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Amine-Grafted Silica Gels for CO_2 Capture Including Direct Air Capture

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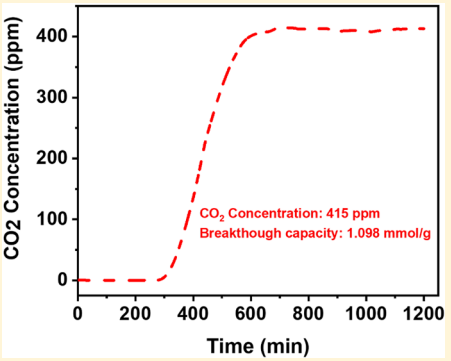
ABSTRACT: A series of commercially available (and low-cost) silica gels were amine-grafted under dry conditions using N^1-(3-trimethoxysilylpropyl)-diethylenetriamine (i.e., "triamine"). CO_2 capture performance, pore properties, and amine loading were investigated, and the results showed that the silica gel with the largest pores (150A) was the most suitable for further enhancement. Amine loading needed to be increased in order to further enhance the CO_2 adsorption capacity. The addition of water during the grafting process was implemented on the 150A silica gel. The wet-grafted 150A silica gel exhibited a 2.3 mmol/g adsorption capacity at 75 °C and 1 bar, which is comparable to the best literature reported values that used similar synthesis methods. The wet-grafted 150A exhibited good cycle stability as well as fast CO_2 uptake rates. The fixed-bed breakthrough capacity for air capture (ambient air with 415 ppm of CO_2 at 25 °C) under dry (0.773 mmol/g) and wet (1.098 mmol/g) conditions are among the highest CO_2 capacities for air capture. The capacity of the low-surface area silica gel (150A, S.A. = 309 m^2/g) rivaled those of the best of the SBA and MCM type materials, which was unexpected. These results indicate that wet-grafted silica gel 150A is a promising and low-cost sorbent for direct capture of CO_2 from ambient air and flue gas applications.



1. INTRODUCTION

Carbon dioxide (CO_2) is a one of the major greenhouse gases that pose a significant threat to the environment. CO_2 concentration in the atmosphere has been increasing at an unprecedented rate, and efforts are being made to develop novel carbon capture and sequestration (CCS) technologies.[1] These technologies are vitally important for curbing global CO_2 emissions.

Amine functionalized siliceous adsorbents are one of the most promising methods for CO_2 capture purposes.[2−12] Under dry conditions, carbamates are formed when CO_2 reacts with the amine groups on siliceous adsorbents; whereas a larger amount of carbamate ion pairs is formed due to the liberation of hydrogen bonded amines under wet conditions.[13,14] Bicarbonate formation is also observed under wet conditions.[5,13,15] Amines are functionalized on the siliceous material through amine grafting using aminosilanes or wet impregnation techniques using amine polymers. Wet impregnated adsorbents possess high CO_2 capture capacity and uptake rates. However, they experience multicycle instability due to leaching and degradation of the amines.[16−20]

In contrast, amine-grafted adsorbents are not susceptible to the aforementioned phenomena. Amine grafting proceeds via a reaction between the surface hydroxyl groups of an adsorbent and alkoxy groups of an aminosilane.[21] While this process yields stable amines that are more tightly bound to the adsorbent, they do not attain the high capacities exhibited by wet impregnated adsorbents. This is mainly due to their low nitrogen content in comparison to wet impregnated adsorbents because amine-grafting depends on the availability of surface hydroxyl groups.[7,8,21] To address this problem, water is added during the grafting process to hydrate the adsorbent surface (increasing the hydroxyl group density).[22] The addition of water as proposed by Feng et al.[22] and Harlick and Sayari[23] could also lead to 1) the hydrolysis of the unreacted alkoxy groups of grafted aminosilanes which would then react with free aminosilane and 2) the formation of siloxane bridges of free aminosilanes to other grafted aminosilanes.[22,23] In addition, N^1-(3-trimethoxysilylpropyl)diethylenetriamine ("triamine") was used as the aminosilane because it possessed 3 amines per silane.[24] This creates adsorbents with a significantly higher nitrogen content due to the somewhat polymeric structure of the amines. The results are promising adsorbents with enhanced CO_2 capture performance.

This wet grafting technique using triamine has been studied by several research groups. Harlick and Sayari[23] and Loganathan et al.[25] synthesized large pore MCM-41 and varied the water amount, silane concentration, and grafting temperature during the grafting process. They were able to achieve a CO_2 adsorption capacity of over 2 mmol/g. Lashaki et al.[26] synthesized SBA-15 with varying pore sizes and volumes and subsequently used water during the grafting

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process. They also reported an enhancement in the CO_2 adsorption capacity after water addition.

