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(54) **Title**: LOW COST IMMOBILIZED AMINE REGENERABLE SOLID SORBENTS

(57) **Abstract**: A method of modifying a chemical interaction between a functional group of an immobilized amine in a solid sorbent composition and a compound that chemically interacts with the functional group to reduce the heat required to desorb the compound from the solid sorbent. A method of inhibiting degradation of an immobilized amine in an immobilized amine solid sorbent. Compositions and methods of use of a low-cost regenerable immobilized amine solid sorbent resistant to degradation.

Low Cost Immobilized Amine Regenerable Solid Sorbents

[0001] This application claims priority from U.S. Provisional Patent Application Ser. No. 61/255,173 filed on October 27, 2009 and from U.S. Provisional Patent Application Ser. No. 61/255,178 filed on October 27, 2009, both of which are incorporated by reference herein.

Background

[0002] The subject matter relates to methods for preparing low-cost regenerable immobilized amine solid sorbents, and compositions and methods for using the same to regenerably remove compounds such as CO_2, SO_2, or other acidic gases from a gas stream.

[0003] Sulfur dioxide (SO_2) in the flue gas of a coal-fired power plant is primarily removed by a wet scrubber method that involves use of large equipment requiring large amounts of energy and the generation of corrosive sulfate by-products. The fixed and operation costs of SO_2 removal due to the foregoing factors can be significantly decreased by using a solid sorbent process.

[0004] It has been shown that SO_2 can be strongly bound on the functional groups of an amine molecule that is immobilized on a solid surface. (Khatri, Rajesh A., et al. Thermal and Chemical Stability of Regenerable Solid Amine Sorbent for CO_2 Capture. Energy & Fuels (2006), 20(4), 1514-1520). However, due to this strong binding, SO_2 is not readily desorbed from the immobilized amine. Attempts to desorb SO_2 species at temperatures above 180°C have caused the decomposition of the immobilized amines.

[0005] To improve the thermal stability of amines on solid sorbents, as well as eliminate degradation problems in the process of removing CO_2, SO_2, or other acidic gases from a

gas stream, and reduce the overall cost of the CO_2, SO_2, or other acidic gases removal process, it has been found that the high temperature decomposition of an immobilized amine on a solid support can be inhibited by the presence of an alcohol species, such as glycol, in the process of producing the sorbent.

Summary

[0006] Provided is a method of modifying a chemical interaction between a functional group of an immobilized amine in a solid sorbent composition and a compound that chemically interacts with the functional group. Modifying the chemical interaction reduces the heat required to desorb the compound from the functional group compared to an unmodified chemical interaction between the functional group and the compound. Modification may be done by causing the chemical interaction between the functional group and the compound to take place in the presence of an alcohol species.

[0007] Further provided is a method comprising inhibiting degradation of a functional group of an immobilized amine in a solid sorbent composition. Inhibition may be accomplished by including an inorganic base in the solid sorbent composition.

[0008] Further provided is a regenerable immobilized amine solid sorbent composition. The composition may comprise a solid support particle and an immobilized amine. The immobilized amine may comprise an adhesive and an amine susceptible to adsorbing a compound. The sorbent composition may additionally comprise an alcohol species capable of lowering the threshold temperature for dissociation of a bond between the compound and the immobilized amine, and an inorganic base.

[0009] Further provided is a method of removing a compound from a gas stream. The method may comprise employing a regenerable solid sorbent in the gas stream. The regenerable solid sorbent may comprise an immobilized amine susceptible to chemosorbing the compound, an alcohol species capable of lowering the threshold temperature for dissociation of the bond between the compound and the amine, and an

inorganic base. The method may further comprise allowing the regenerable solid sorbent to adsorb the compound from the gas stream, and heating the solid sorbent to a temperature above the threshold temperature for dissociation of the bond between the adsorbed compound and the immobilized amine, but below the threshold temperature for dissociation of the immobilized amine.

[0010] Further provided is a dual immobilized amine regenerable solid sorbent composition. The composition comprises solid support particles having pores, pore mouths and a non-porous surface area. The pores may comprise a composition of a first amine susceptible to chemosorbing a first compound, an alcohol species capable of lowering the threshold temperature for dissociation of a bond between the first compound and the first amine, an adhesive, and an inorganic base. The pore mouths and non-porous surface area may comprise a composition of a second amine susceptible to chemosorbing a second compound, an alcohol species capable of lowering the threshold temperature for dissociation of a bond between the second compound and the second amine, an adhesive, and an inorganic base.

[0011] Further provided, is a method of preparing a dual immobilized amine regenerable solid sorbent for adsorbing a first compound and a second compound. The method may comprise impregnating into pores of a solid support a first composition. The first composition may comprise a first amine susceptible to chemosorbing the first compound, an adhesive, an alcohol species capable of lowering the temperature for the dissociation of the bond between the first compound and the first amine, and an inorganic base. The pores may optionally be partially filled with a solvent after impregnating the pores with the first composition. The method may further comprise treating the resultant solid support with a second composition. The second composition may comprise a second amine susceptible to chemosorbing the second compound, an adhesive, an alcohol species capable of lowering the threshold temperature for dissociation of the bond between the second compound and the second amine, and an inorganic base. The method may further comprise, optionally, removing the solvent from the pores.

Brief Description of the Drawings

[0012] By way of example only, certain non-limiting embodiments are described more fully hereinafter with reference tables and to the accompanying figures, wherein:

[0013] FIG. 1 is an explanatory graph of the SO_2 Capture Capacity of a TPS regenerable solid sorbent;

[0014] FIG. 2 is an explanatory graph of the CO_2 Capture Profiles of a TPS regenerable solid sorbent;

[0015] FIG. 3 is an explanatory graph of the CO_2 Capture Capacity of a PhPS regenerable solid sorbent;

[0016] FIG. 4 is an explanatory graph of the SO_2 Capture Profiles of a PhPS regenerable solid sorbent;

[0017] FIG. 5 is an explanatory graph of the H_2S Capture Profiles of a PhPS regenerable solid sorbent;

[0018] FIG. 6 is an explanatory graph of the NO Capture Profiles of a PhPS regenerable solid sorbent.

Detailed Description

[0019] Provided is a method of modifying the chemical interaction of a compound with an immobilized amine to reduce the temperature at which the compound can be desorbed from the immobilized amine. The temperature at which the compound can be desorbed from the immobilized amine can be referred to as the desorption threshold temperature. The desorption threshold temperature can be lowered to a temperature below the temperature at which the immobilized amine would otherwise begin to decompose, or the immobilized amine decomposition threshold temperature. This method may not only can lower the cost of the desorption process by lowering the energy needs for desorption, but may also make it possible to desorb compounds that have heretofore not been desorbable.

[0020] Also provided is a method of reducing degradation of immobilized amine solid sorbents and a method and composition for removing a desired compound from a gas stream while resisting compounds in the gas stream that would otherwise block removal of the desired compound or cause degradation.

[0021] The foregoing methods make possible the production of a low-cost regenerable immobilized amine solid sorbent resistant to degradation. The sorbent composition comprises a solid support containing thereon an immobilized amine. The sorbent can be considered regenerable when it can be exposed to many cycles of adsorbing and desorbing a compound with little or no decomposition of the sorbent. Many cycles can be, for example, and without limitation more than 350 cycles, more than 400 cycles, more than 450 cycles, or more than 500 cycles. In addition, the sorbent composition can be prepared in a manner that inhibits degradation of the immobilized amine and its adsorbent ability. Cost of producing the sorbent, the materials used in the sorbent, and the energy required to desorb compounds from the sorbent can be reduced or minimized.

