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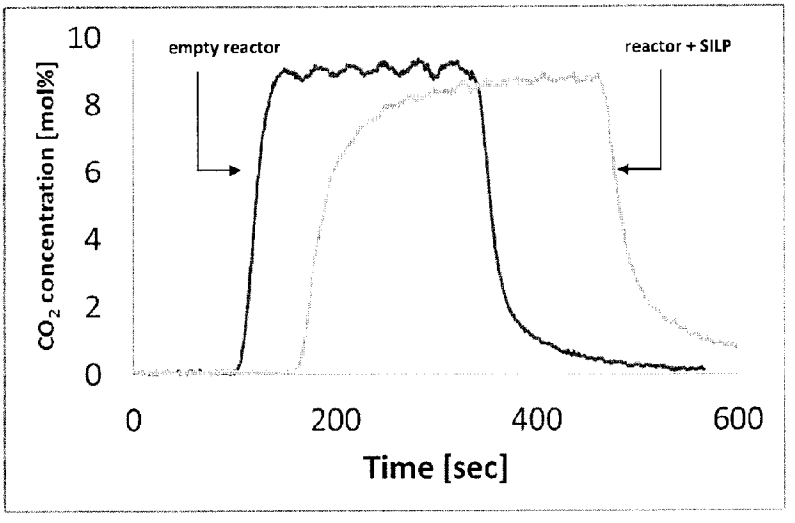
(54) Titre : SORPTION DE CO2 PAR DES LIQUIDES IONIQUES ISSUS D'ACIDES AMINES A SUPPORTS
(54) Title: CO2 SORPTION BY SUPPORTED AMINO ACID IONIC LIQUIDS



(57) Abrégé/Abstract:
Described is a method for absorption of gaseous CO_2 from a gas stream and desorption of the absorbed CO_2, which method comprises contacting said gas stream with a composition at ambient temperature and pressure. The composition comprises: an ionic compound $[A^+][B^-]$ supported on a porous material, wherein $[A^+]$ is an ammonium ion $^+NR_1R_2R_3R_4$, wherein R_1, R_2, R_3 and R_4 are linear C_6 alkyl chains, and $[B^-]$ is an anion selected from the group consisting of L-Isoleucinate, Glycinate, L-Tyrosinate, and L-Prolinate. The CO_2 absorbed on the composition is desorbed by temperature swing absorption (TSA), by increasing the temperature of the composition, by decreasing the total pressure surrounding it and/or by flushing it with a gas stream with no or lower CO_2 content than the gas stream originally applied for the absorption.

Abstract

Described is a method for absorption of gaseous CO_2 from a gas stream and desorption of the absorbed CO_2, which method comprises contacting said gas stream with a composition at ambient temperature and pressure. The composition comprises: an ionic compound $[A^+][B^-]$ supported on a porous material, wherein $[A^+]$ is an ammonium ion $^+NR_1R_2R_3R_4$, wherein R_1, R_2, R_3 and R_4 are linear C_6 alkyl chains, and $[B^-]$ is an anion selected from the group consisting of L-Isoleucinate, Glycinate, L-Tyrosinate, and L-Prolinate. The CO_2 absorbed on the composition is desorbed by temperature swing absorption (TSA), by increasing the temperature of the composition, by decreasing the total pressure surrounding it and/or by flushing it with a gas stream with no or lower CO_2 content than the gas stream originally applied for the absorption.

CO_2 sorption by supported amino acid ionic liquids

Field of the invention

The present invention concerns the absorption and desorption behaviour of carbon dioxide (CO_2) using ionic liquids derived from certain amino acids, adsorbed on porous carrier materials.

Background of the invention

Carbon dioxide is recognized as a greenhouse gas that contributes to climate changes. A major cause of CO_2 emission is from combustion of fossil fuels like oil and coal in production of electricity and heat. The world consumption of coal is expected to increase by 49 % in 2030 and accordingly much attention has been focused on reducing CO_2 emission from power plant flue-gas streams. Currently, aqueous solutions of organic amines are being used to capture CO_2 in scrubbers as carbamates despite concerns about, e.g. low absorbent capacity and energy intensive regeneration by desorption, which may require up to one-third of the total energy output from the power plant. Other technical challenges with amine sorbents include corrosion of steel pipes and pumps as well as thermal and chemical decomposition. In addition concern has been expressed about emission of the amines to the atmosphere leading to serious human health hazards. Solid absorbers also work unsatisfactorily among others due to the high desorption energy required to desorb CO_2 and regenerate the absorber.

In order to overcome these inherent problems, it is highly desired to develop a viable and energy-efficient technology for CO_2 capture by use of alternative, suitable absorbents.

Ionic liquids (ILs) are promising candidates as absorbents in CO_2 removal due to their relatively high thermal stability, exceptionally low vapour pressure and tuneable physicochemical properties [see eg. a) F. Jutz et al. *Chem. Rev.* 2011, 111, 322; b) J. Huang et al. *Aust. J. Chem.* 2009, 62, 298]. There have been many reports on CO_2 capture using common ILs (typically referred to as first-generation ionic liquids), and a maximum CO_2 absorption capacity of 0.75 in mole fraction of CO_2 has been found for $[C_8MIM][PF_6]$ at 40°C under 93 bar pressure [see eg. a) L.A. Blanchard, Z. Gu, Joan F. Brennecke, *J. Phys. Chem.* B 2001, 105, 2437; b) Z. Gu, Joan F. Brennecke, *J. Chem. Eng. Data* 2002, 47, 339; c) Sudhir N. V. K. Aki, Berlyn R. Mellein, Eric M. Saurer, Joan F. Brennecke, *J. Phys. Chem.* B 2004, 108, 20355]. The CO_2

absorption capacity of these kinds of ILs is, however, limited due to the relatively weak physisorption taking place between the IL and CO_2. To circumvent this drawback, Davis and co-workers developed task-specific ionic liquids (TSILs) which are able to chemically bind CO_2 to amine-functionalised imidazolium-based IL at ambient conditions. Even though these TSILs form a chemical bond with CO_2 the absorption capacity was only 0.5 mol of CO_2 per mol of IL (mole ratio of 0.33) due to intermolecular carbamate formation (1:2 mechanism), [see Eleanor D. Bates et al., *J. Am. Chem. Soc.* 2002, 124, 926]. Zhang et al. have proposed a new mechanism for the formation of carbamic acid after CO_2 absorption in phosphonium-based amino acid functionalised ILs [J. Zhang, S. Zhang, K. Dong, Y. Zhang, Y. Shen, X. Lv. Chem. Eur. J. 2006, 12, 4021]. In this mechanism, one mol of CO_2 also reacted with two moles of IL, however in presence of water (1 wt.%) the IL could absorb an equimolar amount of CO_2 via a bicarbonate mechanism (mole ratio of 0.5). Recently, the formation of carbamic acid in amino acid-based ILs was further confirmed by Brennecke and co-workers by examining proline and methionine functionalised phosphonium-based ILs for CO_2 absorption. Here it was shown that one mol of IL can absorb one mol of CO_2 (1:1 mechanism) [see B. E. Gurkan, J. C. de la Fuente, E. M. Mindrup, L. E. Ficke, B. F. Goodrich, E. A. Price, W. F. Schneider, J. F. Brennecke, *J. Am. Chem. Soc.* 2010, 132, 2116]. A few other reports have also published equimolar amount of CO_2 absorption in functionalised ILs, but the typical CO_2-absorption capacity for published IL based solutions is sub-stoichiometric rather than super-stoichiometric.

Chemical absorption (chemisorption) of CO_2 was first observed in imidazolium acetates, where the CO_2 can be trapped either as bicarbonate or, as recently found, also as a carboxylate on carbon position 2 of the imidazole via a carbene mechanism [US Patent App. 10/737,090; US Patent 5,336,298; Maginn, E., DOE Report, quarterly, 01/05- 03/05 2005, 1–12, DOE Scientific and Technical Information, Oak Ridge, TN]. This was recently proven by Rogers and co-workers upon determination of its crystal structure [Gurau G et al. *Angew Chem Int Ed*, 2011, 50:12024–12026]. However, amine functionalized ILs have proven to have a higher CO_2 uptake stoichiometry and has attracted more attention. If an amine functionality is linked to the cation, intermolecular carbamate formation takes place resulting in a maximum stoichiometry of 0.5 moles of CO_2 per mol of IL [[a]Galan Sanchez L et al., Solvent properties of functionalized ionic liquids for CO_2 absorption. Chem Engineer Res Design, 2007, 85: 31–39; [b]Soutullo M et al. Reversible CO_2 capture by unexpected plastic-, resin-, and gel-like ionic soft materials was

discovered during the combi-click generation of a TSIL library. Chem Mater, 2007, 19: 3581–3583]. This has been demonstrated for imidazolium-based cations, where the amine is introduced on one of the alkyl chains. A major drawback of this method is that the already high viscosity of the IL becomes much higher when attaching another functional group to the IL. The important point is, however, that these compounds show much higher CO_2 uptake than their non-functionalized counterparts.

If the amine functionality is attached to the anion of the IL, carbamate species also form, but there is a possibility that the negatively charged functionality on the anion can take up the proton released upon CO_2 capture forming carbamic acid. Then CO_2 can be absorbed with a stoichiometry of up to 1:1, meaning much more efficient use of the IL. However, in most cases, the absorption capacity still corresponds to 0.5:1. This could very well be related to residual water in the IL interfering with the released proton, preventing it from protonating the anionic part.

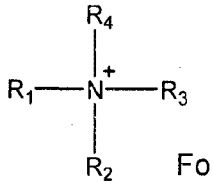
Therefore it must be concluded that despite growing demand, there has not yet been suggested a satisfactory and economically feasible technical solution to the problem of removing CO_2 from eg. flue gases which has a high sorption efficiency, a high capacity and a sufficient robustness to allow for uninterrupted performance over long time periods.

