

(43) International Publication Date
8 November 2012 (08.11.2012)(51) International Patent Classification:
B01D 53/02 (2006.01) *B01J 20/32* (2006.01)
B01J 20/28 (2006.01) *B01J 20/26* (2006.01)

(74) Agent: WILKS, Susan, S.; Corning Incorporated, Intellectual Property Department, SP-Ti-03, Corning, NY 14831 (US).

(21) International Application Number:
PCT/US2012/026291(22) International Filing Date:
23 February 2012 (23.02.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/447,341 28 February 2011 (28.02.2011) US
13/111,360 19 May 2011 (19.05.2011) US

(71) Applicant (for all designated States except US): CORNING INCORPORATED [US/US]; 1 Riverfront Plaza, Corning, NY 14831 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): JIANG, Dayue, D. [CN/US]; 3394 Connocton Road, Painted Post, NY 14870 (US). SONG, Zhen [CN/US]; 3507 Connocton Road, Painted Post, NY 14870 (US). WANG, Jianguo [US/US]; 455 Belwood Drive, Horseheads, NY 14845 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

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

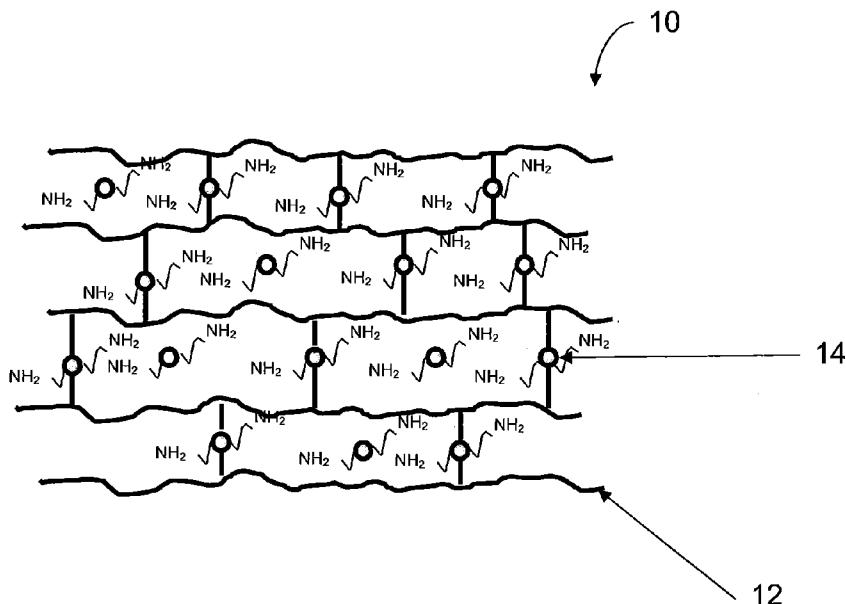
(54) Title: SORBENT ARTICLES FOR CO₂ CAPTURE

Figure 1

(57) Abstract: A sorbent article having a substrate having porous channel walls defining open channels, and an organic-inorganic hybrid sorbent material distributed on a surface of the porous channel walls, wherein the sorbent material is derived from an amino-functionalized alkoxy silane and a polyamine, forming CO₂ adsorption sites within the interior of the porous channel walls is disclosed. The article may be useful, for example, for removing CO₂ from a gas.

SORBENT ARTICLES FOR CO₂ CAPTURE

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority of U.S. Provisional Application Serial No. 61/447,341, filed on February 28, 2011 and U.S. Application Serial No. 13/111,360, filed on May 19, 2011, the contents of which are relied upon and incorporated herein by reference in their entirety.

FIELD OF THE DISCLOSURE

[0002] This disclosure relates generally to sorbent articles comprising an organic-inorganic sorbent material derived from a functionalized alkoxy silanes and polyamines. The sorbent articles may be useful, for example, for removing CO₂ from a gas stream.

BACKGROUND

[0003] Many industrial processes, such as coal gasification, biomass gasification, steam reforming of hydrocarbons, partial oxidation of natural gas, and like processes, produce gas streams that include, for example, CO₂. There are major concerns that such CO₂ is responsible for the greenhouse effect. It is therefore desirable to remove or capture CO₂ from those gas mixtures.

SUMMARY

[0004] Disclosed herein is a sorbent article for removing CO₂ from a gas, the sorbent article comprising a substrate comprising porous channel walls defining open channels, and an organic-inorganic sorbent material distributed on a surface of the porous channel walls, wherein the sorbent material is derived from an amino-functionalized alkoxy silane and a silylated polyamine, wherein the sorbent material is present in an amount equal to or greater than 10 g/l, wherein at least some of the sorbent material resides in the porous channel walls and forms CO₂ sorption sites within the interior of the porous channel walls.

[0005] Also disclosed herein is a sorbent article for removing CO₂ from a gas, the sorbent article comprising a substrate comprising porous channel walls defining open channels, and an organic-inorganic sorbent material distributed on a surface of the porous channel walls, wherein the sorbent material is derived from an epoxide-functionalized alkoxy silane and a polyamine, wherein the sorbent material is present in an amount equal to or

greater than 10 g/l, wherein at least some of the sorbent material resides in the porous channel walls and forms CO₂ sorption sites within the interior of the porous channel walls.

[0006] Also disclosed is a method of removing CO₂ from a fluid, the method comprising contacting the sorbent articles described above with a fluid stream comprising CO₂. The method may further comprise releasing at least a portion of sorbed CO₂ from the sorbent article.

