Research paper

Direct CO₂ air capture with aqueous 2-(ethylamino)ethanol and 2-(2-aminoethoxy)ethanol: ^{13}C NMR speciation of the absorbed solutions and study of the sorbent regeneration improved by a transition metal oxide catalyst

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ABSTRACT

The removal of CO₂ from the atmosphere (DAC technology) has been accomplished at room temperature and pressure with aqueous solutions of 2-(ethylamino)ethanol (EMEA) and 2-(2-aminoethoxy)ethanol (DGA). The absorption efficiency of the sorbents has been investigated in five cycling steps of absorption-desorption, and the speciation of the solutions has been studied by ^{13}C NMR analysis. The CO₂ capture efficiency of both fresh amines is about 88%, and that of the regenerated EMEA solutions decreases to about 79% once the equilibrium between amine regeneration (at 110 °C) and CO₂-loaded amine has been reached. Instead, the efficiency of regenerated DGA progressively decreases to 69% at the end of the fifth cycle. ^{13}C NMR analysis of the absorbed solutions of EMEA indicates that CO₂ is captured as amine carbamate and bicarbonate (nearly 1:1 proportion), whereas DGA carbamate is the sole species of captured CO₂. To improve the efficiency of regenerated DGA solutions, solid WO₃ has been employed as desorption catalyst in five subsequent cycles of absorption and desorption. At equilibrium, the efficiency of CO₂ capture increased to 85%, substantially greater than that of regenerated EMEA. The catalyst has been recovered unchanged at the end of each desorption step.

1. Introduction

The correlation between anthropogenic greenhouse gas (GHG) emissions in the atmosphere and global warming, with the consequent climate change, is nowadays worldwide accepted [1]. The Paris Agreement, adopted at the Paris Climate Conference (COP21) in December 2015, binds the countries that have GHGs reduction obligation to carry out the strategies aimed at holding the increase of the global temperature between 1.5 and 2 °C above the preindustrial level [2]. The increasing use of renewable energy sources (photovoltaic, solar thermal, wind, geothermic, hydroelectric systems) could, at most, balance the increasing energy demand of the unrestrainable growth of the population in the countries in rapid development, to support their economic and industrial growing [2,3]. Carbon dioxide is largely the main component (about 76%) of GHGs, and about half of the anthropogenic CO₂ emissions comes from dispersed sources, mainly from road, sea, air transport, and residential, commercial and service building conditioning

[4]. The chemical capture of CO₂ from large-point sources such as fossil fuel fired power plants, known as carbon capture and sequestration technology (CCS), has been strongly developed in recent decades. Today many efficient sorbents have been formulated and CCS is considered a mature technology that can be fitted at yet working energy and industrial plants, but, obviously, it cannot be applied to sparse emissions [5–9]. To stabilize GHG concentrations in the atmosphere at a level that would prevent further dangerous interference with the climate system, their emissions should match their capture by 2050: to attain that ambitious objective, the removal of CO₂ from the atmosphere, known as Direct Air Capture (DAC) technology, will be crucial [10,11]. The most evident difference of DAC compared to CCS is the very low CO₂ concentration in the air, about 0,04%, with respect to the 8–15% (v/v) of the large stationary sources. This low concentration is a disadvantage for the sustainability of the process, as it reduces the efficiency of the CO₂ chemical capture and increases the capture costs: in particular, the cost of DAC processes usually varies between 200 and 1000 $ per tCO₂, up to

ten times higher than that of traditional CCS processes; only in recent years, thanks to the latest improvements, it has been estimated that the cost of some DAC processes can be lowered to less than 100 $ per tCO₂ [12–15]. Moreover, if the electric energy required for sustaining the entire DAC process is produced by the combustion of fossil fuels, much more CO_2 is emitted by the energy production than that captured from air. Consequently, the DAC technique can become a viable option if less energy intensive absorbents and carbon-free energy sources were employed. In this connection, the great advantage of a DAC plant over a CCS system is its placement anywhere, in sunny or windy areas, benefitting of carbon-free energy sources, or of an excess of electric energy production by conventional power plants, at night time for example [12]. Most of the DAC processes of chemical capture of CO_2 developed to date use solid-based and, among them, immobilized amine/silica sorbents and hollow fiber sorbents have provided promising results, as they combine acceptable capture efficiencies with not excessive operating costs [16–21]. Alkaline liquid absorbents have the potential to capture ultra-diluted CO_2 more quickly and efficiently than solid sorbents. To date, the most studied liquid systems concern alkali hydroxides, KOH and NaOH [22–24], but the high temperatures of their regeneration, and consequently the high energy required, limit their large scale use. Despite the amine solution were the most common sorbents in CCS processes, they have not yet been thoroughly investigated as sorbents in DAC processes, and there are only a few papers dealing with their use [4,25,26]. Recently, our research group has carried out a screening study on different aqueous and nonaqueous alkanolamine solutions, under the same operating conditions, in order to investigate their capability to absorb CO_2 from an air stream [27]. The study, based on a single 24 h-absorption and ^{13}C NMR speciation of the solutions, demonstrated that the rapid formation of amine carbamate is the key factor for an efficient CO_2 capture, and that aqueous primary and secondary unhindered amines are as efficient as alkaline hydroxides, but with a potential energy saving due to the lower regeneration temperatures.

