Application of Polyethylenimine-Impregnated Solid Adsorbents for Direct Capture of Low-Concentration CO_2

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A systematic study of CO_2 capture on the amine-impregnated solid adsorbents is carried out at CO_2 concentrations in the range of 400–5000 ppm, relating to the direct CO_2 capture from atmospheric air. The commercially available polymethacrylate-based HP2MGL and polyethylenimine are screened to be the suitable support and amine, respectively, for preparation of the adsorbent. The adsorbents exhibit an excellent saturation adsorption capacity of 1.96 mmol/g for 400 ppm CO_2 and 2.13 mmol/g for 5000 ppm CO_2. Moisture plays a promoting effect on CO_2 adsorption but depends on the relative humidity. The presence of O_2 would lead to the decrease of adsorption capacity but do not affect the cyclic performance. The diffusion additive is efficient to improve the adsorption capacity and cyclic performance. Moreover, the adsorbents can be easily regenerated under a mild temperature. This study may have a positive impact on the design of high-performance adsorbents for CO_2 capture from ambient air. © 2014 American Institute of Chemical Engineers *AIChE J*, 61: 972–980, 2015

Keywords: CO_2 capture, polyethylenimine, adsorption, resin, low-concentration CO_2

Introduction

Extensive consumption of fossil fuels in modern industrial society has caused a sharp growth of anthropogenic CO_2 emission from 280 to over 390 ppm, which is considered to be a primary factor in global climate change.[1] CO_2 capture from concentrated industrial sources 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.[2–7] Although 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.[8,9] For those, CO_2 capture at the emission source is not practical and economical. A possible pathway to deal with these emissions is to capture CO_2 directly from air, called direct air capture (DAC), which was first proposed by Lackner et al. in 1999.[10] In the long term, DAC may become indispensable for stabilizing the global CO_2 concentration due to the flexibility of the needed infrastructure, which can be placed anywhere.

In addition, efficient and cost-effective removal of low-concentration CO_2 is of great importance in various applications pertaining to energy, environment, and health. From an industrial perspective, the removal of low-concentration CO_2 from air is a growing area of research and development due to its substantial importance for prepurification of air and particularly when atmospheric air is used during the separation of nitrogen and oxygen.[11] Furthermore, in personal confined spaces such as submarines and aerospace shuttles, it has a common requirement to remove CO_2 created by the metabolic processes of the crew. The CO_2 concentration in such closed spaces is typically below 5000 ppm.[12–15] Moreover, efficient CO_2 removal is also critical in mining and rescue missions,[16] diving and most importantly in medical applications such as anesthesia machines.[17] The use of anesthesia machines is still a growing clinical trend worldwide, driven by the need to reduce cost and improve patient care via the use of efficient CO_2 adsorbents. Evidently, there is a pressing need to develop novel adsorbents that can adequately address the growing interest in low CO_2 concentration removal applications.

For trace or low CO_2 concentration removal, a potential adsorbent should combine cost effeiency, optimum uptake, kinetics, energetics, and CO_2 selectivity at trace CO_2 concentration in the presence of humidity. Many classical CO_2 separation processes such as chemical absorbent, cryogenic distillation, and membrane separation are not expected to be economically favorable. The well-studied approaches utilize metal hydroxides or oxides (Ca, Na, etc.) and their conversion into metal carbonates, either in solution or as solids. In general, the regeneration of the carbonate into the original oxide or hydroxide has proven to be quite energy intensive, resulting in high projected energy use and process costs.[18–22] Conversely, physical adsorbents, such as zeolite molecular sieves and activated carbons, can reversibly trap CO_2 by either ion–quadrupole interaction or van der Waals force. The main drawbacks are the quite low heat of adsorption for these materials, leading to shallow adsorption isotherms with

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low adsorption capacities at ultralow pressures. In addition, the presence of water will detrimentally affect the selectivity for CO_2.[23–25]

In recent years, intensive research has focused on the technologies for adsorbing traces of CO_2 using a variety of solid amine adsorbents. The solid amine adsorbents based on primary, secondary, or tertiary amines operate near ambient conditions, are tolerant to water vapor and can be regenerated by mild temperature swings.[2,4] There are three classes of such adsorbent materials: (1) amines covalently bound to the support via the use of grafting chemistry, (2) polymer amines physically impregnated into the support by a "wet impregnation" method, and (3) in situ polymerization of reactive amine monomers on and in the silica support.[26] A variety of solid amine adsorbents have been proposed to take into account their support structure and composition, the type of amine and adsorption capacity. The supports are widely screened including silica materials,[27–35] microporous metal-organic framework,[36,37] carbon nanotubes,[38,39] PMMA-based resins,[15,40] mesoporous carbon,[41,42] mesoporous alumina,[43] and nanofibrillated cellulose.[44,45] The amines generally contain primary or secondary alkylamines and alkanolamines, such as polyethylenimine (PEI),[46–48] tetraethylenepentamine (TEPA),[49–51] and 3-aminopropyltrimethoxysilane.[52] Futhermore, hyperbranched aminosilicas prepared by in situ aziridine polymerization on porous solids have been reported as adsorbents for CO_2 capture from the air.[53,54] Although some valuable progress has been made in CO_2 capture from the ambient air recently, most of the discussion has been based on advancing the support or the amine rather than on a systematic investigation of the process based on kinetic and thermodynamic CO_2 adsorption/desorption process. Moreover, for the design of DAC systems featuring such solid amine adsorbents, detail understanding of the multiple-component adsorption containing N_2, O_2, CO_2, and H_2O is crucial because of the humid and O_2-containing air.

The objective of this work was to systematically study the direct low-concentration CO_2 adsorption behavior of the solid amine adsorbents. The effects of the supports, the types of amines, and loading amount of amine on the CO_2 adsorption capacity were examined to screen the optimized adsorbents. Several macroporous resin supports and polymer amines were selected for the initial studies, and the best performing candidates were further characterized. The CO_2 concentration was investigated to ascertain how the CO_2 concentration affected the steady-state CO_2 adsorption capacity. The desorption behavior was also assessed to build a proper regeneration strategy for dynamic adsorption using fixed-bed columns. Special investigations were focused on the influence of moisture and oxygen in the inlet air on the CO_2 adsorption capacity of the solid amine adsorbents. All materials used in our study are commercially available and the preparation is straightforward, which provide a great potential for trace and low CO_2 concentration removal in general and DAC application in particular.

Experimental

Materials

PEI used in this study was purchased from Aldrich with an average molecular weight of 600 $g \cdot mol^{-1}$. Low molecule amines, including diethanolamine (DEA), diethylenetriamine (DETA) and TEPA, and PEI with molecular weight of 1800 and 10,000 $g \cdot mol^{-1}$ purchased from Sigma-Aldrich Company were used to investigate the effect of amines on the CO_2 adsorption capacity. Five commercial resins, including HP2MGL, SP700, SP835L, D4020, and D3520 purchased from Sigma-Aldrich Company were used to screen the suitable support. The resins were first sieved to collect the fraction in the range of 35–60 mesh (0.25–0.43 mm) and then dried at 100°C for 12 h until no weight loss observed to remove the adsorbed water. Three additives, including cetyltrimethylammonium bromide (CTAB, Aldrich), sorbitan monooleate (Span80, Sinopharm), and polyethylene glycol (PEG, Aldrich) were used to investigate the promotional performance of the adsorbents.