[0007] In an aspect (1), the disclosure provides a sorbent article for removing CO₂ from a gas, the article comprising: a substrate comprising porous channel walls defining open channels and an organic-inorganic hybrid sorbent material distributed on a surface of the porous channel walls; wherein the sorbent material is derived from an amino-functionalized alkoxy silane and a silylated polyamine; wherein the sorbent material is present in an amount equal to or greater than 10 g/l; and wherein at least some of the sorbent material resides in the porous channel walls and forms CO₂ adsorption sites within the interior of the porous channel walls. In an aspect (2), the disclosure provides the article of aspect 1, wherein the sorbent material comprises an SPEI-silica material. In an aspect (3), the disclosure provides the article of aspects 1 or 2, wherein the substrate is honeycomb shaped. In an aspect (4), the disclosure provides the article of any one of aspects 1-3, wherein the porosity of the channel walls is greater than 60%. In an aspect (5), the disclosure provides the article any one of aspects 1-4, wherein the sorbent material is capable of capturing CO₂ at one temperature and releasing the CO₂ at a higher temperature.

[0008] In an aspect (6), the disclosure provides a sorbent article for removing CO₂ from a gas, the article comprising: a substrate comprising porous channel walls defining open channels; and an organic-inorganic hybrid sorbent material distributed on a surface of the porous channel walls; wherein the sorbent material is derived from an epoxide-functionalized alkoxy silane and a polyamine; wherein the sorbent material is present in an amount equal to or greater than 10 g/l; wherein at least some of the sorbent material resides in the porous channel walls and forms CO₂ adsorption sites within the interior of the porous channel walls, and wherein the sorbent material is capable of capturing CO₂ at one temperature and releasing the CO₂ at a higher temperature. In an aspect (7), the disclosure provides the article of aspect 6, wherein the polyamine is a silylated polyamine. In an aspect (8), the disclosure provides the article of aspect 6, wherein the polyamine is a non-silylated polyamine. In an aspect (9), the disclosure provides the article of aspect 8, wherein the

sorbent material is derived from an epoxide-functionalized alkoxysilane and a non-silylated polyamine in the presence of an amino-functionalized alkoxysilane. In an aspect (10), the disclosure provides the article of aspect 6, wherein the sorbent material comprises an SPEI-silica material. In an aspect (11), the disclosure provides the article of any one of aspects 6-10, wherein the substrate is honeycomb shaped. In an aspect (12), the disclosure provides the article of any one of aspects 6-10, wherein the porosity of the channel walls is greater than 60%.

[0009] In an aspect (13), the disclosure provides a method of removing CO₂ from a fluid, the method comprising: contacting an article of aspect 1 or 6 with a fluid stream comprising CO₂. In an aspect (14), the disclosure provides the method of aspect 13, further comprising releasing at least a portion of sorbed CO₂ from the article. In an aspect (15), the disclosure provides an article comprising an organic-inorganic hybrid sorbent material formed into a honeycomb shaped body. In an aspect (16), the disclosure provides an article comprising an organic-inorganic hybrid sorbent material dispersed in a liquid.

[0010] Additional features and advantages will be set forth in the detailed description which follows, and in part will be readily apparent to those skilled in the art from the description or recognized by practicing the embodiments as described in the written description and claims hereof, as well as the appended drawings.

[0011] It is to be understood that both the foregoing general description and the following detailed description are merely exemplary, and are intended to provide an overview or framework to understand the nature and character of the claims.

[0012] The accompanying drawings are included to provide a further understanding, and are incorporated in and constitute a part of this specification. The drawings illustrate one or more embodiment(s), and together with the description serve to explain principles and operation of the various embodiments.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] Figure 1 is a schematic illustration of an embodiment of the organic-inorganic hybrid sorbent.

[0014] Figure 2 shows CO₂ adsorption and desorption according to an embodiment disclosed herein.

[0015] Figure 3 shows CO₂ adsorption and desorption according to an embodiment disclosed herein.

[0016] Figure 4 shows desorption peaks of CO₂ according to an embodiment disclosed herein.

DETAILED DESCRIPTION

[0017] Disclosed herein is a sorbent article comprising a substrate comprising porous channel walls defining open channels, and an organic-inorganic hybrid sorbent material distributed on a surface of the porous channel walls, wherein the sorbent material is derived from an amino-functionalized alkoxy silane and a silylated polyamine, wherein the sorbent material is present in an amount equal to or greater than 10 g/l, wherein at least some of the sorbent material resides in the porous channel walls and forms CO₂ sorption sites within the interior of the porous channel walls. Also disclosed herein is a sorbent article for removing CO₂ from a gas, the sorbent article comprising a substrate comprising porous channel walls defining open channels, and an organic-inorganic sorbent material distributed on a surface of the porous channel walls, wherein the sorbent material is derived from an epoxide-functionalized alkoxy silane and a polyamine, wherein the sorbent material is present in an amount equal to or greater than 10 g/l, wherein at least some of the sorbent material resides in the porous channel walls and forms CO₂ sorption sites within the interior of the porous channel walls. The sorbent articles disclosed may be useful, for example, for removing CO₂ from a gas.

[0018] In embodiments, the organic-inorganic hybrid sorbent is a silylated polyamine. Organic-inorganic hybrid sorbents may comprise amino functionality, allowing them to be used to sorb gases such as CO₂. Embodiments of the organic-inorganic hybrid sorbents have a network of silylated polyamine polymers in which the inorganic moiety is attached to the organic polymer. The result is an organic-inorganic hybrid sorbent with uniform packing densities and microstructural homogeneity that is capable of effectively capturing CO₂ from a mixture of gases.

[0019] A sol comprising a silylated polyamine helps to form a sorbent with uniform density and microstructural homogeneity by polymerization of the silane moiety through a sol-gel process while the amino moiety provides a functional group for capturing CO₂. In embodiments, the methods disclosed herein provide an efficient and cost effective process for making the organic-inorganic hybrid sorbent.