Summary of the invention

It has surprisingly been found that compositions comprising ionic liquids (ILs) based on simple tetraalkylammonium salts of certain amino acids adsorbed on porous (including mesoporous) materials are excellent absorbers of CO_2 having high sorption efficiencies. Thus, absorption of stoichiometric amounts of CO_2 at ambient temperature and pressure (ie. 1 mol CO_2 per mol IL), and in some cases even super-stoichiometric absorption was observed (i.e. more than 1 mol CO_2 per mol IL).

In a first aspect the present invention therefore provides a composition for absorption/desorption of gaseous carbon dioxide (CO_2), which comprises an ionic compound **$[A^+][B^-]$** and a porous material, wherein

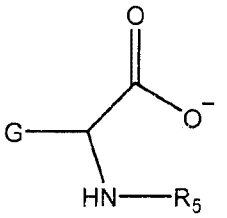
- **$[A^+]$** is an ammonium ion of Formula I



Formula I

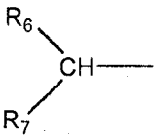
wherein R_1, R_2, R_3 and R_4 are individually selected from linear or branched C_n alkyl chains where n is an integer having a value of at least 4 and not more than 30, and wherein

- **[B^-]** is an anion of Formula II:



Formula II

wherein R_5 is selected from hydrogen or a C_1-C_6 linear or branched alkyl group, and G can be hydrogen or a group of Formula III:



Formula III

wherein

- R_6 is selected from hydrogen or a C_1-C_6 linear or branched alkyl group;
- R_7 can be a C_1-C_6 linear or branched alkyl group or an aromatic group, and
- when R_5 is hydrogen, R_7 may further also be attached to the nitrogen atom to which R_5 is attached, thereby forming a 4-7 membered ring together with said nitrogen.

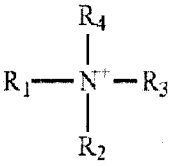
In a second aspect the invention provides a method for absorption of gaseous CO_2 from a gas stream, which method comprises contacting said gas stream with a composition according to the first aspect of the invention.

Reversible CO_2 absorption/desorption was further demonstrated at 80°C without degradation of the supported ionic compound (also referred to in the following as the supported ionic liquid phase (SILP) material), and consecutive absorption-desorption cycles (desorption done at 80°C for 2 h under argon flow) demonstrated complete desorption between each sorption cycle along with preservation of absorption capacities of above 1 mol CO_2 /mol IL for the second and third cycle, respectively.

In a third aspect the invention therefore also allows for desorption of the absorbed CO_2 by increasing the temperature of the composition and/or decreasing the total pressure surrounding it and/or by flushing it with a gas stream with no or lower CO_2 content than the gas stream originally applied for the absorption.

In one aspect, the invention provides a method for absorption of gaseous CO_2 from a gas stream and desorption of the absorbed CO_2, which method comprises contacting said gas stream with a composition at ambient temperature and pressure, wherein the composition comprises: an ionic compound $[A^+][B^-]$ supported on a porous material, wherein $[A^+]$ is an ammonium ion ([N6666]) of Formula I

Formula I



wherein R_1, R_2, R_3 and R_4 are linear C_6 alkyl chains, and $[B^-]$ is an anion selected from the group consisting of L-Isoleucinate ([Ile]), Glycinate ([Gly]), L-Tyrosinate ([Tyr]) and L-Prolinate ([Pro]), and desorbing the CO_2 absorbed on the composition by temperature swing absorption (TSA), by increasing the temperature of the composition, by decreasing the total pressure surrounding the composition, and/or by flushing the composition with a gas stream with no or lower CO_2 content than the gas stream originally applied for the absorption.

Figures

Fig.1 Shows the difference in CO_2 outlet concentration in flow of empty reactor *(left curve)* and with 40 wt% [N6666][Pro] SILP absorber *(right curve)* at 25 °C and 0.09 bar CO_2/He and total gas flow of 55 mL/min.

Fig.2 FT-IR spectrum of [N6666][Asn] as the neat ionic liquid.

Fig.3 FT-IR spectrum of [N6666][Asn] as the SILP version.

Fig.4 FT-IR spectrum of [N6666][Asn] as the SILP version after CO_2 absorption.

Fig. 5 shows Absorp 3.2 TGA program

Fig. 6 shows Absorp 4.0 TGA program

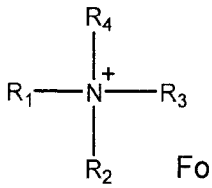
Fig. 7a and 7b shows recycling curves for [N6666][Gly]. Figure 7b shows all the cycles in one graph.

Detailed description of the invention

The inventors have found that compositions comprising ionic liquids (ILs) based on simple tetraalkylammonium salts of certain amino acids adsorbed on high area, porous (including mesoporous) inert materials are excellent absorbers of CO_2 having high sorption efficiencies. Thus, adsorption of stoichiometric amounts of CO_2 at ambient temperature and pressure (ie. 1 mol CO_2 per mol IL), and in some cases even super-stoichiometric absorption was observed (ie. more than 1 mol CO_2 per mol IL). All superstoichiometric uptake amounts must be explained by physical absorption (physisorption) as the ILs of the present invention are only able to bind at most one mol CO_2 by a chemical reaction with the amino group.

In a first aspect the present invention therefore provides a composition for absorption/desorption of gaseous carbon dioxide (CO_2), which comprises an ionic compound **[A^+][B^-]** and a porous material, wherein

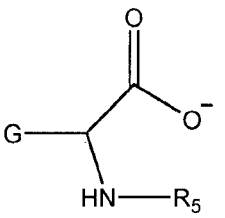
- **[A^+]** is an ammonium ion of Formula I



Formula I

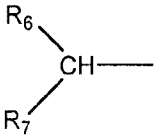
wherein R_1, R_2, R_3 and R_4 are individually selected from linear or branched C_n alkyl chains where n is an integer having a value of at least 4 and not more than 30, and wherein

- $[B^-]$ is an anion of Formula II:



Formula II

wherein R_5 is selected from hydrogen or a C_1-C_6 linear or branched alkyl group, and G can be hydrogen or a group of Formula III:



Formula III

wherein

- R_6 is selected from hydrogen or a C_1-C_6 linear or branched alkyl group;
- R_7 can be a C_1-C_6 linear or branched alkyl group or an aromatic group, and
- when R_5 is hydrogen, R_7 may further also be attached to the nitrogen atom to which R_5 is attached, thereby forming a 4-7 membered ring together with said nitrogen.

Throughout the present application the following abbreviations will be used: [N4444]: tetrabutylammonium, [N6666]: tetrahexylammonium, [N66614]: trihexyltetradecylammonium, [Met]: L-Methionate, [Ile]: L-Isoleucinate, [Gly]: Glycinate, [Asn]: L-Asparaginate, [Tyr]: L-Tyrosinate, [Pro]: L-Prolinate.

In one embodiment R_1, R_2, R_3 and R_4 are alkyl chains of identical length.

In one embodiment R_1 is selected from butyl and hexyl, and R_2, R_3 and R_4 are individually selected from butyl and hexyl.

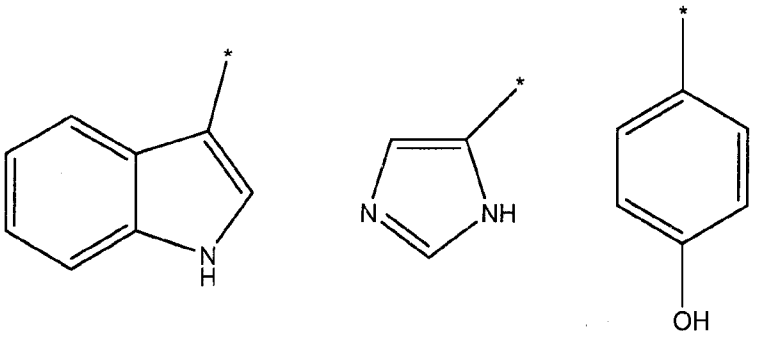
In another embodiment R_1 is a C_n alkyl chain where n is an integer having a value of between 10 and 20, and R_2, R_3 and R_4 are alkyl chains of identical length selected from butyl, pentyl, hexyl, heptyl and octyl.

In a further embodiment R_1 is a C_n alkyl chain where n is an integer having a value of between 10 and 20, and wherein R_2, R_3 and R_4 are individually selected from butyl, pentyl, hexyl, heptyl and octyl.

In one embodiment R_7 is selected from methyl, ethyl, 1-propyl, 2-propyl, 1-butyl, 2-butyl, t-butyl, 1-pentyl, 2-pentyl, 3-pentyl, 1-hexyl, 2-hexyl or 3-hexyl.

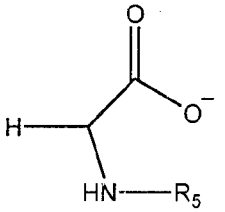
In another embodiment R_7 is an aromatic group selected from benzene, substituted phenyl groups and heteroaromatic groups such as imidazole, pyridine and indole.

In a further embodiment R_7 is an aromatic group selected from the following structures wherein the asterisk (*) denotes the attachment point



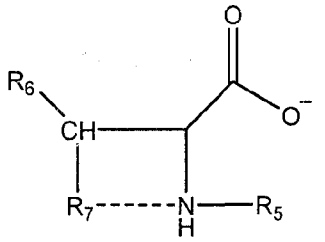
In preferred embodiments **[A^+]** is an ammonium ion selected from tetrabutylammonium, tetrahexylammonium, and trihexyltetradecylammonium.

In one embodiment G is hydrogen, and **[B^-]** becomes an anion of this structure:



wherein R_5 is selected from hydrogen or a C_1-C_6 linear or branched alkyl group.

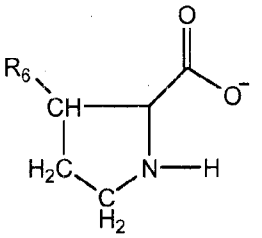
In another embodiment G is a group of Formula III, and **[B⁻]** becomes an anion of this structure:



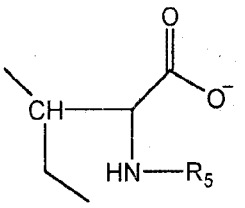
wherein

- R_6 is selected from hydrogen or a C_1-C_6 linear or branched alkyl group;
- R_7 can be a C_1-C_6 linear or branched alkyl group or an aromatic group, and
- the dotted line denotes that when R_5 is hydrogen, R_7 may be attached to the nitrogen atom to which R_5 is attached, thereby forming a 4-7 membered ring together with said nitrogen.

