioxide from the container.

13. A method as recited in claim 12, wherein said purge gas is a gas selected from the group of gases consisting essentially of hydrogen gas, methane gas and synthesis gas.

14. A method as recited in claim 12, wherein said purge gas is a gas introduced to said adsorbent bed container at a pressure of approximately 1 bar.

15. A method as recited in claim 11, further comprising:

filtering the synthesis gas prior to pressurization to remove volatile liquids.

16. A method for separating carbon dioxide gas from a mixture of gases, comprising:

providing a stream of mixed gases containing carbon dioxide;

pressurizing said stream of mixed gases to a pressure between approximately 5 bar and approximately 40 bar;

bringing and maintaining gas stream temperature to a temperature between approximately 300 K and approximately 320 K;

exposing said pressurized mixed gases to a contained bed of at least one metal-organic framework carbon dioxide adsorbent;

collecting gases of said pressurized mixed gas stream that are not adsorbed to the metal-organic carbon dioxide adsorbent for a first period of time;

closing the flow of pressurized mixed gas to the contained bed of adsorbents;

reducing the pressure of the contained bed for a second period of time;

purging said contained bed of adsorbed carbon dioxide sequestered in said adsorbent by opening the flow of pressurized mixed gas stream; and

collecting purged gases from said contained bed.

17. A metal-organic framework carbon dioxide adsorbent, comprising an adsorbent selected from the group of adsorbents consisting essentially of an MOF, Co(BDP), Cu-BTTri, Be-BTB and Mg_2(dobdc).

18. A metal-organic framework carbon dioxide adsorbent, comprising a combination of activated carbon and an adsorbent selected from the group of adsorbents consisting essentially of an MOF, Co(BDP), Cu-BTTri, Be-BTB and Mg_2(dobdc).

19. A carbon dioxide adsorbent and gas separation system as disclosed and described herein.

ABSTRACT

The present invention describes the use of metal-organic frameworks as a new class of adsorbents for use in selective carbon dioxide adsorption via pressure swing adsorption near a temperature of 313 K. These materials selectively adsorb carbon dioxide at high pressures in the presence of hydrogen, and further desorb carbon dioxide upon pressure decrease. Due to their high surface areas and low bulk densities, these materials demonstrate remarkable working capacities for carbon dioxide, making them ideal for use in large scale processing plants and a great improvement on current adsorbents. Five metal-organic frameworks were tested here as representative of different properties available in this broad class of materials, and those with coordinatively unsaturated metal sites display both high selectivities for and working of carbon dioxide.

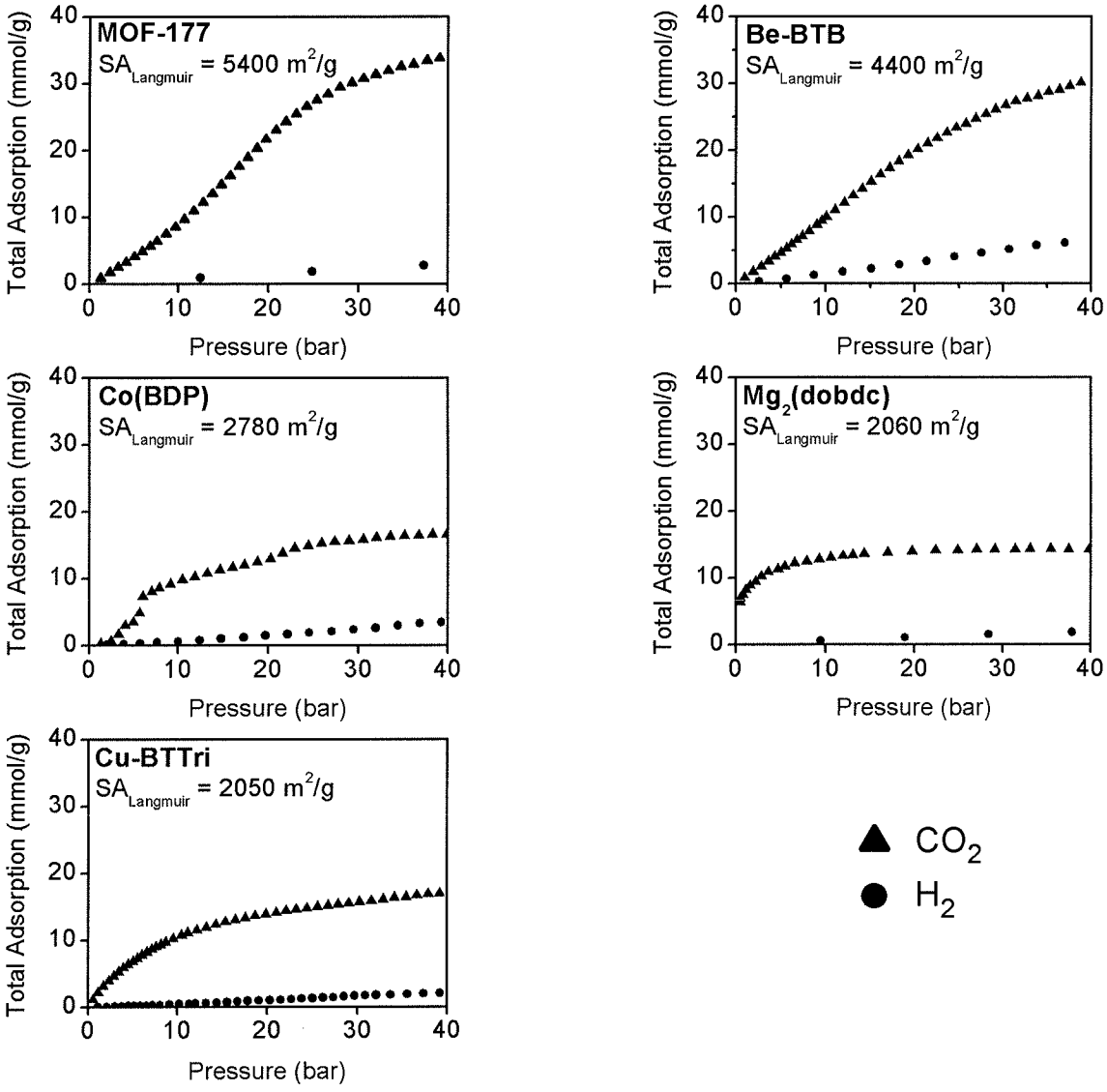
MOF-177
SA Langmuir = 5400 m2/g
Be-BTB
SA Langmuir = 4400 m2/g
Co(BDP)
SA Langmuir = 2780 m2/g
Mg2(dobdc)
SA Langmuir = 2060 m2/g
Cu-BTTri
SA Langmuir = 2050 m2/g
Total Adsorption (mmol/g)
Pressure (bar)
0
10
20
30
40
CO2
H2