The adsorbents were prepared by a wet impregnation method.[55] In a typical preparation, the desired amounts of PEI ($Mw = 600$) were dissolved in 10 g of methanol at 40°C under stirring for 30 min, and then 2 g of the support was added to the above solution and further stirred for 8 h. The slurry was then dried with continuous stirring at 40°C to remove methanol. Then, the adsorbents were dried at 80°C for 12 h under vacuum conditions. The as-prepared adsorbent was denoted as M-a, where M represents the type of resin and a represents the weight percentage of amine in the adsorbent. In addition, to overcome the limitation of the kinetic diffusion, diffusion additives were used, and the samples obtained were denoted as M-R-a-b, where R represents the type of additive and b represents the weight percentage of additive in the adsorbent (PEI + additive + support).

Characterization of the adsorbents

Nitrogen adsorption/desorption isotherms were measured at 77 K with a Quadrasorb SI analyzer. Before the measurements, the samples were degassed in vacuum at 100°C for 12 h. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface area. The pore size distributions were derived from desorption branch using the Barrett–Joyne–Halenda model. The morphologies of the samples were observed by scanning electron microscopy (FEI, Qunta 300).

CO_2 capture measurement

CO_2 Adsorption from Pure CO_2. CO_2 adsorption from pure CO_2 at 0.1 MPa under dry conditions was performed on a TA Instruments Q600 TGA thermogravimetric analyzer. Pure CO_2 (99.99%) was used for the adsorption runs, and purity N_2 (99.999%) was used as a purging gas for CO_2 desorption. In a typical process, about 10 mg of the adsorbent was placed in a platinum sample pan. Before the adsorption test, the adsorbents were pretreated at 100°C under a N_2 flow at 50 $mL \cdot min^{-1}$ for 100 min to remove the moisture and adsorbed CO_2 as much as possible; then the temperature was decreased to the design temperature. The gas was then switched from N_2 to CO_2 (50 $mL \cdot min^{-1}$), and the adsorbent was held at that temperature for 100 min for the adsorption study. The CO_2 capture capacity of the adsorbent in $mmol \cdot g^{-1}$ was calculated from the weight gain of the adsorbent in the adsorption process.

CO_2 Dynamic Adsorption Capacity. The dynamic CO_2 adsorption performance from gas mixtures with different CO_2 concentrations on the adsorbents was conducted in a fixed-bed adsorber operated at a specified temperature. In a typical adsorption process, about 1 g of the adsorbent was

packed in the middle of the adsorber supported with quartz wool. Before the adsorption test, the adsorbent was treated under a N_2 flow of 50 mL/min for 100 min, and then the dry or moist CO_2 (99.99%)/N_2 (99.995%) gas mixture with a certain CO_2 mole fraction was introduced through the tube at a flow rate of 50 mL/min. The flow rate of the gas was controlled by electronic flow control instrument. Therein, the N_2 flow was controlled by two electronic mass flow controllers. One of the N_2 streams was passed through a bubbler-type humidifier contained in a water bath at constant temperature and mixed with the dry gas stream. The relative humidity (RH) of the gas was, thus, controlled by adjusting the ratio of the two streams. RH was measured upstream and downstream of the reactor with electronic sensor. The CO_2 concentration in the influent and effluent gas streams was analyzed at regular intervals, using a gas chromatogram (Shimadzu GC-2014) equipped with a thermal conductivity detector. The adsorption capacity of the adsorbent was calculated by integration of the area above the breakthrough curve and from the CO_2 concentration in the inlet gas, flow rate, adsorption time, and mass of the adsorbent.[55] Q_s represents the saturation adsorption capacity calculated at the saturation time when the outlet concentration is equal to the inlet concentration, while Q_b represents the breakthrough adsorption capacity calculated at the breakthrough time when the outlet concentrations are 5% of the inlet concentration. The effect of O_2 was performed using the feed gas with O_2 concentration of 20.5%. A void space correction was applied for each measurement, in which the breakthrough curve within the system on the valve change and the analyzed change was measured. This correction was derived from separate experiment in which an inert support with an equivalent bulk density to the adsorbent was placed within the fixed bed. The obtained void space adsorption capacity calculated from the breakthrough curve was deducted from the measured adsorption capacity from the dynamic CO_2 adsorption experiment to achieve the CO_2 adsorption capacity. For the CO_2 desorption, the sample was rapidly heated up to a specified desorption temperature under a N_2 flow of 50 mL/min in the fixed bed, followed by holding at the desorption temperature for 120 min. The desorption profiles were gained by analyzing the effluent gas streams using the gas chromatogram at regular intervals. The desorption capacity of the adsorbents were calculated by integration of the area under the desorption profiles and from the flow rate and mass of the adsorbent. The adsorption–desorption cycles were repeated five times to trace the changes of the adsorption capacities.

Results and Discussion

Screening of the supports for the solid amine adsorbents

Macroporous adsorptive resins are commonly used adsorption materials with spherical shape and thermal stability which can be directly used in the fixed bed without any shaping process. Especially, owing to the unique and developed porous structure, the polymer amine could be dispersed into the open framework of the resin at nanoscale dimensions, affording a high gas/amine interfacial area. To screen a suitable support for the CO_2 adsorbents, five commercially available resins derived from two different monomers (polymethacrylate: HP2MGL; polystyrene: D4020, D3520, SP835L, and SP700) were studied. As shown in Table 1, all the resins have total pore volume in the range of 1.2–1.5 $cm^3 \cdot g^{-1}$ for amine loading (here, we used PEI as the referenced polymer amine). After 50 wt. % amine loading, the porosity decreases greatly as a result of a large number of amine molecules filling the pores, however, the adsorbents still maintain a certain amount of porosity and interfacial area, being favorable for CO_2 kinetic diffusion and adsorption. Notably, although SP835L and SP700 have relatively high pore volume and BET surface area, their amine-impregnated derivatives show much low pore volume and surface area. This should be due to the relatively small pore diameter for SP835L and SP700, causing some pore blockages during amine impregnation.

Table 1. Structural Parameters of the Resin Supports and Their PEI-Impregnated Adsorbents

Samples	S_{BET}[a] (cm^2/g)	V_t[b] (cm^3/g)	D_p[c] (nm)
HP2MGL	607.0	1.37	23.6
HP2MGL-50	34.4	0.15	24.8
D4020	399.4	1.30	26.9
D4020-50	32.0	0.19	28.4
D3520	459.4	1.38	27.4
D3520-50	49.5	0.28	29.1
SP835L	1000.5	1.49	12.4
SP835L-50	15.2	0.04	11.2
SP700	1011.8	1.51	13.2
SP700-50	21.8	0.09	11.9

[a] BET surface area.
[b] Total pore volume.
[c] BJH desorption average pore diameter.