[0020] The sol-gel process is a wet-chemical technique well known in the art. It begins with a chemical solution or suspension, the “sol,” which acts as a precursor for an integrated

network, or “gel” of network polymers. The sol has the monomeric units (i.e. the silylated polyamine) and may also have other desired components of the final gel either in solution or as a suspension of submicron particles. The sol-gel process is a dynamic process where polycondensation begins in the sol and proceeds to a gel point. At the gel point, the polymerization is so extensive that it cannot be poured. The sol is cast or deposited before the gel point and polycondensation continues to the gel point after the sol is cast or deposited, particularly as it begins to dry and the sol becomes concentrated. Polycondensation may continue past the gel point, creating a stiffer gel.

[0021] In some embodiments, a sol is prepared by adding the silylated polyamine to an aqueous solvent. The silylated polyamine may be a polyamine having at least one silane or alkoxy silane moiety attached anywhere within the polyamine. The polyamine may be a homopolymer or it may be a heteropolymer. A heteropolymer may have different amine units or it may have a combination of amino and other moieties such as a poly(amino-alcohol). In the sol, the silane moiety of the silylated polyamine undergoes hydrolysis and is partially or fully hydroxylated. If the silane moiety is an alkoxy silane, the alkoxy groups may be replaced by a hydroxyl moiety. In one exemplary embodiment, the silane moiety is a trialkoxysilane and with hydrolysis at least one of alkyloxy groups of the trialkoxysilane replaced with a hydroxyl group. The hydroxyl group can then react with either another hydroxyl moiety or an alkoxy moiety in a second silylated polyamine through a polycondensation reaction. A silica particle/core **14** is formed as the reaction continues (see Figure 1), creating a polymer network and ultimately a gel. The silica core **14** along with the polyamine **12** form the organic-inorganic hybrid sorbent **10**.

[0022] In one embodiment there is provided a method for making an organic-inorganic hybrid sorbent. The method may comprise the steps of preparing a sol comprising at least one silylated polyamine and an aqueous solvent, casting the sol onto a surface and drying the sol to form the organic-inorganic hybrid sorbent. The silylated polyamine may function both as the precursor to the silica core as well as the functional polymer where the amino-moieties sorb the CO₂. The silylated polyamine may be, but is not limited to, silylated polyethylenimine (SPEIm), silylated polyvinylpyridine, silylated polydimethylaminoethylmethacrylate, silylated polyvinylamine, silylated polyallylamine (PAAm) or combinations thereof. In an illustrative embodiment, the silylated polyamine is trimethoxysilylpropyl modified polyethylenimine, silylated polyethylenimine. The sol may

comprise from about 5 wt% to about 40 wt% (or higher) of the silylated polyamine. In an embodiment, the sol may comprise from about 10 wt% to about 20 wt% of the silylated polyamine. It is well known in making sol solutions that the concentration of the silylated polyamine may be such so that the sol does not begin to gel before being cast or deposited on a substrate. The working time for a sol will depend on the silylated polyamine being used as well as concentration and temperature. Those skilled in that art will be able to determine the best concentration for forming a gel from a sol without undue experimentation.

[0023] Likewise, the choice of aqueous solvent may be dependent on the silylated polyamine(s) comprising the sol. By way of non-limiting example, SPEIm may be in aqueous isopropanol. The aqueous solvent may be chosen based on the solubility characteristics of the desired silylated polyamines. Other examples of aqueous solvents may be short alkyl chain alcohols such as methanol and ethanol, either alone or in combination with water.

[0024] In some embodiments, the silylated polyamine is prepared via an in-situ silylating process before preparing the sol, and subsequently the organic-inorganic hybrid sorbent. The polyamine may be in-situ silylated in an aqueous system through a reaction with a silane, for example, glycidylpropyltrimethoxysilane (GPTMOS). In some embodiments, more than one silane may be used. Polyamines suitable for in-situ silylation include, for example, polyethylenimine, polyallylamine, and polyvinylamine.

[0025] The sol can be either cast onto a surface (e.g., by dip-coating or spin-coating), formed into a shaped body, or used to synthesize powders, microspheres, or nanospheres. In one embodiment, the sol is cast on a substrate to produce an organic-inorganic hybrid sorbent article. The substrate may be, but is not limited to, a ceramic honeycomb substrate. In another embodiment, the sol is formed into a shaped body, for example a honeycomb substrate. In yet another embodiment, the dried sol is used to obtain a powdered sorbent.

[0026] Once the sol is cast on the desired surface and/or substrate, the sol and/or subsequent resulting gel may be dried removing the remaining liquid (solvent). As described above, the sol-gel process is a dynamic process and drying the sol may hasten the onset of the gel point.

[0027] In embodiments, the sol, and subsequently the organic-inorganic hybrid sorbent, may further have at least one hydrophilic polymer. The sol may have from about 5 wt% to about 25 wt% of the hydrophilic polymer where the hydrophilic polymer is an alcohol-based polymer or an amino-functionalized alcohol polymer. Non-limiting examples of alcohol-

based polymers may be poly(vinyl alcohol) (PVA) or poly(allyl alcohol) (PAA), poly(hydroxyethyl methacrylate) (PHEMA) or combinations thereof. Non-limiting examples of the amino-functionalized alcohol polymer may be poly(vinyl alcohol-co-vinylamine) (PVAAm), poly(vinyl alcohol-co-allylamine) (PVAAAm), poly(aminopropyl methacrylamide-co-hydroxyethyl methacrylate) (PAPMa-co-HEMA) or combinations thereof. The hydrophilic polymer may be distributed throughout the gel as it is formed and subsequently, the organic-inorganic hybrid composition membrane. It may interact with the silylated polyamine through ionic bonding, hydrogen bonding or by Vander Waal forces. However, it is not necessary that the hydrophilic polymer interact with the silylated polyamine. Optionally, the hydrophilic polymer may be crosslinked to the polyamine either chemically, by radiation or UV, or thermally. It may be crosslinked in the sol or after the gel is formed. If the hydrophilic polymer is an amino-functionalized alcohol polymer, it may provide additional amine functionality for sorbing CO₂.

