Full Length Article

Solid acid catalysts for low-temperature regeneration of non-aqueous sorbents: An innovative technique for energy-efficient CO_2 capture processes

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A B S T R A C T

Chemical absorption of CO_2 from flue gases by using aqueous amine sorbents is regarded as the most mature and effective technology for reducing CO_2 emissions, but the high energy cost of sorbent regeneration has so far greatly limited its industrial application. One of the best strategies developed by researchers in recent years to reduce energy requirements is to improve CO_2 desorption kinetics by adding catalysts during sorbent regeneration. Moreover, non-aqueous sorbents have recently been gaining increasing attention as alternatives to conventional aqueous amines as they have the potential to lower the energy demand for sorbent regeneration. In this paper, we propose an innovative technique that combines and further develops these two emerging technologies, non-aqueous absorbent and catalyst-assisted regeneration, to enable less energy-intensive CO_2 capture processes. In particular, in this screening study, we evaluate the regeneration behaviour of a CO_2-saturated solution of 2-(2-aminoethoxy)ethanol (DGA) in diethylene glycol monomethyl ether (DEGMME) when heated to 85 °C in the absence and presence of different types of solid acid catalysts. In order to assess the potential benefits of this innovative technique over conventional systems, the results obtained were compared with the desorption performance of an aqueous solution of DGA under the same operating conditions and with the same catalysts, which highlighted the possibility of obtaining rapid desorption at relatively low temperatures when conducted with suitable acid catalysts using amines in organic diluents.

Introduction

The increasing concentration of CO_2 in the atmosphere is considered a major cause of the evident global warming and related climate change. The development and deployment of techniques to limit anthropogenic CO_2 emissions is crucial to keep the global temperature rise within 1.5 °C of the pre-industrial level, as envisaged in the 2015 Paris Agreement and subsequent Conferences of the Parties (COP) (UNFCCC - United Nations Framework Convention on ClimateChange, 2021, 2015). The post-combustion CO_2 absorption by chemical capture based on aqueous amines is today regarded as the most mature and effective method for industrial use. In particular, MEA 30% (aqueous solutions of ethanolamine, 30% by weight) have been thoroughly tested on pilot and operating plants (Bui et al., 2018; El Hadri et al., 2017; Feron et al., 2020; Zhang et al., 2017). However, the widespread application of this

technology is still challenging, mainly because of the enormous energy requirement for the sorbent regeneration process (CO_2 desorption at temperatures higher than 120 °C) (He et al., 2023; Liang et al., 2015).

In recent years, researchers have focused their efforts on developing several innovative strategies to reduce the energy demand for desorption while maintaining a CO_2 absorption performance comparable to conventional aqueous MEA (Atzori et al., 2023; Guangjie Chen et al., 2022; Guangying Chen et al., 2022; Shi et al., 2021; Wang et al., 2019). amongst these strategies, the use of solid acid catalysts to improve CO_2 desorption and the use of non-aqueous sorbents are particularly promising.

The implementation of solid acid catalysts in the desorber to enhance sorbent regeneration is a strategy developed very recently for aqueous amine solutions. In these processes, suitable acid catalysts promote the CO_2 release from loaded sorbents at lower temperatures, thus decreasing the total energy consumption (Alivand et al., 2020). In particular, the

addition of catalyst enables sorbent regeneration at temperatures of 85–100 °C, well below conventional temperature used around 120–140 °C, resulting in significative energy savings. Generally, metal oxides, zeolites, modified clays, and silica materials were the catalysts that showed the most beneficial effect in the solvent regeneration (Bhatti et al., 2021b, 2020; Li et al., 2023; Zhang et al., 2023b).

The other innovative strategy considered here involves the use of water-free sorbents. Traditionally, the most studied sorbents for CO_2 capture were aqueous amine, mainly because water is the most common and available diluent. However, high sensible and latent heats of water make the regeneration process of aqueous sorbents extremely energy intensive. Owing to that, recently, an increasing number of researchers are considering using of amine-based sorbents with diluents other than water (Wanderley et al., 2021). Indeed, replacing water with organic solvents redirects the reaction between amine and CO_2 towards less stable carbonated species that can subsequently be decomposed more easily (at $T < 100$ °C). Moreover, the lower heat capacity and heat of vaporization of organic diluents with respect to water could significantly reduce the energy demand of the entire CO_2 capture process (Alkhatib et al., 2022; Barzagli et al., 2022; Heldebrant et al., 2017; Karlsson et al., 2020; Svensson et al., 2014).