[0022] An immobilized amine is a complex in which individual neighboring molecules of the amine have become stationary, or immobilized, relative to one another and possibly a fixed object, such as a solid support particle or a large molecule. In one method, an amine becomes an immobilized amine due to the linking of a fraction of the amine functional groups on individual neighboring amine molecules. Given the proclivity of amines to form bonds with organic compounds, an organic adhesive can be mixed with an amine to bind with a fraction of the amine functional groups on individual amine molecules to cause the linking of the amine functional groups. As the adhesive cures, generally at a temperature of between about 20°C and 160°C, it links neighboring amine molecules together forming an immobilized amine. Prior to curing, the amine/adhesive mixture can then be impregnated on a solid support so that curing of the adhesive will immobilize the amine with respect to the solid support as well. The adhesive is selected based on considerations such as thermal and chemical stability in the immobilized amine, but any chemical compound containing a functional group that reacts chemically with the amine may be an adhesive candidate. In certain embodiments, the

adhesive may be an epoxy, such as, for example and without limitation, a bisphenol epoxy, diglycidyl ether of bisphenol A (DGEBA), EPON-828, or mixtures thereof. The In certain embodiments, the adhesive may be selected from other polymers such as a compound containing isocynate, such as 2,4-tolylene diisocyanate dimer.

[0023] The foregoing method can work with any degree of amine, including but not limited to primary and secondary amines. Although secondary amines generally exhibit a better attraction for chemical absorbency, secondary amines can be expensive. Due to the high cost of secondary amines, the method of immobilizing amines for use in solid sorbents can be useful in lowering the cost of immobilized amine sorbents by allowing use of lower cost primary amines. In particular, the process of bonding an adhesive to a primary group transforms the primary group into a secondary amine functional group. Thus, immobilization can not only prevent an amine from corroding away, but also can be an effective method for lowering the cost of a solid sorbent without sacrificing performance.

[0024] In addition, the amines that can be used comprise aliphatic amines, aromatic amines, or mixtures thereof. While the functional groups on both aliphatic and aromatic amines can attract and adsorb a wide variety of compounds, both have properties that can be utilized for particular purposes. For example, aliphatic amines exhibit the properties of a strong base and can be used to adsorbed compounds that exhibit properties of a weak acid, such as, for example, CO_2. Similarly, aromatic amines exhibit the properties of a weak base, and can be used to adsorbed compounds that exhibit the properties of a strong acid, such as sulfur compounds, for example SO_2.

[0025] Unfortunately, certain compounds form bonds when they chemically adsorb with an immobilized amine that are stronger than the bonds between the adhesive and the amine in the immobilized amine. For such compounds, regeneration of the sorbent by desorption of the compound has not been possible. One example of such a compound, as mentioned above, is SO_2. The bonds of an SO_2 chemically adsorbed on an immobilized

amine have been heated to temperatures of greater than 180°C without desorbing. At this temperature, the immobilized amine decomposes.

[0026] Provided is a method of lowering the desorption threshold temperature of compounds that chemically adsorb on an immobilized amine sorbent, by causing the compounds to adsorb on the immobilized amine in the presence of an alcohol species. Typical operating temperatures at which compounds can be adsorbed can be between 20°C and 80°C. It has been found that an alcohol species can modify the chemical interaction of compounds with the functional groups of the immobilized amine. The modification causes the adsorbed compounds to desorb at a lower temperature compared to when the reaction is not modified. Chemical adsorption can be caused to occur in the presence of an alcohol species, for example, by including the alcohol species in the immobilized amine composition. If the alcohol species is present during the curing stage in the process of preparing the immobilized amine, the alcohol species is present during the chemical interaction. The sorbent also can be suspended in the alcohol species and then introduced to a stream containing the compound to be adsorbed. Another alternative can be to inject an alcohol species mist into a gas stream containing the compound to be adsorbed so that both compound and alcohol species are carried to the adsorption site. The amount of the alcohol species present in the composition can be determined by infra-red spectroscopy. The alcohol species in the composition can be any compound comprising a C-OH group including, but not limited to, alcohols, diols and triols. Some non-limiting examples of alcohols include polyethylene glycol, polyvinyl alcohol, or mixtures thereof.

[0027] Also provided is a method of inhibiting degradation of the functional groups of the immobilized amine. In certain gas streams, such as, for example, flue gas, acidic gases can be present. A gas stream may comprise acidic gases such as sulfur compounds, such as sulfur dioxide (SO_2), hydrogen sulfide (H_2S), carbonyl sulfide (COS), CS_2, thiopene, dibenzothiophene, tetrahydrothiophene (THT), dimethyl sulfide (DMS), mercaptan, tertbutylmercaptant (TBM), 2-methyl-2propanethiol, 1-propanethiol, isobutanethiol, 2-butanethiol, 1-butanethiol, 1-pentanethiol, 1-hexanethiol, and 1-

heptanethiol. A gas stream may comprise acidic gases such as, nitrogen compounds, such as nitric oxide and nitrogen oxide. A gas stream may comprise other acidic gases such as, carbon dioxide. These and other acidic gases can react with a functional group on the immobilized amine, or form compounds that can react with the functional groups, permanently altering the functional group and diminishing the sorbents regenerable sorbent capacity or decomposing the immobilized amine. It has been found that degradation of the amine functional groups can be inhibited with the addition of an inorganic base. An inorganic base may comprise any of the carbonates, bicarbonates, or hydroxyls of any alkali metal or alkali-earth metal. Some non-limiting examples of inorganic bases include Na_2CO_3 and NaOH.

[0028] A sorbent formulation can contain a solid support, an adhesive, an amine, an alcohol species, and an inorganic base. The solid support can be selected based on considerations such as its chemically inert nature with respect to the amine functional group The particles of the solid support can be porous or non-porous and may comprise, for example and without limitation, oxides, such as SiO_2, alumina, calcia, magnesia, or mixtures thereof; metals, for example and without limitation, iron, aluminum, aluminum alloys, steel, steel alloys; carbon materials, for example and without limitation, activated carbon; or combinations thereof.

[0029] The composition can be prepared by mixing the ingredients and impregnating the mixture onto a solid support using impregnation methods known in the art. A solvent can be employed to dissolve the ingredients for thorough mixing, and later removed to allow the adhesive to cure. Solvents may comprise water, organic solvents such as alcohols, ketones, tetrahydrofuran (THF), chlorinated hydrocarbons, aliphatic and aromatic hydrocarbons, or combinations thereof. In certain embodiments, a solvent may be used to wash the solid support to remove excess or un-reacted amine, adhesive, alcohol species and inorganic base. If pellets or granules are desired instead of a powder, the adhesive can be allowed to bond not only between neighboring amine molecules on the same solid support particle, but across particles to bond particles together. A polymer template can be employed to achieve pellets or granules of the desired morphology. The polymer used

as a template should not be reactive toward the amine employed on the sorbent or the adhesive. Some non-limiting examples of polymer templates can be, PEG500, polyvinyl alcohol, or any other water-soluble polymers, or mixtures thereof. Following curing of the amine/adhesive around the polymer template, the polymer template can be washed off to produce void space, serving as macropores and/or micropores to facilitate diffusion of a compound through the sorbent. The entire process can be completed at temperatures between -196°C and 250°C.

[0030] The present subject matter provides for employing the desorption modified immobilized amine regenerable solid sorbent in a gas stream. The sorbent is placed into the gas stream at an operating temperature. The operating temperature can be between 20°C and 80°C, or between 30°C and 70°C, or even between 40°C and 60°C. The sorbent can reside in the gas stream until an amount of a desired compound has adsorbed onto the sorbent. The sorbent may then heated to a temperature above the modified desorption temperature of the chemically adsorbed compound, but below the decomposition threshold temperature of the immobilized amine in the sorbent. Immobilized amines can begin decomposing at around 120°C and the present subject matter allows desorption to occur between 60°C and 120°C, or 70°C and 110°C, or 80°C and 100°C. When the compound has been sufficiently, fully or partially, desorbed and the amine functional groups are sufficiently, fully or partially, regenerated, the sorbent may be placed back into the gas stream for further adsorption.

[0031] In certain embodiments, the subject matter can be used to remove SO_2 from flue gas. In an un-modified immobilized amine sorbent, the desorption threshold temperature of SO_2 can be greater than 180°C, which would cause the decomposition of the un-modified immobilized amine. Creating an immobilized amine with an alcohol species such as polyethylene glycol makes it possible to desorb SO_2 at less than 100°C. In certain embodiments, the subject matter can be used to remove CO_2 from flue gas. By causing CO_2 to be adsorbed in the presence of a polyethylene glycol, CO_2 can be desorbed at temperatures as low as 70°C.