The majority, if not all, of the recent studies on amine-grafted silicas for CO_2 capture was performed on ordered, mesoporous silicas synthesized using templates (SBA-15, MCM-41, MCM-48, KIT-6, etc.), due to their high surface areas and tunable mesopore sizes. However, their production outside a lab setting is often not efficient or economically viable. Commercial silica gels are formed by polymerization of silicic acid, $Si(OH)_4$, via mixing a sodium silicate solution with a mineral acid (e.g., HCl or H_2SO_4). Various silica gels with a wide range of desired pore structures and BET surface areas are produced by controlling the polymerization conditions such as silicate concentration, pH, and temperature. Two common types of silica gels are available commercially: regular density gels (BET S.A. = 750−850 m^2/g, av pore size = 2.2−2.6 nm) and low density gels (BET S.A. = 300−350 m^2/g, av pore size = 10−15 nm).[27] Compared with the ordered, mesoporous silicas, silica gels are commercially available with controlled qualities and substantially lower costs. Moreover, ordered, mesoporous silicas are synthesized in the form of fine powders and need to be pelletized prior to be used for fixed-bed adsorption applications while silica gels can be readily used for amine grafting and fixed-bed adsorption.[27]

Based on a literature review, there have been no studies that explore how the pore structures of silica gels affect the resulting triamine-grafted silica gels. In this study, dry grafting utilizing triamine (in anhydrous toluene) was performed on various commercially available silica gels with varying pore structures with the goal of identifying a favorable silica gel that could be further enhanced using wet grafting. This study also investigated the performance of the silica gel under conditions related to both flue/postcombustion gas and direct CO_2 capture from ambient air.

2. MATERIALS

Silica gel samples with pore sizes of 22, 60, and 150 Å and corresponding mesh sizes of 28−200, 70−230, and 200−425, respectively, were obtained from Sigma-Aldrich. These silica gels were designated as 22A, 60A, and 150A. N^1-(3-Trimethoxysilylpropyl)diethylenetriamine, Pluronic P123, hydrochloric acid (HCl), and tetraethylorthosilicate (TEOS) were obtained from Sigma-Aldrich. Anhydrous toluene was obtained from Fisher Scientific.

2.1. SBA-15. The synthesis of SBA-15 was performed according to the procedure reported by Wang et al.[28] Eight grams of Pluronic P123 was dissolved in 240 mL of H_2O and 40.1 mL of 37% HCl at room temperature. After the complete dissolution of Pluronic P123, the temperature was increased to 35 °C. 18.2 mL of TEOS was then added to the solution dropwise. The mixture was stirred at 35 °C for 24 h, followed by another 24 h at 100 °C. The resulting white solid was collected by filtration, washed with water, and dried at 50 °C overnight. Finally, it was calcined at 550 °C for 6 h under an air flow.

2.2. Dry Grafting. In a typical synthesis, 50 mL of anhydrous toluene was mixed with 5 mL of N^1-(3-trimethoxysilylpropyl)diethylenetriamine in an Erlenmeyer flask, and then 0.5 g of silica gel was added. The mixture was stirred and refluxed at 85 °C for 12 h. The grafted silica gel was filtered and washed with copious amounts of toluene and then dried in a 50 °C oven. Amine-grafted Aldrich silica gels were designated as AG-22A, AG-60A, and AG-150A.

2.3. Wet Grafting. In a typical synthesis, 0.15 mL of H_2O was added rapidly to a solution containing 50 mL of anhydrous toluene and 0.5 g of 150A silica gel. The mixture was stirred at room temperature for 2 h. Five mL of N^1-(3-trimethoxysilylpropyl)diethylenetriamine was then added. The mixture was stirred and refluxed at 85 °C for 12 h. The grafted silica gel was filtered, washed with copious amounts of toluene, and then dried in a 50 °C oven. This synthesis procedure was also performed for SBA-15. Wet-grafted Aldrich silica gels were designated as W-AG-150A.

3. CHARACTERIZATION

Carbon dioxide (0−1 bar) and nitrogen isotherms were measured on a Micromeritics ASAP 2020 sorptometer using a volumetric technique. Carbon dioxide isotherms were measured at 25, 40, 75, and 90 °C. Nitrogen adsorption isotherms were measured at −196 and 25 °C. All samples were degassed overnight at 105 °C prior to all measurements. Thermogravimetric analysis was carried out on a Shimadzu TGA-50H. Amine loading analysis was performed by pretreating the sample under a helium flow for 2 h at 100 °C and then heating to 850 °C at a heating rate of 5 °C/min under a helium and air flow. Adsorption rates were examined using a TGA under a dry 70% CO_2 flow (in He) at 25 °C and 75 °C. Multicycle stability studies were examined using a TGA under a dry 70% CO_2 flow (in He) at 75 °C. The sample was desorbed at 90°C in He after each adsorption cycle.

