A Comprehensive Study of the Impact of Steam on Polyethyleneimine on Silica for CO_2 Capture

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Abstract

An amine sorbent, prepared by impregnation of polyethyleneimine on silica, was tested for steam stability. The stability of the sorbent was investigated in a fixed bed reactor using multiple steam cycles of 90 vol.% H_2O/He at 105 °C and the gas effluent was monitored with a mass spectrometer. CO_2 uptake of sorbent was found to decrease with repeated exposure to steam. Characterization of the spent sorbent using N_2 physisorption, SEM, and thermogravimetric analysis (TGA), showed that the decrease in CO_2 loading can possibly be attributed to a re-agglomeration of the amine in the pores of the silica. No support effect was found in this study. The commercial SiO_2 used, Cariact G10, was found to be stable under the conditions used. While it was found that subjecting the sorbent to several steam cycles decreased its CO_2 uptake, a continuous exposure of the sorbent to steam did not have a significant performance impact. A silanated sorbent, consisting of a mixture of PEI and aminopropyl-triethoxysilane on SiO_2 support, was also investigated for steam stability. Similarly to the non-silanated sorbent, the CO_2 loading of this sorbent decreased upon steam exposure, although a mechanism for this change has not been postulated at this time.

Introduction

The contribution of anthropogenic CO_2 emissions to climate change is of considerable importance, resulting in an increase in research activities relating to the reduction of CO_2 emissions into the atmosphere [1]. As fossil fuels will likely remain the major source of energy for the near future, particularly in the developing world, industrial CO_2 production will likely rise in the coming decades. As a consequence, the development of affordable carbon capture and storage technologies to reduce the harmful impact of CO_2 released during industrial processes is a pressing matter.

The current state-of-the-art technology is CO_2 absorption in aqueous monoethanolamine (MEA) solution [2, 3]. This technology requires a large amount of energy to strip the CO_2 from the spent MEA solution. Consequently, identifying additional potential processes for capturing CO_2 with a more advantageous balance of CO_2 reactivity and lower regeneration energy is of high interest. Solid sorbents, in general, such as zeolites [4-6], metal oxides [7], metal organic frameworks [8], and solid amine sorbents in particular [9-14] may prove viable alternatives for post-combustion CO_2 capture from coal-fired power plants if found less energy intensive than their solvent counterpart.

Solid amine sorbents have been extensively investigated by several groups [9-11, 15-20]. However, most of the work on solid sorbents has focused on improving their CO_2 sorption capacity, their stability in dry inert environments [19-21] and the impact of low concentrations of water vapor during adsorption (under 16 vol.%) on the stability and performance of the sorbents [16, 22, 23]. The customary method of regenerating the sorbents described in the literature consists of a partial pressure swing desorption with an inert sweep gas combined with a temperature swing desorption. The added complexity of the additional step required to separate the CO_2 from the sweep gas is a significant barrier to large scale industrial application. Regeneration of amine based sorbents under a CO_2 sweep could prove to be the best option, yet it may result in a reduction of the working capacity of the sorbent if there is a substantial CO_2 residual loading at regeneration temperature. Regeneration using a steam sweep (direct steam regeneration) may prove a practical technique, given the ease of separating the recovered CO_2 through condensation of H_2O. The steam exposure, however, can impact the sorbents negatively. Few studies on the impact of steam regeneration on amine based sorbents have been reported in the literature [24-27]. Steam regeneration of amine sorbents has been shown to be feasible in a fixed bed reactor [24, 25]. Jones and coworkers [27] found that exposing amine supported on foamed silica to steam conditions in an autoclave for up to 24 h resulted in a decrease in the CO_2 sorption capacity of the sorbents, a decrease postulated to be due to a collapse of the structure of the support.

A continuous flow reactor is a more natural fit to the processing of a continuous emission stream. Consequently, in this work, we are evaluating the stability of a conventional amine sorbent, polyethyleneimine on SiO_2 (nomenclature: PEI-Si) exposed to several cycles of steam as well as different modes of steam introduction in a lab-scale packed bed reactor. As we shall demonstrate, our sample did not suffer the same degradation of the support reported by Li *et al.* [27].

A battery of tests was conducted to discriminate between several proposed avenues of degradation. A possible change in the nature of the amine, a change in the structure of the support, a thermal effect, leaching of the amines, or a change in the dispersion of the amines were considered. Characterization techniques such as thermal gravimetric analysis (TGA), scanning electron microscopy (SEM), and N_2-physisorption of the fresh and spent sorbents were performed to distinguish among the above-mentioned possibilities.

In addition to the conventional amine sorbent, a sorbent with a silane additive, aminopropyl-triethoxysilane, (nomenclature: PEI-Sil-Si) has also been investigated for comparison to published work [25]. It has been reported [28-30] that addition of a silane agent to amine sorbent may improve the interaction of PEI with the support thus improving the dispersion of the amine and therefore the efficiency of the sorbent. However the PEI and the support used in the mentioned work were different from the ones used in this study. And while the impact of steam was also addressed, it was not the goal of that study to thoroughly understand the impact of steam on the sorbents.