With the aim of developing a technique for CO_2 capture with high efficiency and low energy requirement, we decided to combine the two strategies above, resulting in a new technique based on absorption by non-aqueous amine-based solutions and desorption catalysed by acid solids. To verify the suitability of this innovative approach, we carried out a detailed investigation of the desorption performance at low temperature of the same amine in both aqueous and non-aqueous solutions, with and without catalysts. The amine used for this study was 2-(2-aminoethoxy)ethanol (DGA), a highly absorptive primary amine that has a long story for acid gas removal, with fewer corrosion problems than MEA, resulting in potential capital and operating cost savings, as well as improved operation at relatively low pressure (Al-Juaied and Rochelle, 2006; Salkuyeh and Mofarahi, 2012). Moreover, in our recent studies DGA has demonstrated excellent CO_2 absorption efficiencies in both water and organic diluent (Barzagli et al., 2018). Two DGA solutions were prepared with a concentration of 3 mol·L^{-1}: one in water, the other in DEGMME (diethylene glycol monomethyl ether) as organic diluent. DEGMME exhibits interesting chemical-physical characteristics, as it is able to solubilise both amine and its reaction products with CO_2, has a high boiling point (194 °C), viscosity compatible with use in conventional equipment (3.5 cP at 25 °C) and, above all, a much lower heat capacity than water (2260 J·$kg^{-1}·K^{-1}$, with respect to 4184 J·$kg^{-1}·K^{-1}$ of H_2O), which ensures lower energy demand during heating (Bhatti et al., 2021a). The two aqueous and non-aqueous solutions of DGA were first saturated with pure CO_2, and then their desorption performance with and without catalysts was studied at a temperature of 85 °C (significantly lower than conventional temperatures), evaluating the CO_2 released, the rate of CO_2 desorption and the percentage of sorbent regenerated as a function of the desorption time. Five different solid acid catalysts were used for these experimental studies, and in particular two metal oxides (V_2O_5 and WO_3) and three silicate derivatives, namely HCl activated montmorillonite (HCl-MONT), 20%Mo/SBA-15, and 20%Mo/SAPO-11. These acid solids and their precursors have demonstrated in previous studies their catalytic activity in the regenerative processes of aqueous solutions of amines, and in particular with MEA (Barzagli and Mani, 2021; Bhatti et al., 2018, 2017; Li et al., 2023). Moreover, V_2O_5 and WO_3 had already been successfully tested to regenerate non-aqueous solutions of DGA at 90 °C (Bhatti et al., 2021a). Finally, a detailed speciation study (qualitative and quantitative assessment of species in solution) was carried out during the desorption process using ^{13}C NMR analysis for the DGA/H_2O and DGA/DEGMME solutions both in the presence and without the 20%Mo/SAPO-11 catalyst, in order to better understand the different mechanisms of sorbent regeneration under specific operating conditions (Hu et al., 2020; Karlsson et al., 2021; Perinu et al., 2018).

Experimental section

Materials

The primary amine 2-(2-aminoethoxy)ethanol (DGA) and the organic solvent diethylene glycol monomethyl ether (DEGMME) were supplied by Sigma-Aldrich and used without further purification. The non-aqueous sorbent used was prepared by dissolving DGA into DEGMME in order to obtain an amine solution with molar concentration of 3 mol·L^{-1}. Moreover, for comparison purposes, a 3 mol·L^{-1} DGA aqueous solution was also prepared by using deionized water. Previous studies have shown that this amine concentration represents an excellent compromise between high capture efficiency and acceptable viscosity (related to ease of handling) of the CO_2-loaded solution (Bhatti et al., 2021a). Pure CO_2 (Rivoira Spa) was used to saturate amine solutions, while N_2 (Rivoira Spa) was used as gas-carrier during the desorption process. Two flow meters (Cole Parmer) were used to control the flow rates of the two gases. A Varian CP-4900 gas chromatograph (GC) was used to continuously measure the amount of CO_2 released during desorption. The GC was equipped with a PoraPLOT U column (Agilent) and a TCD detector, and was calibrated with 15% and 40% v/v CO_2/N_2 reference mixture and 100% CO_2 reference gas (Rivoira Spa).

Regarding catalysts, tungsten trioxide (WO_3) and divanadium pentoxide (V_2O_5) were supplied by Fisher Scientific and were used as received. The virgin catalyst support used in this study was SAPO-11, a molecular sieve obtained from ACS Materials LLC. Tetraethyl orthosilicate (TEOS, 99.0%), pluronic P123 (M_{avg} 5800), HCl (37%), montmorillonite, and ammonium-molybdate tetra-hydrate were sourced from Sigma-Aldrich.

Catalysts preparation

The production of mesoporous silica SBA-15 was performed using a method outlined in previous literature (Moogi et al., 2020). For a typical batch, calculated amounts of pluronic P-123 ($EO_{20}PO_{70}EO_{20}$) dissolved in water followed by the addition of 2 M HCl solution. TEOS was then added dropwise while under continuous stirring. After 24 h of stirring at 40 °C, the mixture was transferred into a tetrafluropolyethylene (TFPE) bottle and kept in an oven for hydrothermal treatment at 100 °C for 48 h. The resulting SBA-15 micelles were cooled down to ambient temperature, filtered, washed, and dried for 12 h at 105 °C. SBA-15 micelles were then calcined in airflow (0.1 L·min^{-1}) at 550 °C for 6 h. The incipient wetness impregnation method was used to prepare molybdenum-supported catalysts, where calculated amounts of metal precursors (20% Mo) were dissolved in distilled water and added to SAPO-11 and SBA-15 supports while being stirred continuously. The catalysts were dried at 105 °C and then calcined at 550 °C in a nitrogen flow for 6 h. HCl-MONT was also prepared using a method described in our previous work. Briefly, 5 g of MONT clay was slowly added with 100 mL of aqueous HCl solution (4 mol·L^{-1}) in a round-bottom glass flask, then stirred vigorously (600 rpm) at 100 °C for 4 h to allow the acid activation. The sample was then cooled to about 20 °C and washed several times with deionized water, until the filtrate pH was ~7. The collected HCl-MONT was finally dried at 120 °C for 10 h.