[0028] In embodiments, the sol, and subsequently the organic-inorganic hybrid sorbent, may also have at least one alkoxy silane. In illustrative embodiments, the alkoxy silane may be an amine-functionalized alkoxy silane such as, but not limited to, aminopropyltriethoxysilane (APTEOS), (3-trimethoxysilylpropyl)diethylenetriamine (TMSPDETA), glycidylpropyltrimethoxysilane (GPTMOS), N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminoisobutylmethyldimethoxysilane, or combinations thereof. The amine-functionalized alkoxy silanes can form amino-functionalized silica particles through the formation of a silica core as described above for the silylated polyamine. The alkoxy silanes along with the silylated polyamines may form a heterogeneous silica core having both compounds. In some embodiments, non-amino-functionalized silanes/siloxanes may be used, for example, epoxide-functionalized alkoxy silanes may be used.

[0029] The organic-inorganic hybrid sorbent may be disposed on a substrate using a suitable technique such as by applying a solution of the organic-inorganic hybrid sorbent to the substrate. As examples, the organic-inorganic hybrid sorbent can be applied by dipping the substrate in a solution comprising the organic-inorganic hybrid sorbent, by pouring the solution comprising the organic-inorganic hybrid sorbent on the substrate, or by spraying a solution comprising the organic-inorganic hybrid sorbent on the substrate.

[0030] The eventual quantity of organic-inorganic hybrid sorbent formed on the flow-through substrate is dependent on the amount of organic-inorganic hybrid sorbent that is retained by the substrate. The amount of organic-inorganic hybrid sorbent retained by the substrate can be increased e.g., by contacting the substrate with the organic-inorganic hybrid sorbent more than once and allowing the substrate to dry between contacting steps. In addition, the amount of organic-inorganic hybrid sorbent retained by the substrate can be controlled by simply modifying the overall porosity of the substrate (e.g., increasing porosity will increase the amount of organic-inorganic hybrid sorbent retained by the substrate). In some embodiments, the amount of organic-inorganic hybrid sorbent disposed on the flow-through substrate results in greater than 10g/l sorbent loading, greater than 25g/l sorbent loading, greater than 50g/l sorbent loading, greater than 75g/l sorbent loading, greater than 100g/l sorbent loading, greater than 200g/l sorbent loading, greater than 300g/l sorbent loading, greater than 400g/l sorbent loading, or greater than 500g/l sorbent loading .

[0031] In some embodiments, the organic-inorganic hybrid sorbent is distributed on a surface of the porous channel walls of a substrate. For example, the organic-inorganic hybrid sorbent may be distributed on all or a portion of the exposed surfaces of the porous channel walls. In embodiments where the porous channel walls comprise combinations of pore sizes and porous networks throughout the porous channel walls, the organic-inorganic hybrid sorbent may impregnate the porous channel walls of the substrate to any extent. In some embodiments, the organic-inorganic hybrid sorbent is distributed on the surfaces of the porous channel wall and any outer surfaces of the substrate. In some embodiments, the organic-inorganic hybrid sorbent is in the form of an uninterrupted and continuous coating over all or a portion of the surfaces of the substrate. In other embodiments, the organic-inorganic hybrid sorbent comprises cracks, pinholes, or other discontinuities. In some embodiments, the organic-inorganic hybrid sorbent is distributed on the surface of the porous channel walls in a particle form. In embodiments, there is minimal blockage of pores by the organic-inorganic hybrid sorbent.

[0032] In some embodiments, at least a portion of the organic-inorganic hybrid sorbent is chemically bound to at least a portion of flow-through substrate. Thus, in these embodiments, some or all of the organic-inorganic hybrid sorbent can be chemically bound to some or all of the flow-through substrate.

[0033] In some embodiments, at least a portion of the organic-inorganic hybrid sorbent is mechanically bound to at least a portion of flow-through substrate. Thus, in these embodiments, some or all of the organic-inorganic hybrid sorbent can be mechanically bound to some or all of the flow-through substrate.

[0034] In some embodiments, the substrate comprises a glass, glass-ceramic, ceramic, or combinations thereof. Some example substrate materials include cordierite, mullite, clay, magnesia, metal oxides, talc, zircon, zirconia, zirconates, zirconia-spinel, spinel, zeolite, alumina, alumina-titanate, titania, alumino-silicates, silica, silicates, magnesium alumino-silicates, borides, feldspar, fused silica, nitrides, carbides, silicon nitride, metal sulfates, metal carbonates, metal phosphates, or combinations of these.

[0035] In some embodiments, the porous channel walls of the substrate have a surface porosity of greater than 60%, greater than 65%, greater than 70%, or greater than 75%. In some embodiments, the porous walls of the substrate have a surface area of 100 m²/g or more, 150 m²/g or more, 200 m²/g or more, or 250 m²/g or more. In some embodiments, the porous channel walls have pore sizes greater than 10 microns, greater than 25 microns, greater than 50 microns, greater than 75 microns, greater than 100 microns, greater than 125 microns, greater than 150 microns, greater than 200 microns, greater than 500 microns, or combination thereof. In some embodiments, combinations of high porosity and large pores sizes allow for greater sorbent material loading, for example greater amounts of sorbent materials deposition within the pore structure of the porous channel walls.