[0032] The removal of multiple components from a gas stream is also contemplated. A sorbent prepared to handle the challenges of a multi-component gas stream can include a porous solid support with a non-porous surface area. A first composition of an amine, an adhesive, an alcohol species and an inorganic base can be impregnated into the pores of the solid support. A second composition of an amine, an adhesive, an alcohol species and an inorganic base can be impregnated onto the pore mouths and non-porous surface area of the solid support. To keep the second composition out of the pores, the pores can be filled with a solvent, such as, without limitation, water or an organic solvent, after the pores are impregnated with the first composition. When the second composition has been impregnated and cured, the solvent in the pores can be removed, for example, by drying. In addition, before impregnation of the second composition, the first composition can be treated with the compound desired to be adsorbed to allow the amine functional groups to bind with the compound. This dual amine structure can be used to target specific compounds desired to be adsorbed from the gas stream, or for targeting a specific compound while providing alternative sites for adsorbing compounds that would otherwise interfere with the adsorption of the specific compound.

[0033] In certain embodiments, a sorbent is prepared to handle the challenges of removing CO_2 from flue gas containing sulfur compounds and nitrogen compounds. A first immobilized composition is prepared containing an aliphatic amine, a bisphenol epoxy, a polyethylene glycol and Na_2CO_3. The ingredients are dissolved in ethanol (EtOH) and impregnated into the pores of a SiO_2 support. The EtOH is removed by evaporation and the epoxy is allowed to cure, immobilizing the amine. The particles are treated with CO_2 to allow the amine functional groups to bind with CO_2 molecules. The pores are then filled with water to just below the pore mouths and a second composition is prepared. The second composition contains an aromatic amine, a bisphenol epoxy, polyethylene glycol and Na_2CO_3. The second composition is dissolved in EtOH and impregnated onto the pore mouths and non-porous surface area of the SiO_2 particles. The EtOH is removed and the second composition is allowed to cure. The water is removed from the pores and the sorbent is ready to remove CO_2. In this embodiment, the dual amine structure allows CO_2 to adsorb onto the immobilized amine within the pores, while

providing sites on the immobilized amine support surface and pore mouths for the adsorption of sulfur compounds and sulfur by-products as well as nitrogen compounds that would otherwise interfere with the adsorption of the CO_2.

[0034] It will be apparent to those skilled in the art that there may be changes and modifications made to the embodiments described in the examples without departing from the general scope of the provided subject matter. The provided subject matter is intended to include all such modifications and alterations in so far as they come within the scope of the appended claims or the equivalents thereof.

Examples

[0035] **Example 1** – Preparation of novel regenerable solid sorbent formulation:

[0036] Preparation of 10g of "TPS 24/36/40"

[0037] 6g of TEPA (tetraethylene pentamine) was stirred with 9g of PEG (polyethylene glycol 200). A roughly equal volume of EtOH (ethanol) was added to beaker with stirring. The mixture was then poured onto log Silica and stirred until the sorbent was coated properly. The mixture may look like lemon slush when coated properly. The sorbent was then baked at 100 °C until all of the EtOH has evaporated.

[0038] Epoxy Doping

[0039] 0.444g of an epoxy adhesive (EPON) was dissolved in 6-7g EtOH. A hot plate at 70 °C was employed to help dissolution. The EPON/Et0H mixture was then poured on the10g of TPS 24/36/40 and uniformly mixed and baked at 100 °C until all of the EtOH was evaporated.

[0040] Na_2CO_3 addition

[0041] One log of epoxy doped sorbent (the sorbent is denoted as TPS 24/36/40 — 0.222Epon) is weighed out and combined with 0.1g Na_2CO_3 dissolved in 6g of water. The mixture was stirred until all sorbent was coated and then baked in an oven at 100 °C

until all the water evaporated. When all water evaporated, the final product was an opaque white.

[0042] **Example 2** – Preparation and Determination of regenerable SO_2 and CO_2 capture capacity of novel regenerable solid sorbent composition:

[0043] A procedure similar to that of example 1, using a sequential impregnation method and a different sequence was used to prepare four sorbents using two different silica, a granular silica (A) and a powder silica (B). The amount of the raw materials used is listed in Table 1.

Table 1: Compositions of the sorbents prepared in weights

Sample label	EPON	TEPA	PEG	Ethanol	Si02	Na_2CO_3	Water
TPS(A)-E 24/36/40-100 + Na_2CO_3	0.355	0.96	1.44	4	1.6	0.4	2.4
TPS(A)-E 36/24/40-100 + Na2CO_3	0.267	1.44	0.96	6	1.6	0.4	2.4
TPS(B)-E 24/36140-100 + Na_2CO_3	0.355	0.96	1.44	4	1.6	0.4	2.4
TPS(B)-E 36/24/40-100 + Na_2CO_3	0.267	1.44	0.96	6	1.6	0.4	2.4

[0044] Preparation of TPS(A) 24/36/40 (for roughly 4g)

[0045] Mixed the epoxy (EPON) with TEPA and stirred until the EPON dissolved in the TEPA. Added PEG to the EPON/ TEPA mixture and stirred well. Impregnated the mixture onto silica and added ethanol to the silica slurry. The sorbent was heated in an oven at 100 °C to evaporate excess ethanol.

[0046] Na_2CO_3 addition

[0047] Dissolved 0.04g of Na_2CO_3 in water and impregnated the Na_2CO_3 solution onto the above sorbent. The sorbent was heated in an oven at 100 °C to evaporate excess water to obtain an opaque white sorbent.

[0048] The SO_2 and CO_2 capture capacity of these sorbents was determined by the following procedures. In each run, the sorbents were heated for seven minutes in an

oven at 100 °C to remove any adsorbed species CO_2 from the ambient atmosphere. The samples were then saturated with 99% SO_2 or pure CO_2 in continuous flow for 10 minutes. The difference in the weight of the sample before and after the capturing was the amount of SO_2 or CO_2 captured by the particular sorbent. These sorbents were again heated in an oven at 100 °C to remove the saturated CO_2 and further tested for capture capacity. Ten runs are carried out and the SO_2 or CO_2 captured in each individual cycle is calculated. The tested sorbents were kept in oven at 100 °C overnight for evaluation of thermal degradation. These sorbents were further evaluated for SO_2 capture for 3 cycles on day 2 and day 3. The sorbent prepared with powder SiO_2 and 24%TEPA and 36% PEG showed the highest SO_2 capture capacity after three days of degradation studies. The results of SO_2 capture for each run are presented in the graph in Figure 1 and the results for CO_2 capture are presented in the graph in Figure 2.

[0049] The data in Figure 2 represent one of the best sets of data obtained from more than 50 sorbents prepared and tested. These sorbents were subjected to more 35 hours of thermal degradation study at 100°C in air. In this study, the adsorption of CO_2 was carried out at 30 °C and desorption at 100 °C. The CO_2 capture capacity was measured before, during, and after thermal degradation studies.

[0050] Two of the above sorbents have also been tested by ADA Environmental Solution () by adsorption at 55 °C with 12% CO_2, 4% O_2, balance N_2 and desorption at 80-95 °C. The CO_2 capture capacity and stability results obtained by ADA were consistent with those reported in Figure 2.

[0051] With respect to CO_2 capture, we are able to prepare a solid amine sorbent with CO_2 capture capacity of more than 1.5 mmol/g. The sorbent did not degrade under more than 35 hour of thermal treatment. It is expected that this sorbent will sustain more than 500 CO_2 adsorption/desorption cycles without significant degradation.

[0052] **Example 2** – CO_2, SO_2, H_2S and NO capture over m-phenyldiamine/PEG/EPON/SiO_2 sorbents

[0053] The following examples show that m-phenyldiamine/PEG/EPON/SiO_2 + Na_2CO_3 sorbents exhibited capture capacity for CO_2, SO_2, H_2S, and NO. M-phenyldiamine is an aromatic amine. PEG is a glycol, EPON is an epoxy.