The adsorption capacities of these adsorbents were preliminarily evaluated using TGA at different temperatures. As shown in Figure 1, the temperature-relevant adsorption capacities of the adsorbents are obviously dependent on the residual porosity of the adsorbents. At a low temperature, to overcome the kinetic resistance for CO_2 diffusion is a prerequisite for effective CO_2 adsorption. Thus, holding certain gas/sorbent interfacial area, the adsorbents such as HP2MGL, D4020, and D3520 have a high adsorption capacity at a low temperature, which favors for the ambient adsorption and the regeneration by mild temperature swings. In the case of SP835L and SP700 with low residual pore volume and surface area, the CO_2 adsorption is a kinetic

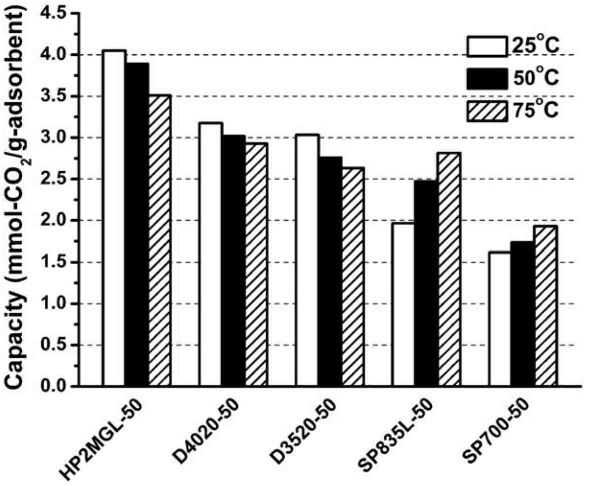

Figure 1. Pure CO_2 adsorption capacity of different supports loaded with 50 wt. % PEI.

The data were from TGA with pure CO_2 gas at 25°C and 0.1 MPa.

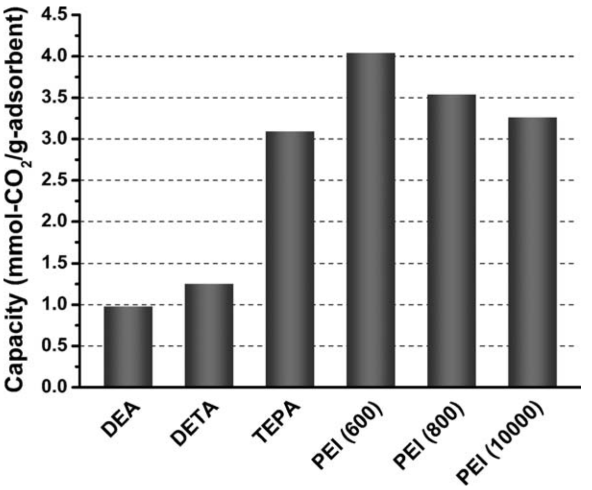

Figure 2. Pure CO_2 adsorption capacity of adsorbents loaded with 50 wt. % different amines.

The data were from TGA with pure CO_2 gas at 25°C and 0.1 MPa.

control process which could be facilitated at a higher temperature. Therefore, the adsorption capacity increases with the increasing temperature, contrary to the other three supports. Among these supports, HP2MGL-based adsorbents exhibit the largest CO_2 adsorption capacities, making them the best candidate.

Effect of amines on CO_2 adsorption

The type of the amines was further screened via TG analysis at 25°C using HP2MGL as support. As presented in Figure 2, the PEI with an average molecular weight of 600 shows the highest adsorption capacity compared to the low molecule amines such as DEA, DETA and TEPA, and high-molecular-weight PEI. The PEI with higher polymerization degree should have large steric hindrance and low fluidity, restraining the internal diffusion of CO_2 and lowering the amine utilization. Conversely, HP2MGL impregnated with low molecule amines (DEA, DETA, and TEPA) have relatively low CO_2 adsorption capacities owing to the weak interaction between the amines and CO_2 or the weak thermodynamic stability of amines.

Effect of the PEI loading on CO_2 adsorption

After the best performing support and amine were screened, the PEI loading amount was optimized to achieve high performance of the HP2MGL-PEI adsorbents. Before testing the adsorption capacity, the porosity of the adsorbents with different PEI contents were investigated by N_2 adsorption and summarized in Table 2. Obviously, the increase of the PEI loading could occupy more mesoporous channels of the support, leading to the decrease of the surface area and pore volume of the adsorbents. Although PEI loading is up to 65 wt. %, no porosity is detected, indicating the complete filling of the mesoporous channels. The CO_2 adsorption capacities at 25°C of these adsorbents were examined by TGA, and the results are shown in Figure 3. The support alone has negligible CO_2 adsorption capacity of ~0.1 mmol·g^{-1}. With the increase of PEI loading, the adsorption capacity gradually increases and achieves a maximum of 4.05 mmol·g^{-1} with an amine utilization of 69% for 50 wt. % PEI loading. With further increase of PEI loading, the adsorption capacity greatly decreases due to the clog of the mesoporous channel, and thus, resisting the further inner diffusion of CO_2 in the PEI films. Many studies have concentrated on the removal of CO_2 at the ambient temperature. Zeleňák et al.[56] demonstrated that support with large pores had a high CO_2 adsorption capacity while three-dimensional accessibility of amine sites inside the pores resulted in faster CO_2 adsorption. Heydari-Gorji et al.[48] reported that at low temperature, adsorbents with relatively low PEI contents were more efficient than their highly loaded counterparts because of the increased adsorption rate. Some typical PEI-modified materials used for CO_2 adsorption at ambient temperature reported in the literatures to date are summarized in Table 3. Under similar conditions, HP2MGL-50 could provide higher adsorption capacity and amine efficient than other PEI-modified adsorbents reported.

Table 2. Structural Parameters of the Support and the PEI-Impregnated Solid Adsorbents

Samples	S_{BET}[a] (cm^2/g)	V_t[b] (cm^3/g)	D_p[c] (nm)
HP2MGL	607.0	1.37	23.6
HP2MGL-30	94.6	0.70	27.1
HP2MGL-40	50.1	0.46	28.6
HP2MGL-50	24.4	0.15	24.8
HP2MGL-60	10.3	0.02	28.5
HP2MGL-65	–	–	–

[a] BET surface area.
[b] Total pore volume.
[c] BJH desorption average pore diameter.

Effect of CO_2 concentration on adsorption breakthrough behavior

The breakthrough adsorption behavior is important characteristic to assess the kinetic performance of adsorbents for CO_2 capture in terms of working capacity. The breakthrough adsorption performance was carried out in the fixed-bed system which has a simple structure to realize the flexibility of the needed infrastructure for the DAC. Figure 4a shows the CO_2 adsorption breakthrough curves, which were investigated experimentally in the CO_2 concentration ranges from 400 ppm to 15% (binary CO_2/N_2 mixture). Once the

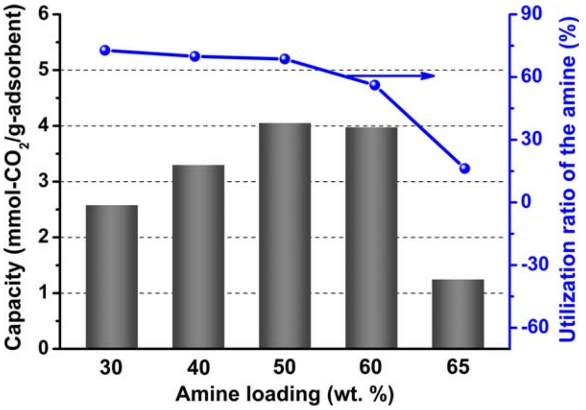

Figure 3. Effect of PEI loading on the pure CO_2 adsorption performance (column) and utilization ratio of the amine (line and symbol) for the PEI-impregnated solid amine adsorbents.