Experimental Section

The sorbent was synthesized by impregnating SiO_2 (Fuji Silysia Cariact grade G-10 HPV, size 75-500 μm) with polyethyleneimine (PEI) (Aldrich PEI Mn-423). A homogeneous solution of PEI and methanol was added to SiO_2 to form a slurry. The slurry was then placed in a rotary evaporator set to 60 °C and left to rotate for 2 h. The methanol was gradually removed using a vacuum pump once the slurry was fully mixed. The resulting solid was then refrigerated. The target PEI loading within the sample was ca. 50 wt. %. The silanated sorbent was prepared following the same procedure except in this case PEI was mixed with aminopropyl-triethoxysilane (Aldrich) $[H_2N(CH_2)_3Si(OC_2H_5)_3]$ and methanol to form the homogeneous solution. The targeted wt. % was between 40 and 45 organic with 5 wt. % being the silane agent: aminopropyl-triethoxysilane.

CO_2 adsorption-desorption cycling was conducted in a lab-scale packed bed reactor (Figure 1) [23, 25]. Typically, 1 g sorbent was loaded into a stainless steel tube (3/8 O.D.). The sample was held in place using quartz wool plugs. The baseline performance of the sorbent was established by testing under dry cycles. A gas stream with a composition of 10 vol. % CO_2/He is passed through the sorbent at 60 °C. Once near equilibrium CO_2 uptake is reached, the sorbent is isolated using two three-way valves. Helium is then used to purge the system after which the reactor is brought back on-line for regeneration. The regeneration consists of two steps: an isothermal pressure swing desorption at 60 °C followed by a temperature swing desorption in which the remaining CO_2 desorbs by ramping the sorbent temperature to 105 °C at 2 °C/min. When steam regeneration was used, the reactor temperature was first increased to 105 °C under stagnant conditions and then the sorbent was swept with 90 vol. % H_2O/He. Helium was added to the steam as a reference gas for the mass spectrometer. After the steam regeneration, the sorbent was dried at 105 °C under He. The sorbent temperature was then decreased to 60 °C. The impact of long exposure time to steam conditions was also investigated. The sorbent was first tested under a full dry cycle, followed by a cycle where adsorption of CO_2 occurred under dry conditions at 60°C and desorption occurred using a stream of 90 vol. % H_2O/ He at 105 °C held for 5 h. The sorbent was dried with a helium sweep at 105 °C after steam regeneration. The sample was then tested under dry cycles to determine its performance after exposure to steam conditions. The gas effluent was monitored with a Thermostar® mass spectrometer.

SEM analysis to investigate morphological changes arising from the steam treatment was carried out on the fresh and spent SiO_2 support using an FEI Quanta 600F scanning electron microscope. Samples were mounted on carbon tape and gold coated. Secondary electron images were collected at 20 kV. The fresh SiO_2 was analyzed as received and the spent SiO_2 was exposed to 5 h of steam at 105 °C to mimic regeneration.

TGA was carried out to determine the total organic amount in the fresh and spent samples using a Thermo Cahn Thermax 300 instrument. The samples were first dried at 100 °C for up to 2 h and then ramped rapidly to 600 °C under N_2. The measured change in weight was correlated to the amount of organic present within the sorbent. N_2 physisorption was carried out using Quantachrome Autosorb 1-C analyzer at 77 K. The sorbents were degassed under vacuum overnight at 70 °C prior to N_2 physisorption.

Results and Discussion

First, we will report on the results of the sorbents without steam to establish a baseline performance.

Sorbents performance under dry conditions

Figure 2 shows the effluent of a typical CO_2 adsorption/regeneration cycle under dry conditions. As can be seen, gas stream with a composition of 10 vol. % CO_2/He adsorption occurred at 60 °C followed by two step regeneration. During isothermal pressure swing desorption at 60 °C, 60 mol. % of total adsorbed CO_2 is desorbed followed by a temperature swing desorption in which the remaining CO_2 desorbs by ramping the sorbent temperature to 105 °C. This dry cycle is used to determine the baseline performance of the sorbents.

Table 1 summarizes the amine loading, CO_2 loading and amine efficiency of PEI-Si and PEI-Sil-Si sorbents. The CO_2 loadings of the sorbents were obtained using a packed bed reactor at 60 °C and atmospheric pressure and the organic loading representing the nitrogen content was obtained using TGA. The amine efficiency was calculated with the assumption that the PEI contains 33 % nitrogen by weight [10].

The CO_2 loadings under dry conditions for PEI-Si and PEI-Sil-Si were found to be similar. A theoretical limit can be calculated by assuming two amine functionalities are stoichiometrically required to adsorb CO_2. Given that primary and secondary amines have an efficiency of 0.5 and assuming that PEI Mn-423 consists of only primary and secondary amines leads to the calculated value of 0.5. Both sorbents exhibited an efficiency lower than 0.5, the theoretical amine efficiency of low molecular weight PEI based sorbents under dry conditions. Nonetheless, the addition of silane seems to improve the efficiency of the amine. This positive impact can be a result of an improved dispersion of the PEI. These results are discussed more thoroughly in a later section.