[0054] **Experimental**

[0055] Sorbent preparation

[0056] For convenience the chemicals in the present study are abbreviated as follows, polyethylene glycol-200 (PEG; P) EPON-826 (EPON; E), m-phenyldiamine (Ph), SiO_2 (S). Two forms of silica were used in this study Tixosil 68 (A) and (B). The sorbent are abbreviated in the following notation and abbreviated as PhPS-E_{10} 24/36/50+Na_2CO_3 for 24 wt% Ph-36 wt% P-40 Wt% S-$E_{(10=\text{mole ratio of EPON/TEPA})}$+$Na_2CO_3$.

[0057] The m-phenyldiamine/PEG/EPON/SiO_2 + Na_2CO_3 sorbents were prepared by dissolving EPON in PEG/ethanol solution under stirring for 5 min followed by addition of m-phenyl diamine pellets. Silica was impregnated with the above mixture and dried in oven at 100 °C for 15-20 min until excess ethanol is evaporated. Aqueous solution of Na_2CO_3 was added to the solid sorbent and dried in oven at 100 °C for 15-20 min to remove the excess water. The specific compositions of sorbents are presented in Table 2.

Table 2 The composition of the different components used in the preparation of sorbents.

Sample label	Ph(g)	PEG(g)	SiO_2(g)	EPON(g)	Na_2CO_3(g)	Water(g)	Ethanol(g)
PhPS(A)-E_{20} 24/36/40-100 + Na_2CO_3	2.4	3.6	4	0.444	0.04	2.4	1
PhPS(A)-E_{10} 36/24/40-100 + Na_2CO_3	3.6	2.4	4	0.666	0.04	2.4	1
PhPS(B)-E_{20} 24/36/40-100 + Na_2CO_3	2.4	3.6	4	0.444	0.04	2.4	2.5
PhPS(B)-E_{10} 36/24/40-100 + Na_2CO_3	3.6	2.4	4	0.666	0.04	2.4	2.5

*removed upon drying

[0058] *CO_2 capture*

[0059] The CO_2 capture capacity of the sorbents is determined by the following procedures. In each run, the sorbents are heated for seven min in an oven at 100 °C to remove any adsorbed CO_2 from the ambient atmosphere. Then the samples are saturated with pure CO_2 in continuous flow for 10 min. The difference in the weight of the sample before and after the CO_2 capture is considered as the amount of CO_2 captured by the particular sorbent. The sorbents are again heated in oven at 100 °C to remove the captured CO_2 and repeat the above steps for further CO_2 capture capacity. The SO_2, H_2S, and NO capture capacity are determined in the same procedures.

[0060] **Results and discussion**

[0061] Figure 3 and Table 3 show the CO_2 capture capacity over **m** phenyldiamine/PEG/EPON/SiO_2 + Na_2CO_3 sorbents. The capture capacity marginally increases during the first day. Treatment of the sorbents in oven at 100 °C for 15 h and retested for CO_2 capture resulted in an increase in the CO_2 capture capacity. Further treatment in oven *at* 100 °C for another 15 h resulted in a small increase in the CO_2 capture capacity. The increase in CO_2 capture capacity is more prominent in case of SiO_2 (B) support.

[0062] Figure 4 and Table 4 show the SO_2 capture over m-phenyldiamine/PEG/EPON/SiO_2 + Na_2CO_3 sorbents. The PhPS (B)-E 24/36/40-100 + Na_2CO_3 sorbent exhibits the highest SO_2 capture capacity. No further heat treatment was performed on these sorbents.

[0063] Figure 5 and Table 5 shows the H2S capture capacity over m phenyldiamine/PEG/EPON/SiO_2 + Na_2CO_3 sorbents. The capture capacity remains constant on three run.

[0064] Figure 6 and Table 6 shows NO capture capacity over m-

phenyldiamine/PEG/EPON/SiO_2 + Na_2CO_3 sorbents. The capture capacity remains constant on three run.

CO_2 capture

Table 3 Results of CO_2 capture of the m-phenyldiamine/PEG/EPON/SiO_2 + Na_2CO_3 sorbents in three successive days.

Day 1 (Fresh samples)						
	CO_2 Capture (mmol)/g			mol CO_2/mol Ph		
Sorbent	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
PhPS(A)-E_{20} 24/36/40-100 + Na_2CO_3	0.254	0.278	0.280	0.028	0.031	0.031
PhPS(A)-E_{10} 36/24/40-100 + Na_2CO_3	0.322	0.207	0.374	0.035	0.023	0.042
PhPS(B)-E_{20} 24/36/40-100 + Na_2CO_3	0.248	0.272	0.296	0.027	0.029	0.032
PhPS(B)-E_{10} 36/24/40-100 + Na_2CO_3	0.258	0.259	0.331	0.029	0.029	0.037
Day 2 (after first thermal degradation at 100 °C for 15h)						
	CO_2 Capture (mmol)/g			mol CO_2/mol Ph		
Sorbent	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
PhPS(A)-E_{20} 24/36/40-100 + Na_2CO_3	0.399	0.313	0.399	0.054	0.043	0.054
PhPS(A)-E_{10} 36/24/40-100 + Na_2CO_3	0.458	0.372	0.429	0.063	0.051	0.059
PhPS(B)-E_{20} 24/36/40-100 + Na_2CO_3	0.383	0.384	0.287	0.058	0.059	0.044
PhPS(B)-E_{10} 36/24/40-100 + Na_2CO_3	0.376	0.406	0.377	0.052	0.056	0.052
Day 3(after second thermal degradation at 100 °C for 15h)						
	CO_2 Capture (mmol)/g			mol CO_2/mol Ph		
Sorbent	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
PhPS(A)-E_{20} 24/36/40-100 + Na_2CO_3	0.435	0.493	0.406	0.060	0.069	0.056
PhPS(A)-E_{10} 36/24/40-100 + Na_2CO_3	0.451	0.331	0.391	0.065	0.048	0.056
PhPS(B)-E_{20} 24/36/40-100 + Na_2CO_3	0.559	0.493	0.528	0.088	0.078	0.083
PhPS(B)-E_{10} 36/24/40-100 + Na_2CO_3	0.514	0.484	0.423	0.074	0.070	0.061

[0065] SO_2 capture

Table 4 Results of SO_2 capture on m-phenyldiamine/PEG/EPON/SiO_2 + Na_2CO_3 sorbents

Day 1 (fresh samples)						
	SO_2 Capture (mmol/g)			mol SO_2/mol Ph		
Sorbent	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
PhPS(A)-E_{20} 24/36/40-100 + Na_2CO_3	1.698	1.537	1.257	0.186	0.168	0.138
PhPS(A)-E_{10} 36/24/40-100 + Na_2CO_3	1.231	1.032	1.080	0.137	0.114	0.120
PhPS(B)-E_{20} 24/36/40-100 + Na_2CO_3	1.890	1.844	1.297	0.211	0.206	0.145
PhPS(B)-E_{10} 36/24/40-100 + Na_2CO_3	1.424	1.324	1.260	0.161	0.149	0.142

[0066] H_2S capture

Table 5 Results of H_2S capture on m-phenyldiamine/PEG/EPON/SiO_2 +Na_2CO_3 sorbents

Day 1 (Fresh samples)						
	H_2S Capture (mmol)/g			mol H_2S/mol Ph		
Sorbent	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
PhPS(A)-E_{20} 24/36/40-100 + Na_2CO_3	0.645	0.526	0.439	0.070	0.057	0.048
PhPS(A)-E_{10} 36/24/40-100 + Na_2CO_3	0.570	0.480	0.450	0.063	0.053	0.050
PhPS(B)-E_{20} 24/36/40-100 + Na_2CO_3	0.623	0.563	0.505	0.068	0.062	0.056
PhPS(B)-E_{10} 36/24/40-100 + Na_2CO_3	0.592	0.594	0.506	0.065	0.065	0.056

[0067] *NO capture*

Table 6 Results of NO capture on m-phenyldiamine/PEG/EPON/SiO_2 + Na_2CO_3 sorbents

Sorbent	NO Capture (mmol/g)			mol NO/mol Ph		
	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
PhPS(A)-E_{20} 24/36/40-100 + Na_2CO_3	0.675	0.607	0.508	0.074	0.067	0.056
PhPS(A)-E_{10} 36/24/40-100 + Na_2CO_3	0.622	0.588	0.381	0.070	0.066	0.043
PhPS(B)-E_{20} 24/36/40-100 + Na_2CO_3	0.471	0.607	0.439	0.052	0.067	0.048
PhPS(B)-E_{10} 36/24/40-100 + Na_2CO_3	0.631	0.666	0.534	0.068	0.072	0.058

[0068] In the preceding description, where a range of values has been provided, it is understood that each intervening value between the upper and lower limit of that range and any other stated or intervening value in that stated range is encompassed within the subject matter. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this subject matter belongs. Although any methods and materials similar or equivalent to those described herein can also be used in the practice or testing of the present subject matter, a limited number of the exemplary methods and materials are described herein.