The data were from TGA with pure CO_2 gas at 25°C and 0.1 MPa. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 3. Comparison of HP2MGL-50 with Other PEI-Modified Adsorbents

Porous Material	*T* (°C)	CO_2 Adsorbed Amount (mmol/g)	Amine Efficiency (%)	Ref
HP2MGL	25	4.05	69.8	This work
MCM-41	25	0.75	12.9	57
Carbon black	25	1.45	25.0	58
PMCM-41	25	1.70	26.6	48
SBA-15	25	2.55	39.9	59
MCF	30	3.39	48.7	60
HMS	30	3.23	50.6	61

adsorbents are exposed to the CO_2 containing stream, CO_2 is completely adsorbed by the adsorbent and the CO_2 concentration is below the detection limit of the gas chromatography. After that, CO_2 begins to break through and is detected in the effluent gas. This breakthrough process is mainly a result of CO_2 diffusion resistance through the PEI films originated from the formation of salt bridges or hydrogen bonded networks of amine-CO_2 zwitterions.[62–65] The breakthrough curves obtained at a low CO_2 concentration (400 and 5000 ppm) show a much longer time with undetectable CO_2 effluent before breakthrough. The breakthrough and saturation adsorption capacities at dynamic conditions of the adsorbents were calculated and shown in Figure 4b. The adsorption capacities gradually decrease with CO_2 concentration decreasing. At a low CO_2 concentration of 5000 ppm, the adsorbent HP2MGL-50 delivers a high breakthrough capacity of 1.63 mmol/g and a saturation adsorption capacity of 2.13 mmol/g. Even at the trace CO_2 concentration of 400 ppm, the adsorbents exhibits an impressive breakthrough

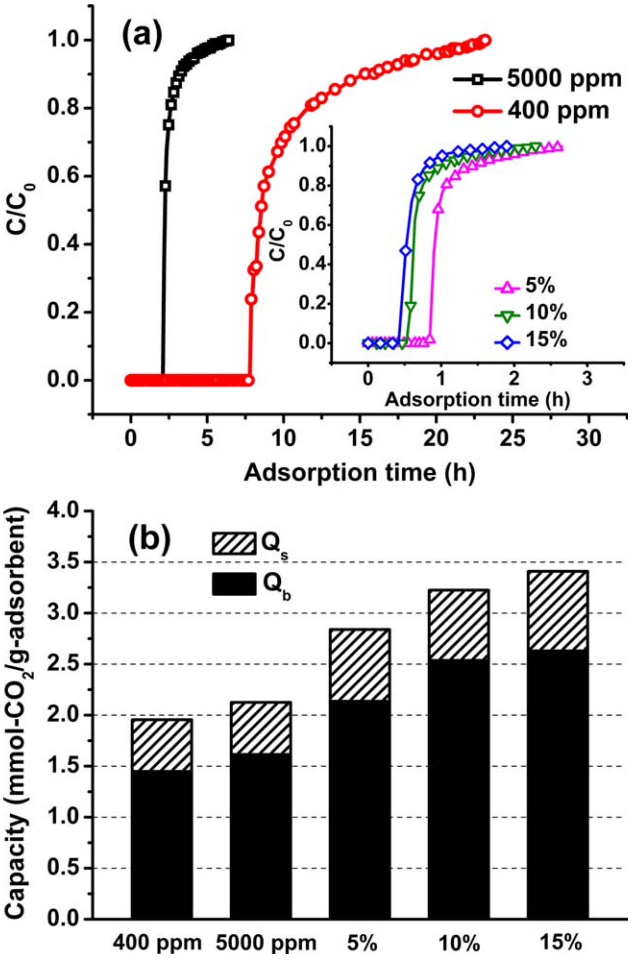

Figure 4. Breakthrough adsorption curves (a) and adsorption capacity (b) on HP2MGL-50 with different CO_2 concentrations in N_2.

The data were from fixed-bed adsorber with different CO_2 concentrations in N_2 at 25°C and 0.1 MPa. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

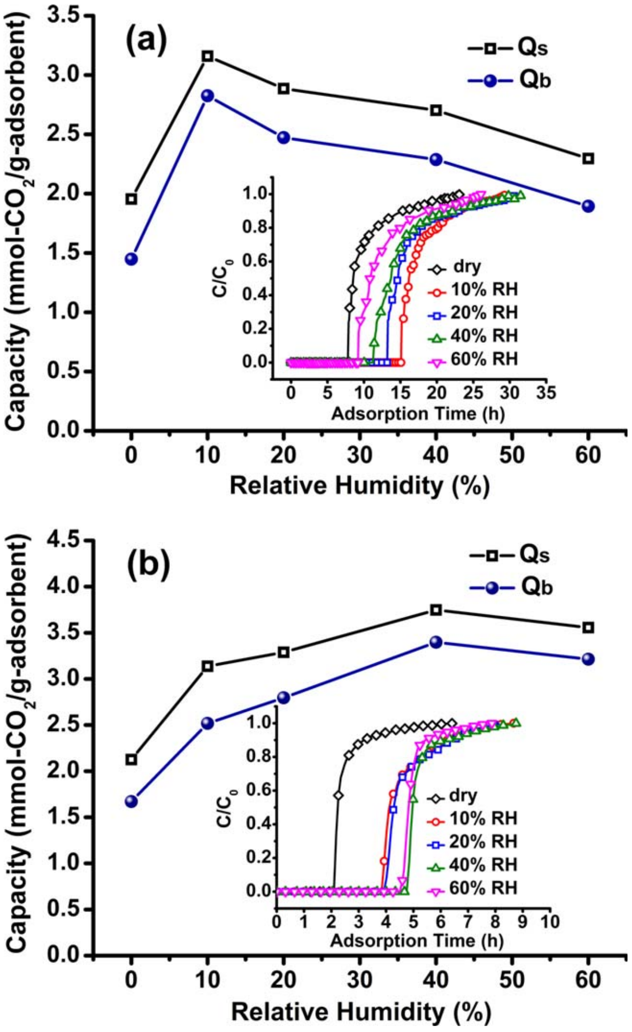

Figure 5. Adsorption capacity and breakthrough adsorption curve (inset) of HP2MGL-50 under different moistures with 400 ppm (a) and 5000 ppm (b) CO_2 in N_2.

The data were from fixed-bed adsorber with CO_2 concentrations of 400 and 5000 ppm in N_2 at 25°C and 0.1 MPa. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

capacity of 1.44 mmol/g, 75% of the saturation adsorption capacity (1.96 mmol/g). The high breakthrough capacity highlights the potential of these adsorbents for low CO_2 concentration applications.

