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Carbon Dioxide Capture from the Air Using a Polyamine Based Regenerable Solid Adsorbent

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Supporting Information

ABSTRACT: Easy to prepare solid materials based on fumed silica impregnated with polyethylenimine (PEI) were found to be superior adsorbents for the capture of carbon dioxide directly from air. During the initial hours of the experiments, these adsorbents effectively scrubbed all the CO_2 from the air despite its very low concentration. The effect of moisture on the adsorption characteristics and capacity was studied at room temperature. Regenerative ability was also determined in a short series of adsorption/desorption cycles.

The ever increasing consumption of fossil fuels by humankind resulted in an accumulation of carbon dioxide in the atmosphere, from a concentration of 270 ppm before the industrial revolution to more than 390 ppm today. It is now widely accepted that anthropogenic CO_2, due to its role as a greenhouse gas, is the major contributor to climate change. Other environmental implications of these emissions, such as ocean acidification, are also becoming increasingly apparent and worrisome. Thus, CO_2 management is one of the most challenging issues of our century. Capture and sequestration of CO_2 (CCS) underground has been proposed, but none of the existing technologies has been proven on the enormous scale needed. We also need to make sure that if billions of tons of CO_2 are pumped underground it also remains there and does not leak out over time. While fossil fuels will be used for as long as they can be easily and economically produced, it should also be clear that their amounts are finite and that they are increasingly depleted. Post-fossil fuel alternative sources of carbon therefore need to be found to fulfill our needs for fuels, hydrocarbons, polymers, and other products presently derived mostly from petroleum oil and natural gas. Instead of considering CO_2 as a problematic and unwanted combustion byproduct, it should be seen as a valuable feedstock for the production of fuels and materials.[1−3] While the required CO_2 can be presently captured from concentrated industrial sources, eventually it will have to be obtained directly from the atmosphere.[4−8]

The capture of CO_2 from concentrated industrial streams such as exhaust gases of coal burning power plants, cement or aluminum factories, and fermentation plants has gained a lot of attention and has been well described in recent publications.[9−13] While about half of the anthropogenic CO_2 emissions are the result of large industrial sources such as power plants and cement factories, the other half originate from small distributed sources such as cars, home heating, and cooking.[14] For those, CO_2 capture at the emission source is not practical and/or economical. A possible pathway to deal with these emissions is to capture CO_2 directly from the air. One of the advantages of CO_2 capture from the atmosphere is that the needed infrastructure can be placed anywhere, preferably where it has the least impact on the environment and human activities or close to CO_2 recycling centers.

CO_2 capture from the air has not been studied extensively, and data on this subject are still limited. Practical applications have been developed for the essential removal of CO_2 from submarines and spacecrafts.[15,16] However, the separation and recovery of CO_2 from ambient air on a larger scale is still in its infancy and has only relatively recently attracted increased interest.[17] Adsorbents based on $Ca(OH)_2$,[18] NaOH,[19−23] and combinations thereof have been suggested, but their regeneration is generally energy intensive. Amine and polyamine based sorbents either chemically bound[24−29] or physically adsorbed[30−35] on a support such as silica, mesoporous solids (MCM-41, MCM-48, SBA-15), and carbon fibers have also been proposed and in some cases tested for CO_2 capture from the air.[36−39] More recently hyperbranched aminosilicas (HAS) prepared by in situ aziridine polymerization on porous solids have been reported as adsorbents for CO_2 capture from the air.[40,41]

Aqueous solutions of primary and secondary amines such as mono- and diethanolamine are used on a large scale to capture CO_2 from industrial streams due to their ability to chemisorb acidic gases like CO_2. In regard to corrosion and degradation issues, these amines are generally used in only 20 to 30% concentration in water. Therefore, a major drawback of the solution state CO_2 capture is the high heat capacity of these aqueous solutions, making the endothermic regeneration step (stripping) very energy intensive and costly. These amines are also more suitable for the capture of CO_2 from gas mixtures, which are practically oxygen free or contain a low concentration of oxygen since these groups of amines tend to degrade over time.[42,43] To lower the energy cost, amines and polyamines deposited on solid supports have been proposed as an alternative to aqueous solutions. Polymeric amines and polyethylenimines (PEIs) in particular have attracted much attention. The reaction of PEI with CO_2 is represented in