The CO_2 breakthrough adsorption measurement was performed using a vertical, fixed-bed with ambient air feed in a down-flow manner. The CO_2 concentration of the effluent gas was continuously monitored with a Vaisala GMP343 CO_2 probe. The Vaisala GMP343 incorporates a silicon-based nondispersive infrared sensor with a measurement range of 0−1000 ppm of CO_2. Unlike SBA-15 and other mesoporous silicas, which come in the form of fine powders, the amine-grafted silica gel is in the form of granular particles with the size range of 28−425 mesh and can be used directly in fixed-bed breakthrough measurements. In a typical measurement, the fixed-bed column was 2 cm in height and 0.35 cm in diameter. An indent and a small piece of quartz wool was used to contain the fixed-bed. Before the adsorption process, the fixed-bed column was degassed at 105 °C for 3 h under nitrogen flow prior to adsorption measurements. The temperature was then reduced to 25 °C, and the feed gas (ambient air) was introduced at a gas-hourly space velocity (GHSV) of 6500 h^{-1}. For the adsorption measurement involving moisture, the feed stream was passed through a bubbler containing a saturated KCl solution at 25 °C before being introduced to the fixed-bed.

4. RESULTS AND DISCUSSION

4.1. Selection of Adsorbent for Optimization.

4.1.1. Pore Properties of Plain and Dry-Grafted Silica Gels. Figures 1 and 2 show the nitrogen adsorption−desorption isotherms at −196 °C of all plain and dry-grafted silica gels. The 60A and 150A silica gel samples exhibited a type IV isotherm which indicates a standard mesoporous material.[29,30] The nitrogen isotherm of 22A exhibited a type I isotherm which corresponds to a microporous material.[30] The BJH (Barrett, Joyner, and Halenda) pore size distribution is centered around 14.97 nm for 150A, 8.15 nm for 60A, and 2.5 nm for 22A, respectively. The BET surface area and total

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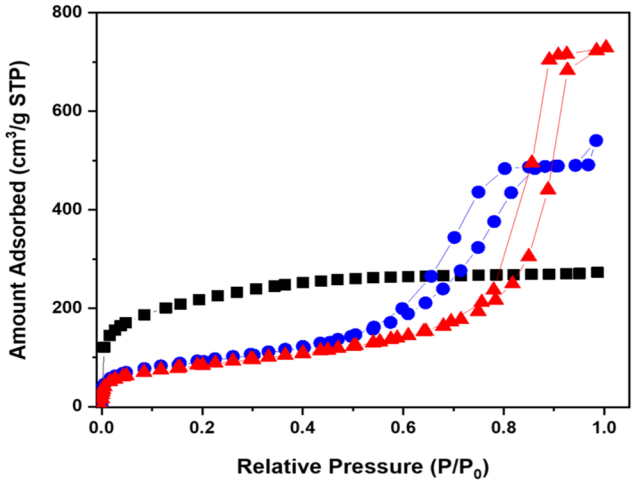

Figure 1. N_2 adsorption−desorption isotherms at −196 °C for silica gels 22A (■), 60A (●), and 150A (▲).

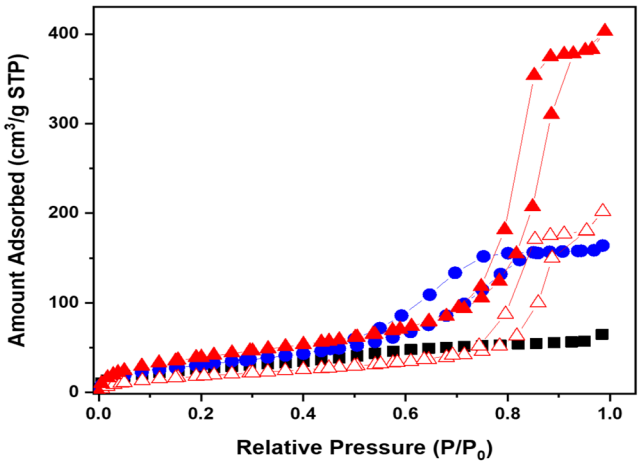

Figure 2. N_2 adsorption−desorption isotherms at −196 °C for amine-grafted silica gels AG-22A (■), AG-60A (●), AG-150A (▲), and W-AG-150A (△).

pore volume are approximately 309 m^2/g and 1.12 cm^3/g for 150A, 338 m^2/g and 0.84 cm^3/g for 60A, and 805 m^2/g and 0.43 cm^3/g for 22A. The physical properties of the samples were varied in order to determine whether these properties would affect the CO_2 adsorption performance; the findings will be discussed subsequently.

In order to investigate the influence of amine grafting on the silica gel samples' physical properties, dry grafting using triamine was performed. The physical properties of plain and dry-grafted samples are summarized in Table 1. There is a marked decrease in surface area, pore size, and pore volume after dry grafting. The silica gel samples with larger pores such as AG-60A and AG-150A showed much lower decreases than the smaller pore silica gel. This decrease can be attributed to the blockage of the pores after triamine grafting, confirming that triamine was successfully grafted on all the silica gel samples.[23−26,31] Furthermore, this establishes that an increase in amine concentration correlates with a decrease in surface area, pore size, and pore volume. It is worth noting that even after triamine grafting, AG-150A still exhibits a type IV isotherm (Figure 2), a pore size of 12.11 nm (Table 1), and pore volume of 0.62 cm^3/g (Table 1), meaning that its

Table 1. Surface Area and Pore Structure Parameters of Silica Gel Samples

sample	BET surface area (m^2/g)	pore diameter (nm)	total pore volume (cm^3/g)
22A	805	2.5	0.43
AG-22A	98.1		0.10
60A	338	8.15	0.84
AG-60A	122	7.03	0.25
150A	309	14.9	1.12
AG-150A	152	12.1	0.62
W-AG-150A	73.1	12.5	0.31

mesopores were largely preserved. The implications of these findings for the CO_2 capture performance are discussed in the following section.