Steam impact on the sorbents

Testing amine sorbents under dry conditions, as usually reported in the literature, does not fully assess their performance. It is important to determine their performance and stability under more realistic conditions. While direct steam sweeping is not the only possible regeneration method for amine sorbents, it is one of the more likely pathways. Consequently, investigating the stability of amine sorbents under steam conditions is crucial and prudent. Moreover, acquiring an understanding of the way steam impacts the sorbents could lead to the identification and synthesis of more stable amine sorbents.

In order to investigate the stability of PEI-Si under water vapor, regeneration of the sorbent following CO_2 adsorption was carried out using 90 vol.% H_2O/He at 105 °C. As mentioned earlier, the sorbent was isolated using two three-way valves following CO_2 adsorption conducted at 60 °C using a flow of 10 vol. % CO_2/He at 100 cc/min. The temperature of the bed was increased to 105 °C prior to regeneration using a steam sweep. The sorbent was cycled six times using this protocol. Sorbent performance was monitored in dry cycles before and after steam. The variation in CO_2 loading on PEI-Si with the number of cycles is shown in Figure 3. The initial and final cycles (cycles 1 and 8) are dry cycles. The CO_2 uptake on the fresh sample was found to be 3.2 mmol/g sorbent, typical for amine sorbents of this type [10]. The variation seen in the second cycle reflects the measurement variation in the unit/mass spectrometer as the sorbent had not yet been exposed to steam. Some of the subsequent cycles also show such variations. However, the trend is towards a decrease in CO_2 capture. A slight decrease in CO_2 uptake from 3.2 to 3.0 mmol/g sorbent (cycle 3) can be seen after one complete cycle with steam regeneration. After two additional cycles with steam regeneration, CO_2 uptake decreased to 2.7 mmol/g sorbent (cycle 4). Subsequently a leveling in CO_2 uptake occurred at 2.8 mmol/g sorbent (cycles 5-7). CO_2 uptake in the final cycle (cycle 8), measured at dry conditions, was found to be 2.8 mmol/g sorbent, a decrease of 12 mol. % from the CO_2 uptake measured on the fresh sorbent under the dry cycle. Most of the loss in CO_2 loading occurred in the first three cycles, with a concomitant loss in overall sorbent performance.

The same experimental protocol was applied to PEI-Sil-Si (Figure 3). CO_2 uptake of the fresh PEI-Sil-Si was 3 mmol/g sorbent. A similar trend occurred with PEI-Sil-Si as seen with PEI-Si under steam regeneration- a decrease in CO_2 loading by ca. 10 mol. %, (3 mmol/g sorbent to 2.7 mmol/g sorbent). The CO_2 loading appears to quasi-stabilize after the 4th cycle, although a slight decrease in CO_2 loading continued.

The amount of moisture adsorbed and desorbed by the sorbents at 105 °C was found to be in the range of 6 to 8 mmol/g sorbent for both sorbents consistent throughout all six cycles. Water uptake may occur either on SiO_2, on the amines, or both. In order to conclusively discriminate between the contribution of SiO_2 and of the amines, moisture loading on bare SiO_2 was determined at 105 °C using a gas stream composition of 90 vol. % H_2O/He. It was found to be only ca. 2.7 mmol/g SiO_2. These results suggest the majority of the water was taken up by the amines. The presence of 5 wt. % aminopropyl-triethoxysilane appears not to alter the water uptake of the sorbent.

Two additional modes of steam addition were investigated to further elucidate the degradation mechanism. Mode 2 of steam addition was similar to the first except that the sorbent was cycled once and held continuously under steam at 105 °C for 5 h. Mode 3 involved only steam (90 vol. % H_2O/He) with no CO_2 added at 105 °C. The sorbents were exposed to six steam cycles consisting of only H_2O adsorption and desorption (drying steps) and every cycle was held approximately 30-40 min resulting in a total time of ca. 3 h. Results allow for separation of the impact of adsorbed CO_2 on the interaction of the sorbent and H_2O during regeneration.

Cycling a sample through six cycles of steam without CO_2 sorption (mode 3) resulted in a similar loss in the performance of PEI-Si as seen in mode 1. Unexpectedly, holding the sorbent at 105 °C for 5 h (mode 2) under steam resulted in a loss of only ca. 3 mol. % CO_2 loading. The impact of steam was more significant for modes 1 and 3, where the sorbent was exposed to H_2O for a total time of around 3.5 h, than when exposed continuously to H_2O for 5 h. The H_2O adsorption/desorption cycle appears to have impacted the loss in CO_2 loading. The five hours continuous exposure to steam of a single cycle showed less impact on the performance of the sorbent even though the steam exposure time was longer. We surmise that the drying step significantly degrades the sorbent. Five hours steam exposure resulted in a greater loss for PEI-Sil-Si than for PEI-Si. It experienced a loss of ca. 8 mol. % CO_2 uptake. Moreover, the silanated sorbent had comparable CO_2 uptake losses for the three steam addition modes. The dissimilarity in the way the two sorbents were affected by the 5 h steam exposure suggests different mechanisms of steam impact on the sorbents.