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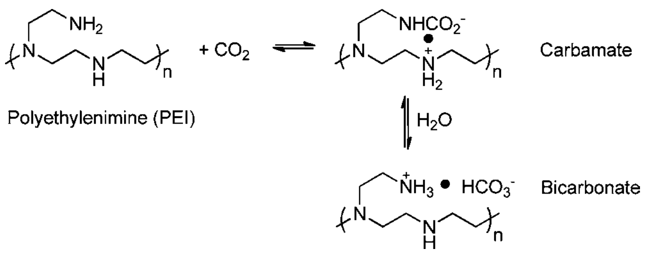
Scheme 1. The repeating unit of the polymer in this scheme is only a simplified model representation showing the three different types of amines present in PEI. The primary and secondary amino group in PEI react with CO_2 to form carbamates. In the presence of water these carbamates can react further to form a bicarbonate species. Following our previous study on PEI impregnated on fumed silica and precipitated silica,[30] we present here our work on the preparation, characterization, and preliminary study of the properties of a silica−organic hybrid adsorbent for CO_2 capture from air.

Scheme 1. Reaction of CO_2 with Amines



We selected branched PEI with a high molecular weight (M_w = 25 000) as an adsorbent material in large part because of its very low volatility. PEI was coated on the surface of fumed silica (FS, Aerosil 380) by mixing it with a methanol solution of PEI followed by evaporation of the solvent. Samples with PEI loadings of 33 and 50 wt % were prepared and labeled FS-PEI-33 and FS-PEI-50, respectively. The Brunauer−Emmett−Teller (BET) method was used to measure the surface area of these samples whereas the total pore volume was determined according to the Gurvitch rule. The physical properties of these adsorbents are provided in Table 1. Not surprisingly, the coating of PEI significantly reduced the surface area of the silica-PEI hybrids compared with the bare fumed silica (329 m^2/g) as can be seen in Table 1. Increasing PEI content lead to a decrease in surface area from 79.9 m^2/g with FS-PEI-33 to 27.2 m^2/g for FS-PEI-50. A similar trend in pore volume was also observed. However, compared to other PEI-based adsorbents on mesoporous supports such as MCM-41[32] or PE-MCM-41,[44] which had surface areas of about 4.5 m^2/g and essentially no porosity for PEI loadings of 50%, the fumed silica based adsorbent still had a relatively high surface area of 27.2 m^2/g for a similar loading and a pore volume of 0.401 cm^3/g. Interestingly, the pore volume measured for the FS-PEI-33 was higher than that for the support itself. This could be due to the fact that fumed silica does not have a defined structure as mesoporous solids such as MCM-41 or SBA-15 but is composed of small particles that form agglomerates with large meso- and macropores. Because of inherent limitations of the N_2 physisorption method, the largest macropores (> ∼200 nm) might not all be accounted for. When PEI is then added to fumed silica, the size of these larger macropores diminishes and falls into the measuring range of the method used (< ∼200 nm), explaining an apparently higher pore volume.[45]

Table 1. Properties of PEI/Fumed Silica Based Adsorbents

PEI content in FS-PEI (%)	Surface area (m^2/g)	Volume of pores (cm^3/g)	CO_2 Adsorption from air (mg/g)	
			Dry condition	Humid condition
0	329	0.908	–[a]	–[a]
33	79.9	1.057	52	78
50	27.2	0.401	75	62

[a] Negligible.

The CO_2 adsorption and desorption measurements were performed in an all-glass, grease-free flow system. The adsorbent, typically 3 g, was packed in a U-shaped glass tube placed in a temperature controlled oil bath. Prior to adsorption measurements the adsorbent was heated to 85 °C under vacuum at a pressure of 65 mTorr for 3 h to remove adsorbed CO_2 and water. The weight loss due to desorption of water and CO_2 was generally between 2 and 10% (see Supporting Information). The weight of the sample after treatment was used to calculate the CO_2 adsorption capacities. For the adsorption tests, ambient air from the laboratory, dried over silica gel, was passed over the adsorbent at a rate of 335 mL/min at 25 °C. The CO_2 concentration of air before and after adsorption was monitored with a Horiba VIA-510 CO_2 analyzer (infrared gas cell) and recorded using LabView 8.6.