4.1.2. CO_2 Capture Performance and Effect of Amine Loading. The CO_2 adsorption isotherm of dry-grafted silica gel samples at 25 °C is presented in Figure 3, and the physical

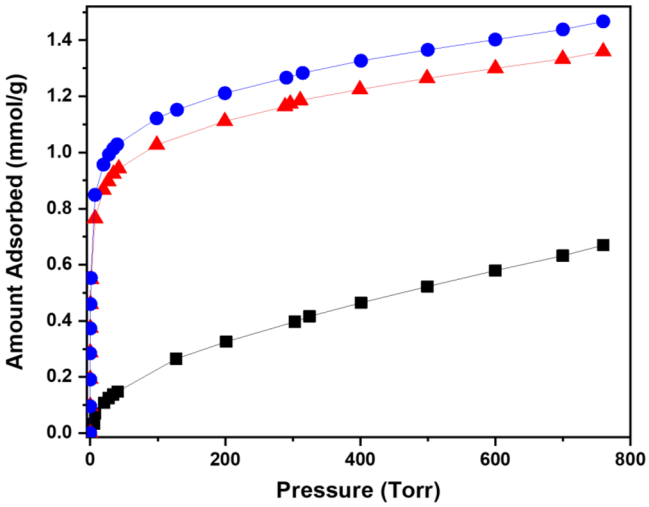

Figure 3. CO_2 adsorption isotherms for AG-22A (■), AG-60A (●), and AG-150A (▲) at 25 °C.

properties are summarized in Table 1. The CO_2 adsorption capacity and amine loading of the dry-grafted silica gels are summarized in Table 2. Figure 3 indicates that AG-150A had a maximum CO_2 capacity of 1.35 mmol/g at 1 bar, which is similar to AG-60A (1.46 mmol/g), another dry-grafted silica gel sample. As displayed in Table 2, silica gel samples with the high amine loading showed the highest CO_2 adsorption

Table 2. CO_2 Adsorption Capacity and Amine Loading of Dry- and Wet-Grafted Silica Gel Samples

sample	CO_2 adsorption capacity (mmol/g, at 25 °C and 1 bar)	amine loading (mmol N/g)	amine efficiency (mol CO_2/mol N; at 25 °C and 1 bar)	CO_2/N_2 selectivity (at 25 °C and 1 bar)
AG-22A	0.66	2.45		
AG-60A	1.46	4.13		
AG-150A	1.35	3.39	0.398	32.9
W-AG-150A	1.97	5.12	0.384	63.1

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capacity. However, additional increases in amine loading past the optimal conditions may lead to a marked decrease in CO_2 adsorption capacity due to pore clogging and the potential for complete blockage.[23−26,31] Therefore, one can conclude that a silica gel sample that provides the possibility of a high amine loading and accessibility without pore blockage or clogging is crucial for enhancing the CO_2 capture performance. The large pore silica gel sample AG-150A meets these conditions and will be used as a support for wet grafting purposes.

4.2. Optimization of 150A (Wet Grafting). The wet grafting procedure chosen for 150A was reported by Lashaki and Sayari.[26] The Sayari group studied triamine functionalized SBA-15 and the impact of pore structure on CO_2 adsorption performance. They concluded that utilizing 0.15 mL of water (under their grafting conditions[26]) was optimal because a further increase in the water amount did not lead to an increase in CO_2 capture capacity. Based on their results, 0.15 mL of water was chosen as the optimal amount for our purposes. In addition, the effect of water addition during grafting was examined and is discussed below.

4.2.1. Pore Properties and Amine Loading of Wet-Grafted 150A (W-AG-150A). Figure 2 shows the nitrogen adsorption−desorption isotherm at −196 °C of W-AG-150A. The pore properties are summarized in Table 1. The nitrogen adsorption isotherm for W-AG-150A exhibited a type IV isotherm which means its mesoporous nature was kept intact. Additionally, according to Figure 2 and Table 1, there is a decrease in nitrogen adsorbed, surface area, pore size, and pore volume after wet grafting. The surface area, pore size, and pore volume decreased by 76%, 16%, and 72%, respectively, which are larger when compared to the dry counterpart. The larger losses, when compared to dry grafting, can be attributed to a greater amount of amine grafted on 150A following wet grafting. This is borne out in Table 2 and in the TGA thermograms presented in Figure 4. Weight loss observed before 150 °C is due to the