Causes of sorbents degradation

We consider several possible causes for the decline in the CO_2 uptake of the sorbent after steam treatments: 1) the effect of the support, 2) a change in the nature of the amine, 3) a thermal effect, 4) a leaching of the amine by water, 5) a change in the distribution of the amine on the support. To investigate each cause fresh and spent sorbents were analyzed using several characterization techniques.

Changes to the support could play a role in the decrease in the performance of the sorbent. It has been reported by Li *et al.* [27] that collapse of the silica support after steam treatment was the cause of the degradation in the performance of their amine sorbent. This particular study prompted the same group to dismiss SiO_2 as an appropriate support for amine sorbents, thus shifting their focus to alumina support [26]. Noteworthy, the particular study used a specific form of SiO_2 –foam like silica. The study used an autoclave to accelerate the aging process, and this experimental methodology selected to investigate the impact of steam on the sorbents could result in condensation of water in the SiO_2 pores. While the authors stated that H_2O does not condense in the pores, no evidence was presented to rule out this possibility [27].

In order to study the effect of steam on the commercial support used in this study, Cariact G10 SiO_2 was pretreated with 90 vol. % H_2O/He at 105 °C for 5 h. The spent sample was then analyzed using SEM and BET. A fresh support was also characterized for comparison. SEM analysis was carried out on the fresh and spent supports and the results are shown in Figure 4. A comparison of the images does not reveal a significant difference in the morphology of the samples at the highest resolution of the instrument (i.e. at very small length scales). At low magnification the support particles do appear to have undergone negligible attrition, likely due to sample handling- loading, unloading of the reactor and sieving.

Available BET surface areas of the fresh and the spent supports were measured from N_2 physisorption isotherms at 77 K. The surface area of the fresh and the spent SiO_2 support were found to be similar, 279 m^2/g and 280 m^2/g, respectively. While the work of Li *et al.* [27] showed their foam-like SiO_2 collapsed after steam treatment, our work clearly shows that any decrease in CO_2 loading in our sample is not due to a collapse of our support. The commercial SiO_2, Cariact G 10, used in this study remains stable under the selected conditions. Thus, we eliminate collapse of the support as a candidate for the degradation mechanism of the sorbent investigated in this work.

The nature of the amine has not been modified due to steam regeneration as has been confirmed by Diffuse Reflectance Infra-red Fourier Transform Spectroscopy (DRIFTS) analysis carried out on both fresh and spent PEI-Si cycled through steam cycles (Figure 5).

In order to eliminate thermal degradation effect, the sorbents were held at 105 °C for 5 hours under helium. The performances of the sorbents post thermal treatment remained the same as on fresh sorbent; and that was the case for both sorbents (not shown).

Leaching of the amines from the support by steam was considered as a possible cause in the lowering of CO_2 uptake of the sorbents. Therefore, to investigate the amine loss, TGA was conducted to determine the amount of organics on the support for the fresh and spent sorbents. For this analysis, the sorbents were first dried at 100 °C for 2 h then heated rapidly to 600 °C under N_2. With the assumption that H_2O has been removed during the 2 h drying step, any further decrease in weight can be attributed to the loss of organics from the sorbent. The organic contents, determined using TGA, on SiO_2 for the fresh and spent sorbents following the three modes of water treatment are summarized in Table 2. For both sorbents, the organic loading on SiO_2 has not measurably changed following the different steam treatments. The fluctuations in the organic wt. % are within the measurement uncertainty of the apparatus. The amount of organics measured was in the range of 44-46 wt. % for PEI-Si and in the range of 38-41 wt. % for PEI-Sil-Si. In addition to TGA, the condensate was tested using a Shimadzu LCMS 2020 by the direct infusion method via a SIL 20AC HT autosampler and dual LC-20 AD binary pumps to determine the amount of PEI. No detectable amount was found (results not shown). These results indicate that leaching of the amines from the sorbent is not a major contributor in the loss of CO_2 uptake following steam treatment. We conclude that in this study the reduction in loading is not due to leaching of the amines.

N_2 physisorption characterization was carried out on the fresh sorbents as well as on the sorbents following steam exposures to further understand the impact of steam on the sorbents. The results are shown in Table 3; the results for SiO_2 are added for comparison. Addition of PEI to silica resulted in a significant decrease in the surface area (SA) from 279 m^2/g to 53 m^2/g and a decrease in the pore volume (PV) from 1.8 cc/g to 0.43 cc/g. Such an impact upon addition of PEI has also been reported in the literature [21, ~~32~~31]. The decrease in the surface area and pore volume was slightly lower for PEI-Sil-Si. For PEI-Si, the decrease was 81 % in SA and 76 % in PV and for PEI-Sil-Si the decrease was 74 % in SA and 68 % in PV. It has been speculated by Fauth *et al.* [25] that the increase in CO_2 uptake efficiency of silanated sorbents with 3-aminopropyltrimethoxy silane was due to a more uniform dispersion of PEI with silane addition. It has to be noted though that the amount of PEI in particular and organics in general is lower for PEI-Sil-Si than for PEI-Si (40 wt. % vs. 46 wt. %). The lower organic amount may account for the differences seen in the surface area and pore volume between PEI-Si and PEI-Sil-Si, and is also consistent with CO_2 loading being lower for PEI-Sil-Si versus PEI-Si.