CO_2 saturation and desorption experiments

DGA/H_2O and DGA/DEGMME solutions were saturated with pure CO_2 (flow rate = 0.230 $molCO_2·h^{-1}$) using a Drechsel washing bottle with a sintered glass diffuser (16–40 μm pores), maintained at 40 °C with a thermostatted bath (Thermo Scientific AC200-A25). To obtain evidence of saturation, the weight of the absorber was constantly monitored during absorption until a constant weight was reached. The CO_2 loading value (mol CO_2 captured/mol amine) was calculated from the maximum increase in weight of the CO_2-saturated solution.
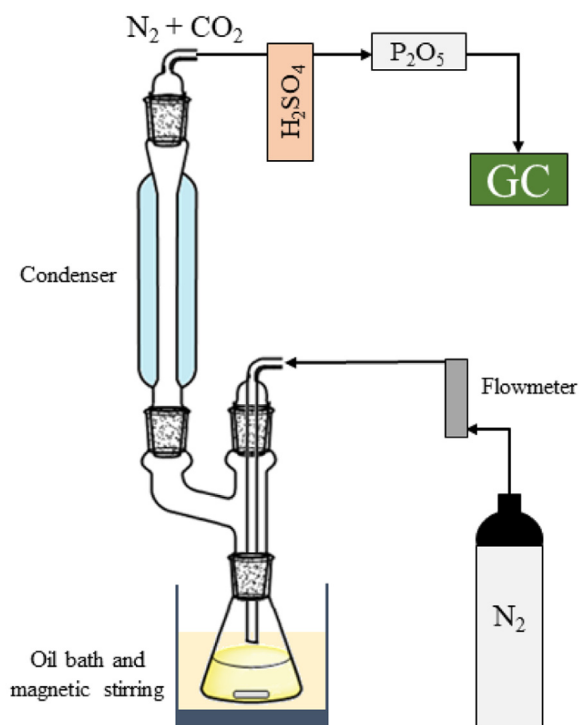
Fig. 1. Simplified sketch of the instrumentation used for CO_2 thermal release experiments.

CO_2 desorption experiments were performed according to a previously validated procedure (Bhatti et al., 2021a). The instrumentation used consisted of a 50 mL conical flask connected to a condenser and an oil bath equipped with a magnetic stirrer (IKA heating bath HBR 4). A simplified representation of the experimental setup is depicted in Fig. 1. Briefly, 25 mL of the CO_2-saturated solution (maintained at 20 °C before being used) was added to the flask and heated to 85 °C. The release of CO_2 was facilitated by magnetic stirring (800 rpm) and by the continuous blowing of a stream of N_2 (flow rate = 410 mL·min^{-1}), which acted as a gas carrier. The CO_2+N_2 gas mixture leaving the solution passed sequentially through a cold condenser to limit evaporation losses of amine and diluent, a concentrated solution of H_2SO_4 to remove any traces of amine, and a desiccant column filled with P_2O_5 to retain any traces of diluent. Finally, the gas mixture was continuously analysed by the GC, which provided the amount of CO_2 desorbed, and consequently the CO_2 desorption rate, throughout the duration of the experiment (60 min). Except for the desorption processes conducted on the two solutions without catalysts (blank), the catalyst under investigation was added directly into the CO_2-loaded solution before heating (1.25 g, about 5% by weight). Each experiment was repeated twice and the deviation from the average value of the released CO_2 was always in the range of 0.5–1.5%.
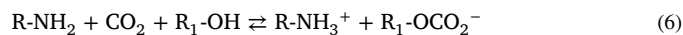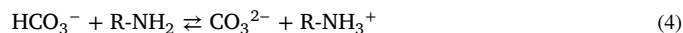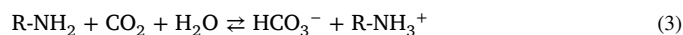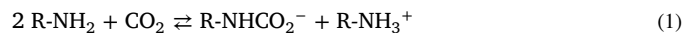
^{13}C NMR speciation study

The speciation of both aqueous and non-aqueous sorbents was determined by ^{13}C NMR analysis of samples collected from the CO_2-saturated solution and during desorption, after 5, 10, 15, 25, 40, and 60 min of heating at 85 °C. The ^{13}C NMR spectra were recorded with a Bruker Avance III 400 spectrometer (100.613 MHz) according to a protocol validated in our laboratories (Barzagli et al., 2013; Bhatti et al., 2021a). $Si(CH_3)_4$ was used as external standard, CH_3CN as internal reference, and D_2O (in a sealed glass capillary) was introduced into the NMR tube to provide the lock signal. The acquisition parameters used are: acquisition time = 1.3632 s, delay time = 2–30 s, pulse angle = 90.0°,

scans = 280–320, data points = 65 K. By integrating the signals at about 40 ppm (relative to the C–CH_2–N carbon in the DGA structure), the relative amounts of DGA carbamate and DGA/DGAH$^+$ (free and protonated amine in rapid equilibrium) can be determined with an estimated error <2%. Similarly, meticulous integration of peaks in the range 158–165 ppm provides a good estimate (error <5%) of the relative quantity of the possible carbonyl species, namely DGA carbamate, DEGMME carbonate and the fast-equilibrating HCO_3^-/CO_3^{2-} ions. Although DGA and DGAH$^+$ provide a unique peak (because of the rapid proton scrambling), their relative quantities can be assessed from the chemical shift (δ, ppm) of their own peak after constructing a suitable calibration line. The limit values found for free DGA and fully protonated DGAH$^+$ in DEGMME were 41.48 ppm and 39.51 ppm, respectively, while in aqueous solution they were 40.24 ppm and 39.27 ppm. Similarly, the position of the unique signal of HCO_3^-/CO_3^{2-} can be exploited to evaluate their relative amount in aqueous solution (Zhang et al., 2023a): the limit values found for carbonate and bicarbonate ions (obviously only in water) were 168.10 ppm and 160.25 ppm, respectively.