[0036] In some embodiments, the substrate has a honeycomb structure comprising an inlet end, an outlet end, and open channels (also referred to as cells) extending from the inlet end to the outlet end. In some embodiments, the honeycomb comprises a multiplicity of channels extending from the inlet end to the outlet end, the channels being defined by intersecting channel walls.

[0037] The substrate may be made using suitable techniques, for example, the substrate may be made by extrusion.

[0038] A sorbent article as disclosed, including any of the embodiments described herein, may be used, for example, for the removal of CO₂ from a gas through contact with the gas. For example, a gas stream may be passed through open channels of a substrate, having an organic-inorganic hybrid sorbent distributed thereon, from the inlet end to the outlet end.

[0039] The terms “sorb,” “sorption,” and “sorbed,” refer to the adsorption, sorption, or other entrapment of the CO₂ on the sorbent article, either physically, chemically, or both physically and chemically.

[0040] In some embodiments, the CO₂ sorption occurs at a temperature up to 30°C, 40°C, 50°C, 60°C, or 70°C.

[0041] The CO₂ removal from a gas may further include the step of releasing the CO₂ from the organic-inorganic hybrid sorbent article. For example at least a portion of sorbed CO₂ is desorbed from the sorbent article by providing the article having CO₂ sorbed thereon, and heating it to a temperature above the desorption temperature of the CO₂. Desorbing of the sorbed CO₂ may also be referred to as regeneration of the sorbent article. The sorbent article may be heated using a suitable method. For example, in one embodiment, the sorbent article may be heated by a flow of hot inert gas such as nitrogen.

[0042] A sufficient temperature to desorb the CO₂ will depend, in part, on the amount of CO₂ that is present. In one embodiment, a sufficient temperature can comprise heating the article at a temperature in the range of from 50°C to 300°C, including, for example, temperatures of 100°C, 150°C, 180°C, or 200°C. In another embodiment, the sufficient heating temperature can be in a range derived from these values, including for example, a range from 90°C to 200°C, or 90°C to 180°C.

[0043] In some embodiments, a sorbent article is capable of more than one cycle of sorption and desorption of CO₂. For example, the sorbent article may be used for CO₂ removal from a gas and regenerated to remove the sorbed CO₂, the article may then be used again for CO₂ removal from a gas. In some embodiments, the sorbent article may be capable of 2 or more, 5 or more, 10 or more, 50 or more, or 100 or more cycles of sorption and desorption of CO₂.

[0044] Various embodiments will be further clarified by the following examples.

Examples 1-3

[0045] In a vial, an amount of a chemical was charged and then an amount of water was added and this was mixed well, for example, 5.0g APTEOS and 5.0g water was mixed well and a 50% aqueous solution was obtained. Three solutions were prepared as shown in Table 1.

Table 1.

Chemical	Description
APTEOS	Prepared into aqueous solution by adding water (a 50% solution was prepared)
SPEI	Prepared into a water/isopropanol solution by adding water (a 25% solution was prepared)
APTEOS/SPEI	Prepared into water/isopropanol solution by adding water (a 37.5 solution with APTEOS:SPEI isopropanol solution at 1:1, wt/wt was prepared)

[0046] Glass wool paper was used as a substrate for examples 1-3. The substrate (its mass was measured before applying the sorbent) was submerged into a solution for 10-15 seconds and then dried at room temperature from hours to overnight (its mass was measured again). The weight gain (the percentage of the solid sorbent with moisture) was obtained by the mass difference (the percent weight gain was about 65% for the tested samples).

[0047] Capability of capturing CO₂ for the resulting samples was conducted in a moisturized CO₂ atmosphere with a small amount of back pressure). Results about the sorption **A**, desorption **B** and estimated moisture **C** capturing for the 1st cycle are listed in Table 2 and plotted in Figure 2.

Table 2.

Tested sample (sorbent attached glass wool paper with sorbent at ~65 wt %)	% sorption (weight gain)	% Desorption (weight loss)	% Moisture (estimated)
Amine-functionalized silica (from APTEOS)	16.5	12.7	5
Silica attached PEI (from SPEI)	27.1	23.1	9
Silica/PEI hybrid (from mixture of APTEOS/SPEI)	25.5	23.1	7

[0048] The sorption was obtained at room temperature for 30-45 minutes with a small back pressure using dry ice as the CO₂ source and the CO₂ gas was passed through a water bath to obtain the moisture; a control test was conducted in a humidified air atmosphere (containing both N₂ and O₂) at the same condition. Just before the test, the testing sample (room temperature dried for over night) was further dried in an oven with a forced air at 100°C for 15 minutes.

[0049] The desorption was achieved at 100°C for 15 minutes in an oven with forced air.

[0050] Moisture is included in the sorption and desorption data, the difference between the sorption and the moisture estimated is used to estimate the CO₂ captured and the difference

between the desorption and the moisture estimated is used to estimate the CO₂ released. The moisture was estimated three ways: 1) the mass difference between the mass after the room temperature dried sample (overnight drying) and the mass after the oven dried sample (100°C for 15 minutes under a forced air) before the sample was tested; 2) the mass difference between the mass just releasing the CO₂ at 100°C for 15 minutes and the mass obtained after placing the sample in hood for over night at room temperature; and 3) the mass difference from the control test – between the mass after dried at 100°C for 15 minutes and the mass after the control test (with the same condition as the CO₂ capturing test except using air to replace CO₂) and then dried at room temperature for overnight.

[0051] The three samples tested in the first cycle were tested for a second cycle and the sorption **A**, desorption **B**, and estimated moisture **C** are plotted in Figure 3.