Upon steam treatment, the surface area and the pore volume of PEI-Si decreased. The decrease in the BET SA for this sorbent was most prominent when the sorbent was cycled through six steam cycles, whereas a similar decrease is seen for the pore volume, when either the sorbent was exposed to six steam cycles or six steam regenerations. TGA results showed no decrease in the amount of organics on the support consistent with the decrease in the BET SA and PV. These results tend to suggest that a re-agglomeration of the amines on the support occurred resulting in a partial blockage of the pores. The decrease in available amines will thus explain the decrease in CO_2 loading.

However, for PEI-Sil-Si, no significant change was found in the BET SA or PV between the fresh and the spent sorbents. The cause of the loss in the CO_2 capacity for PEI-Sil-Si remains undetermined. It is to be noted once more that all modes of steam addition resulted in a similar impact on the performance of PEI-Sil-Si, unlike in the case of PEI-Si. One possibility that could explain the stability in the N_2-physisorption results despite the decrease in the CO_2 capacity is that steam may have initiated a reaction between PEI and the silane additive resulting in a loss of active CO_2 sorption sites and, therefore, a loss in capacity. More work is required and is being pursued to fully understand the steam impact on silanated amine sorbents.

Regeneration kinetics

To investigate the kinetics of steam regeneration in comparison with dry regeneration, PEI-Si was regenerated after CO_2 sorption under similar conditions as when steam regeneration was used, i.e. at 105 °C, except under dry helium conditions. Comparison of dry and steam regeneration curves (Figure 6-a) shows a qualitative difference between the two modes of regeneration. In order to clarify the impact of steam regeneration, the results were plotted as fractional CO_2 desorbed (amount of CO_2 desorbed at time t (n_t) / amount of CO_2 adsorbed at equilibrium (n_{eq})) and fractional CO_2 desorbed rate in Figure 6-b. The initial regeneration rate is found higher for the dry regeneration mode. However, after approximately 1 minute, the rate of regeneration was higher when steam was present. Specifically, at time t = 2 min, 80 mol. % CO_2 desorbed using steam versus 55 mol. % for the dry regeneration. The rapid desorption of CO_2

under steam conditions can be due to an interaction between the steam sweep and the sorbent. Water, unlike helium and other inert sweep gases, has an affinity to the same amine sites that adsorb CO_2 [32]. Hydrogen bond accepting functionalities of PEI interact with water resulting in a more rapid displacement of CO_2 according to the following reaction (1) [33].

$$R_2NCO_2^- + H_2O \leftrightarrow R_2NH^+CO_2^- + OH^- \leftrightarrow R_2NH + CO_2 + OH^- \qquad (1)$$

The initial proton transfer is rapid and the subsequent CO_2 release is the rate limiting step [33]. The slower initial regeneration with steam can be due to the slow diffusion of H_2O compared to helium and H_2O interaction with the amines via hydrogen bonds. However, water, being a displacer will supplant CO_2 more rapidly than helium [32]. A similar trend was seen for PEI-Sil-SI.

Conclusion

The impact of steam on amine sorbents and silanated amine sorbents was investigated in this work. It was found that the SiO_2 used in this sorbent is stable when exposed to steam as shown by N_2-physisorption and SEM analysis results. The commercial SiO_2 support used in this study will likely prove an adequate support for a suitable amine-based sorbent regenerated with steam. However, steam regeneration was shown to impact the amine-based sorbent studied. It was found that under the conditions of the study, steam regeneration likely caused a re-agglomeration of the amine (N_2-physisorption results) which resulted in a blockage of the pores decreasing therefore the number of sites available for CO_2 adsorption. In this work, leaching was not the cause of the decrease in CO_2 loading of the amines as evidenced by TGA results and LCMS analysis. Longer exposures to steam may however result in leaching of the amines. While steam regeneration did decrease the performance of the sorbent, it also exhibited an improvement in the desorption kinetics of CO_2.

Subjecting PEI-Si to several steam cycles resulted in a decrease in CO_2 uptake, but continuously exposing the sorbent to steam did not have a significant performance impact even though the time of exposure was longer in the case of continuous exposure than the total time of cycling exposure. The results suggest that the drying step impacts the degradation of the sorbent.

Addition of silane to the amine sorbent was not found to improve the stability of the sorbent under steam. Nevertheless, aminopropyl-triethoxysilane addition to the PEI-Si seems to improve CO_2 uptake efficiency of the sorbent and the stability of the BET SA and PV upon steam exposure as measured by N_2-physisorption. The impact of the different modes of steam addition was found to differ for PEI-Sil-Si suggesting a different deactivation mechanism. Work is continuing on the investigation into the silanated sorbent and on understanding the role of the silane.

Figure 1. Schematic of the laboratory scale fixed bed reactor.

Figure 2. Effluent of a typical CO_2 adsorption/desorption cycle under dry conditions, as collected by the mass spectrometer.