Results and discussion

Chemical equilibria in CO_2 capture processes

Before studying their desorption performance with and without catalysts, the DGA/H_2O and DGA/DEGMME solutions (amine concentration = 3 mol·L^{-1}) were saturated with pure CO_2 at a temperature of 40 °C, as described in Section 2.3, and their CO_2 loadings (mol CO_2 captured/mol amine) were determined from the increase in weight of the CO_2-saturated solution at the end of the experiment. The loading value obtained in aqueous solution was 0.647, while that in DEGMME was 0.576. Moreover, solution samples were analysed by ^{13}C NMR spectroscopy to qualitatively and quantitatively determine the species present. The spectra obtained are shown in Fig. 2, and the species present are those expected from reactions 1–6, which describe the CO_2 capture by DGA in different diluents (El Hadri et al., 2017; Zhang et al., 2016).

$$2 \text{ R-NH}_2 + CO_2 \rightleftarrows \text{R-NHCO}_2^- + \text{R-NH}_3^+ \tag{1}$$

$$\text{R-NHCO}_2^- + CO_2 + 2 H_2O \rightleftarrows 2 \text{ HCO}_3^- + \text{R-NH}_3^+ \tag{2}$$

$$\text{R-NH}_2 + CO_2 + H_2O \rightleftarrows \text{HCO}_3^- + \text{R-NH}_3^+ \tag{3}$$

$$\text{HCO}_3^- + \text{R-NH}_2 \rightleftarrows \text{CO}_3^{2-} + \text{R-NH}_3^+ \tag{4}$$

$$CO_2 + \text{CO}_3^{2-} + H_2O \rightleftarrows 2 \text{ HCO}_3^- \tag{5}$$

$$\text{R-NH}_2 + CO_2 + \text{R}_1\text{-OH} \rightleftarrows \text{R-NH}_3^+ + \text{R}_1\text{-OCO}_2^- \tag{6}$$

According to reaction 1, the primary alkanolamine DGA, denoted here as R-NH$_2$ ($R = \text{–CH}_2\text{CH}_2\text{–O–CH}_2\text{CH}_2\text{–OH}$), reacts with CO_2 to produce DGA carbamate (R-NHCO$_2^-$) and the protonated species DGAH$^+$ (R-NH$_3^+$), irrespective of the type of diluent used. In contrast, carbonate and bicarbonate ions can only be produced in water (reactions 2–5). Organic diluents with a hydroxyl group such as DEGMME, denoted here as R_1–OH ($R_1 = \text{–CH}_2\text{CH}_2\text{–O–CH}_2\text{CH}_2\text{–O–CH}_3$), can also react with both CO_2, when alkaline species such as DGA are present, to form the corresponding alkyl carbonate R_1-OCO$_2^-$ (reaction 6). This reaction is kinetically and thermodynamically less favourable than the others and, in fact, generally occurs during prolonged absorption, when the amount of free amine is low; moreover, the alkyl carbonate formed has low stability
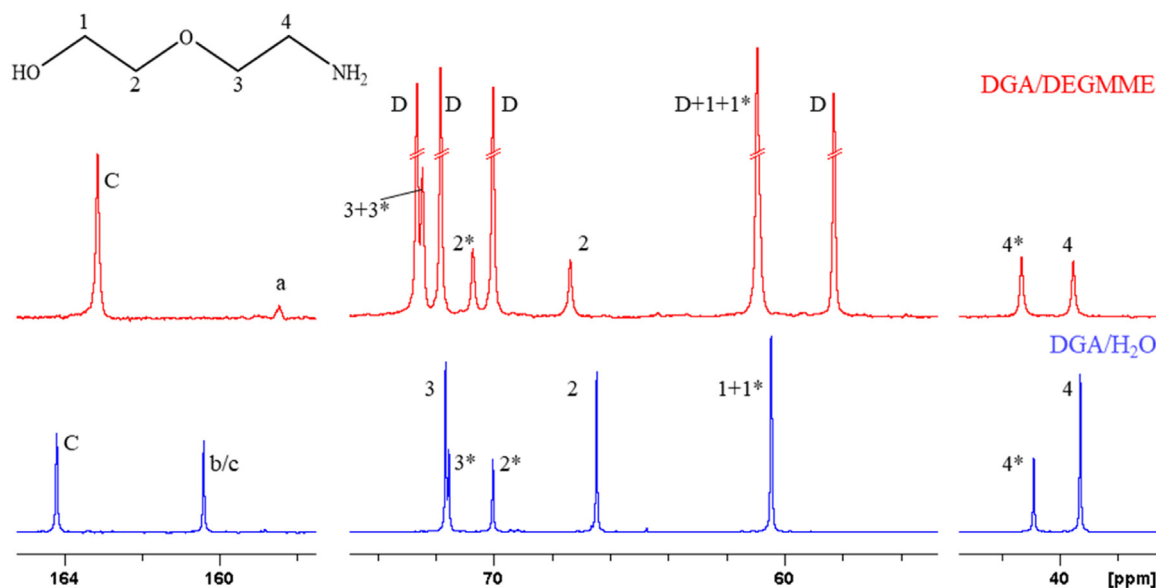
Fig. 2. ^{13}C NMR spectra of DGA/DEGMME and DGA/H$_2$O solutions after CO$_2$ saturation. The carbon atoms of DGA and DGAH$^+$ (unique signal) are indicated by numbers, and asterisks denote the carbon atoms of DGA carbamate. *D* indicates DEGMME signals. The carbonyl carbons of DEGMME carbonate, HCO$_3^-$/CO$_3^{2-}$ and DGA carbamate are indicated by *a, b/c* and *C*, respectively (peak intensity not scaled).