By continuing this research, in the study here reported we investigated the ultra-dilute CO_2 capture with two different aqueous alkanolamines in several absorption and desorption cycles, in order to verify the feasibility of regenerated amines for reuse in continuous DAC systems. The experiments were carried out with aqueous solutions of 2-(ethylamino)ethanol (EMEA) and 2-(2-aminoethoxy)ethanol (DGA). In our previous study [27], these two amines had provided the same high CO_2 absorption efficiency (among the highest of all tested amines) despite different reaction mechanisms. Actually, DGA (primary amine) reacts with aerial CO_2 forming only carbamate, while EMEA also forms bicarbonate [27]. Therefore, it seemed interesting to us to further investigate their performance under different operating conditions: the CO_2 absorption efficiency was evaluated by means of 5 subsequent absorption experiments, each lasting 24 h; the thermal regeneration of the CO_2-loaded solution was accomplished at 110 °C for 90 min. The ^{13}C NMR analysis at the end of each absorption and desorption step allowed us to identify and quantify the species in solution, providing important information on the reaction mechanism [28–31].

Moreover, the use of an acid catalyst to improve the efficiency of the desorption was also evaluated. Recently, it has been shown that the addition of a solid acid catalyst (such as HZSM-5, γ-Al₂O₃, metal oxides) to CO_2-loaded aqueous amines increases the desorption kinetics and allows lower regeneration temperatures, that turn out to the advantage of energy saving and less thermal and oxidative degradation of the amines used [32–39]. Here, we investigated the effect of tungsten trioxide, WO₃, as a catalyst for the desorption of aqueous solution of DGA, in order to improve the ultra-diluted aerial CO_2 absorption efficiency of its regenerated solutions. Despite the increasing number of papers reporting catalyst-aided sorbent regeneration for CCS, to the best of our knowledge this is the first experimental application of a catalyst in a DAC process.

2. Material and methods

2.1. General information

All chemicals were reagent grade and were used as received. 2-(2-aminoethoxy)ethanol (DGA, CAS: 929–06-6), 2-(ethylamino)ethanol (EMEA, CAS: 110–73-6) were purchased by Sigma-Aldrich while tungsten trioxide (WO₃) was supplied by Fisher Scientific. A digital gas mass flow controller (Aalborg) and a gas meter (Cole Parmer) were used to regulate and measure the flow rate of atmospheric air. The percentage of aerial CO_2 before and after the capture process was measured with a Varian CP-4900 gas chromatograph (GC). The CO_2 percentage measured in the atmospheric air was 0.044%. XRD data was collected on a X'Pert PRO diffractometer (Panalytical, Almelo, the Netherlands) with Cu Kα radiation (λ = 1.5418 Å) equipped with a PIX-CEL solid-state fast detector and a focusing mirror (scanning range 2θ = 20–60° with a 0.01° increments of 2θ).

2.2. CO₂ capture from air

The CO_2 capture from the air was performed using the same apparatus and procedure as described in details in our previous DAC experimental work [27]. Briefly, 0.100 dm³ of the aqueous amine solution (1.50 mol dm⁻³) was charged into the absorber, a home-built glass cylinder with the internal diameter of 56 mm and height 400 mm, maintained at 25 °C by circulating a thermostatted liquid (by means of a Julabo model F33-MC bath) through the external jacket of the column. In order to maximize the contact surface between air and absorbent, the column was packed with glass rings (diameter = 5 mm). The system operates in countercurrent: atmospheric air is fed from the bottom of the absorber at a flow rate of 46.2 dm³ h⁻¹ (CO₂ = 0.044%) and the aqueous amine is fed from the top of the column; a peristaltic pump (Masterflex) allows the continuous circulation of the aqueous amine from the bottom to the top of the column at a flow rate of 0.300 dm³ h⁻¹. The air exiting from the top of the column flows in turn through a cool condenser (at −5 °C), a concentrated H₂SO₄ solution and a gas purification tower filled with P₂O₅, in order to remove any traces of water and amine before the GC analysis. The comparison between the percentage of CO_2 in the air before and after the reaction with the amine allows to continuously evaluate the CO_2 absorption efficiency (abs%). Each absorption lasts 24 consecutive hours.