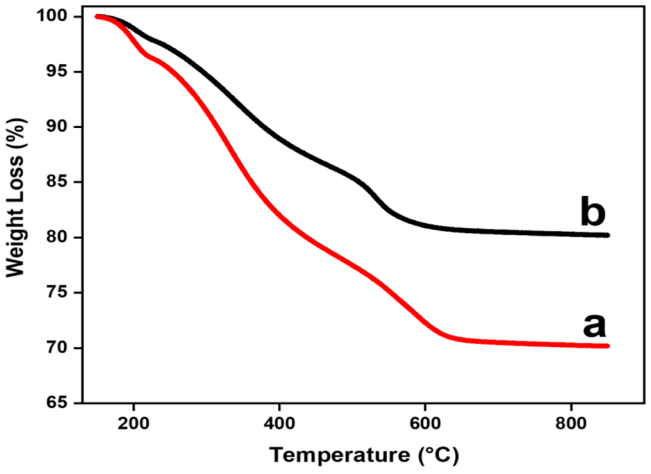

Figure 4. TGA thermograms of (a) wet-grafted W-AG-150A and (b) dry-grafted AG-150A in air flow.

desorption of atmospheric CO_2 and adsorbed water as well as the removal of methoxy ligands; as such, it was omitted.[32,33] The weight loss observed above 150 °C is a result of the decomposition of the grafted amine.[8,32] The weight leveled off around 600 °C, which signifies that grafted amine underwent degradation and air oxidation from 150 to 600 °C. W-AG-150A exhibited a 29.9% weight loss while its dry counterpart AG-150A exhibited only a 19.8% weight loss. These results indicate that the addition of water during grafting plays an important role in increasing amine concentration.

4.2.2. CO_2 Capture Capacity. The CO_2 and N_2 adsorption isotherms of AG-150A and W-AG-150A at 25 °C are presented in Figure 5. CO_2 adsorption measurements were performed to

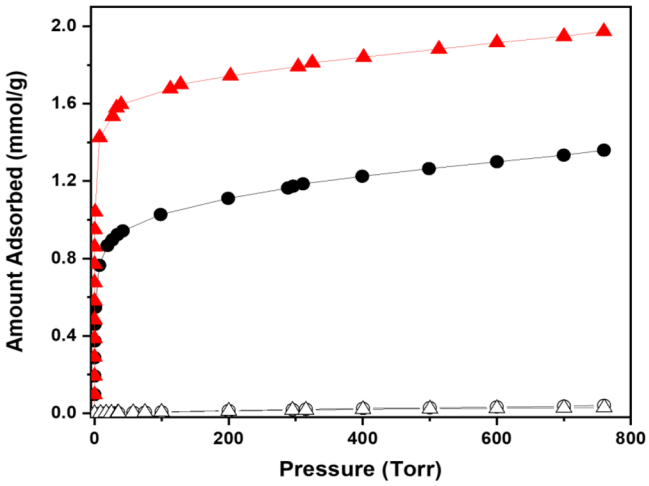

Figure 5. CO_2 (filled symbols) and N_2 (open symbols) adsorption isotherms for dry-grafted AG-150A (●) and wet-grafted W-AG-150A (▲) at 25 °C.

verify that the increase in amine loading would result in enhancing the CO_2 capture capacity. Figure 5 shows a sharp vertical increase in the low-pressure region between 0 and 0.2 bar, which corresponds to the strong interaction between the amine groups and CO_2 molecules.[8] In this region, there is a much higher increase for W-AG-150A, when compared to AG-150A. This is because AG-150A does not contain as many amine groups, so the interaction strengths between the support and CO_2 molecules are weaker.[25] This result indicates that the wet-grafted sample is promising for direct air capture. Moreover, a further increase from 0.2 to 1 bar corresponds to physical adsorption (via van der Waals interactions) of CO_2 on the samples.[25] The CO_2 adsorption capacity at 1 bar and 25 °C for W-AG-150A is 1.97 mmol/g, which is 46% higher than AG-150A.

Another factor to examine for amine-grafted adsorbents is amine efficiency (mol CO_2/mol N). Under dry conditions, the maximum theoretical amine efficiency is 0.5, and values above the theoretical value correspond to wet conditions.[23] From Table 2, AG-150 and W-AG-150A exhibited maximum amine efficiencies of 0.398 and 0.384, respectively. It is evident that after wet grafting there is a negligible decrease in amine efficiency. This proves that a large portion of the grafted amines on W-AG-150A contributed to the adsorption of CO_2 and that the higher amine loading did not impact the accessibility of the amines.