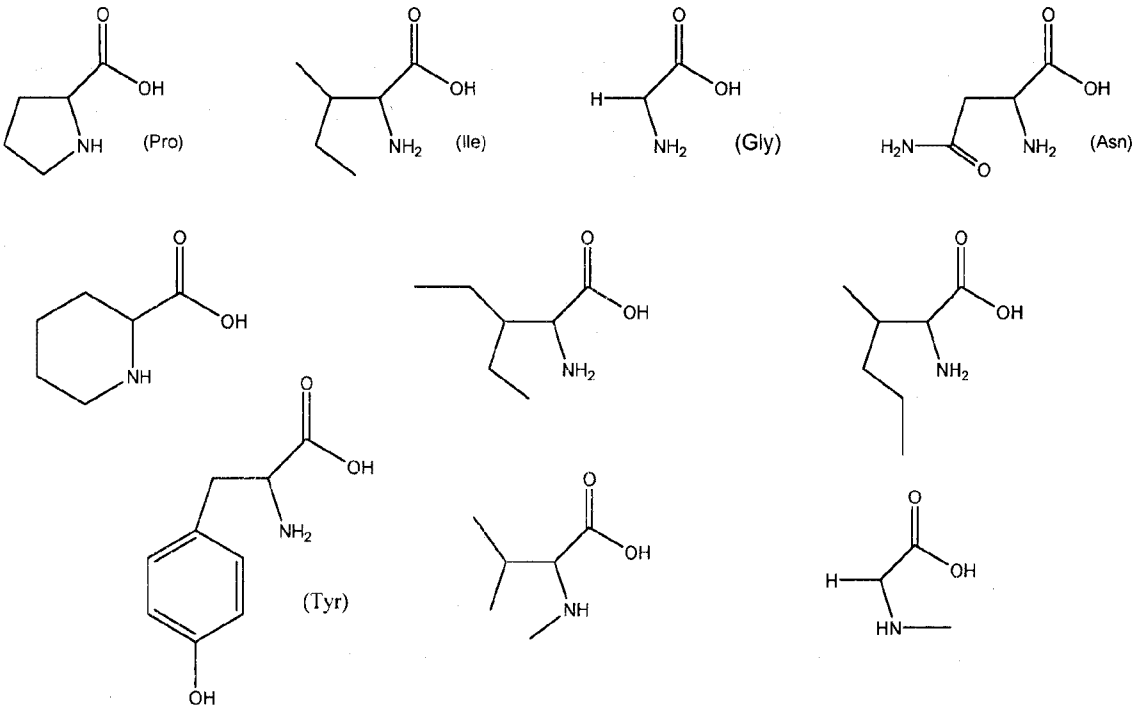
In a preferred embodiment R_5 is hydrogen, R_6 is selected from hydrogen or a C_1-C_6 linear or branched alkyl group and R_7 is an ethyl group further attached to the nitrogen atom to form a 5-membered ring, such that **[B⁻]** becomes an anion of this structure:



In another preferred embodiment R_5 is selected from hydrogen or a C_1-C_6 linear or branched alkyl group, R_6 is methyl and R_7 is an ethyl group, such that **[B⁻]** becomes an anion of this structure:



In further embodiments **[B⁻]** is an anion of one of the following amino acids:



Good to excellent absorption of CO_2 was observed for the following ionic compounds of the invention: [N4444][Met], [N6666][Ile], [N6666][Gly], [N6666][Asn], [N6666][Pro] and [N6666][Tyr], all impregnated on hydrophobic SiO_2 (Table 1 and 2).

In a preferred embodiment **[B⁻]** is thus an anion selected from L-Methionate, L-Isoleucinate, Glycinate, L-Asparaginate, L-Tyrosinate and L-Prolinate.

In a particularly preferred embodiment, **[B⁻]** is an anion selected from L-Isoleucinate, Glycinate and L-Prolinate.

In one preferred embodiment, **[A⁺][B⁻]** is [N6666][Ile].
In another preferred embodiment **[A⁺][B⁻]** is [N6666][Gly].
In a particularly preferred embodiment, **[A⁺][B⁻]** is [N6666][Pro].
In one preferred embodiment, **[A⁺][B⁻]** is [N66614][Pro].

In an embodiment the porous material is selected from porous (including mesoporous) inorganic, carbonaceous or a polymeric materials such as, but not limited to, silica, including

mesoporous silica, controlled pore glass, alumina, titania (anatase), zirconia, alkaline earth metal oxides, clays and zeolites, or mixtures hereof.

In separate embodiments the porous material is selected from **PG75-120** (mesh size 80-120, mean pore diameter 74 Å, pore distribution ±7:0%, pore volume 0.47 cc/g, surface area 152.7 m^2/g), **PG500-80** (mesh size 20-80, mean pore diameter 547 Å, pore distribution ±6:3%, pore volume 1.06 cc/g, surface area 44.5 m^2/g), **PG2000-200** (mesh size 120-200, mean pore diameter 1932 Å, pore distribution ±7:3%, pore volume 0.86 cc/g, surface area 11.32 m^2/g) and **Silica gel 90** (mesh size 80-120, mean pore diameter 74 Å, pore distribution ±7:0%, pore volume 0.47 cc/g, surface area 152.7 m^2/g).

In an embodiment the composition according to the **first aspect** of the invention contains between 5-45 % w/w of the ionic compound **$[A^+][B^-]$**, such as 10% w/w, 20% w/w, 30% w/w or 40% w/w.

In another embodiment the composition according to the **first aspect** of the invention contains between 5-45% w/w, such as 10% w/w, 20% w/w, 30% w/w or 40% w/w, of an ionic compound selected from [N4444][Met], [N6666][Ile], [N6666][Gly], [N6666][Asn], [N6666][Pro] and [N6666][Tyr].

In yet another embodiment the composition according to the **first aspect** of the invention contains about 40% w/w of an ionic compound selected from [N6666][Ile], [N6666][Gly] and [N6666][Pro].

In specific embodiments, the composition of the **first aspect** has a total CO_2 absorption capacity of over about 1 mol CO_2/mol ionic liquid, such as over 0.9 mol CO_2/ mol ionic liquid, over 1.1 mol CO_2/ mol ionic liquid, over 1.2 mol CO_2/ mol ionic liquid, over 1.3 mol CO_2/ mol ionic liquid, over 1.4 mol CO_2/ mol ionic liquid, over 1.5 mol CO_2/ mol ionic liquid, over 1.6 mol CO_2/ mol ionic liquid or over 1.7 mol CO_2/ mol ionic liquid.

In other specific embodiments, the composition of the **first aspect** has a total CO_2 absorption capacity of over about 3% w/w CO_2, such as over 3.4% w/w CO_2, over 3.6% w/w, over 3.7% w/w, over 4.4% w/w, over 4.5% w/w or over 4.6% w/w.

In a second aspect the invention provides a method for absorption of gaseous CO_2 from a gas stream, which method comprises contacting said gas stream with a composition according to the first aspect of the invention.

In an embodiment the composition of the **first aspect** of the invention has an absorption capacity of over 1 mol CO_2/mol of the ionic compound **[A^+][B^-]** at a CO_2 concentration of less than 0.1 bar.

In a further embodiment the invention provides a method according to the **second aspect** of the invention, wherein the absorption takes place from a gas stream which contains 1 – 100 mol% CO_2 with an absorption capacity of over 1 mol CO_2/mol of the ionic compound **[A^+][B^-]**.

In a particular embodiment, the contact between the gas stream and the absorbent composition of the invention takes place in a suitable reactor which could be a fixed-bed or movable-bed reactor using an appropriately shaped form of the composition of the invention to provide low resistance to the gas stream and thus an accompanying acceptable pressure drop across the reactor.

In particular embodiment, the gas stream is a flue-gas stream generated from combustion by large point stationary sources such as power plants.

In specific embodiments, the gas stream contains less than about 15% CO_2 such as 15% CO_2, 14% CO_2, 13% CO_2, 12% CO_2, 11% CO_2, 10% CO_2, 9% CO_2or between 10-15% CO_2.

In a further particular embodiment, the gas stream contains significant amounts of water vapor, such as 3-5% H_2O, 5-7% H_2O, 7-10% H_2O, 10-12% H_2O, 12-14% H_2O 14-16% H_2O or more than 16% H_2O.

The compositions of the invention may be part of a composite material e.g. combined with fiber materials or other materials which improve the mechanical strength, but do not lower gas diffusion severely.

Reversible CO_2 absorption/desorption was further demonstrated at 80°C without degradation of the supported ionic compound (also referred to in the following as the supported ionic liquid phase (SILP) material), and consecutive absorption-desorption cycles (desorption done at 80°C for 2 h under argon flow) demonstrated complete desorption between each sorption cycle along with preservation of absorption capacities of around or above 1 mol CO_2 /mol IL for the second and third cycle, respectively.

Consecutive absorption-desorption cycles for the 40 wt% [N6666][Pro] SILP absorber (desorption done at 80°C for 2 h under argon flow) demonstrated further complete desorption between each sorption cycle, and preservation of good absorption capacities of 1.05 and 1.17 mol CO_2 /mol IL for the second and third cycle, respectively (see table 4).

Figure 7a shows recycling curves for [N6666][Gly] and figure 7b shows all the cycles shown in one graph. A very small loss of capacity is seen from the first to subsequent cycles. The absorption stoichiometry is around 1.00 mol of CO_2 per mol IL in this material. Absorption kinetics is very fast.

In a third aspect the invention also provides a method for desorption of the absorbed CO_2 by increasing the temperature of the saturated composition and/or decreasing the total pressure surrounding it and/or by flushing it with a gas stream with no or lower CO_2 content than the gas stream originally applied for the absorption.