2.3. CO₂ desorption without and with catalyst

The CO_2 desorption experiments were performed with a gastight apparatus already described [40]. In brief, the CO_2-loaded amine solution obtained in the 24 h absorption step was charged in a 0.250 dm³ conical flask, and stirred with a magnetic stirrer for 90 min at 110 °C. The flask was equipped with a condenser to prevent any water or amine loss, and connected to two 0.250 dm³ gas burettes through a three-way valve. The burettes were filled with CO_2 saturated water and equipped with a pressure-equalizing device. During the experiment, one burette was filled with CO_2 and simultaneously the other was emptied, thus allowing a continuous measure of the collected gas.

In the catalyst-aided desorption experiments, 5.00 g of WO₃ were added to 0.100 dm³ (about 5% by weight) of the CO_2-loaded amine solution into the flask. At the end of the regeneration step, the amine solution was cooled to room temperature and the solid WO₃ was separated by filtration, washed and dried at 110 °C for 24 h, in order to be reused in the subsequent desorption step.

2.4. ¹³C NMR analysis

The ^{13}C NMR spectroscopy has been used to identify and quantify the species in solution after each absorption and desorption step. The spectra were recorded with a Bruker Avance III 400 spectrometer

operating at 100.613 MHz by using a procedure that has been already described in previous works [41,42], with a pulse sequence with proton decoupling and NOE suppression. The acquisition parameters were: pulse angle = 90.0°, acquisition time = 1.3632 s, delay time = 2–30 s, data points = 65 K, number of scans = 250–500. All the data were processed by using Bruker Topspin software. Tetramethylsilane and acetonitrile were used as external standard and internal reference, respectively. A sealed glass capillary containing deuterium water (Aldrich) was inserted inside the NMR tube with the solution sample in order to provide a good signal for deuterium lock.

The accurate peak integration for each –CH_2– resonance allows to measure the relative amount of carbamate with respect to the total amine, calculated as the ratio between the area of the carbamate peak and the sum of the areas of the peaks of carbamate and of the rapidly equilibrating (free amine)/(protonated amine). Increasing the acquisition time and/or the relaxation delay (up to 60 s) does not produce substantial changes in the relative peak areas of the –CH_2– carbon atoms that contain the same number of attached protons [43].

The relative amounts of carbamate and fast exchanging bicarbonate/carbonate ion were quantified by integrating the carbon resonances in the range 167–163 ppm. The ^{13}C atoms of bicarbonate, carbonate and carbamate functionality have no attached hydrogen, and consequently they show a longer relaxation time than that of –CH_2– groups, resulting in lower intensity resonances. Nonetheless, a careful peak integration of the carbon resonances could provide an estimation (5% deviation) of the relative amounts of the species formed.

3. Results and discussion

3.1. Cycles of CO_2 absorption and amine regeneration without catalyst

In this experimental study we evaluated the capacity of two different aqueous amines, namely the primary amine 2-(2-aminoethoxy)ethanol (DGA) and the secondary amine 2-(ethylamino)ethanol (EMEA), as sorbents for regenerative DAC processes. In our previous screening study [27], those amines showed similar (and high) aerial CO_2 absorption efficiencies, despite a different reaction mechanisms, and it seemed interesting to us to in depth investigate their properties in absorption–desorption subsequent cycles. In a regenerative process of CO_2 capture, an efficient desorption of the CO_2 loaded sorbent is of paramount importance so that the regenerated sorbent could maintain a high absorption efficiency. To verify the feasibility of regenerated amine solutions for reuses, we conducted five consecutive absorption–desorption cycles.