FIG. 1

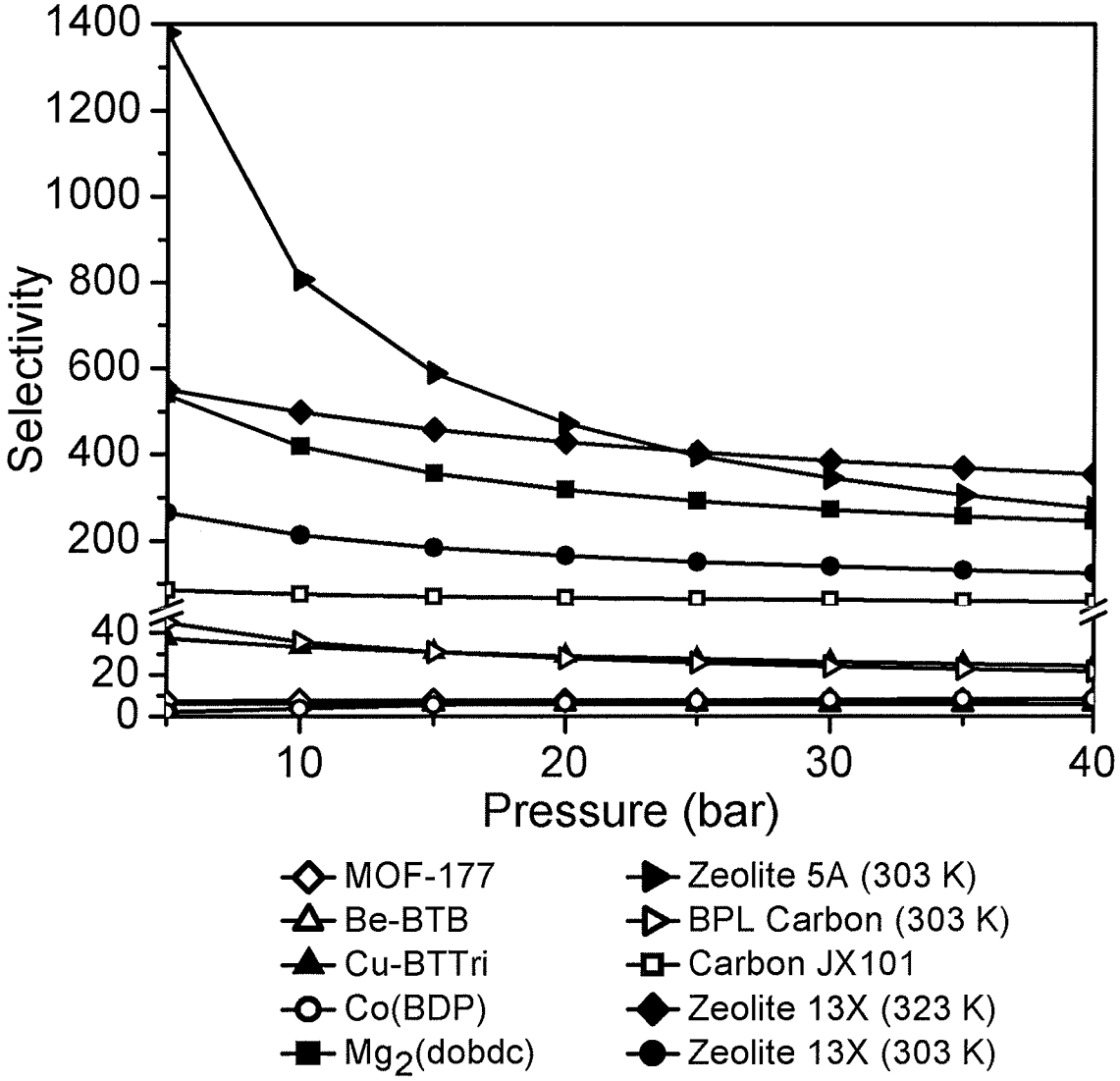
1400
1200
1000
800
600
400
200
40
20
0
Selectivity
10
20
30
40
Pressure (bar)
MOF-177
Be-BTB
Cu-BTTri
Co(BDP)
Mg2(dobdc)
Zeolite 5A (303 K)
BPL Carbon (303 K)
Carbon JX101
Zeolite 13X (323 K)
Zeolite 13X (303 K)