Experimental

All chemicals were purchased from Sigma-Aldrich in p.a. quality and used as received.
Glass, controlled pore series: **PG75-120** (mesh size 80-120, mean pore diameter 74 Å, pore distribution ±7:0%, pore volume 0.47 cc/g, surface area 152.7 m^2/g), **PG500-80** (mesh size 20-80, mean pore diameter 547 Å, pore distribution ±6:3%, pore volume 1.06 cc/g, surface area 44.5 m^2/g), **PG2000-200** (mesh size 120-200, mean pore diameter 1932 Å, pore distribution ±7:3%, pore volume 0.86 cc/g, surface area 11.32 m^2/g). **Silica gel 90** (mesh size 80-120, mean pore diameter 74 Å, pore distribution ±7:0%, pore volume 0.47 cc/g, surface area 152.7 m^2/g).

Silica gel 60 (Merck) was calcined at 600 °C for 6 h prior to use to obtain hydrophobic silica. All silica and SILP materials were stored in a desiccator over solid NaOH. ^{1}H NMR spectra were recorded on a Varian Mercury 300 (300 MHz) and are reported relative to the residual solvent peak (δ = 4.79 for D_2O and δ = 2.50 for d_6-DMSO). ^{13}C NMR spectra were recorded on a Varian Mercury 300 (75.5 MHz) or a Varian Inova 500 (125 MHz) and are reported relative to the residual solvent peak (δ = 39.52 for d_6-DMSO). FT-IR measurements were carried out with a Bruker ALPHA-P FT-IR spectrophotometer using an ATR platinum with diamond crystal. OPUS 6.5 software was used to analyze the samples. Spectra were taken with 24 scans unless otherwise stated.

Structures of synthesized ionic liquids are given in **Table 1.**

TGA analysis, general procedure

Thermo gravimetric analysis (TGA) was performed on a Mettler Toledo TGA/DSC 1 STAR System with a Gas Controller GC 100 and a flow of nitrogen of 70 mL/min. A crucible was weighed inside the TGA instrument and approximately 10 mg of IL or 25 mg of SILP was transferred to it before reinsertion. The weight was noted and during measurements samples were heated from 40 to 600 °C at a constant heating rate of 10 °C/min.

Two ways of performing the TGA including recycling (flow absorption-desorption studies) are used in the present recycling studies. The two different TGA methods are illustrated graphically in **fig 5** (Absorp 3.2) and **fig 6** (Absorp 4.0). In the absorp 3.2 method the sample is heated to 80 °C in 180 min to remove remaining solvent followed by cooling to 25 °C with CO_2 absorption in 120 min, heating etc. In the absorp 4.0 method the initial heating is conducted at 100°C and after the cooling to 25°C, the sample is left for 10 min under N_2 before CO_2 is lead over the sample (for 60 min), and intermediate heating steps are performed at 80 °C etc. In both methods the sample starts taking up N_2 during the cooling step. The same is seen with pure SiO_2 so a theory is that all the N_2 uptake stems from SiO2 N_2 uptake.

Synthesis of Tetrabutylammonium Methionate [N4444][Met] – Table 1, entry 1

General procedure 1: 9.72 g of tetrabutylammonium hydroxide ([N4444][OH], 40 wt% in water, 15 mmol) was added to a 50 mL round-bottom flask along with a magnet stirrer. 2.45 g of L-

methionine (16 mmol) was added and the edge of the flask was washed with 2 mL of water. The mixture was stirred overnight at rt to ensure full deprotonation of the amino acid. The magnet was removed and the water was evaporated at 10 mbar and 40°C for 1 h. Excess amino acid was removed by adding 10 mL of cold acetonitrile. The flask was immersed into an icebath and allowed to precipitate for 1 h, followed by separation by a glas frit. The solvent was evaporated at 200 mbar and 40°C for 1 h followed by 10 mbar and 40°C for 1 h. ^{1}H and ^{13}C NMR spectra were taken in D_2O and confirmed the identity of the ionic liquid. Purity of the IL was estimated by integration of visible impurities in the ^{1}H NMR spectrum.

^{1}H NMR (500 MHz, D_2O) d = 3.40 (dd, J = 7.2, 5.6 Hz, 1H), 3.20 (m, 8H), 2.58 (t, J = 7.8 Hz, 2H), 2.13 (s, 3H), 1.97 (m, 1H), 1.85 (m, 1H), 1.66 (m, 8H), 1.36 (m, 8H), 0.96 (t, J = 7.4 Hz, 12H); ^{13}C NMR (75 MHz, D_2O) d = 181.85, 58.19, 55.43, 52.14, 34.29, 30.01, 23.29, 19.35, 14.41, 13.19; IR (ATR platinum diamond 1 Refl): 3359, 3285, 2960, 2935, 2874, 1584, 1487, 1464, 1380, 1326. Yield ≥99 %. Purity≥ 99 % w/w.

Synthesis of Tetrahexylammonium Isoleucinate [N6666][Ile] – entry 2

Following general procedure 1, tetrahexylammonium isoleucinate ([N6666][Ile]) was synthesised and its identity was confirmed by ^{1}H and ^{13}C NMR.

^{1}H NMR (300 MHz, D_2O) d = 3.24 – 3.09 (m, 8H), 3.07 (d, J = 5.3 Hz, 1H), 1.64 (br. s, 8H), 1.51 – 1.23 (m, 25H), 1.23 – 1.01 (m, 1H), 0.87 (m, 18H); ^{13}C NMR (75 MHz, D_2O) d = 181.57, 61.27, 58.21, 38.81, 30.92, 25.47, 24.41, 22.14, 21.31, 15.97, 13.77, 11.68; IR (ATR platinum diamond 1 Refl): 3381, 3288, 2955, 2926, 2860, 1583, 1487, 1465, 1379, 1327.

Yield ≥99 %. Purity≥ 99 % w/w.

Synthesis of Tetrahexylammonium Glycinate [N6666][Gly] – entry 3

Following general procedure 1, tetrahexylammonium glycinate ([N6666][Gly]) was synthesised and its identity was confirmed by ^{1}H and ^{13}C NMR.

^{1}H NMR (500 MHz, d_6-DMSO) d = 3.69 (m, 8H), 2.66 (s, 2H), 1.57 (br. s, 8H), 1.29 (br. s, 24H), 0.88 (t, J = 6.6 Hz, 12H); ^{13}C NMR (75 MHz, d_6-DMSO) d = 174.40, 57.58, 46.29, 30.60, 25.44, 21.89, 21.01, 13.69; IR (ATR platinum diamond 1 Refl): 3362, 3293, 2954, 2925, 2858, 1593, 1489, 1466, 1378, 1324.

Yield ≥99%. Purity≥ 99 % w/w.

Synthesis of Tetrahexylammonium Asparaginate [N6666][Asn] – entry 4

Following general procedure 1, tetrahexylammonium asparaginate ([N6666][Asn]) was synthesised and its identity was confirmed by ^{1}H and ^{13}C NMR. ^{1}H NMR (300 MHz, D_2O) d = 3.56 (dd, J = 9.1, 4.7 Hz, 1H), 3.17 (m, 8H), 2.65 (dd, J = 14.8, 4.7 Hz, 1H), 2.40 (dd, J = 14.8, 9.1 Hz, 1H), 1.64 (br. s, 8H), 1.32 (br. s, 24H), 0.87 (t, J = 6.8 Hz, 12H); ^{13}C NMR (75 MHz, D_2O) d = 181.26, 176.79, 58.27, 53.44, 40.58, 30.54, 25.30, 21.85, 21.07, 13.36; IR (ATR platinum diamond 1 Refl): 3490, 3363, 3296, 3181, 2954, 2927, 2859, 1667, 1590, 1487, 1466, 1378.

Yield ≥99 %. Purity≥ 99 % w/w.

Synthesis of Tetrahexylammonium Prolinate [N6666][Pro] – entry 5

Following general procedure 1, tetrahexylammonium prolinate ([N6666][Pro]) was synthesised and its identity was confirmed by ^{1}H and ^{13}C NMR.

^{1}H NMR (300 MHz, D_2O) d = 3.42 (dd, J = 8.1, 6.1 Hz, 1H), 3.16 (m, 8H), 2.99 (m, 1H), 2.70 (m, 1H), 2.04 (m, 1H), 1.58 (m, 11H), 1.29 (br. s, 24H), 0.85 (t, J = 6.7 Hz, 12H); ^{13}C NMR (75 MHz, D_2O) d = 182.05, 61.63, 58.27, 46.17, 42.99, 30.91, 30.66, 25.35, 21.96, 21.14, 13.53; IR (ATR platinum diamond 1 Refl): 3291, 2954, 2927, 2859, 1590, 1487, 1466, 1373.

Yield ≥99 %. Purity≥ 99 % w/w.

Synthesis of Tetrahexylammonium Tyrosinate [N6666][Tyr] – entry 6

Following general procedure 1, tetrahexylammonium tyrosinate ([N6666][Tyr]) was synthesised and its identity was confirmed by ^{1}H and ^{13}C NMR. However, for the precipitation of excess amino acid, 10 mL of cold MeOH was used instead of MeCN. This IL is sensitive to light and was therefore wrapped in aluminum foil during synthesis and storage.

^{1}H NMR (300 MHz, D_2O) d = 6.99 (d, J = 8.5 Hz, 1H), 6.61 (d, J = 8.5 Hz, 1H), 3.40 (dd, J = 7.6, 5.0 Hz, 1H), 3.11 (m, 8H), 2.87 (dd, J = 13.6, 5.0 Hz, 1H), 2.66 (dd, J = 13.8, 7.6 Hz, 1H), 1.61 (br. s, 8H), 1.30 (br. s, 24H), 0.81 (m, 12H); ^{13}C NMR (75 MHz, d_6-DMSO) d = 176.63, 160.67, 129.51, 126.61, 116.09, 58.45, 57.64, 42.28, 30.62, 25.46, 21.92, 21.01, 13.83; IR (ATR platinum diamond 1 Refl): 3233, 2954, 2926, 2859, 1589, 1513, 1486, 1466, 1380. Yield ≥99 %. Purity≥ 96 % w/w.