[0052] The thermal stability and antioxidation performance was evaluated by the color change through heating samples in an oven at 100°C with forced air. Samples that changed color (from colorless to light brown and dark brown) at the earliest time were considered to have poor thermal stability and anti-oxidation performance.

[0053] The amino-functionalized silica particle (from the APTEOS) possesses a good thermal stability and antioxidation performance according to the thermal test, but shows the lowest sorption capability because of a relative low amount of amino-groups. The silica attached PEI possesses a good capability of capturing the CO₂, but the thermal stability and antioxidation performance is undesirable. The silica/PEI hybrid derived from APTEOS/SPEI combines the advantages of the two materials and demonstrates a capability of capturing CO₂ close to the silica attached PEI and the thermal stability and anti-oxidation performance close to the amino-functionalized silica.

Example 4

[0054] A silica/PEI hybrid sorbent solution as prepared above was distributed on a high porosity honeycomb substrate. The amount of solid sorbent material on the substrate was about 10 weight percent. CO₂ capture capability of the sample was tested using a gas stream of 9.2% CO₂, 5.5% H₂O, and balance N₂. Adsorption was tested at room temperature. Four cycles of different adsorption time were measured, from 10 minutes to 20 minutes. No water adsorption peak was detected, but a water desorption curve was observed at temperature less than 100°C. The CO₂ capture capacity was stable over the 4 cycles. CO₂ adsorption occurs

within 3 minutes. An increase in sample temperature was observed during adsorption. The CO₂ capture efficiency of this sample was about 35%.

[0055] The sample was then heated to 120°C to desorb the CO₂. Two desorption peaks were observed, as shown in Figure 4. One peak at about 38°C to 40°C, represents physiosorbed CO₂. The second peak at about 108°C represents chemisorbed CO₂. The amount of physiosorbed to chemisorbed CO₂ ratio is about 6:1.

[0056] Unless otherwise expressly stated, it is in no way intended that any method set forth herein be construed as requiring that its steps be performed in a specific order. Accordingly, where a method claim does not actually recite an order to be followed by its steps or it is not otherwise specifically stated in the claims or descriptions that the steps are to be limited to a specific order, it is no way intended that any particular order be inferred.

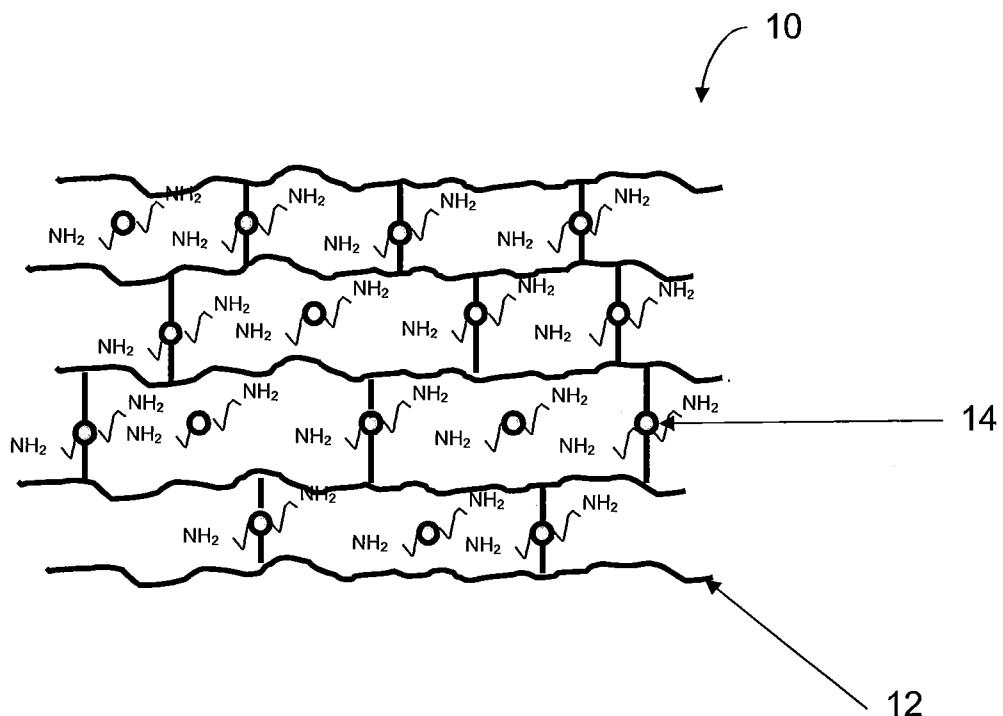
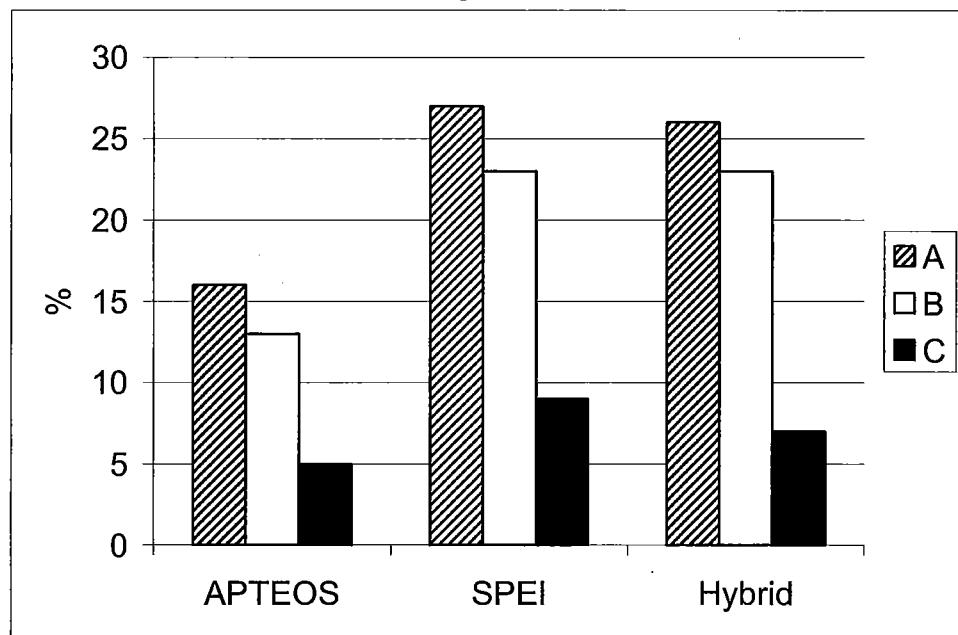
[0057] It will be apparent to those skilled in the art that various modifications and variations can be made without departing from the spirit or scope of the invention. Since modifications combinations, sub-combinations and variations of the disclosed embodiments incorporating the spirit and substance of the invention may occur to persons skilled in the art, the invention should be construed to include everything within the scope of the appended claims and their equivalents.