FIG. 2A

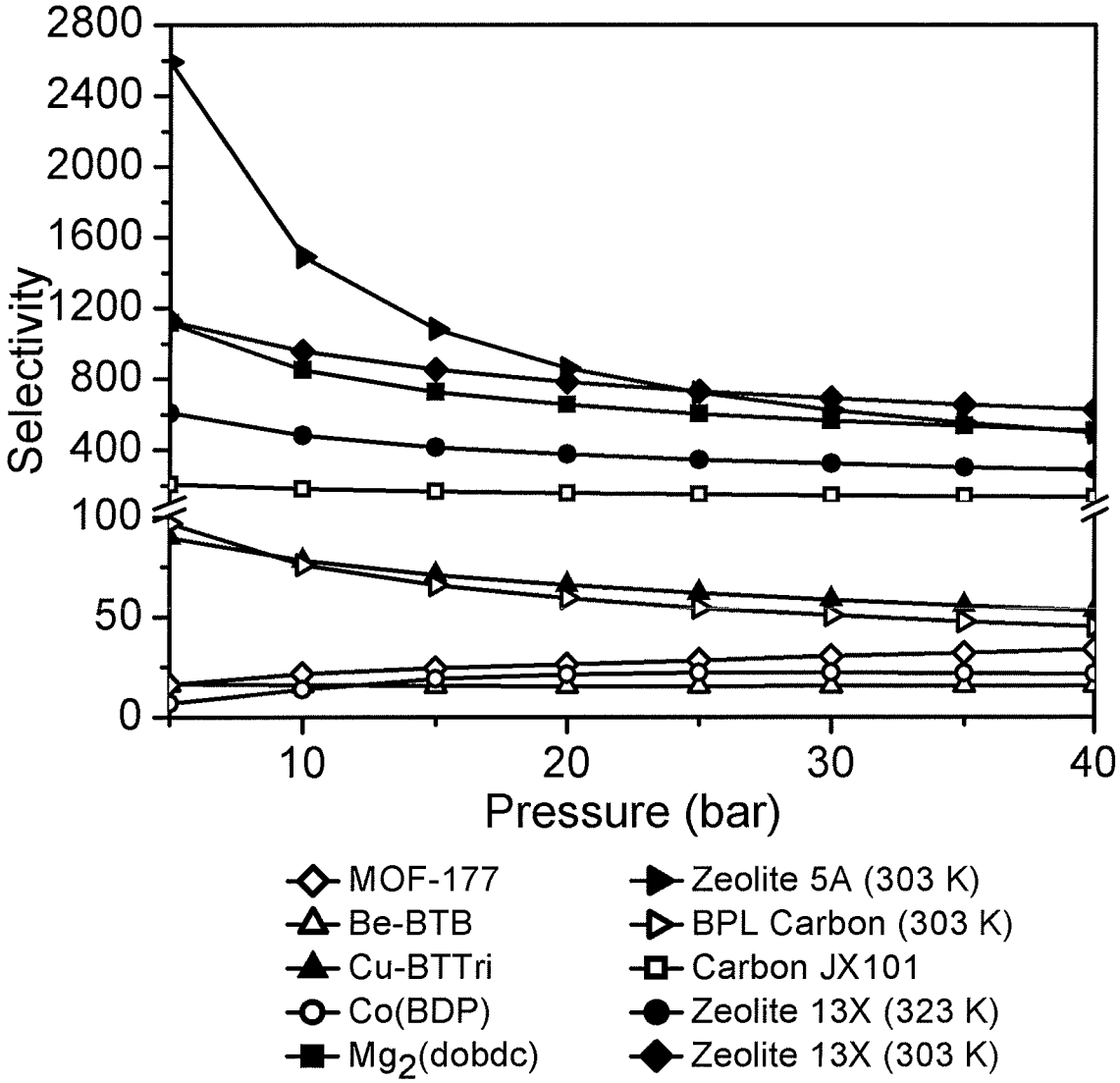
2800
2400
2000
1600
1200
800
400
100
50
0
Selectivity
10
20
30
40
Pressure (bar)
MOF-177
Be-BTB
Cu-BTTri
Co(BDP)
Mg2(dobdc)
Zeolite 5A (303 K)
BPL Carbon (303 K)
Carbon JX101
Zeolite 13X (323 K)
Zeolite 13X (303 K)