Thermal stability of SILP absorbers

The ILs of particular interest according to the present invention are ones with a capability of capturing CO_2 from a dilute stream, such as off-gas from combustion, and concurrent release of the gas by temperature swing absorption (TSA). For this purpose the amino acid functionalized ILs according to the present invention and their corresponding SILP materials were synthesized and analyzed for temperature stability.

The temperature stability of the ILs was estimated by TGA, and the point of decomposition was determined by initial curvature of both the curve representing the weight as well as the heat flux to the sample. The points of decomposition for all the pure ILs were measured to be 140–150 °C except for [N6666][Tyr] which decomposed at approximately 130 °C. After impregnation on SiO_2 (see below example) the resulting SILP materials showed comparable or slightly higher temperature stabilities vis-a-vis their IL counterparts, thus making them applicable for TSA.

Synthesis of Hydrophobic Silica.

Approximately 15 g of SiO_2 (marked Silica 60) was calcined at 600°C for 6 h. The hydrophobic silica was stored in a desiccator over NaOH(s). This hydrophobic silica is used as a support material in the following.

Synthesis of Supported Ionic Liquid Phase absorber materials

2 g of [N6666][Met] was added to a 100 mL round-bottom flask along with a magnet stirrer. 10 mL of MeOH was added followed by 3 g of hydrophobic silica. The suspension was stirred overnight. The magnet was removed and the solvent was evaporated at 330 mbar and 40°C for 1 h followed by 10 mbar and 40°C for 1 h. The sticky solid was weighed and transferred to a glass fritted funnel and Ar was flowed through it for approximately three days at approximately 70 mL/min to remove remaining solvent. The dry SILP was transferred to a small container and stored in a desiccator over NaOH(s). All other examined SILP absorbers with 10–40 wt% IL loading were prepared by a similar method as described above (see Table 2).

The used carrier material, SiO_2, was chosen due to easy access and convenient calcination. It also has a high surface area and a mesoporous structure, both of which are important for a support material. Other support materials relevant in the context of the present invention

include controlled pore glasses, alumina, titania (anatase), zirconia, alkaline earth metal oxides, clays and zeolites, or mixtures hereof.

CO_2 Absorption Studies

CO_2 absorption capacities of the SILP absorbers:

The equilibrium CO_2 absorption capacities of the SILP absorbers were determined under 1 bar of CO_2 pressure using the following method: A glass reactor was dried in an oven at 120 °C overnight, assembled hot, and allowed to cool for approximately 1 h. After weighing 1–2 g of SILP was transferred to the reactor where after it was degassed with helium (approximately 70 mL/min) for 24 h or until no further weight loss was observed. Subsequently, the reactor was subjected to a stream of approximately 50 mL/min of CO_2 gas (99.9%, Air Liquide Denmark) and the weight increase of the reactor followed periodically for 48 h. The absorption dynamics using a SILP absorber was demonstrated in a flow-setup at 0.09 bar CO_2 pressure (in He) using the following method: 0.78 g of a SILP absorber with 40 wt% [N6666][Pro] was loaded between glass wool into a glass tube reactor with inner diameter of 1 cm. The system was then purged with helium (50 mL/min) for approximately 30 min, where after a flow of CO_2 (5 mL/min) was directed into the helium stream and the CO_2 concentration at the reactor outlet was continuously measured using a CO_2 BINOS 100 detector (Rosemount Analytical, Solon, OH, USA). A blank experiment was also performed without absorber material in the reactor.

The absorption measurements revealed a number of the prepared amino acid-based SILP absorbers to provide excellent CO_2 uptake, as shown in Table 1 and Table 2. Hence, many of the SILP materials absorbed superstoichiometric amounts of CO_2, which is surprising considering the very slight physical solubility of CO_2 in ILs in general, and specifically at ambient pressure. All superstoichiometric uptake amounts are assigned to physical absorption (physisorption) as the ILs of the present invention are only able to bind one mol CO_2 by a chemical reaction with the amino group. Accordingly, the ILs of the invention very likely have accessible cavities for CO_2 to intercalate, possibly aided by attraction to the negatively charged carboxylate moiety present in the amino acid anions.

To determine if the superstoichiometric uptake had anything to do with the support porosity, specifically trapping of CO_2 or IL in its pores, a series of lower loading SILP materials based

on [N6666][Pro] was synthesised. After synthesis they were not characterised, only dried and submitted to CO_2 absorption experiments (Table 3).

The SILP material with 10 wt% [N6666][Pro] loading showed a particular high equilibrium absorption capacity of 1.74 mol CO_2 mol IL (at 25 °C, 1 bar CO_2). At higher loadings this ratio decreased gradually, as expected, indicating that the support affected the capacity although absorption by the SiO_2 was subtracted in the reported data. ILs have a high degree of ordering in the liquid state [[a]Jacquemin J, et al. High-pressure volumetric properties of imidazolium-based ionic liquids: Effect of the anion. *J Chem Engineer Data,* 2007, 52: 2204–2211; [b]Huang X et al. Why is the partial molar volume of CO2 so small when dissolved in a room temperature ionic liquid? *J.Am Chem Soc,* 2005, 127: 17842–17851], and this ordering might be further promoted by impregnation on a solid surface [[a]Gottfried JM et al., Surface studies on the ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate using X-ray photoelectron spectroscopy (XPS). *Z für Physikalische Chem*, 2006, 220: 1439–1453; [b]Steinrück H-P. Recent developments in the study of ionic liquid interfaces using X-ray photoelectron spectroscopy and potential future directions. *Phys Chem Chem Phys*, 2012, 14: 5010–5029]. The surface-induced ordering of the IL would then extend some distance into the bulk liquid, and the effect is therefore more pronounced with low loading.

To further assess the CO_2 absorption abilities of the SILP materials, flow absorption-desorption studies (recycle studies) were performed using the 40 wt% [N6666][Pro] SILP absorber, which possessed the highest CO_2 mass uptake, with a gas stream of 0.09 bar CO2 (i.e. 9 mol%) in He. The result showed that insertion of the amino acid-based SILP material into the CO_2-containing stream led to a fast CO_2 gas uptake and a "silent" time of approximately 50 sec before breakthrough compared to a blank run without absorber material, see **Figure 1**. This corresponds roughly to utilization of one third of the SILP material's maximum gas uptake capacity. Consecutive absorption-desorption cycles for the 40 wt% [N6666][Pro] SILP absorber (desorption done at 80°C for 2 h under argon flow) demonstrated further complete desorption between each sorption cycle, and preservation of good absorption capacities of 1.05 and 1.17 mol CO_2 /mol IL for the second and third cycle, respectively (see table 4). For CO_2 uptake the last column should be examined, as it has been corrected for uptake of CO_2 by SiO_2, while for the desorption steps, the third column should be examined. This number has not been corrected for uptake of CO_2 by the support material and will therefore be zero when

the initial weight of the sample has been reached. As seen in table 4, the CO_2 uptake becomes negative at the second and third desorptions. As the subsequent uptake of CO_2 is superstoichiometric, this is probably not due to decomposition or evaporation of the active compound, but more likely to be desorption of solvent or moisture captured in the SILP material.

Consecutive absorption-desorption cycles for the 40 wt% [N6666][Gly] SILP absorber (desorption done at 80°C for 2 h under argon flow, see figure 7a and 7b) demonstrated further complete desorption between each sorption cycle, and preservation of good absorption capacities for the second, third and fourth cycle, respectively (see table 5). A very small loss of capacity is seen from the first to subsequent cycles. The absorption stoichiometry is around 1.00 mol of CO_2 per mol IL in this material. Absorption kinetics is very fast.

The recycle studies conducted for, [N6666][Gly] can be seen in **Fig. 7.** Fig. 7a is raw data where the background is "drifting". This is probably due to evaporation of solvent. The graphs are normalized so that the lowest point in the first cycle has the value 0 and the rest is calculated from there which means that the lowest point in the following cycles are below 0. Fig. 7b is corrected for this shifting, and is parallel displaced upwards so that all the cycle graphs begins in 0. The scale has been recalculated to a fraction of theoretically maximal CO_2 uptake by the SILP material.

These results clearly demonstrate the potential to use amino acid derived SILP absorbers for post-combustion CO_2 capture at relevant gas concentration levels by TSA operation.

FT-IR analysis, general procedure

A background spectrum was taken and sample was transferred to the ATR crystal to completely cover it. For liquid samples, a few drops were used, and for solid samples approximately 10 mg was used and pressed against the ATR crystal using the pressure arm. All spectra were recorded with 24 scans and corrected for background noise before analysis.

The active part for CO_2 absorption in the synthesized SILP materials is the amino acid anions. Thus, upon uptake of CO_2 some noteworthy changes in the IR spectrum of the anions are expected if carbamate formation occurs, as also previously shown by Brennecke *et al.* [Gurkan

BE et al. Equimolar CO_2 absorption by anion-functionalized ionic liquids. *J Am Chem Soc,* 2010, 132: 2116–2117].

In all the FT-IR spectra of the SILP materials before and after CO_2 absorption, significant changes in both the N-H stretching region and/or the 1700–1300 cm^{-1} region were observed (see exemplary Figure 2-4 for [N6666][Asn]). This leads to the conclusion that CO_2 indeed was chemically absorbed up to 1 mol CO_2 per mol IL via the nitrogen moiety of the amino acid anions in the SILP materials, as expected.

Fig 2-4 were recorded for [N6666][Asn] and SILP versions thereof. For the neat IL [N6666][Asn] itself four N-H stretch bands are seen in the spectrum, while only two poorly resolved bands are seen in the SILP spectrum. After CO_2 absorption, one of these bands has become strong. The 1700-1300 cm^{-1} region also shows clear signs of chemical uptake of CO_2 with the appearance of a C=O stretch at 1646 cm^{-1} and a band at 1581 cm^{-1} that might come from a now visible N-H bending motion.