[0069] It must be noted that as used herein and in the appended claims, the singular forms "a", "an", and "the" include plural referents unless the context clearly dictates otherwise.

What is claimed is:

1. A method of modifying a chemical interaction between i) an amine functional group of an immobilized amine in a solid sorbent composition, and, ii) a gaseous compound that chemically interacts with the amine functional group, by causing the adsorption of the gaseous compound on the immobilized amines in the presence of an alcohol species.
2. The method of claim 1 wherein the immobilized amine is prepared from an aliphatic or aromatic amine and an epoxy on a solid support, said solid support comprising an oxide, a metal, a carbon material, or a combination thereof.
3. The method of claim 1 wherein the chemically adsorbed compound is an acidic gas, said acidic gas comprising, sulfur dioxide, hydrogen sulfide, carbonyl sulfide, CS_2, thiopene, dibenzothiophene, tetrahydrothiophene, dimethyl sulfide, mercaptan, tertbutylmercaptant, 2-methyl-2propanethiol, 1-propanethiol, isobutanethiol, 2-butanethiol, 1-butanethiol, 1-pentanethiol, 1-hexanethiol, and 1-heptanethiol, nitric oxide, nitrogen oxide, carbon dioxide, or some combination thereof.
4. The method of claim 1 wherein the alcohol species is a glycol.
5. A method comprising:
    a. inhibiting degradation of amine functional groups of an immobilized amine in a solid sorbent composition
    b. by including an inorganic base in the solid sorbent composition.
6. A regenerable immobilized amine solid sorbent composition comprising:
    a. a solid support particle,
    b. an immobilized amine,
        i. wherein the immobilized amine comprises an adhesive and an amine susceptible to adsorbing a compound,
    c. an alcohol species capable of lowering the threshold temperature for dissociation of a bond between the compound and the immobilized amine, and;
    d. an inorganic base.
7. The composition of claim 5 wherein the solid support particle is SiO_2.
8. The composition of claim 5 wherein the amine is an aliphatic or aromatic amine.

9. The composition of claim 5 wherein the adhesive is an epoxy.
10. The composition of claim 5 wherein the alcohol species is a polyethylene glycol.
11. The composition of claim 5 wherein the inorganic base is Na_2CO_3.
12. A method of removing a compound from a gas stream comprising:
    a. employing a regenerable solid sorbent in the gas stream, wherein the regenerable solid sorbent comprises,
        i. an immobilized amine susceptible to chemosorbing the compound,
        ii. an alcohol species capable of lowering the threshold temperature for dissociation of the bond between the compound and the amine, and
        iii. an inorganic base,
    b. allowing the regenerable solid sorbent to adsorb the compound from the gas stream, and;
    c. heating the solid sorbent to a temperature above the threshold temperature for dissociation of the bond between the adsorbed compound and the immobilized amine, but below the threshold temperature for dissociation of the immobilized amine.
13. The method of claim 12 wherein the gas stream is flue gas, the compound is CO_2, the solid support is SiO_2, the amine is an aliphatic amine, the adhesive is an epoxy, the alcohol species is a polyethylene glycol and the inorganic base is Na_2CO_3.
14. The method of claim 12 wherein the gas stream is flue gas and the compound is SO_2, the solid support is SiO_2, the amine is an aromatic amine, the adhesive is an epoxy, the alcohol species is a polyethylene glycol and the inorganic base is Na_2CO_3.
15. A method of preparing a dual immobilized amine regenerable solid sorbent for adsorbing a first compound and a second compound, comprising:
    a. impregnating into pores of a solid support a first composition comprising,
        i. a first amine susceptible to chemosorbing the first compound,
        ii. an adhesive,
        iii. an alcohol species capable of lowering the threshold temperature for dissociation of the bond between the first compound and the first amine, and
        iv. an inorganic base,

b. optionally partially filling the pores with a solvent after impregnating the pores with the first composition,

c. treating the resultant solid support with a second composition comprising,

i. a second amine susceptible to chemosorbing the second compound,

ii. an adhesive,

iii. an alcohol species capable of lowering the threshold temperature for dissociation of the bond between the second compound and the second amine, and,

iv. an inorganic base, and;

d. optionally, removing the solvent from the pores.

16. The method of claim 15 wherein the first compound is CO_2 and the first composition comprises an aliphatic amine, a polyethylene glycol, an epoxy and Na_2CO_3, and the second compound is SO_2 and the second composition comprises an aromatic amine, a polyethylene glycol, an epoxy and Na_2CO_3.

17. The method of claim 16 wherein the solvent is water.

18. A dual immobilized amine regenerable solid sorbent composition, comprising:

a. solid support particles having pores, pore mouths and a non-porous surface area,

b. wherein the pores contain a composition of a first amine susceptible to chemosorbing a first compound, an alcohol species capable of lowering the threshold temperature for dissociation of a bond between the first compound and the first amine, an adhesive, and an inorganic base, and;

c. wherein the pore mouths and non-porous surface area contain a composition of a second amine susceptible to chemosorbing a second compound, an alcohol species capable of lowering the threshold temperature for dissociation of a bond between the second compound and the second amine, an adhesive, and an inorganic base.

19. The composition of claim 18 wherein the solid support particles are SiO_2 particles, the first compound is CO_2, the amine susceptible to chemosorbing a first compound is an aliphatic amine, the alcohol species is a polyethylene glycol, the adhesive is an epoxy and the inorganic base is Na_2CO_3.

20. The composition of claim 18 wherein the solid support particles are SiO_2 particles, the second compound is SO_2, the amine susceptible to chemosorbing a second compound is an aromatic amine, the alcohol species is a polyethylene glycol, the adhesive is an epoxy and the inorganic base is Na_2CO_3.