Effect of moisture on CO_2 adsorption

The presence of moisture is inevitable in the ambient air, which would affect the CO_2 adsorption performance. Here, a series of breakthrough experiments were studied using 400 and 5000 ppm CO_2/N_2 gas mixtures in dry condition as well as with various RH at room temperature (25°C and 0.1 MPa). As shown in Figure 5, when moist gas mixtures are used, the CO_2 breakthrough time increases in contrast to dry gas mixture, revealing that moisture has a positive effect on the adsorption of CO_2 over the adsorbents. At CO_2 concentration of 400 ppm, the saturation adsorption capacity is improved to a maximum of 3.16 mmol/g at a RH of 10%. At 5000 ppm CO_2, the saturation adsorption capacity exhibits a maximum of 3.74 mmol/g while the RH is 40%. In the previous report,[66] the moisture was found to play a promoting effect on the adsorption of high-concentration CO_2 over the solid amine adsorbents due to its proton transfer function in the reaction of CO_2 and amine groups. In the case of trace or low-concentration CO_2 removal, it also plays a promoting effect but is more sensitive that depends on the RH, which is distinct from the results reported by Steinfeld and coworkers.[45] This should be ascribed to the competitive adsorption between CO_2 and H_2O at the same adsorption sites. Thus, the moisture should be appropriately controlled to optimize low-concentration CO_2 capture for DAC applications.

Effect of oxygen on cyclic adsorption behavior

Oxygen gas is the second most common component of the atmosphere, taking up 20.8% of its volume. Moreover, oxygen is one of an oxidizing agent which could oxidize the organic polymer compounds. Therefore, it is necessary to investigate the effect of oxygen on adsorption capacity during the temperature swing adsorption–desorption cycles.[67–69] All the regenerations were performed at 100°C using pure N_2 as a purging gas for CO_2 desorption. As shown in Figure 6, the saturation adsorption capacity decreases significantly from 2.13 mmol/g for O_2-free gas to 1.84 mmol/g for 20.5% O_2-containing gas in the case of 5000 ppm CO_2 removal. This recession may be due to the competitive adsorption between CO_2 and O_2 and the irreversible loss of some CO_2 adsorption active sites caused by the oxidation during the first CO_2 adsorption–desorption process. Furthermore, the active sites for O_2 adsorption and oxidation are limited, leading to the stable CO_2 adsorption capacity during the next four cycles. To verify this assumption, we designed a gas switch experiment. Specifically, the feed gas was first used as 5000 ppm CO_2/99.5% N_2 and switched to 5000 ppm CO_2/79% N_2/20.5% O_2 at the second cycle, and then switched back to 5000 ppm CO_2/99.5% N_2 in the next three cycles. Once the adsorbents are exposed in the O_2 containing stream, some CO_2 adsorption active sites are occupied by O_2 and cannot be recovered and utilized for the consequent adsorption cycles even using O_2-free stream. This result confirms that irreversible reactions such as the oxidation of amine groups occur during CO_2/O_2 coadsorption process. The experiment analysis and mechanism study of the

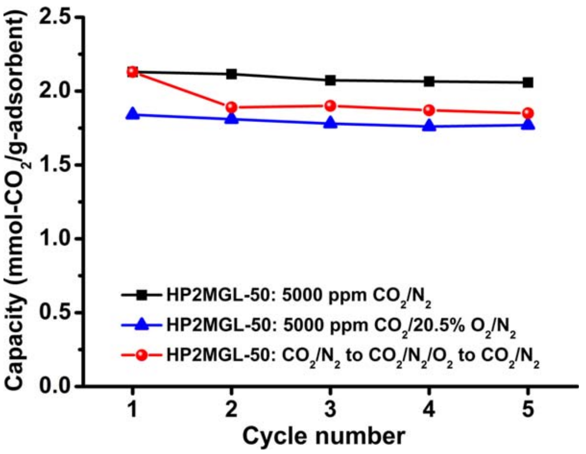

Figure 6. Effect of oxygen on cyclic saturated adsorption capacity of HP2MGL-50 for 5000 ppm CO_2.

Data were from fixed-bed adsorber with 5000 ppm CO_2 gas for adsorption at 25°C and with pure N_2 gas for desorption at 100°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

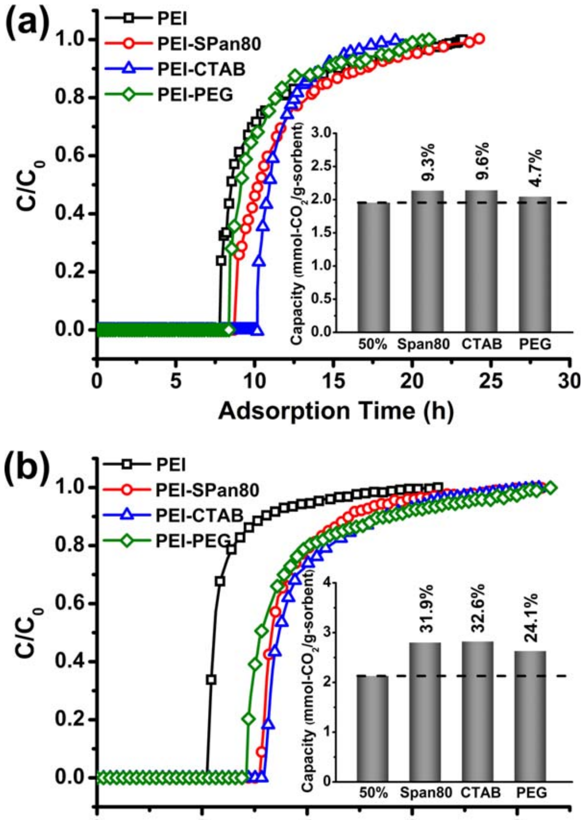

Figure 7. Effect of diffusion additives on the breakthrough adsorption curve and saturated adsorption capacity (inset) of the adsorbent with 50 wt. % PEI and 5 wt. % diffusion additive at 400 ppm (a) and 5000 ppm CO_2 (b).

The data were from fixed-bed adsorber with CO_2 concentrations of 400 and 5000 ppm in N_2 at 25°C and 0.1 MPa. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

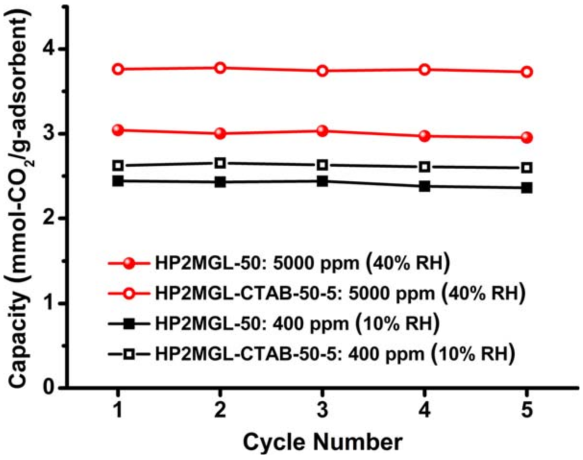

Figure 8. Cyclic adsorption of CO_2 by HP2MGL-50 and HP2MGL-CTAB-50-5.

The solid square and open square were from fixed-bed adsorber with a RH of 10% and 400 ppm CO_2/79.5% N_2/20.5% O_2 at 25°C and 0.1 MPa. The solid circle and open circle were from fixed-bed adsorber with a RH of 40% and 5000 ppm CO_2/79% N_2/20.5% O_2 at 25°C and 0.1 MPa. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

irreversible oxidation reactions on the adsorbents will be performed in the near future and reported elsewhere.