Equally important are the conditions related to flue/postcombustion gas. Flue gas needs to be cooled to around 44 to 70 °C.[34] The CO_2 isotherms of W-AG-150A at 25 and 75 °C presented in Figure 6 address its CO_2 capture capacity at those conditions. There is a noticeable increase in CO_2 adsorption capacity as the temperature increases. For flue gas (~0.15 bar CO_2), the CO_2 adsorption capacity of W-AG-150A increased from 1.69 mmol/g (25 °C) to 1.83 mmol/g (75 °C). At 1 bar, the CO_2 adsorption capacity increased from 1.97

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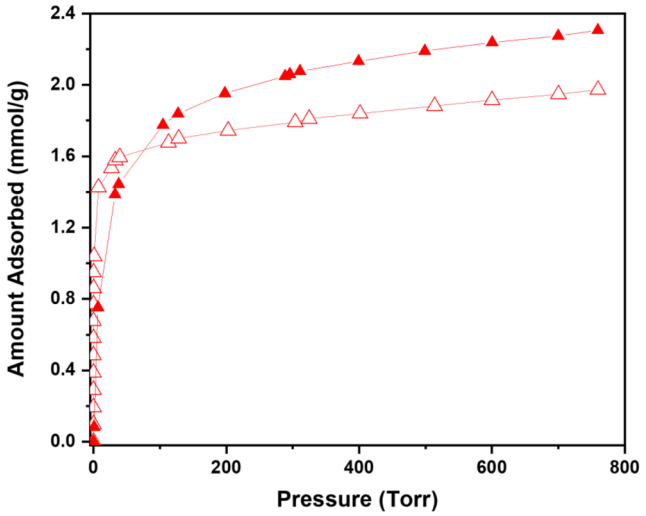

Figure 6. CO_2 adsorption isotherms for wet-grafted W-AG-150A at 25 °C (△) and 75 °C (▲).

mmol/g (25 °C) to 2.3 mmol/g (75 °C). Notably, however, the CO_2 adsorption capacity decreased beyond 75 °C as evidenced in Figure 7. At 90 °C, the CO_2 adsorption capacity

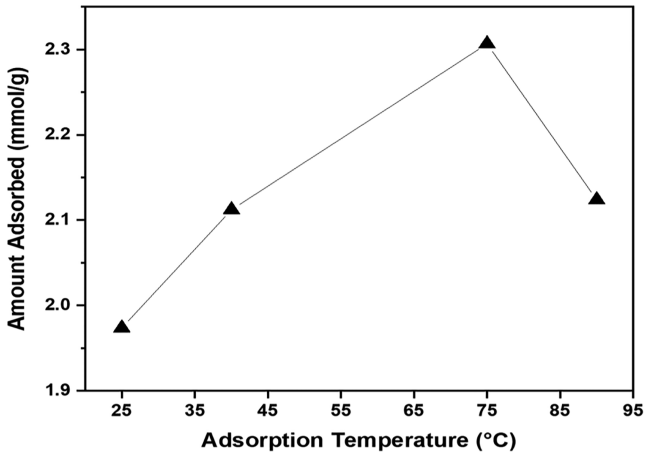

Figure 7. CO_2 adsorption capacity of wet-grafted W-AG-150A at 1 bar and different temperatures.

was 2.12 mmol/g at 1 bar. This phenomenon is typical for wet impregnated adsorbents using polyethyleneimine (PEI) and wet-grafted adsorbents with a high degree of aminosilane polymerization.[6,24−26,35,36] These adsorbents, similar to W-AG-150A, achieved their highest CO_2 adsorption capacity at 75 °C. This can be explained by diffusion limitations within the pores which caused some of the amines to be inaccessible.[6,25] However, as the temperature increases, the polymer-like amines become more mobile, allowing CO_2 access to more amines.[6,25] Even so, as the temperature rises beyond 75 °C, the thermodynamic equilibrium shifts, and the CO_2 adsorption capacity decreases.[6,25]

In addition, flue gas is composed of mostly nitrogen and carbon dioxide.[34] Therefore, the selectivity of CO_2 over N_2 for promising adsorbents is an important metric that must also be evaluated. The N_2 adsorption isotherms of AG-150A and W-AG-150A at 25 °C are presented in Figure 5. At 25 °C, the amount of nitrogen adsorbed on AG-150A and W-AG-150A was insignificant. AG-150A exhibited a CO_2/N_2 single-component selectivity of 119 at 0.15 bar and 32 at 1 bar. Similarly, W-AG-150A exhibited a CO_2/N_2 selectivity of 195 at 0.15 bar and 63 at 1 bar. Thus, the CO_2/N_2 selectivity for W-AG-150A is 1.6 times at 0.15 bar and 1.9 times higher at 1 bar than AG-150A. This means the addition of water during the grafting process to increase amine concentration did not abate the CO_2/N_2 selectivity. Moreover, it is expected that the CO_2/N_2 selectivity will be higher at 75 °C (as N_2 adsorption will decrease).

The results from this study as well as from the literature utilizing similar methods are summarized in Table 3. W-AG-150A is evidently highly competitive, with similar or higher CO_2 adsorption capacity than all the adsorbents.