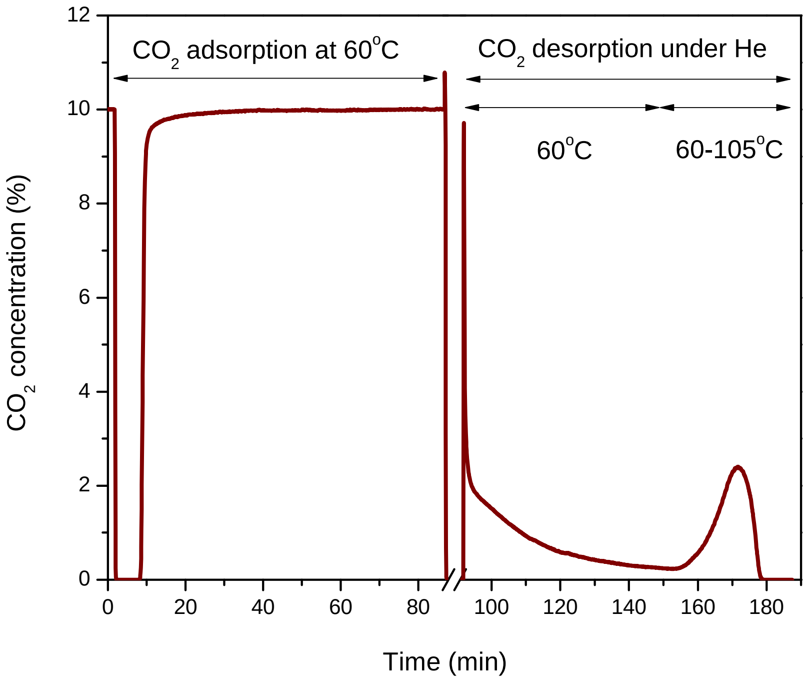


Figure 3. Impact of steam regeneration on the performance of PEI-Si and PEI-Sil-Si. In cycles 1 and 8, the sorbents were regenerated in 100% He using the two steps of regeneration: a pressure swing at 60 °C followed by a temperature swing to 105 °C. In cycles 2 to 8, the sorbents were regenerated in 90 vol. % H_2O/He at 105 °C.

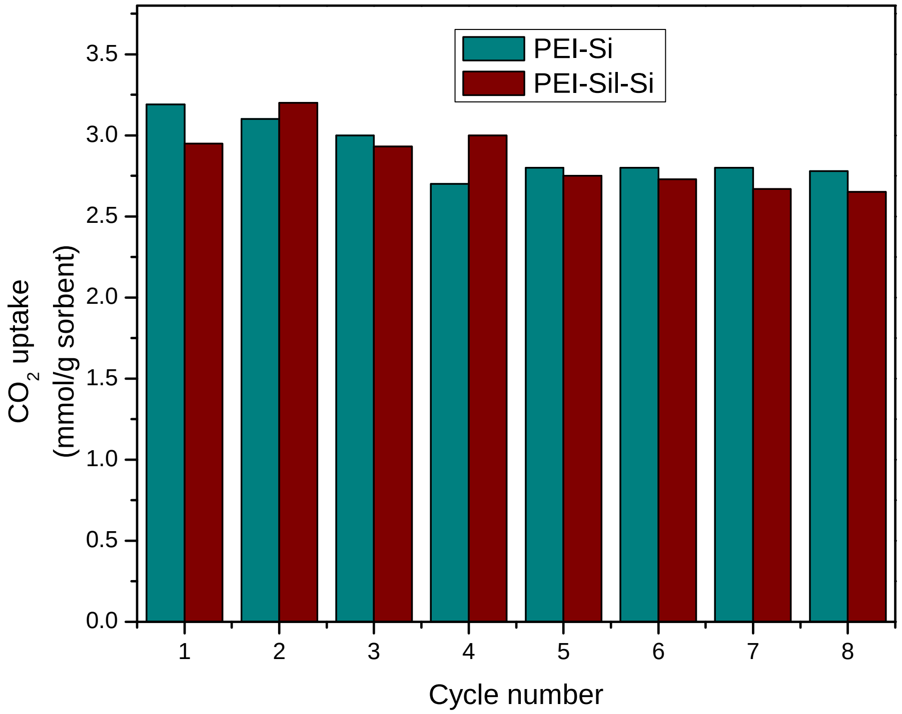
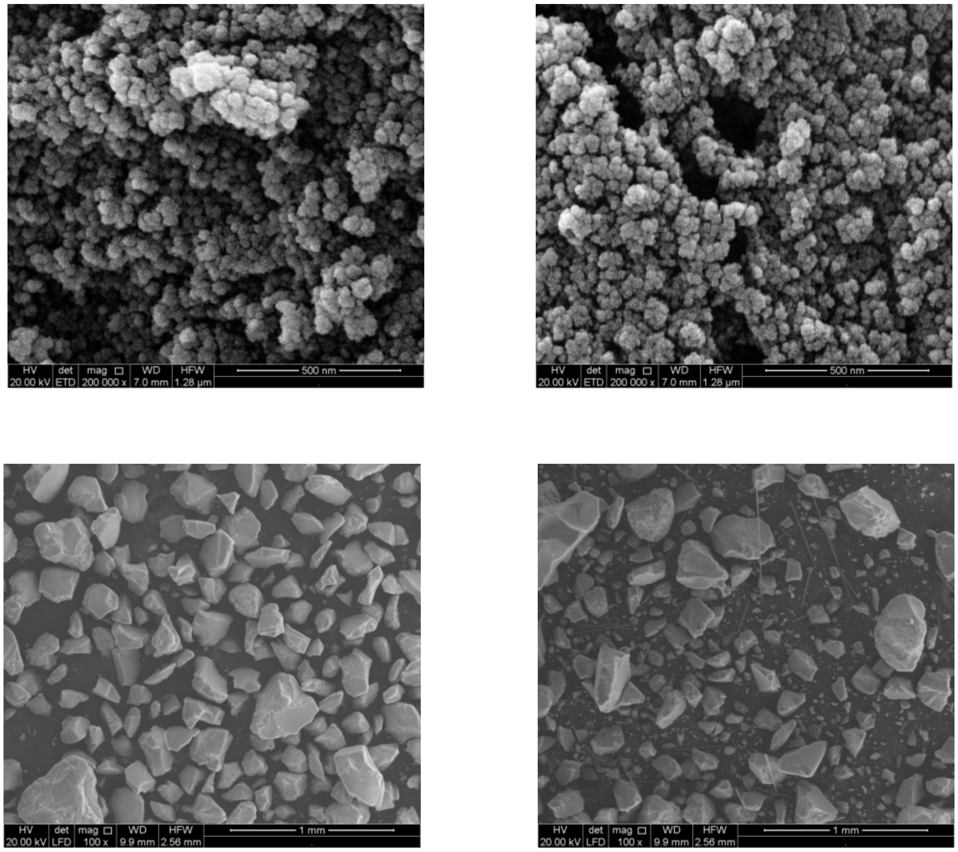