Figure 1 represents the results obtained for the CO_2 adsorption at 25 °C on FS-PEI-50. The first segment of the curve shows the CO_2 concentration of the air when the adsorbent was bypassed (420 ppm). After opening of the flow to the adsorbent, complete adsorption of CO_2 was observed with a CO_2 concentration close to 0 ppm. After this initial adsorption period, the adsorbent started to get saturated and a slow increase in CO_2 concentration in the outlet gas was observed until complete saturation. From 0.6 to 7.1 h, when the outlet gas was practically CO_2-free, 2.39 mmol of CO_2 were removed from the air. An additional 2.25 mmol of CO_2 were adsorbed during the partial CO_2 removal period until complete saturation. A total of 4.64 mmol of CO_2 were thus adsorbed from ambient air by 2.72 g of adsorbent, representing 1.71 mmol CO_2 per g or 75 mg CO_2 per g of adsorbent.

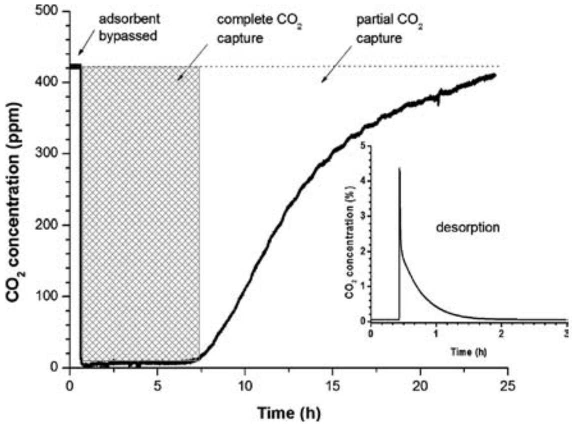


Figure 1. Adsorption of CO_2 from the air at 25 °C on FS-PEI-50. Inset: Desorption at 85 °C.

Ideally, CO_2 adsorbents should be regenerable, meaning that they should be able to undergo numerous adsorption/desorption cycles without noticeable loss in adsorption capacity. The endothermic regeneration step needs to be performed under relatively mild conditions to avoid excessive energy use. To test its regenerability, the FS-PEI-50 adsorbent previously used for CO_2 adsorption from air was heated under vacuum at 85 °C for 3 h combining pressure and temperature swings. The adsorbent was then used again for CO_2 adsorption from the air. These adsorption/desorption cycles were repeated four times with no noticeable decrease in adsorption capacity. The total CO_2 adsorption capacity varied from 73 to 75 mg CO_2/g adsorbent (1.65 to 1.71 mmol/g). At the same time, between 34.7 and 38.6 mg CO_2/g were adsorbed during the initial period, where complete CO_2 adsorption from the air was observed.

Another method of regeneration was also tested in which the adsorbent was submitted to a temperature-swing desorption of the adsorbed gases at 85 °C in the presence of 335 mL/min dry air. The CO_2 concentration of the output gases as a function of time is given in Figure 1 (inset). The CO_2 concentration shows an initial maximum value of 4.34%. In 1 h, essentially all the CO_2 was desorbed. Following this desorption step, an adsorption step gave an adsorption of 75 mg/g, the same as in the first run. This indicates that the PEI coating did not significantly degrade in the presence of oxygen at 85 °C. However, studies with numerous adsorption/desorption cycles are needed to assess the long-term stability of PEI under these conditions. The low regeneration temperature allows the use of low value "waste heat" readily available in many industrial processes. Heat from the sun could also be used, making a practical application of these adsorbents more promising.

It has been shown that the presence of water generally increases the CO_2 adsorption capacity of amines by allowing the formation of bicarbonates (see Scheme 1).[38,44,46] In this case, only one amino group is necessary for every CO_2 molecule instead of two in the case of carbamate formation in the absence of water. A similar effect was expected for FS-PEI-50. However, when experiments were conducted at 25 °C with a relative humidity (RH) of 67% in the gas flow, no positive effect could be detected. On the contrary, the total adsorption capacity decreased somewhat to 62 mg CO_2/g.