Effect of diffusion additives on CO_2 adsorption

When the adsorbent is exposed to CO_2, the reaction between fresh amine groups and CO_2 could form ammonium carbamates, hindering the CO_2 diffusion from the surface into the deeper films of the amines, especially in the case of low CO_2 concentration with the low-concentration gradient. To further advance the adsorbents for low-concentration CO_2 capture, we use a facilitating CO_2 diffusion strategy raised in our previous contributions.[61] Three polymer surfactants (Span80, CTAB, and PEG) were added to the PEI at a fixed HP2MGL/PEI/surfactant weight ratio of 45/50/5. The adsorption capacities of the surfactant-promoted adsorbents exposed to 400 and 5000 ppm CO_2/N_2 gas mixtures at 25°C are shown in Figure 7. As expected, all additives used in this work could improve the CO_2 adsorption capacity to a certain degree. These CO_2-neutral polymer surfactants are hoped to break the bulk amine films or their CO_2 adsorption product (ammonium carbamates) from a compact entity into a dual interpenetrating polymer composite, allowing the easy diffusion of more CO_2 into the deeper amine films. Consequently, the adsorbents offer an increased number of reactive sites and higher utilization efficiency of the amine groups, leading to an enhanced CO_2 adsorption capacity. Among these additives, CTAB is a most effective promoter, which exhibits the improved saturation adsorption capacity of 9.6% and 32.6% for CO_2 concentration of 400 and 5000 ppm, respectively. It is worth noting that the improvement of 400 ppm CO_2 is lower than that of 5000 ppm CO_2. This may be attributed to the low diffusion force deriving from the low-concentration gradient at 400 ppm CO_2 which would weaken the positive impact of the promoter.

CO_2 adsorption with oxygen and moisture

For the direct CO_2 capture from the air, detail investigating of CO_2, H_2O, and O_2 adsorption–desorption is crucial. Therefore, the low-concentration CO_2 adsorption over the adsorbents with or without CTAB additive was investigated experimentally using column breakthrough tests exposed to 5000 ppm CO_2/79% N_2/20.5% O_2 with a RH of 40% and 400 ppm CO_2/79.5% N_2/20.5% O_2 with a RH of 10%, respectively. As shown in Figure 8, due to the compromise between the positive effect of moisture and the negative effect of O_2, the adsorbent HP2MGL-50 exhibits a relatively high saturation adsorption capacity of 3.04 mmol/g for 5000 ppm CO_2 and a capacity of 2.44 mmol/g for 400 ppm CO_2 with a good cycling ability. Furthermore, with the promotion of CTAB, the adsorbent HP2MGL-CTAB-50-5 could direct capture 3.76 and 2.63 mmol/g CO_2 from the 5000 and 400 ppm CO_2 steam, respectively. These results suggest that the as-prepared adsorbents are robust enough to allow repeated temperature swing cycles under humidified and O_2-containing conditions and, thus, can provide a stable air capture capacity during multiple adsorption/desorption operations.

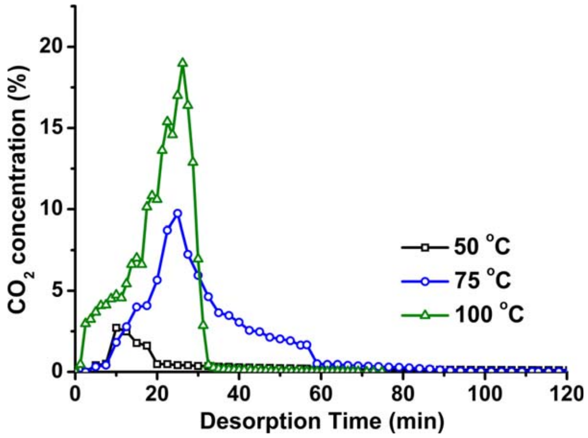

Figure 9. Effect of temperature on the CO_2 desorption as a function of time.

Data were from fixed-bed adsorber with 5000 ppm CO_2 gas for adsorption at 25°C and with pure N_2 gas for desorption. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Desorption behavior

To study the CO_2 desorption behavior, HP2MGL-50 was submitted to regeneration by temperature swing under a flow of N_2 after the adsorption saturation at 5000 ppm CO_2 flow. Temperatures of 50, 75, and 100°C were tested for the regeneration experiments. The CO_2 concentrations of the outlet gases as a function of regeneration time are presented in Figure 9. High temperature is apparently beneficial to the regeneration efficiency. Only 40% CO_2 adsorbed could be released at 50°C even extension of the regeneration time to 120 min. On the contrast, about 99% CO_2 adsorbed could be desorbed during the first 32 min at a mild temperature of 100°C. The industrially and economically acceptable desorption technology such as steam stripping and temperature-vacuum swing processes are currently being developed and will be reported in a future contribution.

Conclusions

In summary, we have experimentally studied CO_2 capture on the amine-impregnated resin adsorbents under conditions relevant to the direct capture of low-concentration CO_2. The adsorbents were easily prepared from widely available and industrially produced resins and were able to adsorb CO_2 reversibly under mild conditions in repeated adsorption/desorption cycles. The adsorbents have an extraordinary capture capacity with CO_2 concentration ranging from 400 ppm to 15% at ambient temperature. Especially, at the very low CO_2 concentration of 400 ppm, they are able to remove efficiently all CO_2 in the initial hours of the experiments and exhibit an saturation adsorption capacity of 1.96 mmol/g. For the adsorption of low-concentration CO_2, there would be an optimal RH to achieve the maximum adsorption capability. A further increase in the moisture leads to a decrease in the promotion. Oxygen could react irreversibly with the amine groups, leading to the loss of CO_2 adsorption active site and the resulting decreased adsorption capacity compared with the O_2-free gas. The diffusion-promoted strategy is efficient to improve the adsorption capacity with an enhanced saturation capacity of 9.6% and 32.6% for CO_2 concentration of 400 and 5000 ppm, respectively. Moreover, the solid amine adsorbent shows an excellent adsorption capacity with a good regenerability for CO_2 capture from the ambient air with moisture, based on the balance of positive effect of moisture and negative effect of O_2. This study presents a detailed analysis of the CO_2 capture on the amine-impregnated solid adsorbents. These materials, if incorporated into suitable, scalable processes, would one day be important components of practical air capture technologies including prepurification of air during the separation of nitrogen and oxygen and trace CO_2 removal in personal confined spaces such as submarines and aerospace shuttles.