In the present work the capture of CO_2 from atmospheric air was performed with 0.100 dm^3 of a 1.50 mol dm^{-3} aqueous solution of the selected amine, as described in Section 2.2. The CO_2 absorption efficiency (abs%), defined as the ratio between the amount of captured CO_2 and the CO_2 in the air stream, was continuously monitored throughout the experiment (24 h). At the end of each absorption, the solution was regenerated with the procedure described in Section 2.3, at a temperature of 110 °C for 90 min and under magnetic stirring. At the end of the desorption, the solution was cooled and used for a new absorption step. The whole procedure was repeated five times for both the amine solutions.

The average values of the aerial CO_2 absorption efficiency (abs%) obtained in subsequent absorption steps are shown in Fig. 1 for both aqueous DGA and EMEA.

The aqueous solutions of fresh DGA and EMEA have high CO_2 absorption efficiencies (abs%), 88.4% and 87.7% respectively (step 1, Fig. 1), that are consistent with the values reported in our previous screening study [27]. In the subsequent absorption–desorption cycles, however, the two amines provide some different results. As shown in Fig. 1, the absorption efficiency of regenerated aqueous EMEA significantly decreases in the second step, but remains almost constant in the subsequent three cycles, whose percentages are 79.7%, 78.6% and
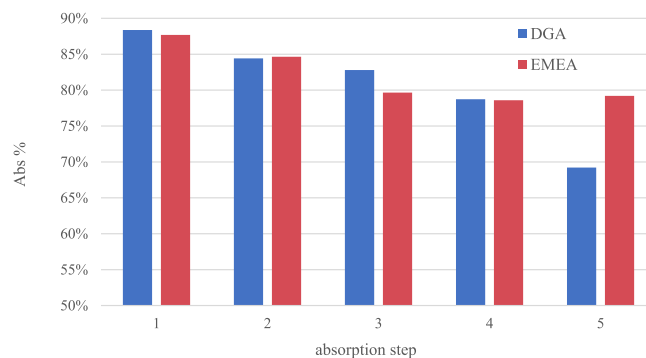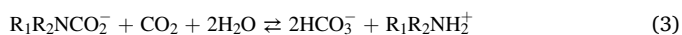

Fig. 1. The CO_2 absorption efficiency (abs%) of fresh aqueous DGA and EMEA (step 1) compared with that of four times regenerated amines (steps 2–5).

79.8%, respectively. On the contrary, the abs% of aqueous DGA decreases continuously in each subsequent absorption step, to the low value of 69.2% in step 5. Those results indicate that DGA isn't a suitable solvent for a DAC process, where absorption and desorption occur continuously over time, at least under the operating conditions we have used.

In order to understand the different behavior of the two amines, samples of the solutions at the end of each absorption and desorption step were checked by ^{13}C NMR spectroscopy, to identify and quantify the carbonated species in solution. As an example, Fig. 2 shows the spectra of EMEA and DGA at the end of the fifth absorption step. From the accurate integration of the peak signal of each –CH_2– resonance we computed the percentage of amine carbamate with respect to overall amine, and from the peak integration of the carbonyl atoms in the range 167–163 ppm we estimated the relative amounts of carbamate and fast exchanging bicarbonate/carbonate ion. The speciation results recovered from ^{13}C NMR spectra are reported in Table 1.

Aqueous solutions of primary and secondary amine (R_1R_2NH, in primary amine R_1 = H) react with the ultra-diluted CO_2 in a gas stream to form the corresponding amine carbamate ($R_1R_2NCO_2^-$), bicarbonate and carbonate ions, according the following reactions [44]:

$$2R_1R_2NH + CO_2 \rightleftarrows R_1R_2NCO_2^- + R_1R_2NH_2^+ \qquad (1)$$

$$R_1R_2NH + CO_2 + H_2O \rightleftarrows HCO_3^- + R_1R_2NH_2^+ \qquad (2)$$

$$R_1R_2NCO_2^- + CO_2 + 2H_2O \rightleftarrows 2HCO_3^- + R_1R_2NH_2^+ \qquad (3)$$

$$R_1R_2NH + HCO_3^- \rightleftarrows CO_3^{2-} + R_1R_2NH_2^+ \qquad (4)$$

$$CO_2 + CO_3^{2-} + H_2O \rightleftarrows 2HCO_3^- \qquad (5)$$

As shown in Fig. 2 (peaks at 163.9 and 166.4 ppm), and reported in Table 1, the reaction between aqueous EMEA and ultra-diluted CO_2 leads to the formation of a nearly equal amount of carbamate and bicarbonate/carbonate. Instead, the speciation of carbonated products after each desorption step is about 57% carbamate and 43% bicarbonate/carbonate, and indicates that more bicarbonate/carbonate is desorbed than carbamate. It's noteworthy that, since the second desorption step, the percentage of the residual carbonated species in solution remains almost constant. In other words, once the absorption–desorption equilibrium is reached, the 90 min desorption at 110 °C regenerates so much EMEA that the subsequent absorption occurs without further decreasing.