Tables

Table 1: CO_2 absorption at room temperature and structure of ionic liquids.

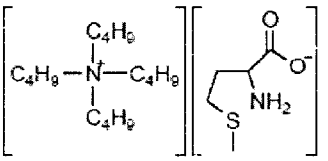
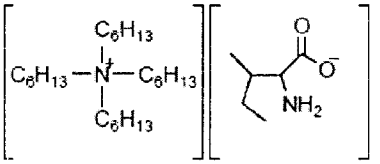
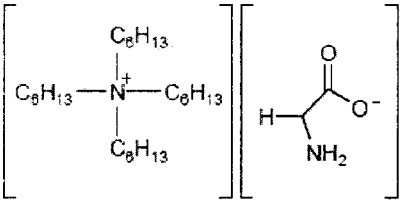
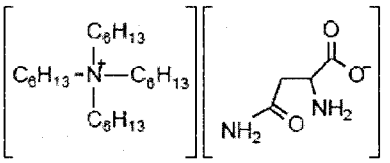
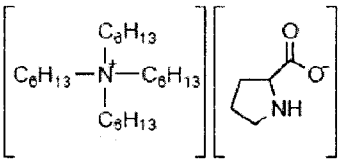
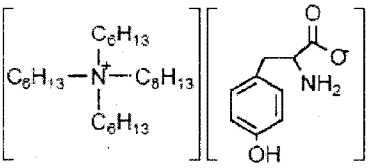
Table 2: CO_2 absorption capacities for selected SILP absorbers

Table 3: SILP loading and CO_2 absorption by a series of $[N_{6666}][Pro]$ materials

Table 4: Recycling CO_2 absorption capacities for $[N_{6666}][Pro]$ SILP loading 40wt%.

Table 5: Recycling CO_2 absorption capacities for $[N_{6666}][Gly]$ SILP loading 40wt%

Table 1

Entry	Ionic liquid	Structure	Abs. Capacity[a]
1	$[N_{4444}][Met]$		0.95
2	$[N_{6666}][Ile]$		1.21
3	$[N_{6666}][Gly]$		1.11
4	$[N_{6666}][Asn]$		0.94
5	$[N_{6666}][Pro]$		1.13
6	$[N_{6666}][Tyr]$		1.13

[a] mol CO_2/mol IL. Corrected for uptake by SiO_2

25°C, 1 bar CO_2; SILP loading 40 wt.%

Table 2

Ionic liquid[b]	SILP loading (wt.%)	Abs. Capacity[a]	
		Mol CO_2/mol IL	Wt.% CO_2
$[N_{6666}][Ile]$	40	1.21	4.4
$[N_{6666}][Gly]$	40	1.11	4.5
$[N_{6666}][Asn]$	40	0.94	3.4
$[N_{6666}][Tyr]$	40	1.13	3.7
$[N_{6666}][Pro]$	10	1.74	1.6
$[N_{6666}][Pro]$	30	1.34	3.8
$[N_{6666}][Pro]$	40	1.23	4.6

a) 25°C, 1 bar CO_2; b) [N6666]: tetrahexylammonium, [Ile]: L-Isoleucinate, [Gly]: Glycinate, [Asn]: L-Asparaginate, [Tyr]: L-Tyrosinate, [Pro]: L-Prolinate.

Table 3

Entry	Ionic liquid	SILP loading (% w/w)	Abs. Capacity[a]
7	$[N_{6666}][Pro]$	10.2	1.74
8	$[N_{6666}][Pro]$	30.5	1.34
9	$[N_{6666}][Pro]$	40.0	1.23

[a] mol CO_2/mol IL. Corrected for uptake by SiO_2

25°C, 1 bar CO_2;

Table 4

Cycle	Conditions	Abs. stoich.	Corr. abs. stoich.
1	CO_2, rt, 3d	1.51	1.23
	Ar, 80°C, 3h	0.00	-0.28
2	CO_2, rt, 1d	1.32	1.05
	Ar, 80°C, 2h	-0.46	-0.74
3	CO_2, rt, 2d	1.45	1.17
	Ar, 80°C, 24h	-0.49	-0.77

Uptake of moles of CO_2 per mole of IL by [N6666][Pro] during recycling.

Table 5

Ionic liquid	Cycle 1[a]	Cycle 2[a]	Cycle 3[a]	Cycle 4[a]
[N6666] [Gly] SILP loading 40%	1.01	0.98	0.96	0.95

[a]The absorption capacity is measured as mol CO_2/mol IL, the absorption takes place at 25°C.

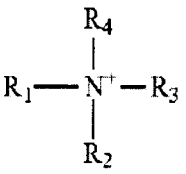
CLAIMS:

1. A method for absorption of gaseous CO_2 from a gas stream and desorption of the absorbed CO_2, which method comprises contacting said gas stream with a composition at ambient temperature and pressure, wherein the composition comprises:

an ionic compound $[A^+][B^-]$ supported on a porous material, wherein

$[A^+]$ is an ammonium ion ([N6666]) of Formula I

Formula I



wherein R_1, R_2, R_3 and R_4 are linear C_6 alkyl chains, and

$[B^-]$ is an anion selected from the group consisting of L-Isoleucinate ([Ile]), Glycinate ([Gly]), L-Tyrosinate ([Tyr]) and L-Prolinate ([Pro]), and

desorbing the CO_2 absorbed on the composition by temperature swing absorption (TSA), by increasing the temperature of the composition, by decreasing the total pressure surrounding the composition, and/or by flushing the composition with a gas stream with no or lower CO_2 content than the gas stream originally applied for the absorption.

2. The method according to claim 1, wherein the absorption takes place from a gas stream which contains 1-100 mol % CO_2 with an absorption capacity of over 1 mol CO_2/mol of the ionic compound $[A+][B^-]$.

3. The method according to claim 1 or 2, wherein the gas stream is a flue-gas stream generated from combustion by large point stationary sources.

4. The method according to claim 3, wherein the large point stationary sources are power plants.

5. The method according to any one of claims 1 to 4, wherein the contact between the gas stream and the composition takes place in a fixed-bed or movable-bed reactor.

6. The method according to any one of claims 1 to 5, wherein the anion is selected from the group consisting of L-Isoleucinate ([Ile]), Glycinate ([Gly]) and L-Prolinate ([Pro]).

7. The method according to any one of claims 1 to 5, wherein the porous material is selected from the group consisting of porous inorganic, carbonaceous, and polymeric materials.

8. The method according to claim 7, wherein the porous material is selected from the group consisting of mesoporous inorganic, carbonaceous, and polymeric materials.

9. The method according to claim 7, wherein the porous material is selected from the group consisting of silica, hydrophobic mesoporous silica, controlled pore glass, alumina, titania, zirconia, alkaline earth metal oxides, clays and zeolites, or mixtures thereof.

10. The method according to claim 9, wherein the titania is an anatase.

11. The method according to any one of claims 1 to 10, wherein the composition contains between 5-45% w/w of the ionic compound $[A^+][B^-]$.

12. The method according to claim 11, wherein the composition contains 10% w/w of the ionic compound $[A^+][B^-]$.

13. The method according to claim 11, wherein the composition contains 20% w/w of the ionic compound $[A^+][B^-]$.

14. The method according to claim 11, wherein the composition contains 30% w/w of the ionic compound $[A^+][B^-]$.

15. The method according to claim 11, wherein the composition contains 40% w/w of the ionic compound $[A^+][B^-]$.

16. The method according to any one of claims 1 to 10, wherein the composition contains 40% w/w of an ionic compound selected from the group consisting of [N6666][Ile], [N6666][Gly] and [N6666][Pro].

Fig. 1

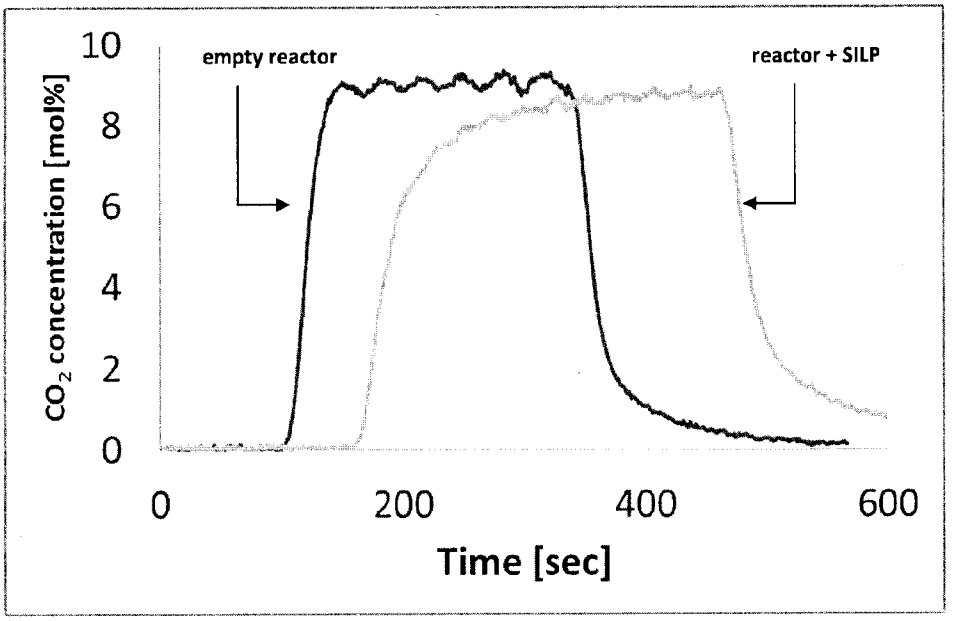

empty reactor
reactor + SILP
CO_2 concentration [mol%]
10
8
6
4
2
0
0
200
400
600
Time [sec]