(Barzagli et al., 2019; Karlsson et al., 2021). The spectra in Fig. 2 clearly shows that CO$_2$ is absorbed almost exclusively as DGA carbamate (reaction 1, DGA/CO$_2$ stoichiometry = 2/1) when the reaction takes place in DEGMME, whereas in aqueous solution CO$_2$ is captured both as carbamate and bicarbonate (reaction 2, DGA/CO$_2$ stoichiometry = 1/1), in comparable amounts: this explains the higher loading value obtained in H$_2$O than in organic solvent.

Catalyst-assisted sorbent regeneration

To evaluate the potential benefits of combining the use of non-aqueous sorbents with the use of catalysts to facilitate regeneration compared to conventional sorbents, the CO$_2$ desorption performance of saturated solutions of DGA/DEGMME and DGA/H$_2$O without and with five distinct catalysts was studied. The catalysts used were two metal oxides, V$_2$O$_5$ and WO$_3$, and three silicate derivatives, namely HCl-MONT, 20%Mo/SBA-15, and 20%Mo/SAPO-11, which have already proven to be active with several aqueous solutions of amines and, in the case of metal oxides, also with non-aqueous DGA sorbents (Bhatti et al., 2021a, 2020). Desorption experiments were carried out at T = 85 °C on aliquots (0.025 L) of the previously saturated solutions according to the procedure described in Section 2.3. For each solution, desorption was performed without catalysts (blank) and with 1.25 g (5% wt) of each of the five selected catalysts. During the 60-minute experiment, the CO$_2$ released was continuously measured by the GC, as described in Section 2.3; from these data, the rate of CO$_2$ desorption (mmolCO$_2$·min^{-1}), the cumulative quantity of CO$_2$ desorbed (mmol) and the percentage of regenerated sorbent were calculated. All results obtained with and without catalysts during the desorption experiments for aqueous and non-aqueous DGA solutions are given in the Supporting Information in Tables S1 and S2, respectively. Moreover, the most significant data for comparing the different regeneration performances are shown here in Table 1.

Once the experiments were completed, the catalysts were recovered from the regenerated solutions by filtration, with the exception of V$_2$O$_5$, which is soluble in both water and DEGMME at the desorption temperature and cannot be completely separated even after cooling.

For both DGA solutions, the change in CO$_2$ desorption rate (mmol·min^{-1}) in the absence and presence of the different catalysts over the desorption time is illustrated in Fig. 3.

Either in aqueous and non-aqueous solutions, all the catalysts tested were able to significantly increase the rate of CO$_2$ desorption with respect to the solution without catalysts (blank) during the first few minutes of desorption. As the regeneration proceeded (and the residual CO$_2$ in the solutions decreased), the desorption rates for all solutions tended to decrease, and similar values were recorded. In the DGA/H$_2$O solution, the maximum desorption rate obtained with the catalysts decreases in the order 20%Mo/SAPO-11 > 20%Mo/SBA-15 > V$_2$O$_5$ > WO$_3$ ≈ HCl-MONT. In particular, 20%Mo/SAPO-11 and 20%Mo/SBA-15 recorded the highest absolute desorption rate values, of 2.70 and 2.24 mmol·min^{-1}, respectively (Table 1), and a maximum desorption rate increase of up to 520% and 415%, respectively, compared to the aqueous blank (Table S1). Differently, in DEGMME, the best performing catalysts are metal oxides, and the beneficial effect on sorbent regeneration decreases in the order V$_2$O$_5$ > WO$_3$ > 20%Mo/SAPO-11 > 20%Mo/SBA-15 > HCl-MONT. The addition of V$_2$O$_5$ to the DGA/DEGMME solution resulted in a maximum desorption rate value of 3.19 mmol·min^{-1} (Table 1) and a maximum desorption rate increase of 86% compared to the non-aqueous blank (Table S2).

Most notably, Fig. 3 clearly shows that the rate of CO$_2$ desorption at 85 °C of DGA in the organic diluent is significantly higher than in water under the same operating conditions. Without addition of any catalyst, the CO$_2$ desorption rate of blank DGA/DEGMME is higher than that of blank DGA/H$_2$O (the maximum values are 2.16 and 1.75 mmol·min^{-1}, respectively). The addition of catalysts significantly increases the desorption rate for both solutions, however the values obtained in non-aqueous solution are still higher. Moreover, these higher values are maintained for longer periods of time, thus allowing more CO$_2$ to be desorbed for the same amount of time. This situation can be better understood by looking at Fig. 4, which shows the percentage of sorbent regeneration (ratio of the amount of CO$_2$ desorbed to the amount of CO$_2$ absorbed in the saturated solution) as a function of time for both aqueous and non-aqueous solutions.

Due to the highest (and longer lasting) desorption rate values, DGA/DEGMME is already 50% regenerated within 14 min without catalysts and even within 11 min with the addition of V$_2$O$_5$. The same percentage of regeneration in DGA/H$_2$O is only achieved between 27 min (with 20%Mo/SAPO-11) and 33 min (blank). In organic diluent, regeneration at 85 °C is around 90% at the end of the 60-minute heating
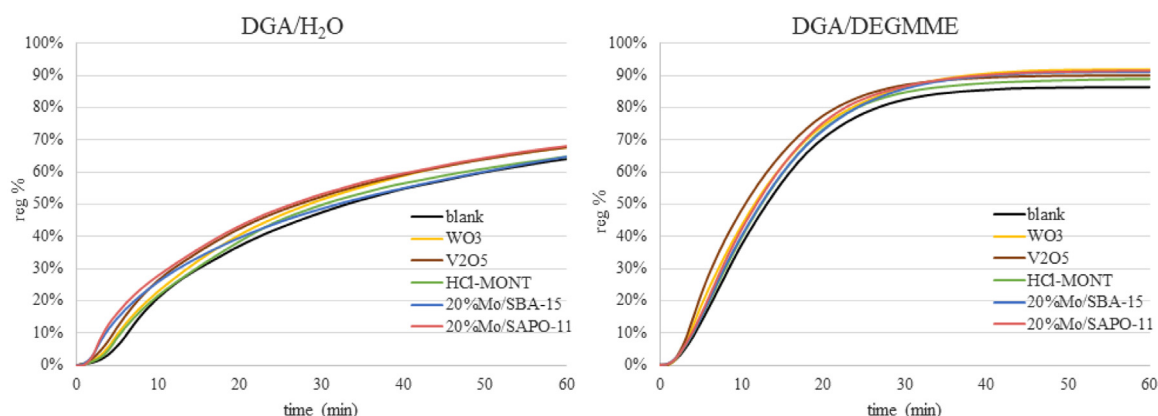
Table 1