FIG. 2B

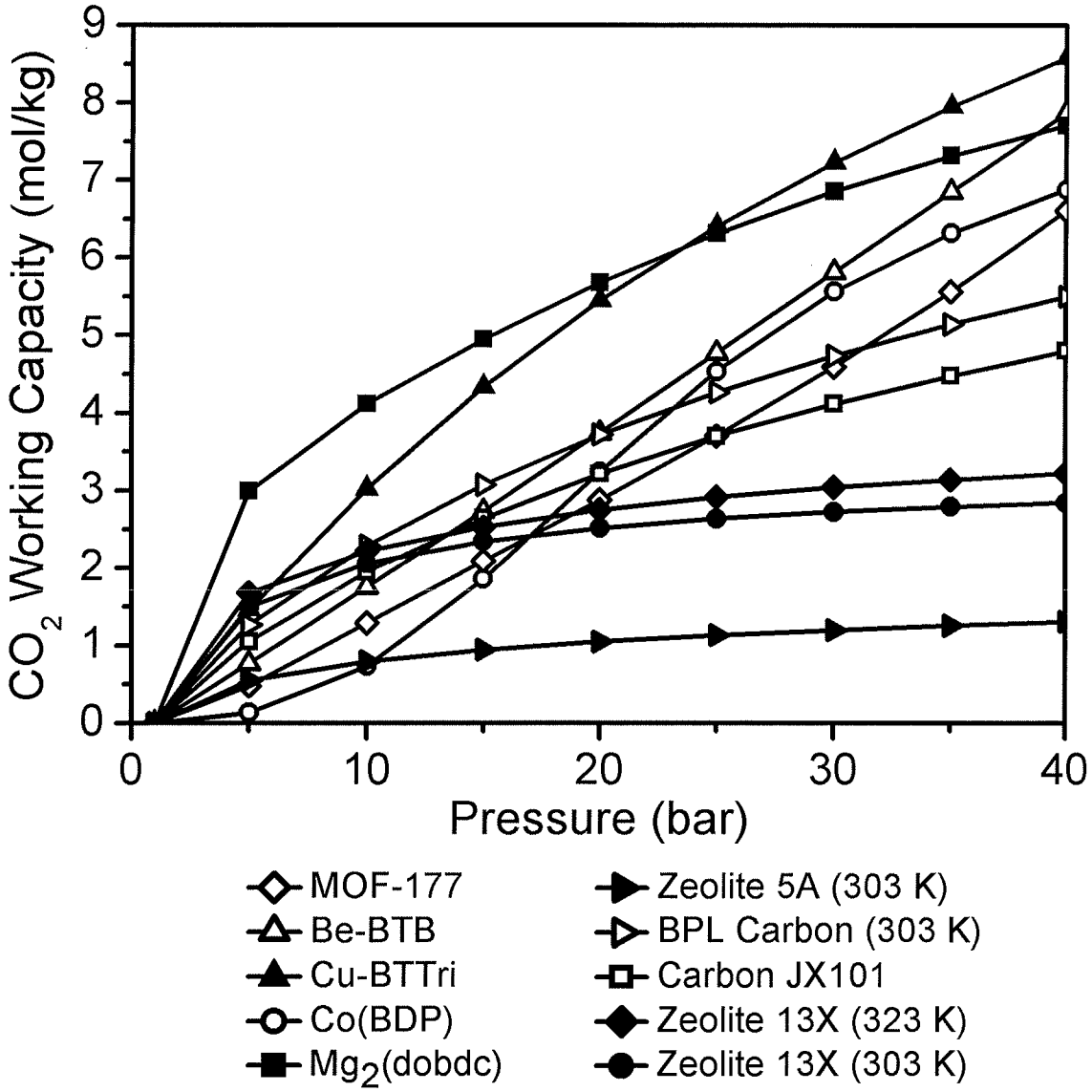
CO_2 Working Capacity (mol/kg)
0
1
2
3
4
5
6
7
8
9
0
10
20
30
40
Pressure (bar)
MOF-177
Be-BTB
Cu-BTTri
Co(BDP)
Mg_2(dobdc)
Zeolite 5A (303 K)
BPL Carbon (303 K)
Carbon JX101
Zeolite 13X (323 K)
Zeolite 13X (303 K)