Fig. 2

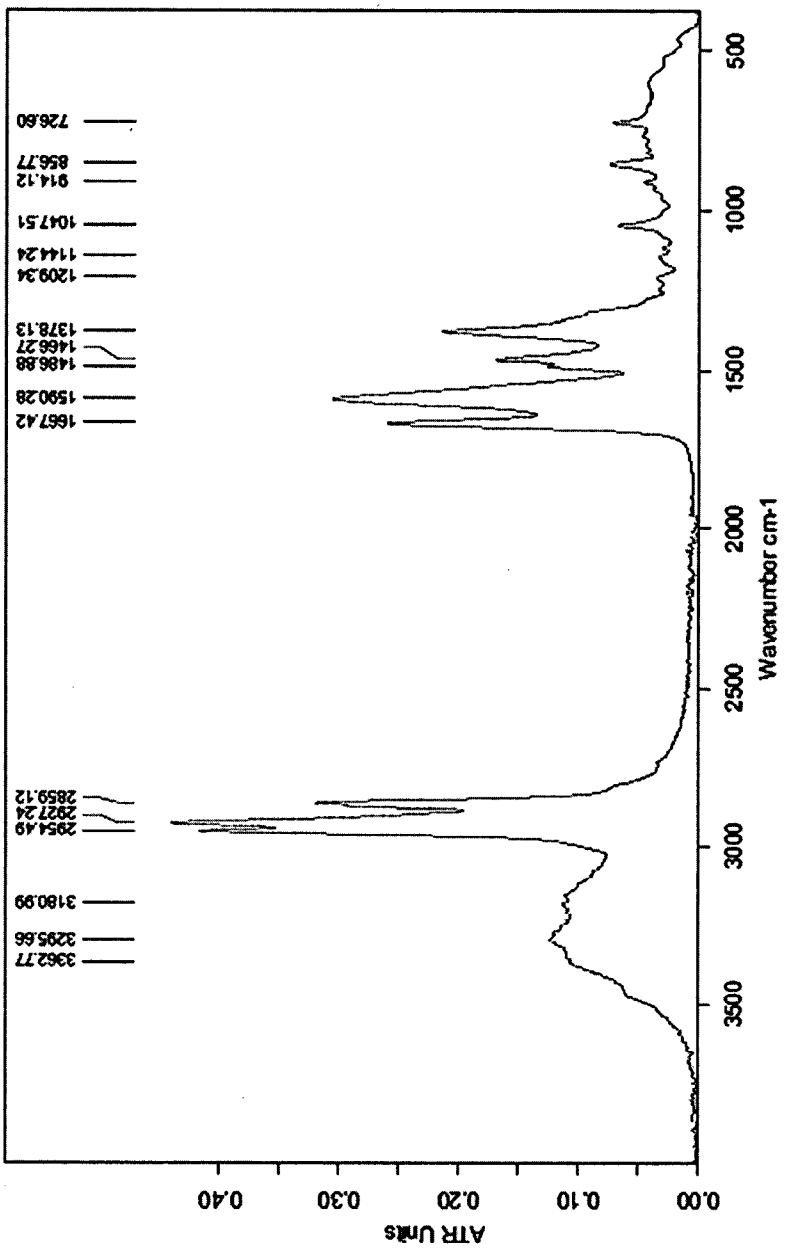

ATR Units
0.00
0.10
0.20
0.30
0.40
Wavenumber cm-1
500
1000
1500
2000
2500
3000
3500
726.60
856.77
914.12
1047.51
1144.24
1209.34
1378.13
1466.27
1486.88
1590.28
1667.42
2854.49
2927.24
2859.12
3180.99
3295.66
3362.77

Fig. 3

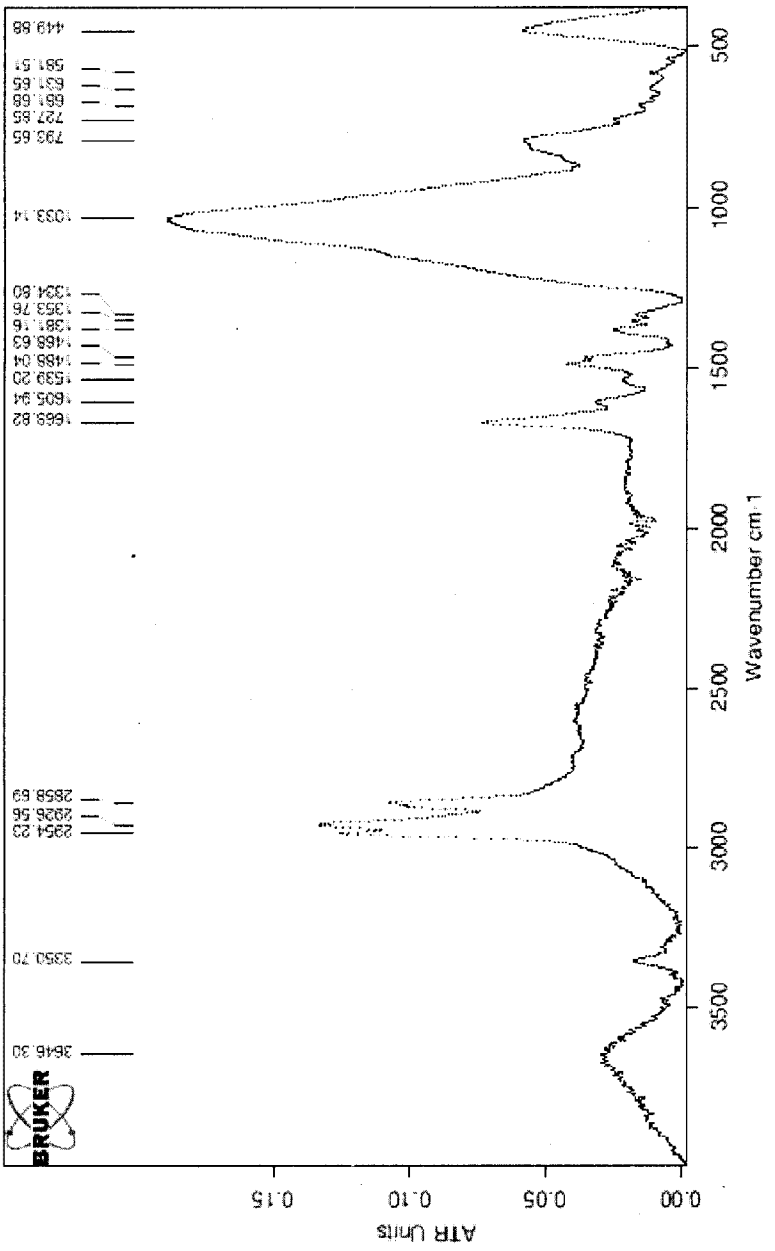

3646.30
3350.70
2954.23
2926.56
2858.69
1668.82
1605.94
1539.20
1488.04
1468.63
1387.16
1353.76
1324.80
1033.14
795.65
727.85
691.68
631.65
591.51
449.88
BRUKER
ATR Units
0.00
0.05
0.10
0.15
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

Fig. 4

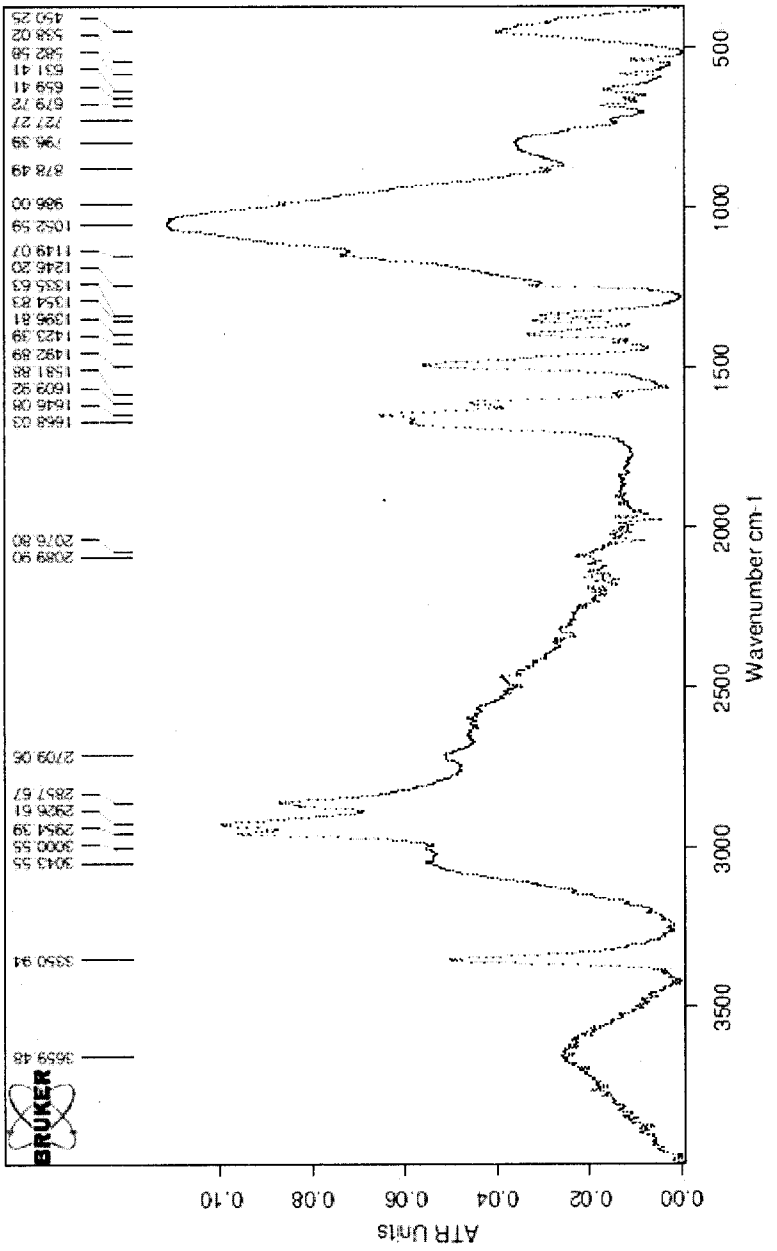

ATR Units
0.00
0.02
0.04
0.06
0.08
0.10
Wavenumber cm-1
500
1000
1500
2000
2500
3000
3500
BRUKER
3659.48
3350.94
3043.55
3000.55
2954.39
2926.51
2857.67
2709.06
2089.90
2076.80
1868.03
1646.08
1609.92
1581.88
1492.89
1423.39
1396.81
1354.83
1335.63
1246.20
1149.07
1052.59
986.00
878.49
796.39
727.27
679.72
659.41
631.41
582.58
538.02
450.25