On the other hand, the ultra-diluted aerial CO_2 is captured by aqueous solutions of DGA almost exclusively as carbamate (Fig. 2 and Table 1). The possible formation of a negligible amount of bicarbonate/carbonate would be no detectable in the ^{13}C NMR analysis. By considering the desorption steps (Table 1), the amount of residual carbamate in the desorbed solutions increases progressively from the first (10.2%) to the fifth step (25.6%). In this case, the equilibrium is not reached, the
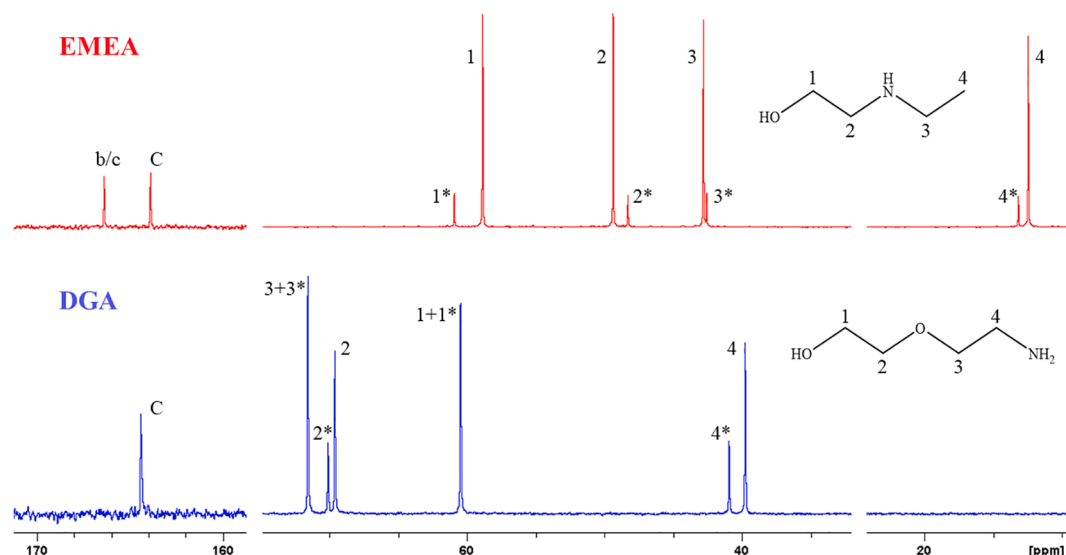
Fig. 2. ^{13}C NMR spectra of aqueous EMEA and DGA at the end of the fifth absorption step. Asterisks denote the carbon backbones of amine carbamate. C and b/c indicate the carbonyl atoms of amine carbamate and of bicarbonate/carbonate, respectively. The intensity of the signals in the range 160–170 ppm is not in scale.

Table 1
^{13}C NMR analysis of the species in solution at the end of each absorption and desorption step.

Amine	step	Absorption			Desorption		
		% carb[a]	speciation[b]		% carb[a]	speciation[b]	
			C	b/c		C	b/c
EMEA	1	11.9%	50.0%	50.0%	9.7%	56.9%	43.1%
	2	17.5%	49.3%	50.7%	12.4%	56.3%	43.7%
	3	22.4%	48.3%	51.7%	13.3%	57.0%	43.0%
	4	23.7%	49.3%	50.7%	12.9%	57.3%	42.7%
	5	23.3%	50.3%	49.7%	13.2%	57.1%	42.9%
DGA	1	12.4%	100%	0%	10.2%	100%	0%
	2	21.9%	100%	0%	14.1%	100%	0%
	3	25.2%	100%	0%	17.0%	100%	0%
	4	27.5%	100%	0%	20.0%	100%	0%
	5	29.7%	100%	0%	25.6%	100%	0%

[a] Percentage of the total carbonated species formed (sum of carbamate, bicarbonate and carbonate) with respect to overall amine in solution.
[b] Speciation of the carbonated species formed, reported as the relative percentage of amine carbamate (C) and of bicarbonate/carbonate ion (b/c).

desorption process is not capable to regenerate enough DGA and consequently the CO_2 absorption efficiency progressively decreases.