Parameters for evaluating the regeneration performance of aqueous and non-aqueous DGA solutions with and without catalysts: maximum desorption rate, total amount of CO_2 released, CO_2 loading after desorption, percentage of final regeneration, time required to regenerate 50% of the sorbent.

| catalyst | DGA/H_2O solution – CO_2 loading after saturation: 0.647 | | | | | |
	Max des. rate (mmol·min^{-1})	Time at max des. rate (min)	Total CO_2 des. (mmol)	CO_2 Loading after des.	Sorbent regen. (%)	Time for 50% regen. (min)
Blank (no cat.)	1.75	7′	31.17	0.232	64.2	33'
WO_3	1.78	5′	32.93	0.208	67.8	29′
V_2O_5	1.90	5′	32.87	0.209	67.7	28′
HCl-MONT	1.76	5′	31.44	0.228	64.8	31′
20%Mo/SBA-15	2.24	3′	31.54	0.227	65.0	32′
20%Mo/SAPO-11	2.70	3′	33.01	0.207	68.0	27′

| catalyst | $DGA/DEGMME$ solution – CO_2 loading after saturation: 0.576 | | | | | |
	Max des. rate (mmol·min^{-1})	Time at max des. rate (min)	Total CO_2 des. (mmol)	CO_2 Loading after des.	Sorbent regen. (%)	Time for 50% regen. (min)
Blank (no cat.)	2.16	9′	37.35	0.078	86.4	14′
WO_3	2.69	5′	39.65	0.048	91.7	12′
V_2O_5	3.19	5′	38.93	0.057	90.1	11′
HCl-MONT	2.21	7′	38.43	0.064	88.9	13′
20%Mo/SBA-15	2.35	7′	39.33	0.052	91.0	13′
20%Mo/SAPO-11	2.49	7′	39.56	0.049	91.5	12′
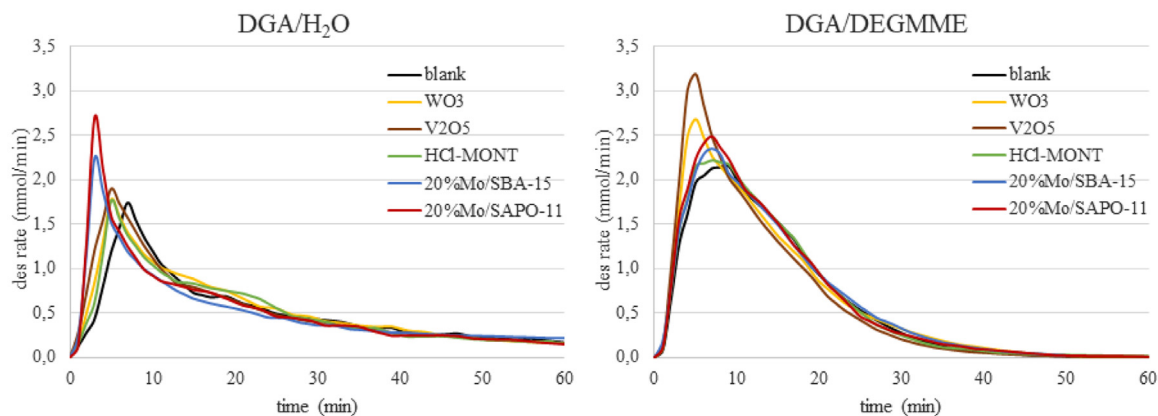
Fig. 3. Variation of the rate of CO_2 desorption (mmolCO_2·min^{-1}) in the absence and presence of the different catalysts over the desorption time (at 85 °C).

Fig. 4. Variation of sorbent regeneration percentage (%) in the absence and presence of the different catalysts over the desorption time (at 85 °C).

time, whereas in water regeneration values are around 65% (Table 1). Since the CO_2 loading of DGA in organic diluent is lower than in water, the percentage of regeneration alone may not be sufficient to assess the desorption performance: it is therefore necessary to verify the actual amount of CO_2 desorbed (mmol) at the end of the process. However, even these values confirm that desorption is higher in DEGMME (total