Figure 4. SEM analysis on SiO_2- (a) fresh SiO_2, (b) spent SiO_2. First row images: mag. 200,000. Second row images: mag. 100.



(a) (b)

Figure 5. FT-IR spectra of fresh PEI-Si (top) and spent PEI-Si cycled through six steam cycles (bottom).

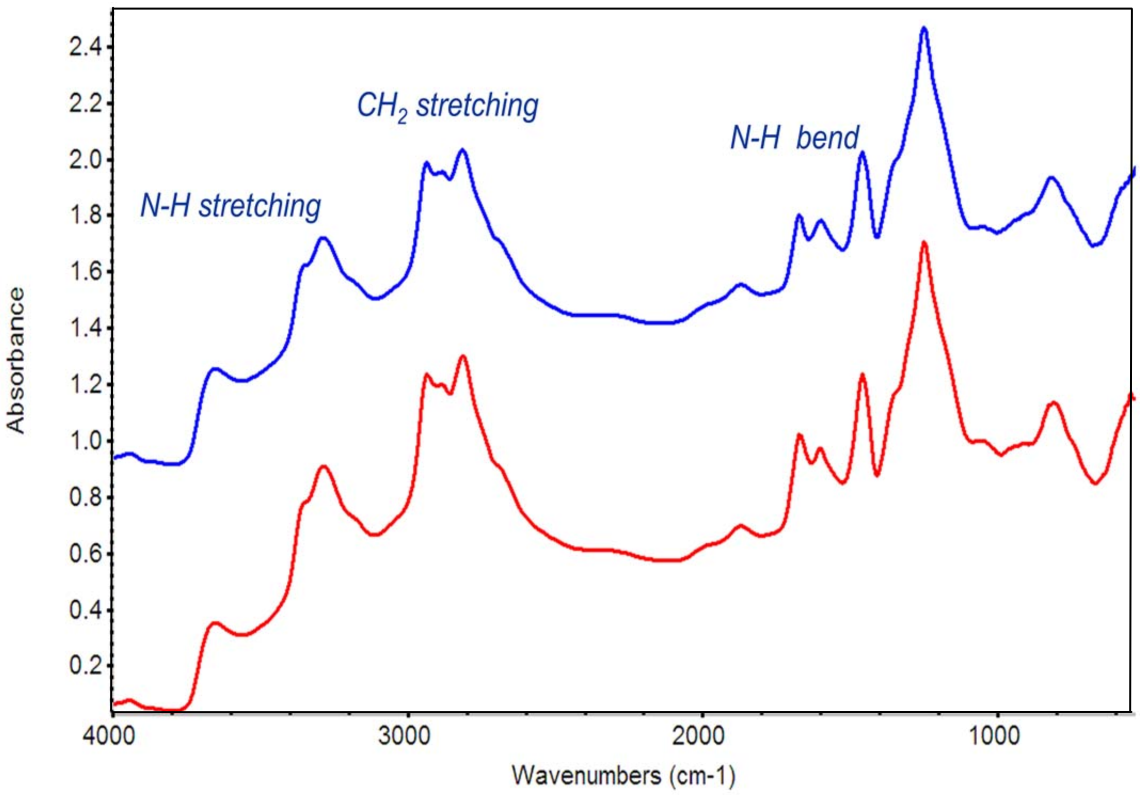


Figure 6. (a) Effluent of desorbed CO_2: comparison of dry vs. steam regeneration at 105 °C on PEI-Si, (b) Comparison of fractional CO_2 desorbed (CO_2 desorbed at time t/ CO_2 adsorbed at equilibrium) and fractional CO_2 desorbed rate (min-1) of PEI-Si: dry vs. steam regeneration.