The lower regeneration efficiency of DGA compared to EMEA is due to the more unfavorable reverse of reaction (1) in comparison to reverse of reaction (2). We found in our previous studies on liquid amines [8,44] that the formation of the carbamate derivative (reaction (1)) is more kinetically favored than bicarbonate/carbonate. The great excess of DGA compared to the low amount of captured CO_2 favors the rapid formation of carbamate (low activation energy), but it is a disadvantage to the reverse of reaction (1), because of its higher activation energy. In other words, the decomposition of carbamate is slower than that of bicarbonate/carbonate. Moreover, it may be of interest to note that a possible endothermic reaction that produces carbamate could be a severe hindrance to the thermal decomposition of DGA carbamate, as we have already found for some amine carbamates [45,46]. In summary, under the same desorption time and temperature, the presence of HCO_3^- in solution allows a more efficient regeneration of aqueous EMEA solution compared to DGA.

3.2. DAC process with catalyst-aided sorbent regeneration

The primary goal of every regenerative process of CO_2 capture is to maximize the regeneration of the sorbent solution in order to maintain high absorption efficiency after the subsequent absorption steps.

One strategy to promote the amine regeneration can be the addition of an acid catalyst to the solution during the desorption step (reaction (6)).

$$R_1R_2NCO_2^- + [H_3O^+(\text{catalyst})] \rightleftharpoons R_1R_2NH + H_2O + CO_2 + \text{catalyst} \quad (6)$$
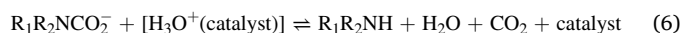
It has been reported [38,39,47] that some transition metal oxides can be a good option for catalyst-aided amine regeneration processes, due to the acid sites (transition metal oxides at higher oxidation number are Lewis acid) over their surfaces, in conjunction with aqueous solutions ($H_2O\cdot WO_3 + H_2O \rightleftharpoons HWO_4^- + H_3O^+$).

In order to verify the feasibility of a catalyst-aided sorbent regeneration in a DAC process, DGA solution is more suitable than EMEA, because the high absorption efficiency (88.4%) of the fresh DGA was not kept after the first step, so that its absorption percentage drops to 69.2% at the end of the five experiments.

On the basis of the aforementioned literature [38,39,47], we carried out some preliminary tests aimed at identifying an effective solid catalyst for the desorption of CO_2-loaded DGA aqueous solution with the lowest possible solubility at high temperature: compared with ZnO, V_2O_5, Al_2O_3 and a molecular sieve, WO_3 was found to be the best choice. We used the regenerated fifth aqueous DGA solution for a further 24 h-absorption experiment (the sixth). As expected, the CO_2 absorption efficiency (64.7%) further decreased compared to the fifth absorption (69.2%, Table 1). To evaluate the effectiveness of that catalyst in our operating conditions, at the end of the sixth absorption step, the CO_2-loaded amine solution was divided into two equal portions. The first half (approximately 0.050 dm^3) was desorbed without catalyst, as blank, while the other half was desorbed by adding 2.50 g of WO_3 (about 5% by weight) to the flask. The two portions of solution were desorbed under the same operating conditions, at the temperature of 110 °C for 90 min. Samples of aqueous DGA after the absorption step and after the desorption of the two different portions (with and without catalyst) were checked by ^{13}C NMR spectroscopy. The spectra are shown in Fig. 3, and the analytical results are reported in Table 2. CO_2 absorbed (mol) is calculated as the difference between the amount of carbamate at the end of the sixth absorption step and the amount of carbamate at the end of the fifth desorption (corresponding to 0.0375 mol, calculated from
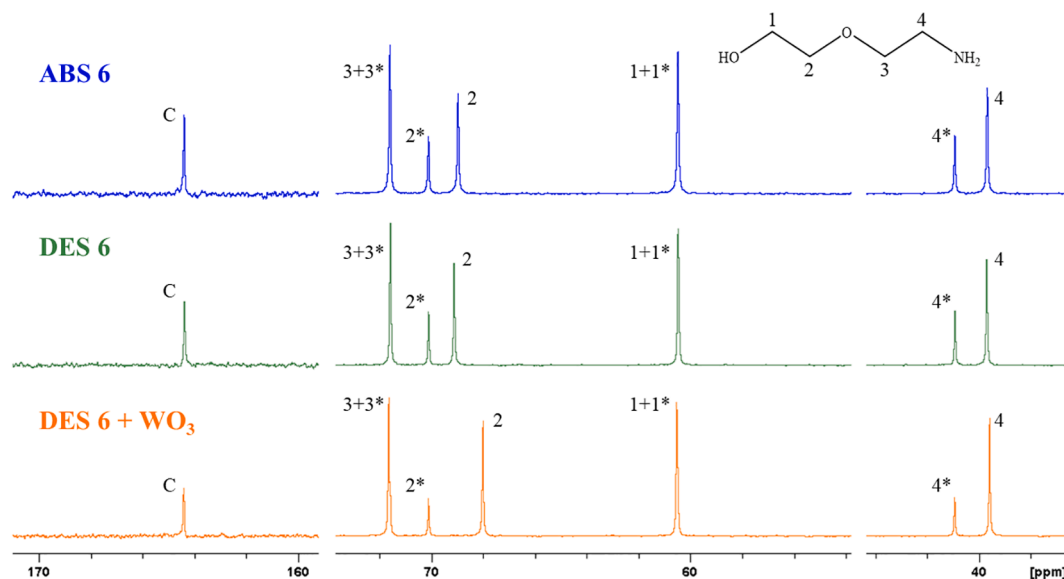
Fig. 3. ^{13}C NMR spectra of aqueous DGA at the end of the sixth absorption step and of the subsequent desorption steps, without and with WO$_3$. Asterisks denote the carbon backbones of DGA carbamate, while C indicates its carbonyl atoms. The intensity of the signals in the range 160–170 ppm is not in scale.