CO_2 desorbed between 37 and 40 mmol) than in the DGA/H_2O solution, which desorbed between 31 and 33 mmol of CO_2 (Table 1). CO_2 loading values at the end of desorption also confirm that non-aqueous solutions are substantially regenerated and ready for subsequent absorption (loadings between 0.048 and 0.078), whereas aqueous solutions exhibit higher CO_2 loadings, in the range 0.207–0.232 (Table 1)
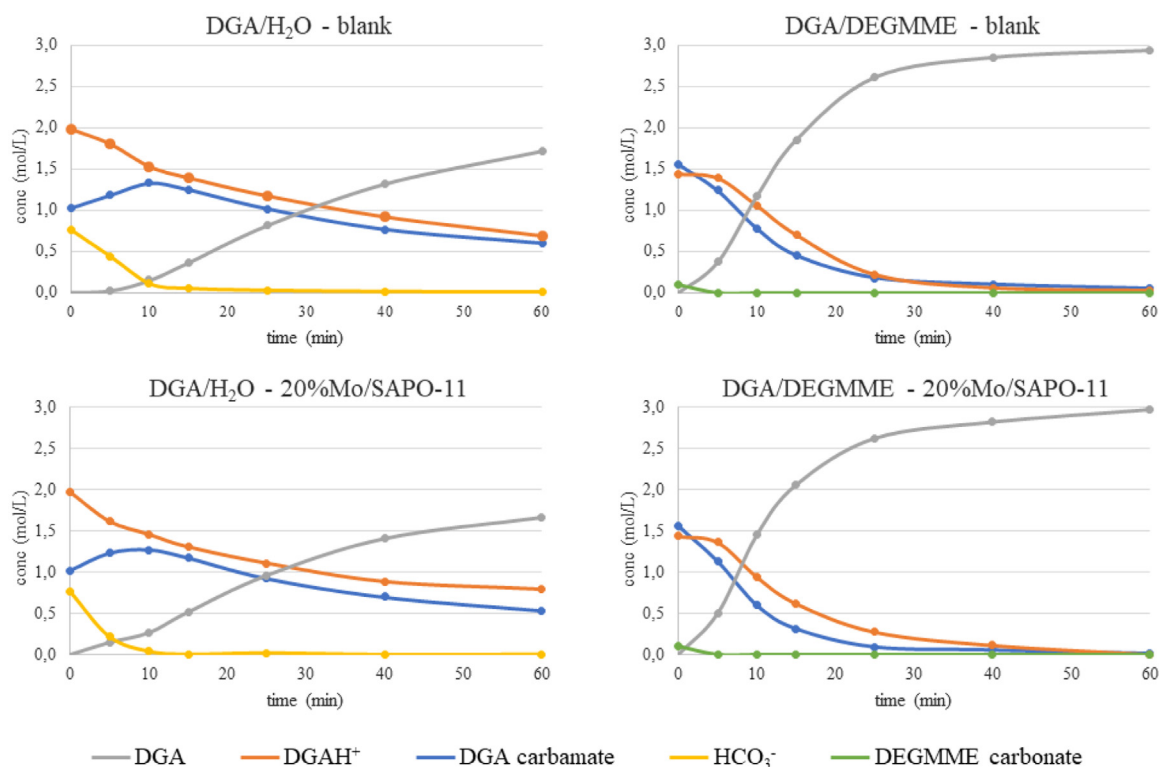
Fig. 5. Variation over time of the concentration (mol·L^{-1}) of the different species in DGA aqueous and non-aqueous systems, without and with 5 wt% 20%Mo/SAPO-11 catalyst, calculated by ^{13}C NMR analysis.

These results confirm the potential energy savings resulting from the use of amines in organic diluents, which are capable of almost complete regeneration at much lower temperatures than those conventionally used in industrial plants with aqueous MEA (120–140 °C). Furthermore, it is clear from Figs. 3 and 4 that the effect of solid acid catalysts is to significantly enhance desorption (and thus regeneration) especially in the first 10–15 min of heating: faster regeneration is of crucial importance in the design of continuous CO_2 absorption and desorption plants.

^{13}C NMR study of the desorption mechanism

In order to better understand the different behaviour during desorption, a detailed ^{13}C NMR study was carried out to identify the species present in the solutions during the regeneration and determine their concentration. Specifically, solution samples were taken (and analysed) after 5, 10, 15, 25, 40, and 60 min of heating at 85 °C. The comparison was made for both DGA solutions in the absence and presence of 20%Mo/SAPO-11, which proved to be the most efficient catalyst in H_2O, and also worked in organic diluent.

The results of this study are presented in Fig. 5. In particular, for each solution-catalyst combination, the graphs show the change in concentration (mol·L^{-1}) over the desorption time for free amine (DGA), protonated amine (DGAH$^+$), DGA carbamate, bicarbonate ion (only in aqueous solutions) and DEGMME carbonate (only in organic diluent). The initial values (at time = 0 min) are those for saturated solutions (shown in Fig. 2). The carbonate ion (present only in water) has not been reported as its concentration is negligible at time zero and is not detectable during regeneration.

The speciation profiles are significantly different between aqueous and non-aqueous solutions. In agreement with the desorption performance results, Fig. 5 highlights that the concentration of DGA increases very rapidly in DEGMME, until it reaches a concentration very close to 3 mol·L^{-1}, i.e., the initial concentration. On the contrary, in aqueous so-
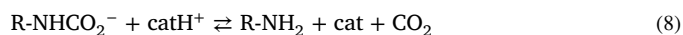
lution, the concentration of DGA increases more slowly and after 60 min barely reaches 1.7 mol·L^{-1}, even in the presence of the catalyst.

Another difference clearly seen in Fig. 5 concerns the decomposition of the compounds produced in the CO_2-saturated solution. In DGA/DEGMME solutions, the main absorption product is DGA carbamate. During the regeneration process, it decomposes quite rapidly in the first 15 min, and then slowly reaches concentrations close to zero as desorption continues. The presence of the catalyst accelerates the decomposition of DGA carbamate, as evident by comparing its concentrations between 5 and 25 min with or without 20%Mo/SAPO-11.