Under similar conditions, humidity had a substantial promoting effect on an adsorbent with lower PEI content, namely FS-PEI-33. Using this adsorbent, an adsorption of 78 mg CO_2/g could be achieved at an RH of 67%. This represents 1.74 mmol CO_2/g. Interestingly, under dry conditions, FS-PEI-33 adsorbed less than FS-PEI-50, 52 vs 75 mg CO_2/g, as shown in Table 1. The initial period during which all the CO_2 in the gas is adsorbed was however longer for the adsorbent containing less PEI (8.3 h). This initial period was followed by a much faster rate of saturation of the adsorbent than observed for FS-PEI-50 as can be seen in Figure 2. The difference in behavior could be explained by gas diffusion into the adsorbents. With a lower loading in PEI, the polymeric amine is better dispersed on the surface of the support, allowing an easier access to amino groups for the incoming gases. At higher loadings, a larger part of the amino groups in PEI might not be as accessible due to a poorer dispersion on the support's surface and agglomeration of the coated particles. The BET data showing a surface area of 27.2 and 79.9 m^2/g for FS-PEI-50 and FS-PEI-33, respectively, support this explanation. So does the pore volume, decreasing from 1.057 cm^3/g for FS-PEI-33 to 0.401 cm^3/g for FS-PEI-50. This would also explain why the time needed for saturation of the adsorbent is much longer for the adsorbent with a higher PEI loading where the reaction is more diffusion controlled. Water might have a detrimental effect on the adsorbent with higher PEI content by blocking the access to some of the already difficult to reach amino groups. So, although the adsorbent contains more amino groups, the CO_2 adsorption is more effective on the adsorbent containing less but better dispersed PEI. Under dry conditions, on FS-PEI-33 the amount of CO_2 adsorbed per g of PEI was 156 mg/g, whereas it was 150 mg/g for FS-PEI-50. In the presence of water, these values were 230 and 124 mg CO_2/g PEI, respectively. PEI use was almost two times more efficient at a lower loading. A similar trend was already reported in the case of adsorption of pure CO_2.[30]

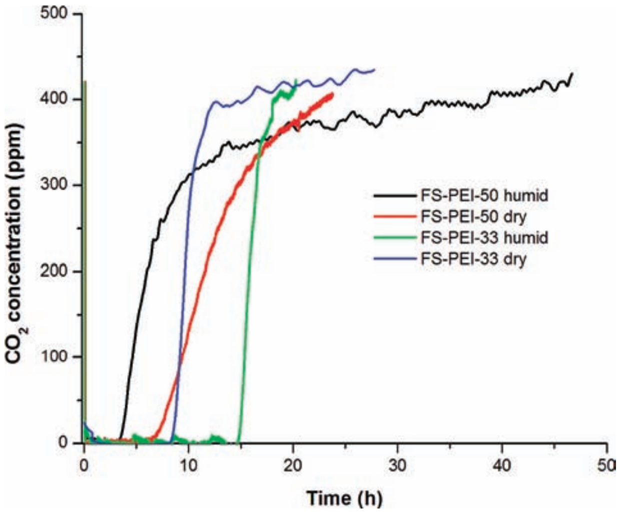


Figure 2. Adsorption of CO_2 from the air at 25 °C on FS-PEI-50 and FS-PEI-33 under dry and humid conditions.

Our reported values under humid conditions are among the highest reported for CO_2 adsorption from the air! The 1.74 mmol/g adsorption of FS-PEI-33 obtained under humid conditions was noticeably higher than the one reported for a hyperbranched aminosilica (1.44 mmol/g) with a comparable organic amine content of 36% and closer to the ones obtained on an HAS with a higher organic content of 42.5% (1.72 mmol/g).[40,41] Triamine-grafted pore-expanded mesoporous silica (TRI-PE-MCM-41), on the other hand, exhibited a CO_2 adsorption capacity of 0.98 mmol/g.[37] Operating under humid conditions has a further advantage: Recently, the presence of water has been shown to greatly improve the stability of solid amine based adsorbents by avoiding the formation of urea.[44]

The novel PEI on fumed silica adsorbents used here are solids, which are easy to prepare from readily available materials. They are able to reversibly adsorb CO_2 under mild conditions in repeated cycles and represent promising candidates for the capture of CO_2 from dilute sources and especially from the atmosphere. They can operate under both dry and humid conditions. The fact that they can be used under humid conditions is an advantage compared to zeolites, which lose most of their CO_2 adsorption capacity in the presence of water. They could be utilized to purify gas streams from CO_2 in submarines and other closed environments as well as for applications such as alkaline fuel cells for which it is important to have an air source free of CO_2 to avoid the formation of carbonates by reaction with a strongly basic electrolyte (generally NaOH or KOH). The supply of CO_2-free air is equally important for inexpensive and robust iron-air batteries being currently developed in our laboratory for large scale energy storage in grid applications, which also necessitate basic electrolytes for their operation.

Being a solid adsorbent, FS-PEI avoids many of the problems associated with existing CO_2 separation technologies relying on liquid amine based scrubbers. Clearly, adsorbents based on supported amines are promising inexpensive materials for the capture of CO_2 from the atmosphere and warrant further studies.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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