FIG. 3A

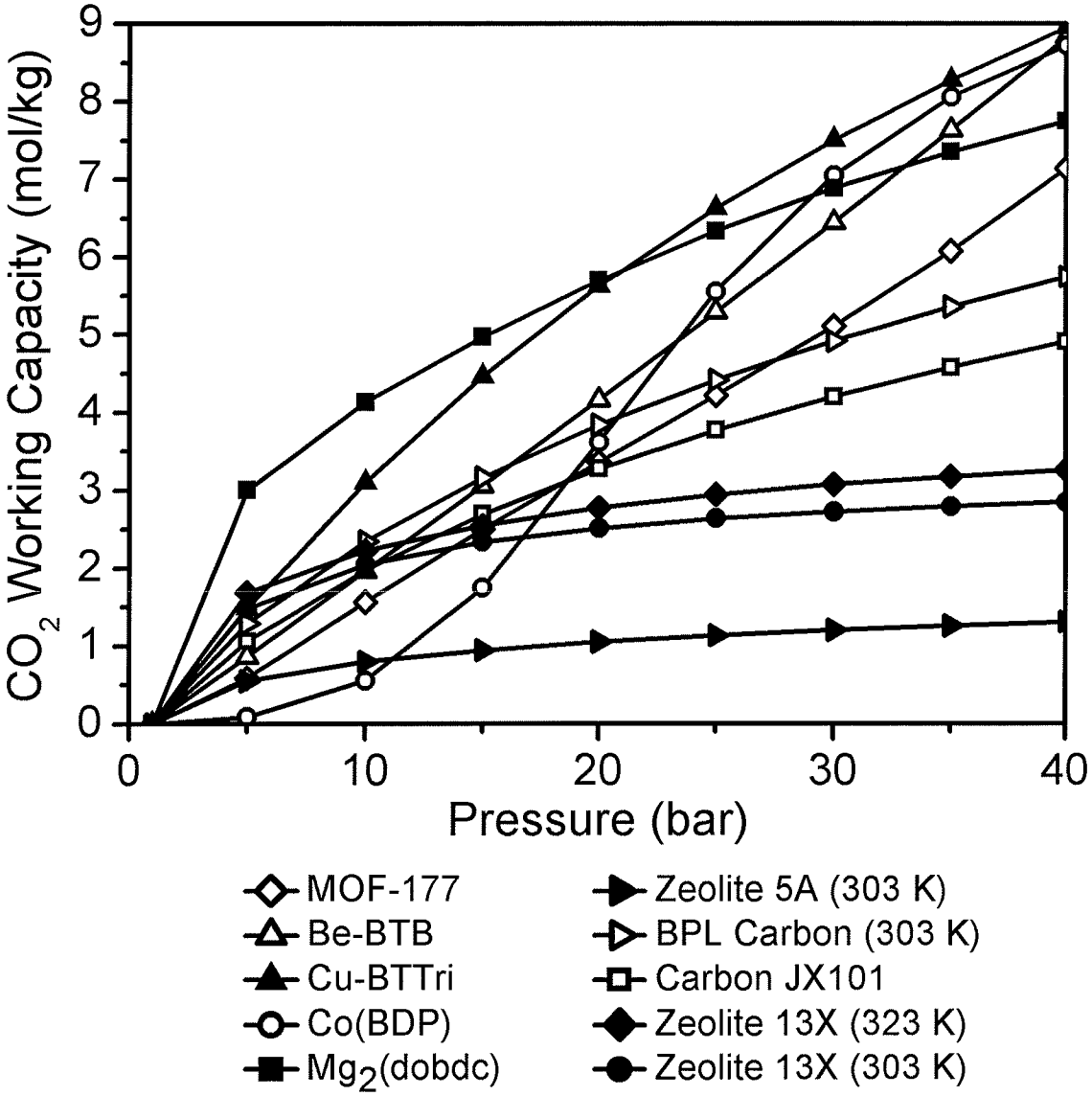
CO_2 Working Capacity (mol/kg)
0
1
2
3
4
5
6
7
8
9
0
10
20
30
40
Pressure (bar)
MOF-177
Be-BTB
Cu-BTTri
Co(BDP)
Mg_2(dobdc)
Zeolite 5A (303 K)
BPL Carbon (303 K)
Carbon JX101
Zeolite 13X (323 K)
Zeolite 13X (303 K)