Fig. 5

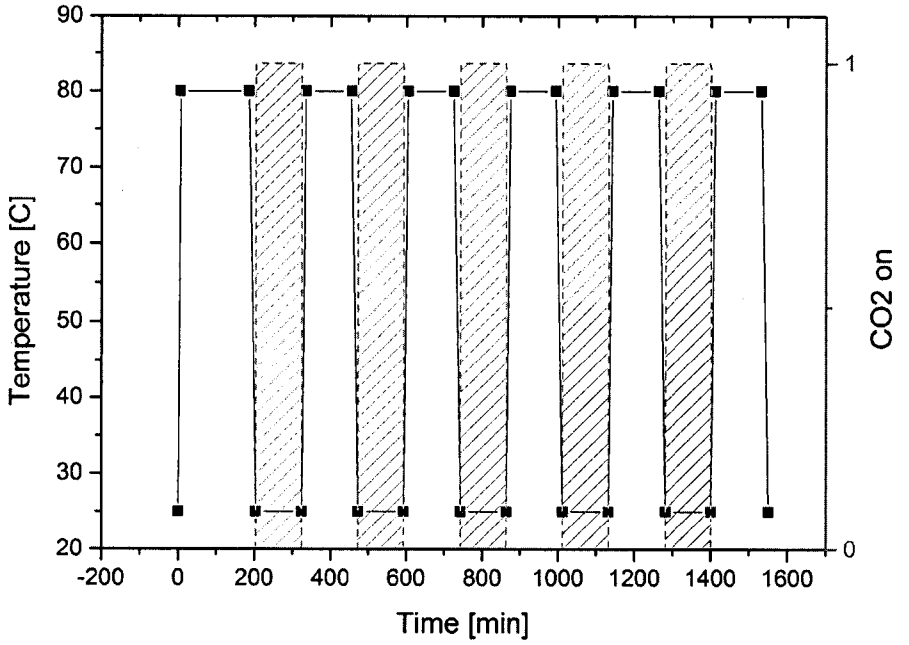

Temperature [C]
CO2 on
Time [min]
90
80
70
60
50
40
30
20
1
0
-200
0
200
400
600
800
1000
1200
1400
1600

Fig. 6

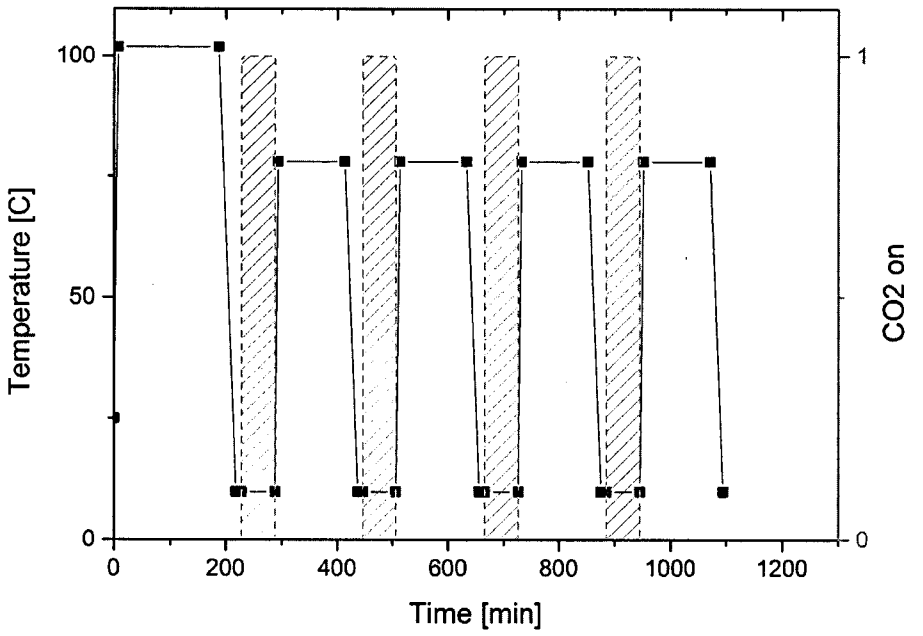

Temperature [C]
CO2 on
Time [min]
100
50
0
1
0
0
200
400
600
800
1000
1200

Fig. 7a

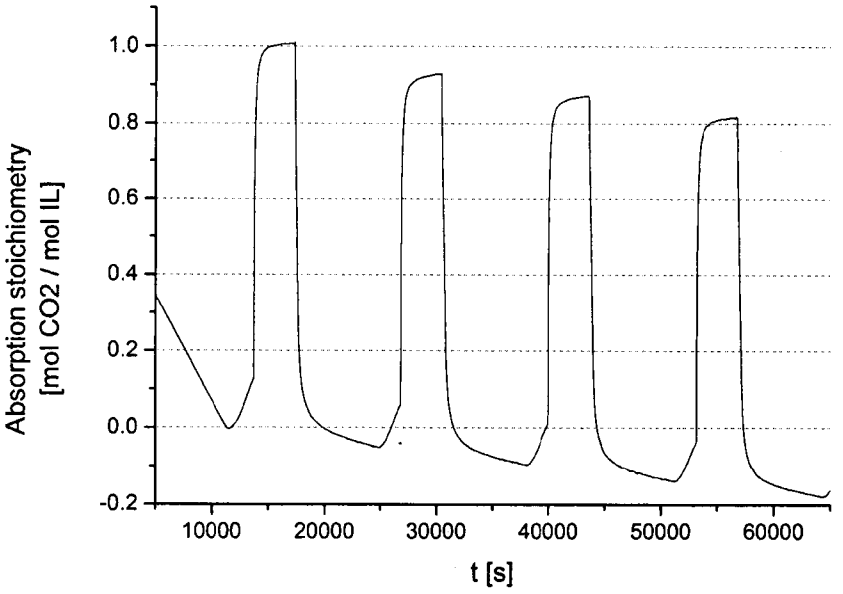
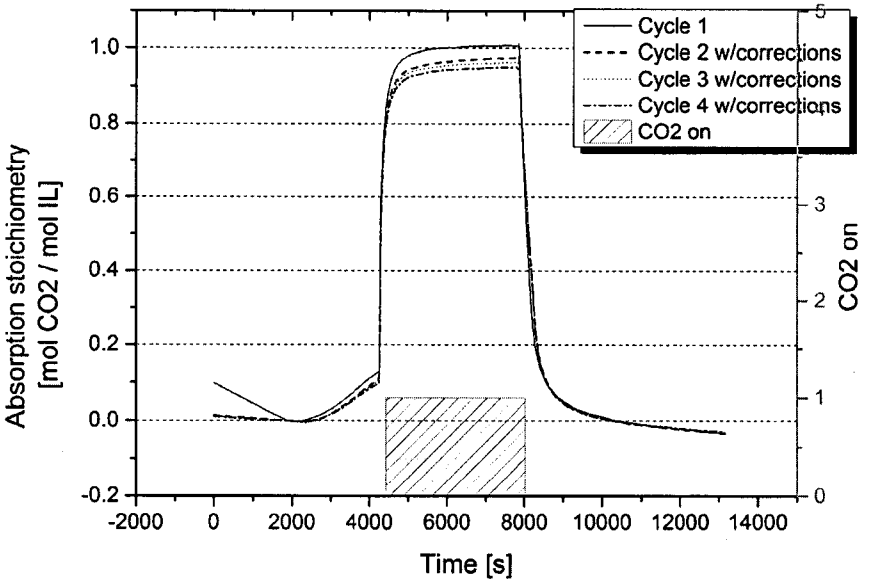
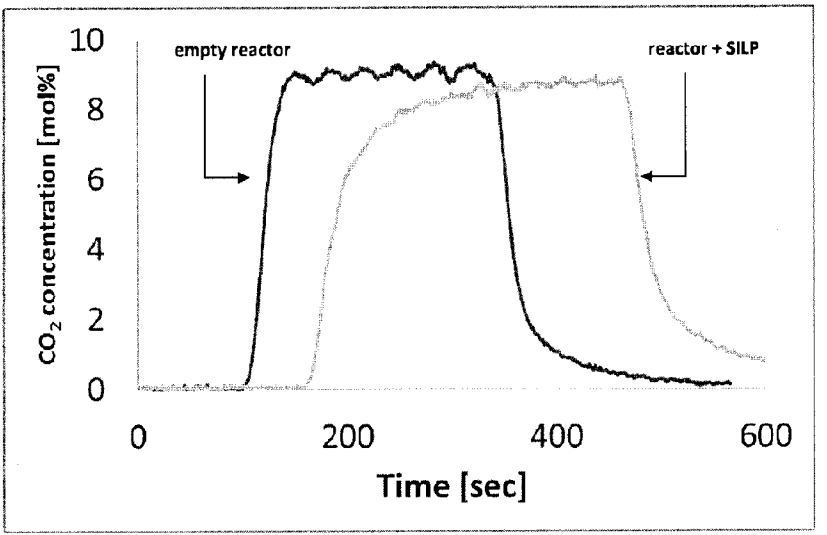

Absorption stoichiometry
[mol CO2 / mol IL]
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
10000
20000
30000
40000
50000
60000
t [s]

Fig. 7b


Cycle 1
Cycle 2 w/corrections
Cycle 3 w/corrections
Cycle 4 w/corrections
CO2 on
Absorption stoichiometry
[mol CO2 / mol IL]
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-2000
0
2000
4000
6000
8000
10000
12000
14000
Time [s]
5
3
2
1
0
CO2 on


empty reactor
reactor + SILP
CO_2 concentration [mol%]
10
8
6
4
2
0
0
200
400
600
Time [sec]