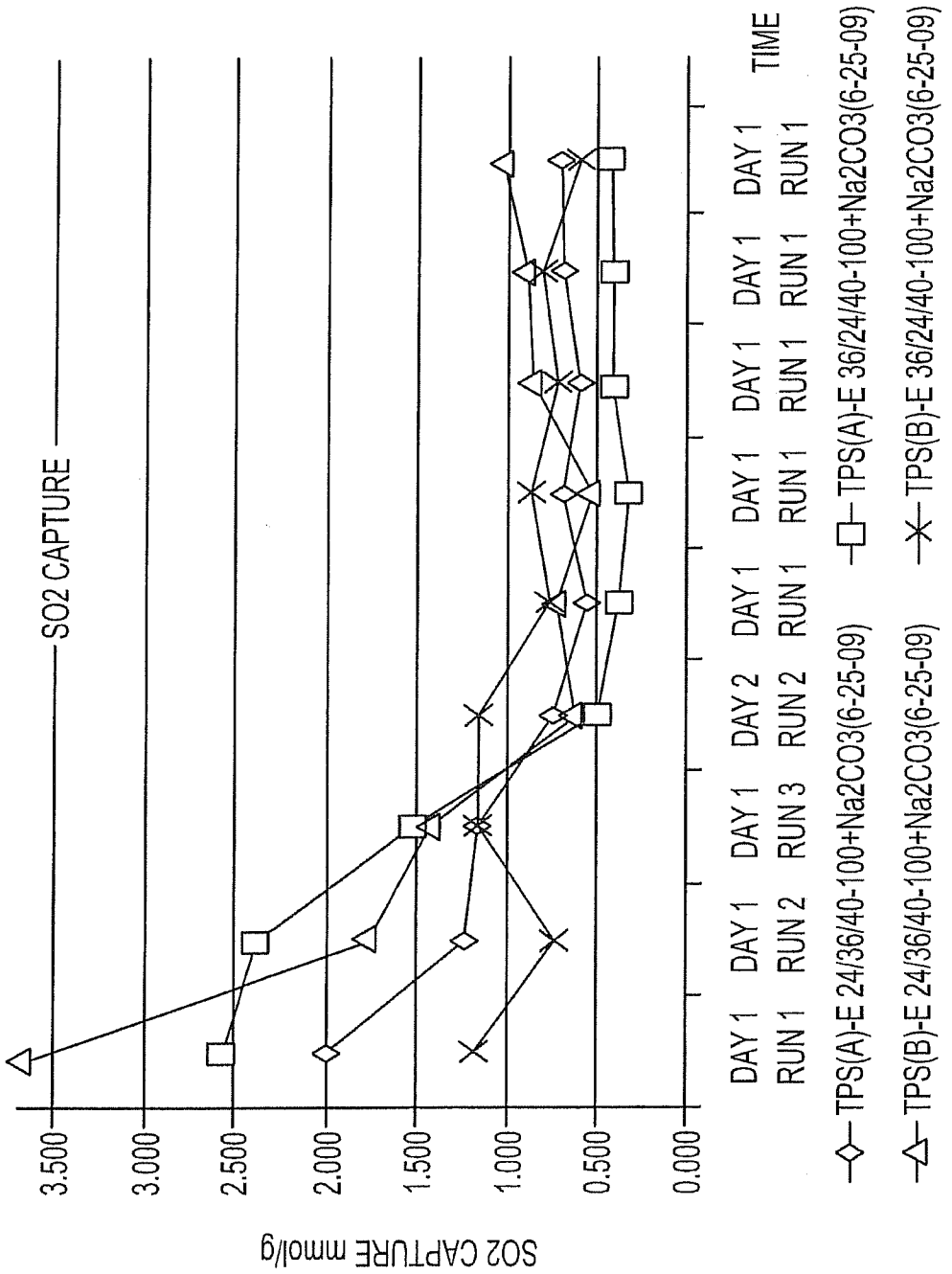

SO2 CAPTURE
3.500
3.000
2.500
2.000
1.500
1.000
0.500
0.000
SO2 CAPTURE mmol/g
DAY 1 DAY 1 DAY 1 DAY 2 DAY 1 DAY 1 DAY 1 DAY 1 DAY 1 TIME
RUN 1 RUN 2 RUN 3 RUN 2 RUN 1 RUN 1 RUN 1 RUN 1 RUN 1
TPS(A)-E 24/36/40-100+Na2CO3(6-25-09)
TPS(A)-E 36/24/40-100+Na2CO3(6-25-09)
TPS(B)-E 24/36/40-100+Na2CO3(6-25-09)
TPS(B)-E 36/24/40-100+Na2CO3(6-25-09)

FIG. 1

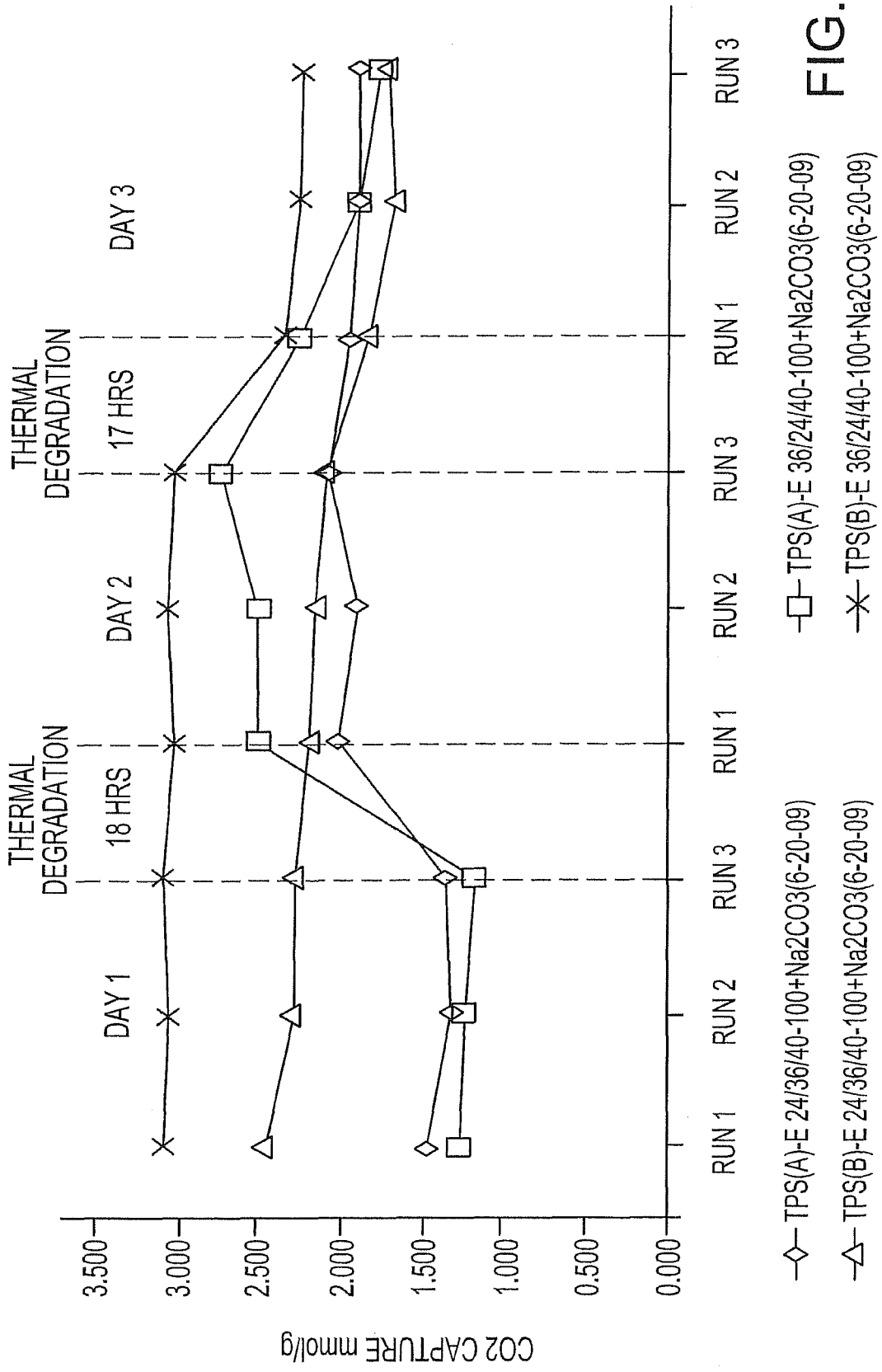

CO2 CAPTURE mmol/g
3.500
3.000
2.500
2.000
1.500
1.000
0.500
0.000
DAY 1
DAY 2
DAY 3
THERMAL DEGRADATION
18 HRS
THERMAL DEGRADATION
17 HRS
RUN 1
RUN 2
RUN 3
RUN 1
RUN 2
RUN 3
RUN 1
RUN 2
RUN 3
TPS(A)-E 24/36/40-100+Na2CO3(6-20-09)
TPS(B)-E 24/36/40-100+Na2CO3(6-20-09)
TPS(A)-E 36/24/40-100+Na2CO3(6-20-09)
TPS(B)-E 36/24/40-100+Na2CO3(6-20-09)
CO2 CAPTURE