FIG. 3B

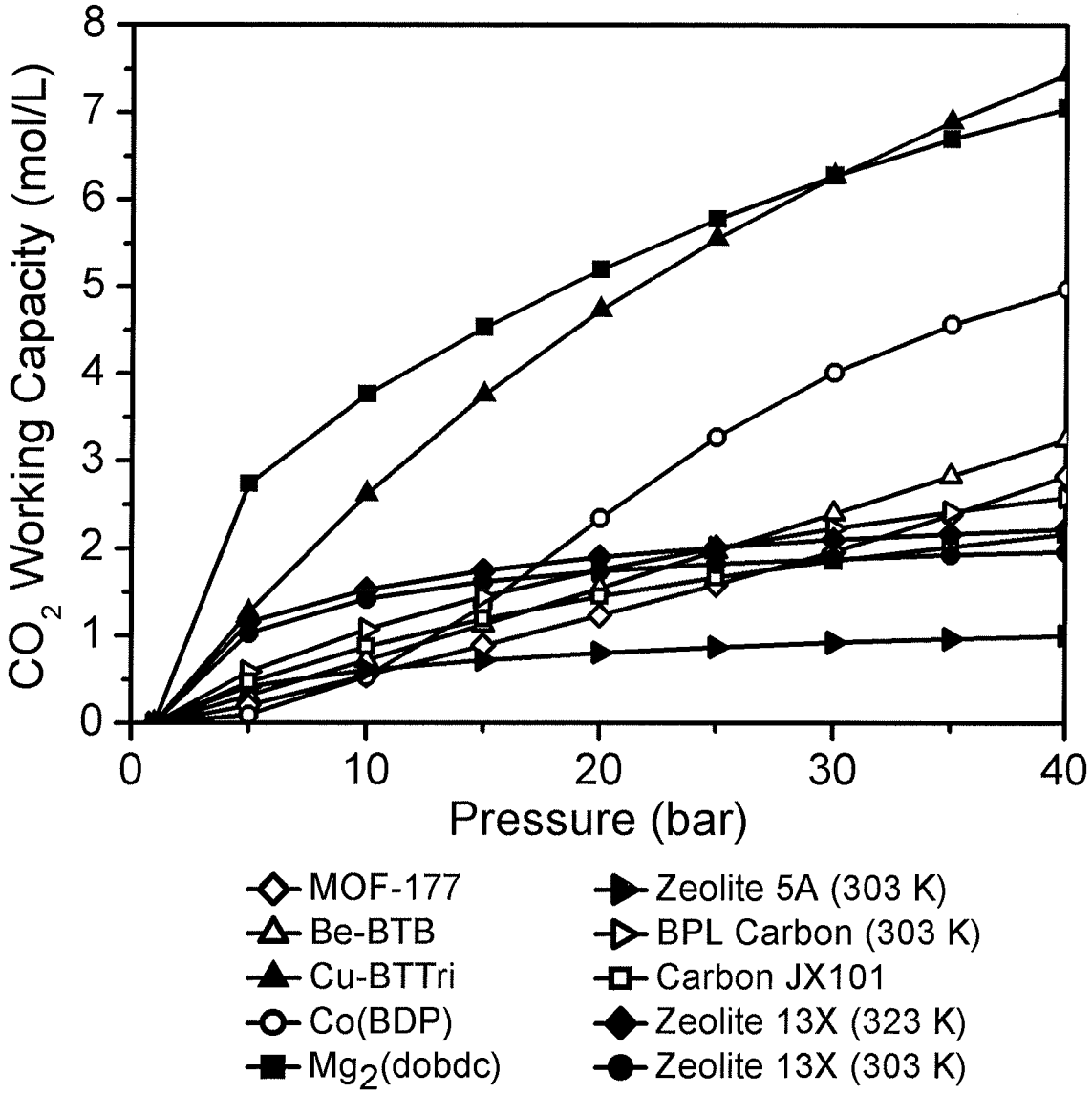
CO_2 Working Capacity (mol/L)
0
1
2
3
4
5
6
7
8
0
10
20
30
40
Pressure (bar)
MOF-177
Be-BTB
Cu-BTTri
Co(BDP)
Mg_2(dobdc)
Zeolite 5A (303 K)
BPL Carbon (303 K)
Carbon JX101
Zeolite 13X (323 K)
Zeolite 13X (303 K)

FIG. 4A

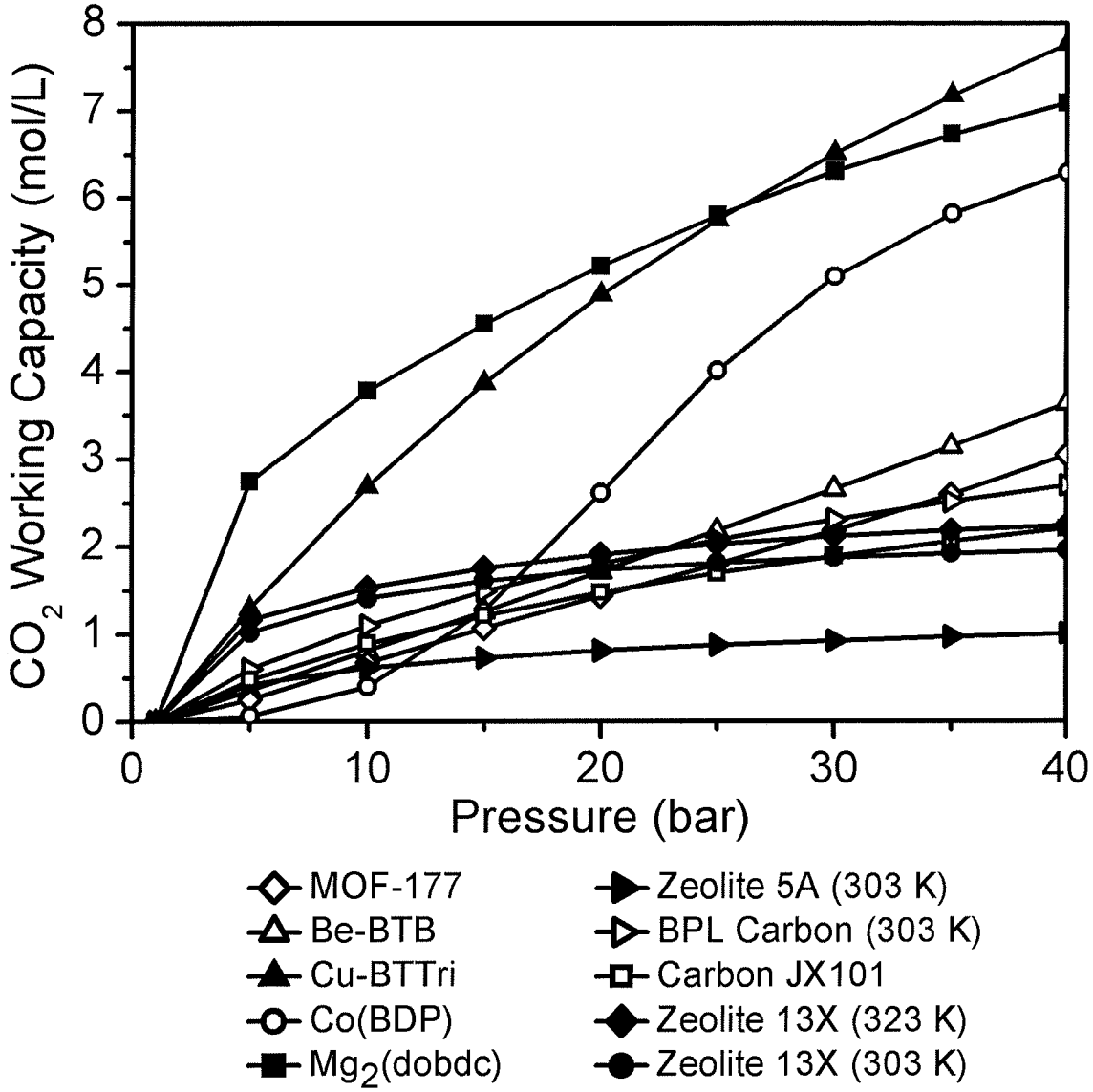
8
7
6
5
4
3
2
1
0
CO_2 Working Capacity (mol/L)
0
10
20
30
40
Pressure (bar)
MOF-177
Be-BTB
Cu-BTTri
Co(BDP)
Mg_2(dobdc)
Zeolite 5A (303 K)
BPL Carbon (303 K)
Carbon JX101
Zeolite 13X (323 K)
Zeolite 13X (303 K)