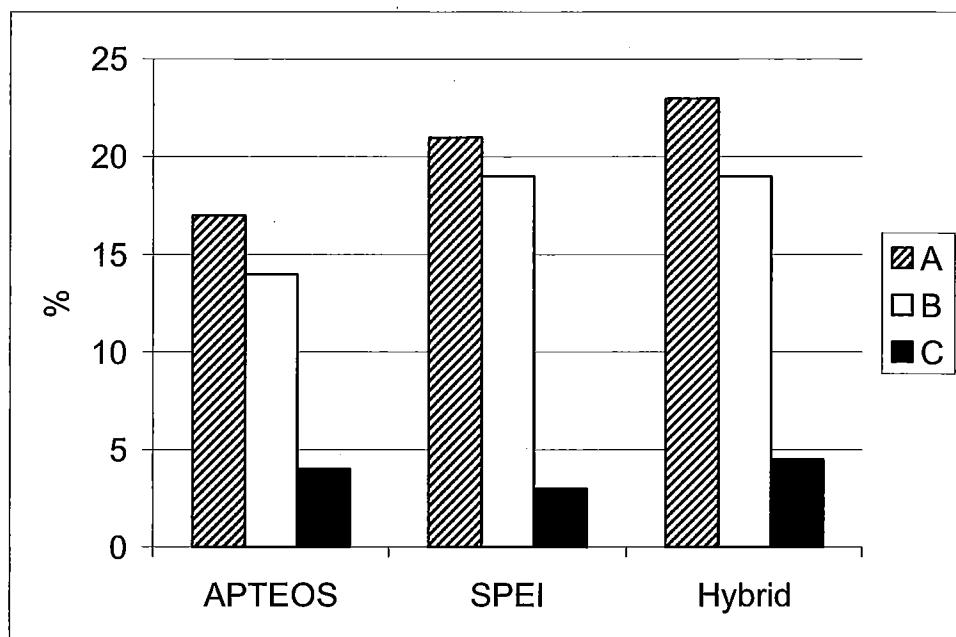
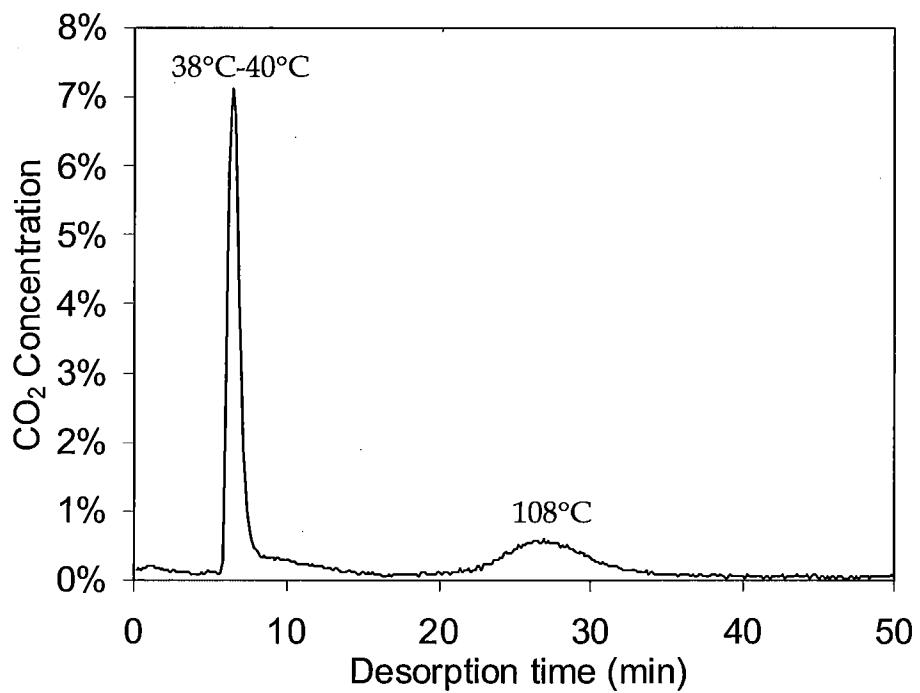
What is claimed is:

1. A sorbent article for removing CO₂ from a gas, the article comprising:
 - a substrate comprising porous channel walls defining open channels; and
 - an organic-inorganic hybrid sorbent material distributed on a surface of the porous channel walls;
 - wherein the sorbent material is derived from an amino-functionalized alkoxysilane and a silylated polyamine;
 - wherein the sorbent material is present in an amount equal to or greater than 10 g/l;
 - wherein at least some of the sorbent material resides in the porous channel walls and forms CO₂ adsorption sites within the interior of the porous channel walls.
2. The article of claim 1, wherein the sorbent material comprises an SPEI-silica material.
3. The article of claim 1 or 2, wherein the substrate is honeycomb shaped.
4. The article of any one of claims 1-3, wherein the porosity of the channel walls is greater than 60%.
5. The article any one of claims 1-4, wherein the sorbent material is capable of capturing CO₂ at one temperature and releasing the CO₂ at a higher temperature.