Table 3. Summary of Wet-Grafted Silica Adsorbents and Their CO_2 Capture Capacities

		CO_2 adsorption capacity			
sample	amine used	CO_2 partial pressure (bar)	temp (°C)	capacity (mmol/g, dry)	ref
MCM-41	triamine	0.2	75	2.1	25
KIT-6	APTES	1	25	1.56	31
SBA-15	diamine	0.15	60	1.36	37
SBA-15	triamine	0.15	60	1.58	37
SBA-15	triamine	0.05	25	1.88	26
SBA-15	triamine	0.89	75	2.3	24
SBA-15	triamine	1	25	0.13	present work
W-AG-150A	triamine	1	25	1.97	present work
W-AG-150A	triamine	1	75	2.3	present work

4.2.3. Uptake Rates. The adsorption rates of CO_2 were measured for W-AG-150A at 25 and 75 °C using the gravimetric method. The measurement was carried out by introducing W-AG-150A to a 70% CO_2/He feed gas mixture at time = 0, from an initially helium flow, at the desired temperature. As shown in Figure 8, the CO_2 adsorption capacity after 200 min is 65.9 mg/g at 25 °C and 75.2 mg/g at

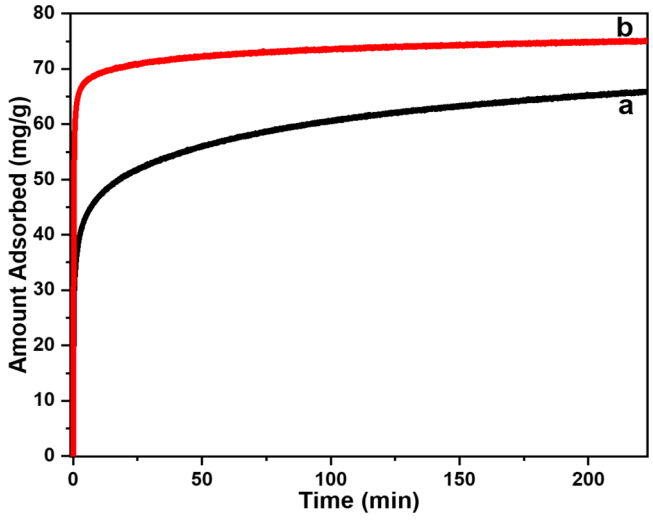

Figure 8. CO_2 uptake rates on wet-grafted W-AG-150A at 25 °C (a) and 75 °C (b) under a 70% CO_2 (in He) flow.

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75 °C. As stated earlier, the increased adsorption capacity at 75 °C is due to the enhanced accessibility of the amines by CO_2.

Furthermore, the uptake rates can be expressed by a diffusion time constant (D/R^2, where D is pore diffusivity, and R is the radius of the particle).[32] The diffusion time constant can be calculated from the TGA data presented in Figure 8. This is the first time the uptake rates are reported for CO_2 in wet amine-grafted silica gel. The calculated D/R^2 is summarized in Table 4. From Table 4, it is evident that the uptake rates at 75 °C are markedly higher (52%) than at 25 °C. This elevated rate of adsorption at 75 °C is due to the increased kinetic energy of the CO_2 molecules as temperature increases, leading to faster diffusion of the CO_2 molecules in the pores.[25]

Table 4. Diffusion Time Constants (D/R^2) for W-AG-150A at 25 and 75 °C

temp (°C)	D/R^2 (1×10^{-3}), s^{-1}
25	2.767
75	5.242

4.2.4. Cyclic Stability. For practical applications, it is imperative that the promising adsorbent is stable after multiple cycles. The multicycle stability of W-AG-150A was carried out at 75 °C (highest performing condition). W-AG-150A was regenerated at 90 °C in He after each adsorption measurement, and it took approximately 3 min to fully regenerate. After the 17 cycles, there was no significant loss in CO_2 adsorption capacity at 75 °C (Figure 9). The observed losses can be attributed to the formation of urea groups after repeated adsorption/desorption cycles at high temperatures as well as possible carbamate decomposition.[26,38] However, the formation of the urea groups, which serve to deactivate grafted amines, can be inhibited by performing CO_2 adsorption in wet conditions.[26,38] Finally, it can be concluded that the CO_2 adsorption capacity did not change significantly after multiple cycles which is consistent with previous findings for wet-grafted adsorbents and indicates that W-AG-150A exhibits multicycle stability.[24,25,31]

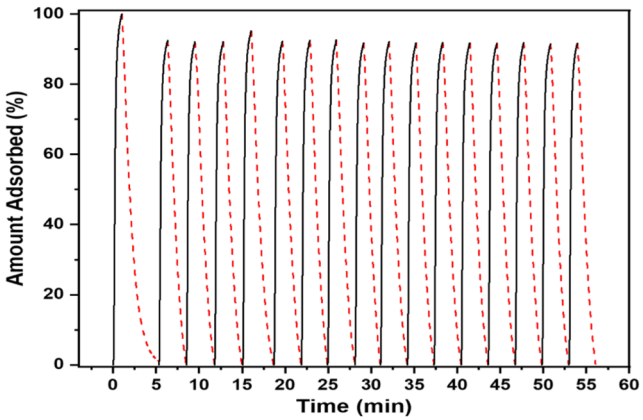

Figure 9. Cyclic stability studies (70% CO_2 (in He) flow; desorption in He at 90 °C (dashed line)) of wet-grafted W-AG-150A at 75 °C and 1 bar.