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Literature Cited

1. Eisenberger PM, Cohen RW, Chichilnisky G, Eisenberger NM, Chance RR, Jones CW. Global warming and carbon-negative technology: prospects for a lower-cost route to a lower-risk atmosphere. *Energy Environ.* 2009;20:973–984.
2. Choi S, Drese JH, Jones CW. Adsorbent materials for carbon dioxide capture from large anthropogenic point sources. *ChemSusChem* 2009;2:796–854.
3. Macdowell N, Florin N, Buchard A, Hallett J, Galindo A, Jackson G, Adjiman CS, Williams CK, Shah N, Fennell P. An overview of CO_2 capture technologies. *Energy Environ. Sci.* 2010;3:1645–1669.
4. Wang Q, Luo J, Zhong Z, Borgna A. CO_2 capture by solid adsorbents and their applications: current status and new trends. *Energy Environ. Sci.* 2011;4:42–55.
5. Goeppert A, Czaun M, Prakash GKS, Olah GA. Air as the renewable carbon source of the future: an overview of CO_2 capture from the atmosphere. *Energy Environ. Sci.* 2012;5:7833–7853.
6. Goeppert A, Czaun M, May RB, Prakash GKS, Olah GA, Narayanan SR. Carbon dioxide capture from the air using a polyamine based regenerable solid adsorbent. *J. Am. Chem. Soc.* 2011; 133:20164–20167.
7. Goldberg DS, Lackner KS, Han P, Slagle AL, Wang T. Co-location of air capture, subseafloor CO_2 sequestration, and energy production on the Kerguelen Plateau. *Environ. Sci. Technol.* 2013;47:7521–7529.
8. IPCC. *IPCC Fourth Assessment Report: Climate Change 2007*. Cambridge, UK: Cambridge University Press, 2007.
9. Jones CW. CO_2 capture from dilute gases as a component of modern global carbon management. *Annu. Rev. Chem. Biomol. Eng.* 2011;2: 31–52.
10. Lackner KS, Ziock H-J, Grimes P. Carbon dioxide extraction from air: is it an option? In: *The 24th International Conference on Coal Utilization & Fuel Systems*. Clearwater, Florida, 1999.
11. Rege SU, Yang RT, Buzanowski MA. Adsorbents for air prepurification in air separation. *Chem. Eng. Sci.* 2000;55:4827–4838.
12. Mulloth LM, Finn JE. Carbon dioxide adsorption on a 5A zeolite designed for CO_2 removal in spacecraft cabins. NASA Ames Research Center, 1998:1.
13. U.S. Department of Labor Occupational Safety & Health Administration. *Occupational Safety and Health Standards*, Washington, DC, 1910 Z 1910.1000 TABLE Z-1.
14. Knox JC. International space station carbon dioxide removal assembly testing. Society of Automotive Engineers, Inc., NASA Marshall Space Flight Center. 2000.
15. Satyapal S, Filburn T, Trela J, Strange J. Performance and properties of a solid amine sorbent for carbon dioxide removal in space life support applications. *Energy Fuels* 2001;15:250–255.
16. Moore P. Miner protection. *Mineral. Mag.* 2007;196:35–41.
17. Dosch MP. *The Anesthesiagas Machine*. 2006. Available at www.udmercy.edu/crna/agm, accessed on August 2, 2014.
18. Keith DW, Ha-Duong M, Stolaroff JK. Climate strategy with CO_2 capture from air. *Clim. Change* 2006;74:17–45.
19. Zeman FS, Lackner KS. Capturing carbon dioxide directly from the atmosphere. *World Res. Rev.* 2004;16:157–172.
20. Baciocchi R, Storti G, Mazzotti M. Process design and energy requirements for the capture of carbon dioxide from air. *Chem. Eng. Process.* 2006;45:1047–1058.
21. Zeman F. Energy and material balance of CO_2 capture from ambient air. *Environ. Sci. Technol.* 2007;41:7558–7563.
22. Pielke RA. An idealized assessment of the economics of air capture of carbon dioxide in mitigation policy. *Environ. Sci. Policy* 2009;12: 216–225.
23. Choi S, Drese JH, Eisenberger PM, Jones CW. A new paradigm of anthropogenic CO_2 reduction: adsorptive fixation of CO_2 from the ambient air as a carbon negative technology. *AIChE Annual Meeting, Nashville, TN*, 2009.
24. Li G, Xiao P, Zhang J, Webley PA, Xu D. The role of water on postcombustion CO_2 capture by vacuum swing adsorption: bed layering and purge to feed ratio. *AIChE J.* 2014;60:673–689.
25. Moloney P, Huffman C, Gorelik O, Nikolaev P, Arepalli S, Allada R, Springer M, Yowell L. Advanced life support for space exploration: air revitalization using amine coated single wall carbon nanotubes. In: Materials for Space Applications, Symposium on Materials for Space Applications. Boston, November 29–December 03, 2004 (Chipara M, Edwards DL, Benson RS, Phillips S, editors). *MRS Proceedings* 2005;851:59–64.
26. Bollini P, Didas SA, Jones CW. Amine-oxide hybrid materials for acid gas separations. *J. Mater. Chem.* 2011;21(39):15100–15120.
27. Belmabkhout Y, Serna-Guerrero R, Sayari A. Amine-bearing mesoporous silica for CO_2 removal from dry and humid air. *Chem. Eng. Sci.* 2010;65:3695–3698.
28. Belmabkhout Y, Serna-Guerrero R, Sayari A. Adsorption of CO_2-containing gas mixtures over amine-bearing pore-expanded MCM-41 silica: application for gas purification. *Ind. Eng. Chem. Res.* 2009; 49:359–365.
29. Liu YM, Ye Q, Shen M, Shi JJ, Chen J, Pan H, Shi Y. Carbon dioxide capture by functionalized solid amine sorbents with simulated flue gas conditions. *Environ. Sci. Technol.* 2011;45:5710–5716.
30. Cui S, Cheng WW, Shen XD, Fan MH, Russell A, Wu ZW, Yi XB. Mesoporous amine-modified SiO2 aerogel: a potential CO_2 sorbent. *Energy Environ. Sci.* 2011;4:2070–2074.
31. Chen C, Yang ST, Ahn WS, Ryoo R. Amine-impregnated silica monolith with a hierarchical pore structure: enhancement of CO_2 capture capacity. *Chem. Commun.* 2009;0:3627–3629.
32. Qi G, Wang Y, Estevez L, Duan X, Anako N, Park AH, Li W, Jones CW, Giannelis EP. High efficiency nanocomposite sorbents for CO_2 capture based on amine-functionalized mesoporous capsules. *Energy Environ. Sci.* 2011;4:444–452.
33. Chaikittisilp W, Khunsupat R, Chen TT, Jones CW. Poly(allylamine)-mesoporous silica composite materials for CO_2 capture from simulated flue gas or ambient air. *Ind. Eng. Chem. Res.* 2011;50: 14203–14210.
34. Chaikittisilp W, Lunn JD, Shantz DF, Jones CW. Poly(L-lysine) brush-mesoporous silica hybrid material as a biomolecule-based adsorbent for CO_2 capture from simulated flue gas and air. *Chem. Eur. J.* 2011;17:10556–10561.