6. A sorbent article for removing CO₂ from a gas, the article comprising:
 - a substrate comprising porous channel walls defining open channels; and
 - an organic-inorganic hybrid sorbent material distributed on a surface of the porous channel walls;
 - wherein the sorbent material is derived from an epoxide-functionalized alkoxy silane and a polyamine;
 - wherein the sorbent material is present in an amount equal to or greater than 10 g/l;
 - wherein at least some of the sorbent material resides in the porous channel walls and forms CO₂ adsorption sites within the interior of the porous channel walls, and wherein the sorbent material is capable of capturing CO₂ at one temperature and releasing the CO₂ at a higher temperature.
7. The article of claim 6, wherein the polyamine is a silylated polyamine.
8. The article of claim 6, wherein the polyamine is a non-silylated polyamine.
9. The article of claim 8, wherein the sorbent material is derived from an epoxide-functionalized alkoxy silane and a non-silylated polyamine in the presence of an amino-functionalized alkoxy silane.
10. The article of claim 6, wherein the sorbent material comprises an SPEI-silica material.
11. The article of any one of claims 6-10, wherein the substrate is honeycomb shaped.
12. The article of any one of claims 6-10, wherein the porosity of the channel walls is greater than 60%.

13. A method of removing CO₂ from a fluid, the method comprising:
contacting an article of claim 1 or 6 with a fluid stream comprising CO₂.
14. The method of claim 13, further comprising releasing at least a portion of sorbed CO₂ from the article.

**Figure 1****Figure 2**

**Figure 3****Figure 4**

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/026291

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/02 B01J20/28 B01J20/32 B01J20/26
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01D B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2010/212495 A1 (GADKAREE KISHOR PURUSHOTTAM [US] ET AL) 26 August 2010 (2010-08-26) abstract paragraph [0041]; figure 3 paragraph [0044] - paragraph [0048] ----- -/-/	1,3,5, 13,14

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

1 August 2012

14/08/2012

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040,
 Fax: (+31-70) 340-3016

Authorized officer

Klemps, Christian

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/026291

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	LEAL O ET AL: "Reversible adsorption of carbon dioxide on amine surface-bonded silica gel", INORGANICA CHIMICA ACTA, ELSEVIER BV, NL, vol. 240, 1 January 1995 (1995-01-01), pages 183-189, XP002298347, ISSN: 0020-1693, DOI: 10.1016/0020-1693(95)04534-1 Section: "2.1. Surface modification"; page 184, left-hand column page 185, left-hand column; figure 2 page 187, left-hand column - right-hand column; figure 9; table 1 -----	1,5,13, 14
X	DE LATHOUDER ET AL: "Polyethyleneimine (PEI) functionalized ceramic monoliths as enzyme carriers: Preparation and performance", JOURNAL OF MOLECULAR CATALYSIS. B, ENZYMATIC, ELSEVIER, AMSTERDAM, NL, vol. 50, no. 1, 21 November 2007 (2007-11-21), pages 20-27, XP022356529, ISSN: 1381-1177 Section: "2.1. Materials"; page 21, right-hand column Section: "2.2. Sample preparation"; page 22, left-hand column; table 1 -----	1-12
X	HUI WANG ET AL: "MFI Zeolite with Small and Uniform Intracrystal Mesopores", ANGEWANDTE CHEMIE INTERNATIONAL EDITION, vol. 45, no. 45, 17 October 2006 (2006-10-17), pages 7603-7606, XP55028920, ISSN: 1433-7851, DOI: 10.1002/anie.200602595 Scheme 1; page 7604, left-hand column Section: "Experimental Section"; page 7605, right-hand column -----	1,2,5
X	DE LATHOUDER K M ET AL: "A novel structured bioreactor: Development of a monolithic stirrer reactor with immobilized lipase", CATALYSIS TODAY, ELSEVIER, NL, vol. 105, no. 3-4, 15 August 2005 (2005-08-15), pages 443-447, XP027834589, ISSN: 0920-5861 [retrieved on 2005-08-15] abstract Section: "2.2. Methods"; page 444, right-hand column; figure 1 -----	6-12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2012/026291

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.: because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-5(completely); 13, 14(partially)

relating to sorbent article comprising a substrate comprising porous channel walls defining open channels; and an organic-inorganic hybrid sorbent material distributed on a surface of the porous channel walls; wherein the sorbent material is an epoxy-functionalized silane and a polyamine; wherein at least some of the sorbent material resides in the porous channel walls; further to a method of removing CO₂ from a fluid by contacting the sorbent article with a fluid stream comprising CO₂

2. claims: 6-12(completely); 13, 14(partially)

relating to a sorbent article comprising a substrate comprising porous channel walls defining open channels; and an organic-inorganic hybrid sorbent material distributed on a surface of the porous channel walls; wherein the sorbent material is an epoxy-functionalized alkoxy silane and a polyamine; wherein at least some of the sorbent material resides in the porous channel walls; further to a method of removing CO₂ from a fluid by contacting the sorbent article with a fluid stream comprising CO₂

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2012/026291

Patent document cited in search report	Publication date	Patent family member(s)			Publication date
US 2010212495	A1 26-08-2010	CN EP US WO	102365123 A 2401054 A2 2010212495 A1 2010099208 A2		29-02-2012 04-01-2012 26-08-2010 02-09-2010