Table 2
Amount of carbamate in aqueous DGA, CO$_2$ absorbed and desorbed at the end of the sixth absorption and desorptions steps.

DGA 6th cycle	Carbamate		CO$_2$ absorbed	CO$_2$ desorbed	
	%[a]	mol[b]	mol	mol[b]	%
Absorption	34.0%	0.0510	0.0135	–	–
Des (blank)	29.5%	0.0443	–	0.0067	49.6%
Des + WO$_3$	23.8%	0.0358	–	0.0152	113%

[a] Percentage of DGA carbamate with respect overall amine determined by ^{13}C NMR analysis.
[b] Values referred to 0.100 dm^3 of solution.

Table 1). CO$_2$ desorbed (mol) was calculated as the difference between the amount of carbamate at the end of absorption and that present at the end of desorption (referred to 0.100 dm^3 of solution). The percentage of desorption is calculated from the ratio between CO$_2$ desorbed and CO$_2$ absorbed in the sixth cycle.

The data show the improvement of CO$_2$ desorption in the presence of WO$_3$: a greater amount of CO$_2$ is released with catalyst than without catalyst for the same desorption time interval and at the same temperature. It should be noted the percentage of CO$_2$ desorbed is even higher than 100%: this result indicates that the catalyst promotes the 100% desorption of the amount of CO$_2$ captured in the sixth absorption step, and even more CO$_2$ is desorbed, coming from the residual carbamate of previous desorption steps.

To provide a confirmatory evidence to the preliminary results of the effective catalytic action of WO$_3$, we carried out a new series of 5 absorption/desorption cycles, with 0.100 dm^3 of a fresh solution of DGA (1.5 mol dm^{-3}). In each desorption step, the solution recovered from the absorber was added with 5% wt of WO$_3$. At the end of the regeneration step, the solid WO$_3$, separated from the solution by filtration, was dried and used for the subsequent desorption steps. At the end of the first desorption step, we found that a very small amount of WO$_3$ remained dissolved in the solution. On the contrary, at the end of the subsequent desorption steps the catalyst was always recovered quantitatively.

The results, reported in Fig. 4, show that the absorption efficiency of aerial CO$_2$ remains almost constant at high values (about 85%) since the second step. As a matter of fact, the small amount of WO$_3$ solubilized did not significantly affect the efficiency of the subsequent absorptions. In the presence of catalyst, the process for carbamate decomposition takes
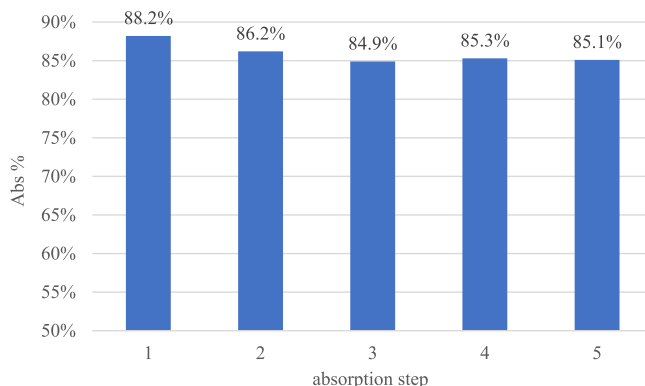