In non-aqueous systems, the decomposition reaction of DGA carbamate is the reverse of reaction 1:

$$R\text{-}NHCO_2^- + R\text{-}NH_3^+ \rightleftarrows 2\ R\text{-}NH_2 + CO_2 \tag{7}$$
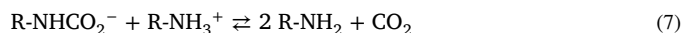
As reported in one of our previous studies (Bhatti et al., 2021a), the presence of an acid catalyst presumably increases the number of protons available for the reaction with carbamate, thereby increasing the rate of decomposition according to reactions 8 and 9 (Alivand et al., 2020; Zhang et al., 2018).

$$R\text{-}NHCO_2^- + catH^+ \rightleftarrows R\text{-}NH_2 + cat + CO_2 \tag{8}$$

$$R\text{-}NH_3^+ + cat \rightleftarrows R\text{-}NH_2 + catH^+ \tag{9}$$

Finally, DEGMME carbonate was not detected in any of the samples collected during regeneration: due to its low initial concentration and poor stability, it was fully decomposed within the first 5 min of desorption, according to (reverse) reaction 6.

Differently, in the aqueous solution, the regeneration of DGA depends on the decomposition of both carbamate and bicarbonate, which are in similar concentrations when the solution is saturated with CO_2. The speciation study highlights an interesting behaviour, not to be expected considering only the species decomposition reactions (inverse of

reactions 1–5): in fact, during the first 10 min of heating, the carbamate concentration increases instead of decreasing. At the same time, a decrease in DGAH$^+$ and, even more markedly, in HCO$_3^-$ can be seen. These trends suggest that a reaction between bicarbonate and protonated species to form DGA carbamate is prominent in the initial phase of desorption, according to reaction 10 (Barzagli et al., 2009).

$$2 \ HCO_3^- + R\text{-}NH_3^+ \rightleftarrows R\text{-}NHCO_2^- + CO_2 + 2 \ H_2O \qquad (10)$$
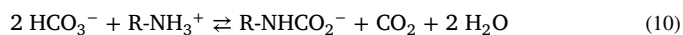
This reaction explains both the CO$_2$ desorption recorded with gas chromatograph (Fig. 3) and the very limited regeneration of DGA at the beginning of the desorption (Fig. 5). After 10 min the bicarbonate concentration is almost zero, and the DGA carbamate begins to decompose. The increment in the rate of desorption recorded in the presence of the 20%Mo/SAPO-11 (Fig. 3) is attributable to the more rapid decrease in the bicarbonate concentration: by comparing the speciation curves, the concentration of HCO$_3^-$ after 5 min of heating is significantly lower in the presence of the catalyst than in the blank. In this case, the acid solid presumably catalyses the protonation of bicarbonate (reaction 11), and is restored by subtracting a proton from DGAH$^+$ (reaction 12), which is also confirmed by the higher concentration of DGA present.

$$HCO_3^- + catH^+ \rightleftarrows H_2O + CO_2 + cat \qquad (11)$$

$$R\text{-}NH_3^+ + cat \rightleftarrows R\text{-}NH_2 + catH^+ \qquad (12)$$
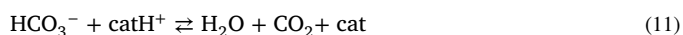
Conclusions

To overcome the current constraints of conventional carbon capture technologies, mainly related to the high energy cost of desorption, in this study we proposed an innovative technique for CO$_2$ capture that combines the use of non-aqueous sorbents with the use of acid catalysts for regeneration. To summarize, the regeneration performance of the primary amine DGA was studied with two co-solvents, traditionally used water and organic DEGMME, in the presence and absence of five different acidic catalysts. Opposed to the conventional 120–140 °C regeneration temperature, the sorbent regeneration was studied at a mild temperature of 85 °C, and the rate of CO$_2$ desorption, the quantity of CO$_2$ released, and the percentage of sorbent regenerated were used as the key performance indicators. As a finding of this study, the proposed new technique combining non-aqueous sorbents with acidic catalysts for desorption demonstrated significantly superior regenerative performance to both non-aqueous sorbents without catalysts and, to a greater extent, to solutions of the same amine in water. The use of V$_2$O$_5$ in the desorption of the DGA solution in DEGMME resulted in the highest desorption rate value of 3.19 mmol·min^{-1}, which was significantly better than both that obtained with the same solution without catalyst (2.16 mmol·min^{-1}) and those obtained in aqueous DGA solutions (1.75 mmol·min^{-1} without catalyst, 2.70 mmol·min^{-1} with 20%Mo/SAPO-11). Similar results were also obtained with WO$_3$, with the advantage over V$_2$O$_5$ of being insoluble and thus easily separable at the end of desorption. In the organic diluent, it was observed that the desorption rate values remained high for a longer time than in water: as a consequence, in the non-aqueous solution, it was possible to regenerate the sorbent by 50% after 11–14 min, whereas in water this percentage was obtained only after 27–33 min. Moreover, the addition of catalysts in non-aqueous sorbent allowed regeneration values of around 90% to be achieved after 60 min of heating to 85 °C, significantly better than those obtained in water (65–68%). The ^{13}C NMR speciation analysis of the desorption processes clarified the degradation mechanism of the amine carbamate, thus explaining the different behaviour in the different DGA-diluent-catalyst combinations.

In conclusion, initial evaluations of this proposed new approach suggest great potential for CO$_2$ capture efficiencies from gaseous mixtures,

coupled with regenerative processes at a significantly lower energy cost than conventional aqueous MEA technologies. Further investigation will be required to identify the best combination of amine, organic diluent, and catalyst to minimise energy expenditure while maximising CO$_2$ capture efficiency, as well as to assess its sustained performance over time, including amine stability under the chosen operating conditions and catalyst reusability.

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.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ccst.2023.100124.

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