FIG. 2

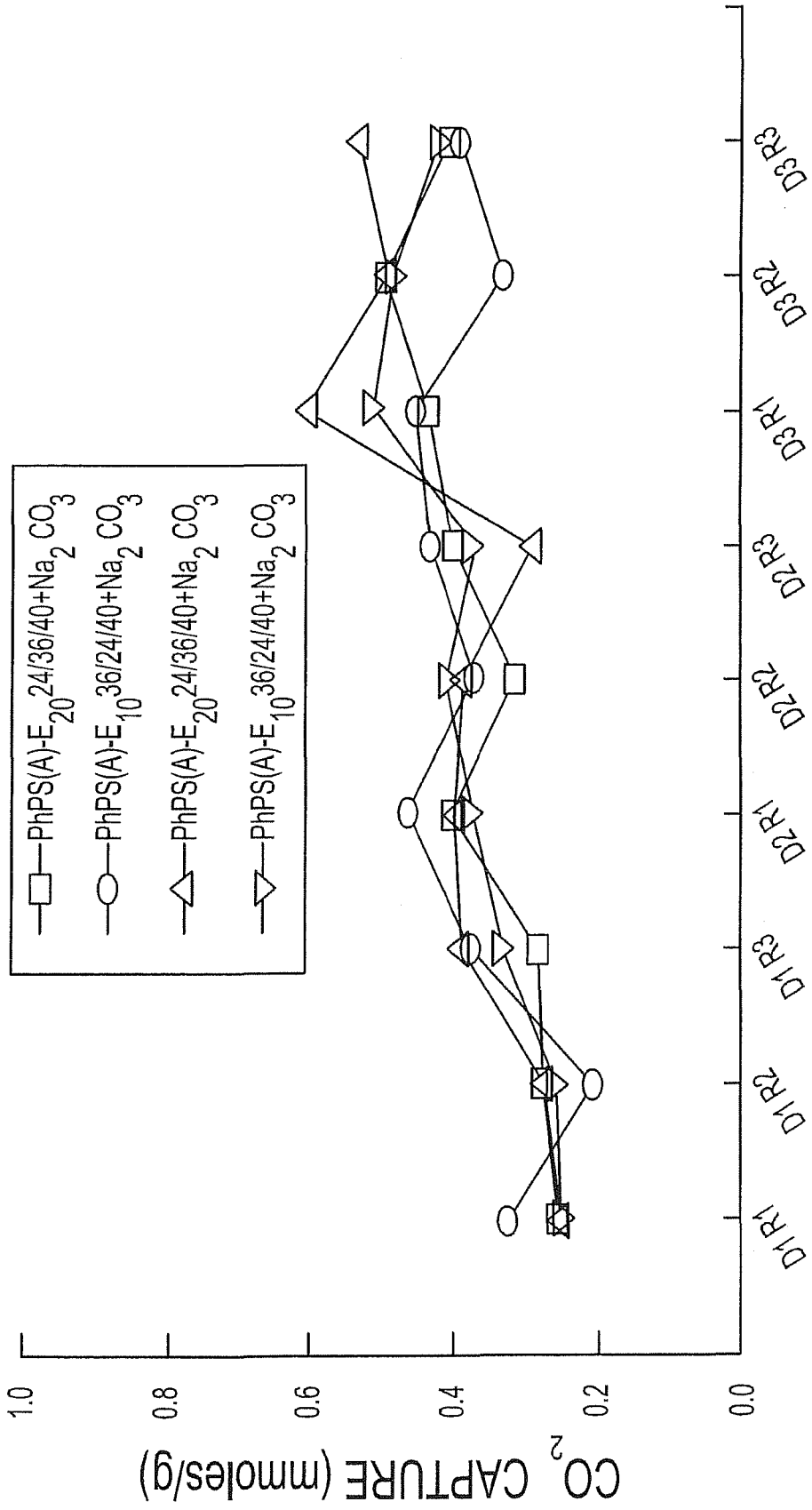
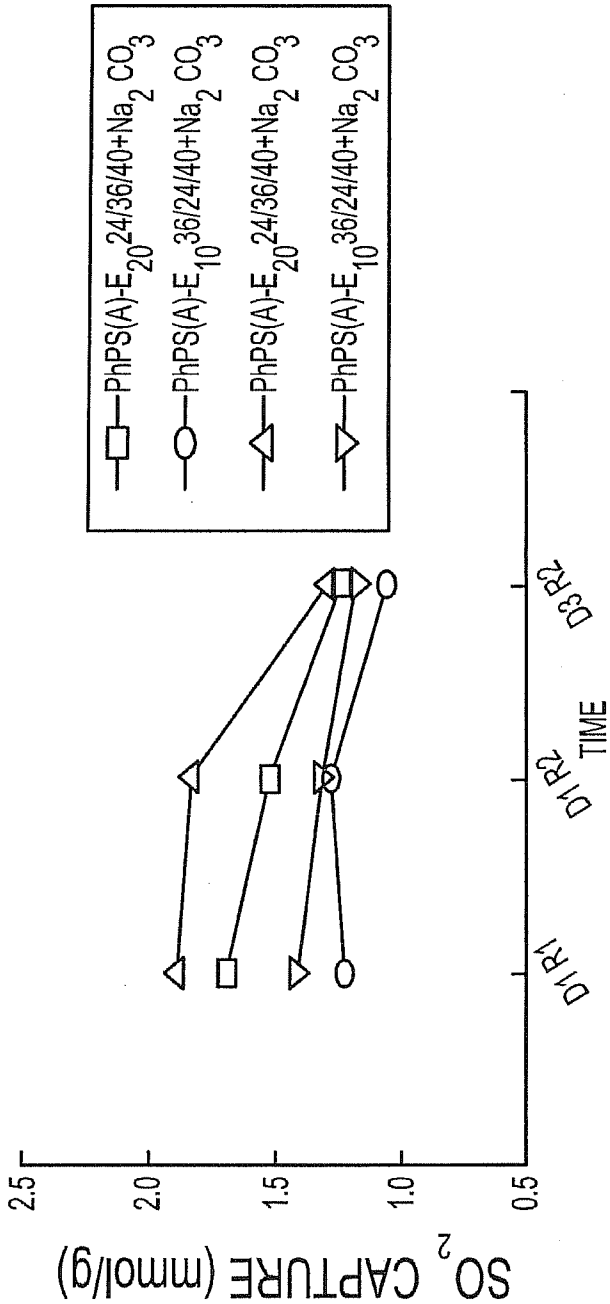


FIG. 3

CO_2 capture profiles of m-phenyldiamine/PEG/EPON/Sio_2 +Na_2CO_3 sorbents

(D-DAY OF EXPERIMENT; R-RUN NUMBER)

FIG. 4


PhPS(A)-E20 24/36/40+Na2 CO3
PhPS(A)-E10 36/24/40+Na2 CO3
PhPS(A)-E20 24/36/40+Na2 CO3
PhPS(A)-E10 36/24/40+Na2 CO3
SO2 CAPTURE (mmol/g)
2.5
2.0
1.5
1.0
0.5
D1,R1
D1,R2
D3,R2
TIME