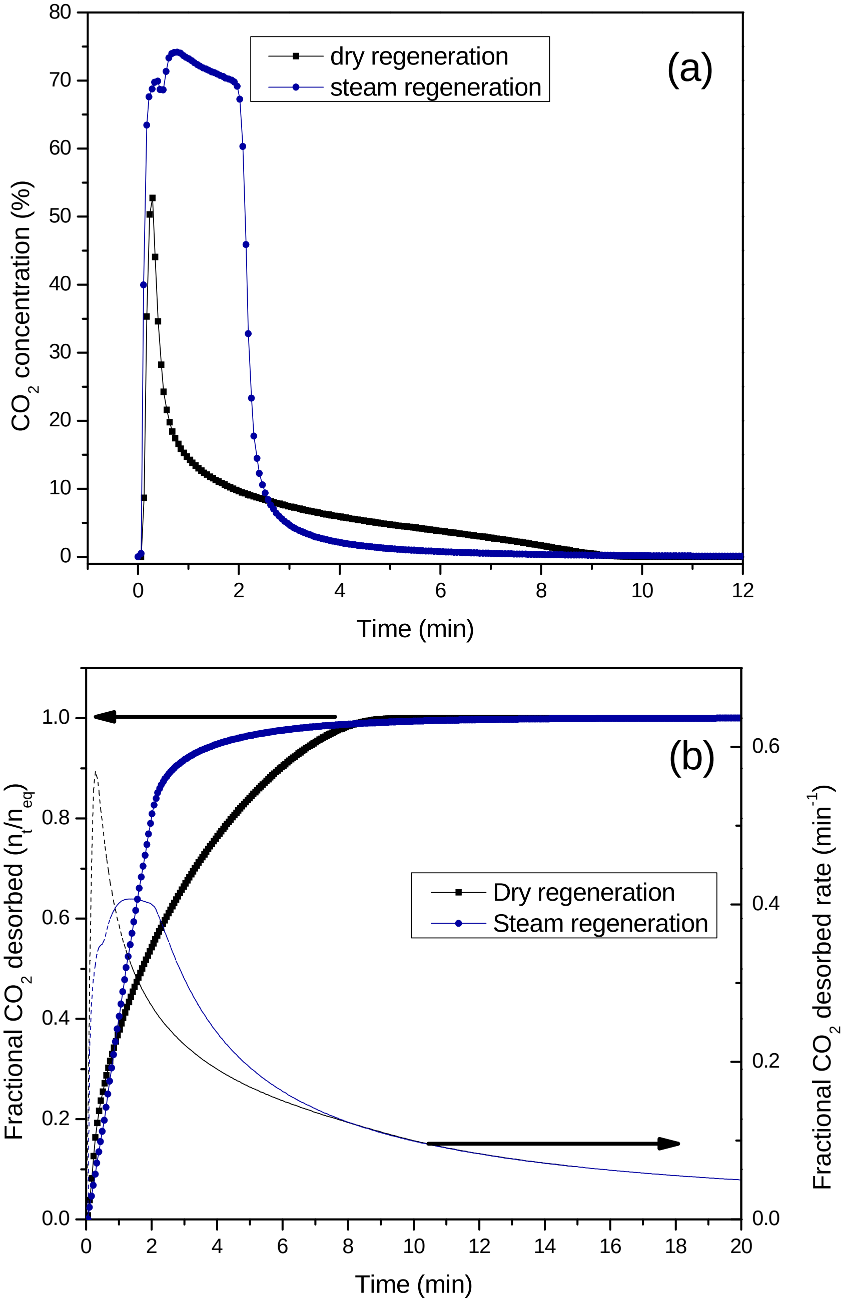


Table 1. Wt. % organics, amine loading, CO_2 loading, and amine efficiency of the PEI-Si and PEI-Sil-Si.

Sorbent	organic wt%	mmolN/gsorbent	CO_2 loading (mmolCO_2/gsorbent)	efficiency
PEI-Si	46	10.73	3.2	0.3
PEI-Sil-Si	39.2	9.10	3	0.33

Table 2. Wt. % organics for fresh and pretreated PEI-Si and PEI-Sil-Si.

Pretreatment	None	5 h steam	6 steam exposures	6 steam cycles
PEI-Si	46	44	46	46
PEI-Sil-Si	39.2	41.4	38.3	40.2

% error:± 5

Table 3. N_2-Physisorption characterization of PEI-Si and PEI-Sil-Si sorbents before and after various steam conditions.

	BET SA (m^2/g)			PV (cc/g)		
Pretreatment	SiO_2	PEI-Si	PEI-Sil-Si	SiO_2	PEI-Si	PEI-Sil-Si
None	279	53	71	1.8	0.43	0.56
6 steam exposures	-	48	65	-	0.32	0.55
6 steam cycles	-	35	73	-	0.28	0.56

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Note

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