35. Wurzbacher JA, Gebald C, Steinfeld A. Separation of CO_2 from air by temperature-vacuum swing adsorption using diamine-functionalized silica gel. *Energy Environ. Sci.* 2011;4:3584–3592.
36. McDonald TM, Lee WR, Mason JA, Wiers BM, Hong CS, Long JR. Capture of carbon dioxide from air and flue gas in thenalkylamine-appended metal-organic framework mmen-Mg2(dobpdc). *J. Am. Chem. Soc.* 2012;134:7056–7065.
37. Choi S, Watanabe T, Bae TH, Sholl DS, Jones CW. Modification of the Mg/DOBDC MOF with amines to enhance CO_2 adsorption from ultradilute gases. *J. Phys. Chem. Lett.* 2012;3:1136–1141.
38. Su F, Lu C, Cnen W, Bai H, Hwang JF. Capture of CO_2 from flue gas via multiwalled carbon nanotubes. *Sci. Total Environ.* 2009;407: 3017–3023.
39. Ye Q, Jiang JQ, Wang CX, Liu YM, Pan H, Shi Y. Adsorption of low-concentration carbon dioxide on amine-modified carbon nanotubes at ambient temperature. *Energy Fuels* 2012;26:2497–2504.
40. Chen ZH, Deng SB, Wei HR, Wang B, Huang J, Yu G. Polyethylenimine-impregnated resin for high CO_2 adsorption: an efficient adsorbent for CO_2 capture from simulated flue gas and ambient air. *ACS Appl. Mater. Interfaces* 2013;5:6937–6945.
41. Wang JT, Wang M, Zhao BB, Qiao WM, Long DH, Ling LC. Mesoporous carbon-supported solid amine sorbents for low-temperature carbon dioxide capture. *Ind. Eng. Chem. Res.* 2013;52:5437–5444.
42. Arenillas A, Smith KM, Drage TC, Snape CE. CO_2 capture using some fly ash-derived carbon materials. *Fuel* 2005;84:2204–2210.
43. Chaikittisilp W, Kim H-J, Jones CW. Mesoporous alumina-supported amines as potential steam-stable adsorbents for capturing CO_2 from simulated flue gas and ambient air. *Energy Fuels* 2011;25: 5528–5537.
44. Gebald C, Wurzbacher JA, Tingaut P, Zimmermann T, Steinfeld A. Amine-based nanofibrillated cellulose as adsorbent for CO_2 capture from air. *Environ. Sci. Technol.* 2011;45:9101–9108.
45. Wurzbacher JA, Gebald C, Piatkowski N, Steinfeld A. Concurrent separation of CO_2 and H_2O from air by a temperature-vacuum swing adsorption/desorption cycle. *Environ. Sci. Technol.* 2012;46:9191–9198.
46. Ma XL, Wang XX, Song CS. Molecular "basket" sorbents for separation of CO_2 and H_2S from various gas streams. *J. Am. Chem. Soc.* 2009;131:5777–5783.
47. Zhang Z, Ma X, Wang D, Song C, Wang Y. Development of silica-gel-supported polyethylenimine sorbents for CO_2 capture from flue gas. *AIChE J.* 2012;58:2495–2502.
48. Heydari-Gorji A, Belmabkhout Y, Sayari A. Polyethylenimine-impregnated mesoporous silica: effect of amine loading and surface alkyl chains on CO_2 adsorption. *Langmuir* 2011;27:12411–12416.
49. Yue MB, Sun LB, Cao Y, Wang Y, Wang ZJ, Zhu JH. Efficient CO_2 capturer derived from as-synthesized MCM-41 modified with amine. *Chem. Eur. J.* 2008;14:3442–3451.
50. Bhagiyalakshmi M, Yun LJ, Anuradha R, Jang HT. Utilization of rice husk ash as silica source for the synthesis of mesoporous silicas and their application to CO_2 adsorption through TREN/TEPA grafting. *J. Hazard. Mater.* 2010;175:928–938.
51. Liu SH, Wu CH, Lee HK, Liu SB. Highly stable amine-modified mesoporous silica materials for efficient CO_2 capture. *Top. Catal.* 2010;53:210–217.
52. Knowles GP, Graham JV, Delaney SW, Chaffee AL. Aminopropyl-functionalized mesoporous silicas as CO_2 adsorbents. *Fuel Process. Technol.* 2005;86:1435–1448.
53. Choi S, Drese JH, Eisenberger PM, Jones CW. Application of amine-tethered solid sorbents for direct CO_2 capture from the ambient air. *Environ. Sci. Technol.* 2011;45:2420–2427.
54. Choi S, Gray ML, Jones CW. Amine-tethered solid adsorbents coupling high adsorption capacity and regenerability for CO_2 capture from ambient air. *ChemSusChem* 2011;4:628–635.
55. Wang XX, Ma XL, Xu XC, Sun L, Song CS. Mesoporous-molecular-sieve-supported polymer sorbents for removing H_2S from hydrogen gas streams. *Top. Catal.* 2008;49:108–117.
56. Zeleňák V, Badaničová M, Halamova D, Čejka J, Zukal A, Murafa N, Goerigk G. Amine-modified ordered mesoporous silica: effect of pore size on carbon dioxide capture. *Chem. Eng. J.* 2008;144:336–342.
57. Xu XC, Song CS, Andresen JM, Miller BG, Scaroni AW. Preparation and characterization of novel CO_2 "molecular basket" adsorbents based on polymer-modified mesoporous molecular sieve MCM-41. *Microporous Mesoporous Mater.* 2003;62:29–45.
58. Wang DX, Ma XL, Sentorun-Shalaby C, Song CS. Development of carbon-based "molecular basket" sorbent for CO_2 capture. *Ind. Eng. Chem. Res.* 2012;51:3048–3057.
59. Heydari-Gorji A, Yang Y, Sayari A. Effect of the pore length on CO_2 adsorption over amine-modified mesoporous silicas. *Energy Fuels* 2011;25:4206–4210.
60. Yan W, Tang J, Bian ZJ, Hu J, Liu HL. Carbon dioxide capture by amine-impregnated mesocellular-foam-containing template. *Ind. Eng. Chem. Res.* 2012;51:3653−3662.
61. Wang JT, Long DH, Zhou HH, Chen QJ, Liu XJ, Ling LC. Surfactant promoted solid amine sorbents for CO_2 capture. *Energy Environ. Sci.* 2012;5:5742–5749.
62. Danckwerts PV. The reaction of CO_2 with ethanolamines. *Chem. Eng. Sci.* 1979;34:443–446.
63. Caplow M. Kinetics of carbamate formation and breakdown. *J. Am. Chem. Soc.* 1968;90:6795–6803.
64. Soutullo MD, Odom CI, Wicker BF, Henderson CN, Stenson AC, Davis JH. Reversible CO_2 capture by unexpected plastic-, resin-, and gel-like ionic soft materials discovered during the combi-click generation of a TSIL library. *Chem. Mater.* 2007;19:3581–3583.
65. Gutowski KE, Maginn EJ. Amine-functionalized task-specific ionic liquids: a mechanistic explanation for the dramatic increase in viscosity upon complexation with CO_2 from molecular simulation. *J. Am. Chem. Soc.* 2008;130:14690–14704.
66. Xu XC, Song CS, Miller BG, Scaroni AW. Influence of moisture on CO_2 separation from gas mixture by a nanoporous adsorbent based on polyethylenimine-modified molecular sieve MCM-41. *Ind. Eng. Chem. Res.* 2005;44:8113–8119.
67. Heydari-Gorji A, Sayari A. Thermal, oxidative, and CO_2-induced degradation of supported polyethylenimine adsorbents. *Ind. Eng. Chem. Res.* 2012;51:6887–6894.
68. Calleja G, Sanz R, Arencibia A, Sanz-Pérez ES. Influence of drying conditions on amine-functionalized SBA-15 as adsorbent of CO_2. *Top. Catal.* 2011;54:135–145.
69. Bollini P, Choi S, Drese JH, Jones CW. Oxidative degradation of aminosilica adsorbents relevant to postcombustion CO_2 capture. *Energy Fuels* 2011;25:2416–2425.

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