4.2.5. Fixed-Bed Breakthrough Curves. Fixed-bed adsorption breakthrough experiments were performed on W-AG-150A, using ambient air feed (with 415 ppm of CO_2), at a high gas hourly space velocity of 6,500 h^{-1}. The results for dry (pre-dried with 3A zeolite) and wet feed conditions are presented in Figure 10. The sharp breakthrough curves indicated the lack of mass transfer limitation. The calculated CO_2 adsorption capacity under dry and wet conditions was 0.773 and 1.098 mmol/g, respectively. The increased breakthrough capacity and longer breakthrough time are typical for measurements performed in wet conditions. This phenomenon occurs because under wet conditions, a larger amount of carbamate ion pairs is formed due to the liberation of hydrogen bonded amines under wet conditions.[13,14] The formation of bicarbonates is also observed under wet conditions.[5,13,15] To the best of our knowledge, 1.098 mmol/g is the highest recorded adsorption capacity for an amine-grafted silica gel and amine-grafted SBA-15.[39,40] These results indicate that this adsorbent would be well-suited for capturing CO_2 directly from ambient air.

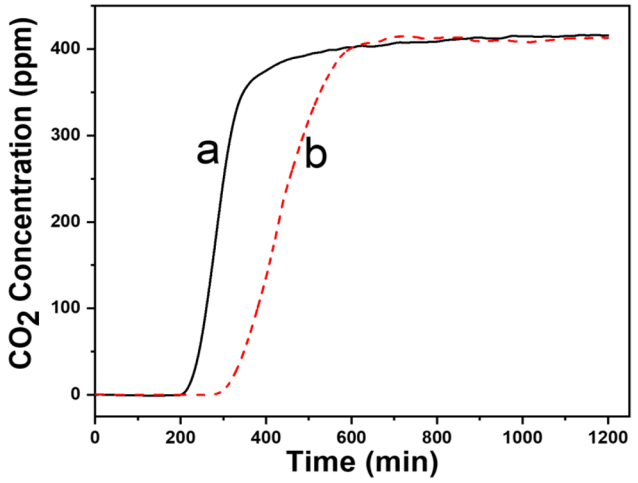

Figure 10. CO_2 breakthrough curves for wet-grafted W-AG-150A under an ambient air feed at 25 °C, 0.96 bar, and R.H. 0.0% (a) and at 25 °C, 0.96 bar, and R.H. 60% (b). Space velocity = 6,500 h^{-1}.

In addition, Stuckert et al. performed breakthrough experiments utilizing similar operating conditions as this work on zeolites (Li-LSX, K-LSX, and NaX) and amine-grafted SBA-15.[40] The breakthrough capacity of W-AG-150A (0.773 mmol/g) under dry conditions was similar to Li-LSX (0.82 mmol/g), the best performing zeolite, and significantly higher than K-LSX (0.25 mmol/g), NaX (0.32 mmol/g), and amine-grafted SBA-15 (0.09 mmol/g). Under wet conditions, the CO_2 adsorption capacity of W-AG-150A and amine-grafted SBA-15 increased by 42% (1.098 mmol/g) and 44% (0.13 mmol/g), respectively. Conversely, the zeolites experienced almost a total loss of all CO_2 adsorption capacity. This has been observed for others zeolites under wet conditions.[16] When compared to Li-LSX, K-LSX, NaX, and amine-grafted SBA-15, W-AG-150A's breakthrough performance was comparable under dry conditions and superior under wet conditions due to the positive influence of moisture on CO_2 adsorption capacity.

5. CONCLUSION

In this work, various commercially available silica gels with a wide range of pore structures were dry-grafted using triamine. CO_2 adsorption results, pore properties, and amine loading analysis performed on these samples provided insight as to

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which silica gel would be suitable for further enhancement. Silica gel 150A (with the highest pore size and pore volume but the lowest BET surface area) was chosen for further enhancement due to its favorable characteristics. The enhancement process involved the addition of water during grafting to increase the amine concentration, which in turn enhances CO_2 capture performance. The addition of 0.15 mL of water (under specified grafting conditions) during grafting resulted in a CO_2 adsorption capacity of 1.83 mmol/g at 75 °C and 0.15 bar and 2.3 mmol/g at 75 °C and 1 bar. CO_2/N_2 pure-component selectivity was enhanced, and the wet-amine-grafted W-AG-150A displayed excellent amine efficiency, cyclic stability, and fast uptake rates. Breakthrough adsorption experiments with ambient air feed performed under dry and wet conditions indicate that W-AG-150A is an excellent adsorbent for direct air capture purposes. Due to its commercial availability, low-cost, and excellent CO_2 capture performance, W-AG-150A can be considered a promising amine-functionalized adsorbent for direct air capture as well as flue gas CO_2 capture applications.

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The authors declare no competing financial interest.

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