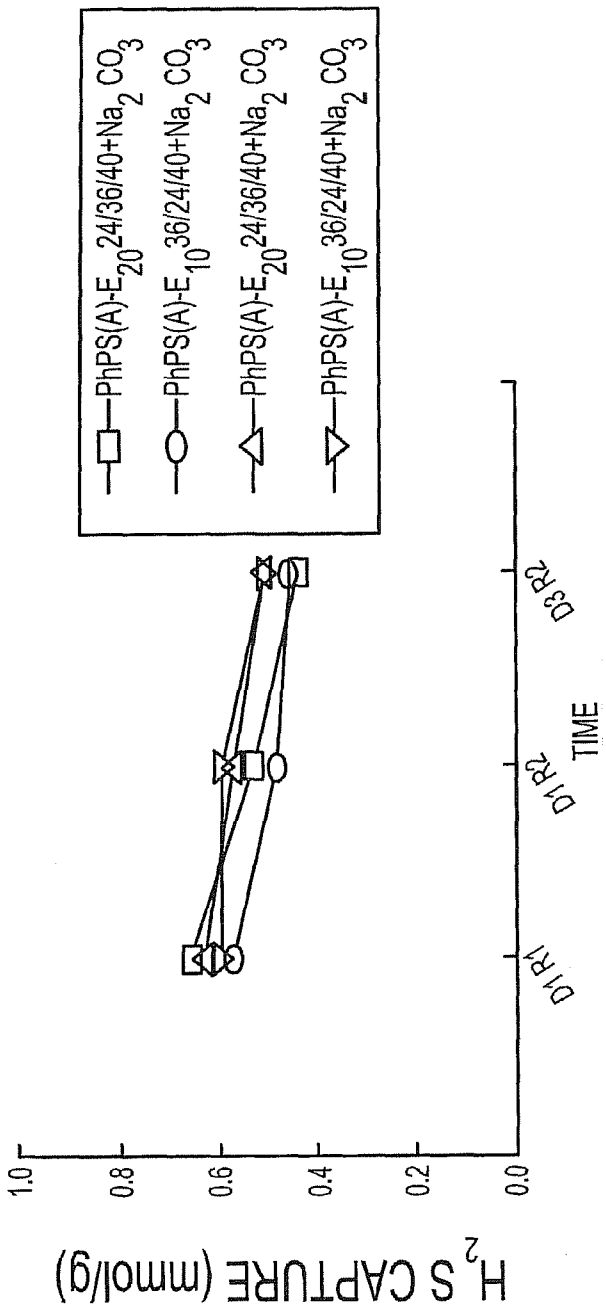

PhPS(A)-E20 24/36/40+Na2 CO3
PhPS(A)-E10 36/24/40+Na2 CO3
PhPS(A)-E20 24/36/40+Na2 CO3
PhPS(A)-E10 36/24/40+Na2 CO3
H2S CAPTURE (mmol/g)
1.0
0.8
0.6
0.4
0.2
0.0
D1R1
D1R2
D3R2
TIME

FIG. 5

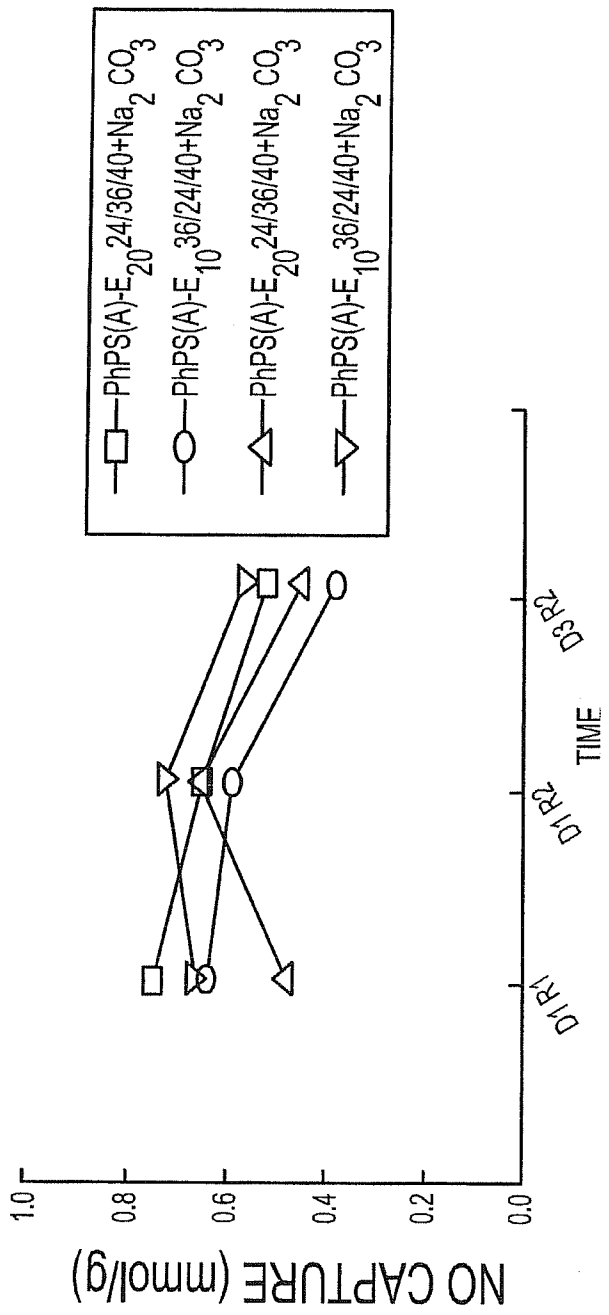

PhPS(A)-E20 24/36/40+Na2 CO3
PhPS(A)-E10 36/24/40+Na2 CO3
PhPS(A)-E20 24/36/40+Na2 CO3
PhPS(A)-E10 36/24/40+Na2 CO3
NO CAPTURE (mmol/g)
1.0
0.8
0.6
0.4
0.2
0.0
D1R1
D1R2
D8R2
TIME

FIG. 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/054277

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J20/04 B01J20/10 B01J20/22 B01J20/32 B01J20/34
B01D53/62 B01D53/50
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J B01D

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2009/061470 A1 (UNIV AKRON [US]; CHUANG STEVEN [US]) 14 May 2009 (2009-05-14) claims 1, 2, 5-7, 8-10 page 7, line 30 - line 33 page 8, line 2 - line 10 page 18, line 23 - page 19, line 3 ----- -/--	1-4

[X] Further documents are listed in the continuation of Box C.

[X] 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 document 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
17 March 2011	06/07/2011

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Kaluza, Nicoleta

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/054277

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Jak Tanthana: "Study of Amine Impregnated on Silica Support for CO2 Capture", University of Akron, Ohio, USA , 1 August 2008 (2008-08-01), pages I-VIII, 42-43,70-73, XP002628496, Retrieved from the Internet: URL:http://etd.ohiolink.edu/send-pdf.cgi/Tanthana%20Jak.pdf?akron1216213754 [retrieved on 2011-03-05] page 42 - page 43 figures 4.13,4.14 page 70 - page 72	1-4
X	US 5 376 614 A (BIRBARA PHILIP J [US] ET AL) 27 December 1994 (1994-12-27) column 2, line 48 - line 50 column 2, line 66 - column 3, line 2 column 3, line 26 - line 31 column 3, line 45 - line 51 column 4, line 7 - line 18 column 4, line 52 - column 5, line 36 claims 1,4	1-4
X	Duane D. Miller: "In Situ Infrared Study of G-S /L-S Adsorption and Photocatalytic Processes", University of Akron, Ohio, USA , 1 August 2009 (2009-08-01), pages I-XII, 145-150, XP002628497, Retrieved from the Internet: URL:http://etd.ohiolink.edu/send-pdf.cgi/Miller%20Duane%20D.pdf?akron1248780285 [retrieved on 2011-03-05] page 145 - page 148 figure 5.7 tables 5.1,5.2	1-4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2010/054277

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.:

1-4

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: 1-4

A method of modifying a chemical interaction between an amine functional group of an immobilized amine in a solid support composition and a gaseous compound to be absorbed in the presence of an alcohol species;

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2. claim: 5

A method to inhibit the degradation of an amine functional group from an amine-based solid sorbent composition

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3. claims: 13(completely); 6-12(partially)

An aliphatic amine based sorbent composition and its use to remove CO2 from a gas stream

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4. claims: 14(completely); 6-12(partially)

An aromatic amine based sorbent composition and its use to remove SO2 from a gas stream

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5. claims: 15-20

A dual amine sorbent composition for adsorbing two different compounds from gas streams and its prepation

---

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2010/054277

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2009061470 A1	14-05-2009	CN 101909743 A	08-12-2010
		EP 2214814 A1	11-08-2010
		US 2010263534 A1	21-10-2010
US 5376614 A	27-12-1994	DE 69305534 D1	21-11-1996
		DE 69305534 T2	20-02-1997
		EP 0673279 A1	27-09-1995
		JP 2635446 B2	30-07-1997
		JP 7509659 T	26-10-1995
		WO 9413386 A1	23-06-1994
		US 5492683 A	20-02-1996