Fig. 4. CO$_2$ absorption efficiency (abs%) of aqueous DGA in the five subsequent absorption experiments, with catalyst-aided desorption steps.

less time under similar heating rate, resulting in an increase in amine regeneration rate. Consequently, the absorption efficiency in steps 2–5 aren't substantially different from that of the fresh amine (step 1).

Finally, the stability of the catalyst over time was confirmed by XRD comparison between fresh WO$_3$ and that recovered at the end of the fifth desorption; the spectra are shown in Fig. 5.

4. Conclusions

In order to find efficient and sustainable sorbents suitable for the DAC technology, we have investigated the performances of aqueous 2-(ethylamino)ethanol (EMEA) and 2-(2-aminoethoxy)ethanol (DGA) through five subsequent cycles of CO$_2$ absorption and amine regeneration. The regenerated amines are less efficient than the fresh ones, as expected, and EMEA features substantial differences from DGA. Once EMEA reached the steady state between the reactions of CO$_2$ capture and amine regeneration (at 110 °C), the regenerated absorbents attained the constant efficiency of 79%. On the contrary, regenerated DGA progressively decreased its efficiency to 69% at the end of the fifth experiment. As inferred from ^{13}C NMR analysis of the absorbed DGA, CO$_2$ is only captured as amine carbamate, whose thermal decomposition is slower than that of bicarbonate contained in EMEA absorbed solution. The efficiency of regenerated DGA is substantially improved (up to 85%) by
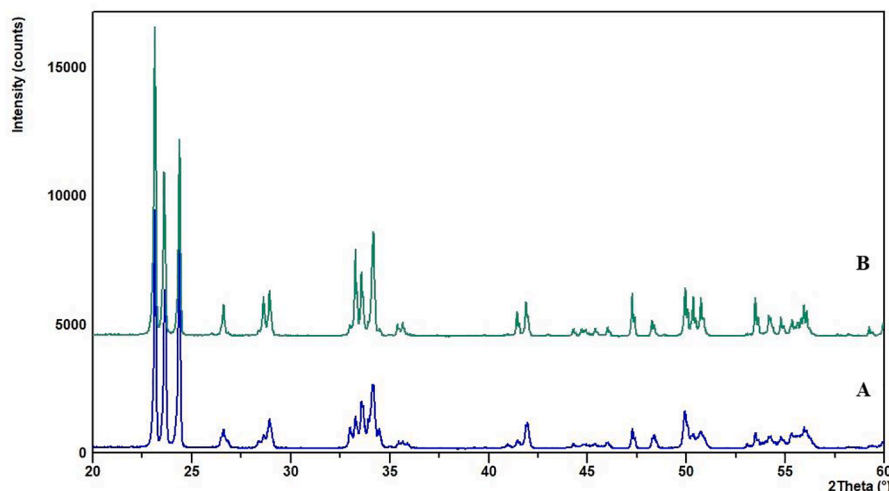
Fig. 5. XRD patterns of (A) fresh WO_3 and (B) WO_3 recovered after the fifth desorption step.

WO_3 catalyst (5% wt), which accelerates the carbamate decomposition and CO_2 release. The catalyst is recovered unchanged at the end the sorbent regeneration. In summary, the high efficiency of aqueous solutions of EMEA and of catalyzed DGA entails potential advantages for their application to DAC technology. Notwithstanding, we are aware that further experiments carried out with the absorbents that are simultaneously recycled between the absorber and the desorber are required. Those experiments have the purpose of finding the operating conditions (temperature, pressure, properly designed apparatuses, amine concentrations and their recycling rate) that could maximize the capture efficiency with sustainable energy costs. As a final remark, ^{13}C NMR analysis proves to be an invaluable aid in giving reliable information on the composition of H_2O/amine/CO_2 systems, and therefore on the mechanisms of CO_2 capture and amine regeneration.

CRediT authorship contribution statement

Francesco Barzagli: Conceptualization, Investigation, Writing - original draft, Writing - review & editing. **Fabrizio Mani:** Conceptualization, Writing - original draft, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

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