FIG. 4B

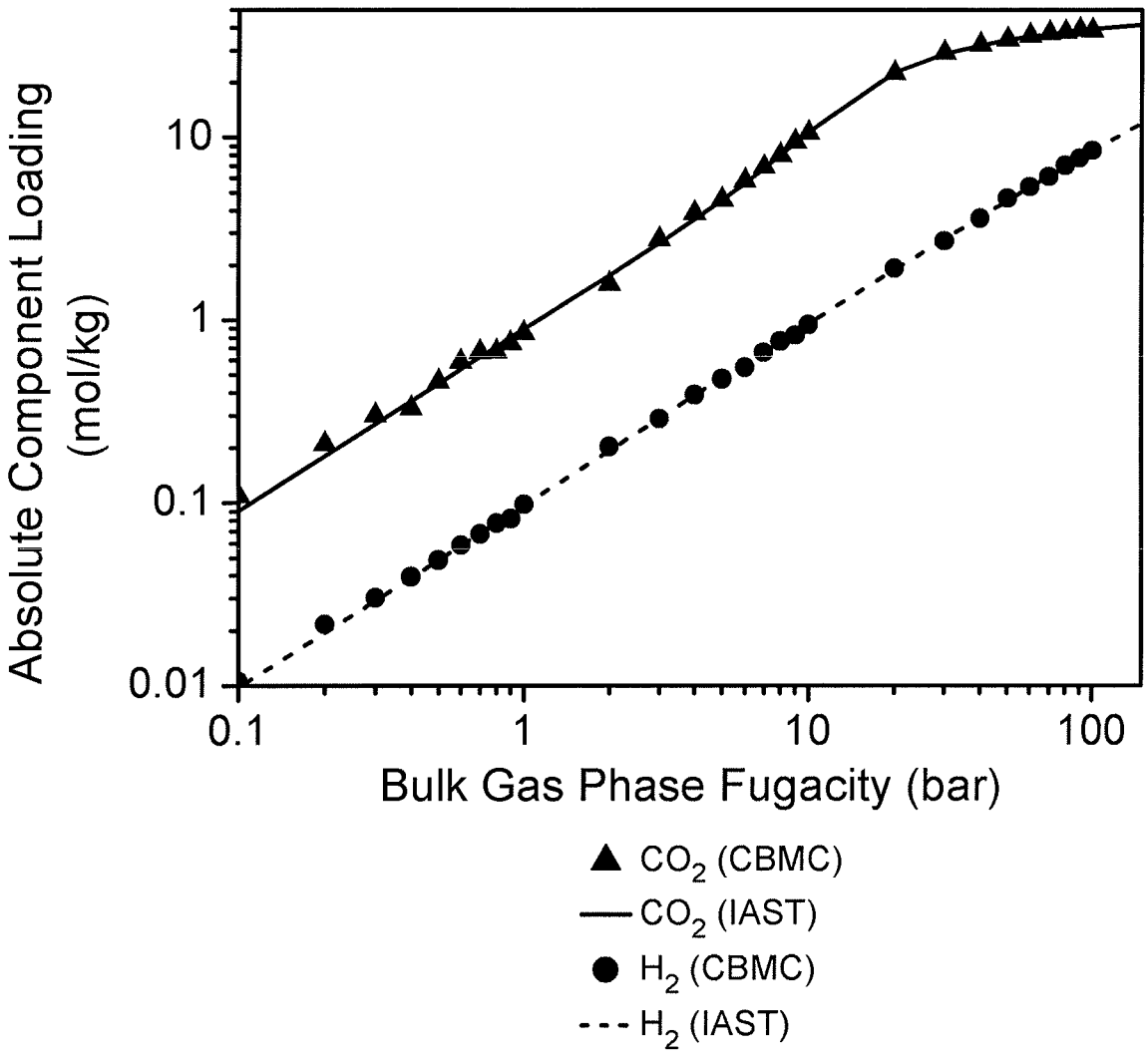
Absolute Component Loading (mol/kg)
10
1
0.1
0.01
0.1
1
10
100
Bulk Gas Phase Fugacity (bar)
CO2 (CBMC)
CO2 (IAST)
H2 (CBMC)
H2 (IAST)

FIG. 5A

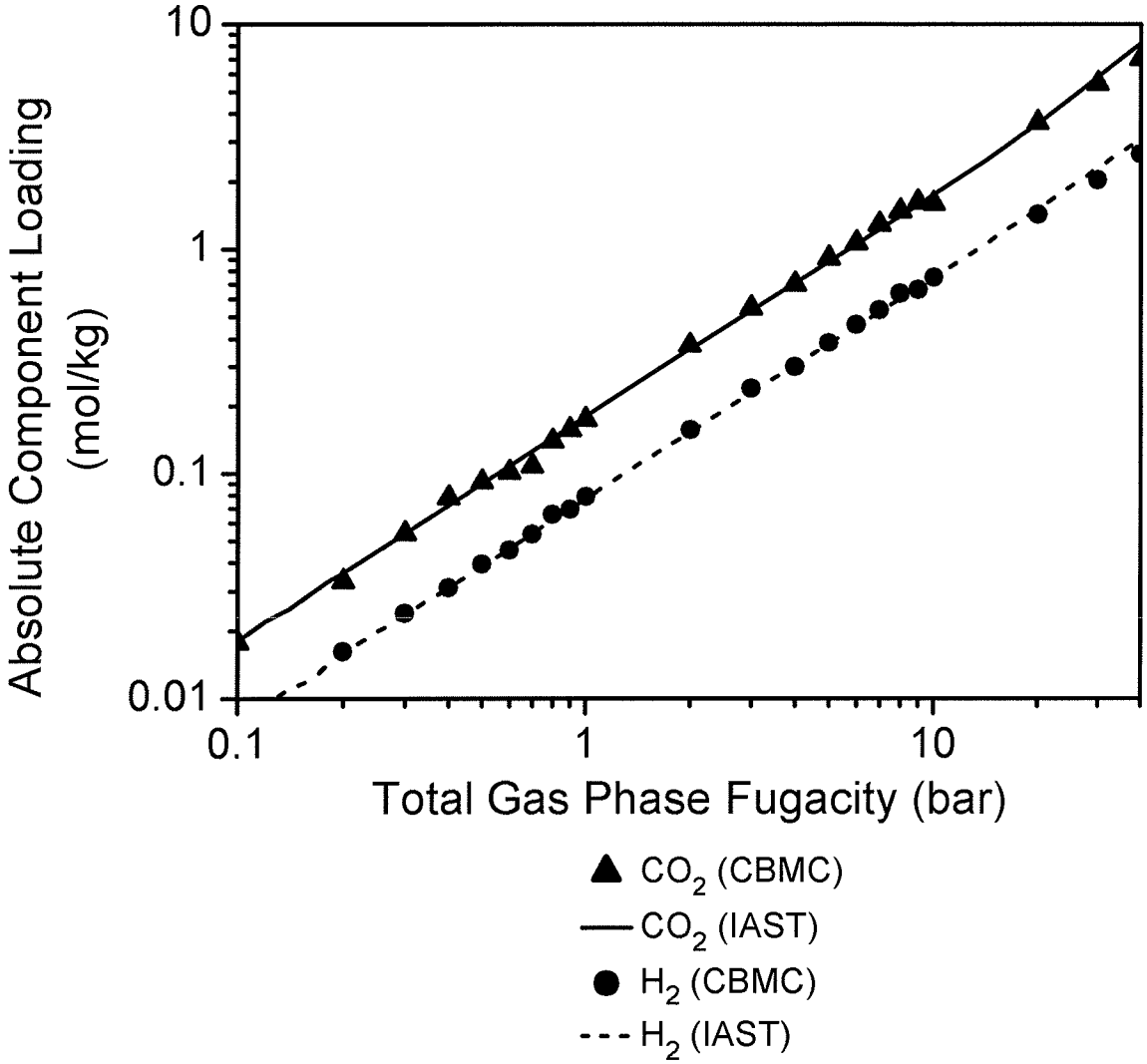
Absolute Component Loading (mol/kg)
10
1
0.1
0.01
0.1
1
10
Total Gas Phase Fugacity (bar)
CO2 (CBMC)
CO2 (IAST)
H2 (CBMC)
H2 (IAST)

FIG. 5B