

Supporting Information

Improving the Direct Air Capture Capacity of Grafted Amines via Thermal Treatment

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Experimental Section

Materials

Reagent grade or above toluene, hexanes, methanol, 37% hydrochloric acid, poly(ethylene glycol)-*block*- poly(propylene glycol)-*block*-poly(ethylene glycol) (Pluronic P-123), and tetraethyl orthosilicate (TEOS) were purchased from Millipore Sigma or VWR. (2-aminoethyl)-3-aminopropyltrimethoxysilane (ethyl diamine), 3-aminopropyl trimethoxysilane (propyl monoamine), and (6-aminohexyl)aminopropyl trimethoxysilane (hexyl diamine) were purchased from Gelest Inc. Catalox HP 14/150 alumina was provided by Sasol, SS 6*137 silica was provided by Saint Gobain, and Aeroxide P25 titania was provided by Evonik. UHP nitrogen, air, helium, 410 ppm carbon dioxide in nitrogen (simulated air), and 4% carbon dioxide in nitrogen were purchased from Airgas. All materials were used as received without further purification.

Synthesis of amine-grafted sorbents

The synthesis of SBA-15 followed previously reported procedures.¹ In brief, 636 mL of DI water was mixed with 120 mL of 37% hydrochloric acid and 24 g of Pluronic P-123 in a 2 L Erlenmeyer flask. 46.3 g of tetraethyl orthosilicate (TEOS) was added dropwise to the solution while stirring. Next, the solution was heated to 40 °C while stirring for 20 hours. The stir bar was then removed, and the solution heated further to 100 °C for 24 hours. The solution was removed from heat and quenched with 400 mL of DI water. The solid SBA-15 was filtered from solution and rinsed with ~5 L of DI water before drying in a 75 °C oven for at least 8 hours. Finally, the SBA-15 was calcined in air with the following heating protocol: heat to 200 °C (1 °C/min); hold at 200 °C for 1 hour; heat to 550 °C (1 °C/min); hold at 550 °C for 12 hours; cool to room temperature.

The aminosilane grafting to the oxide supports all followed the same basic procedure.¹ The support material was dried overnight at 100 °C under vacuum before functionalization. In a round bottom flask, 1 g of oxide ($\text{Al}_2\text{O}_3/\text{SiO}_2/\text{TiO}_2$) was stirred in 50 mL of toluene. Next, 200 μL of water was added to the stirred solution and allowed to equilibrate for at least 1 hour. The aminosilane was diluted in 2 mL of toluene then added dropwise to the stirring solution. The aminosilane concentration was used to control the grafting density, with 1.5, 2.25, and 3 mol/kg (mol aminosilane/kg oxide support) used to functionalize the low, medium, and high loading ethyl diamine SBA-15 samples, respectively. All other samples were grafted using 3 mol/kg aminosilane solutions. The flask was then purged with argon, fitted with a condenser, and heated to 80 °C for

~18 hours. The functionalized oxides were filtered, washed with ~100 mL each of toluene, methanol, and hexanes before drying under vacuum at 100 °C.

Characterization

Physisorption

Nitrogen physisorption at 77 K was measured on a Gemini VII 2390p (Micromeritics). Samples were dried at 100 °C overnight before analysis. The synthesized SBA-15 had a BET surface area of 735 m²/g and pore volume of 0.866 cm³/g at $p/p^0 = 0.99$.

Elemental Analysis

Elemental analysis was performed by Midwest Microlab. C, H, and N analysis on each sample was performed in duplicate and the results averaged. Samples were dried at 80 °C under vacuum for 2 hours before analysis.

Thermogravimetric Analysis

The CO₂ capacity, aminosilane loading, and decomposition products were measured in a SDT 650 DSC/TGA (TA Instruments) with an OmniStar GSD 350 mass spectrometer (Pfeiffer Vacuum) attached to the outlet of the furnace. The sample and balance gas flow rates were 100 mL/min.

The amine loading was determined by comparing the mass loss during heating of the grafted samples to the bare oxides. Samples were degassed at 100 °C for 1 hour before heating to 900 °C at 10 °C/min in air. Table S1 lists the amine loadings determined via TGA.

Table S1. Amine loading density determined via TGA. An average of 2.5 out of 3 silanes per aminosilane molecule are assumed to be grafted to the oxide surface.

Sample	Support	Support Surface Area (m ² /g)	Amine Loading (mmol/g)	Silane Density (#/nm ²)
Ethyl diamine - low	SBA-15	726	2.22	1.1
Ethyl diamine - medium	SBA-15	726	2.96	1.6
Ethyl diamine - high	SBA-15	726	3.42	1.9
Propyl monoamine	SBA-15	726	2.10	1.7
Hexyl diamine	SBA-15	726	2.80	1.6
Ethyl diamine	Al ₂ O ₃	97	3.25	9.1
Ethyl diamine	SiO ₂	160	2.67	6.0
Ethyl diamine	TiO ₂	43	2.03	14

Figure S1 and Table S2 show the temperature and gas profiles used for the CO₂ adsorption experiments.

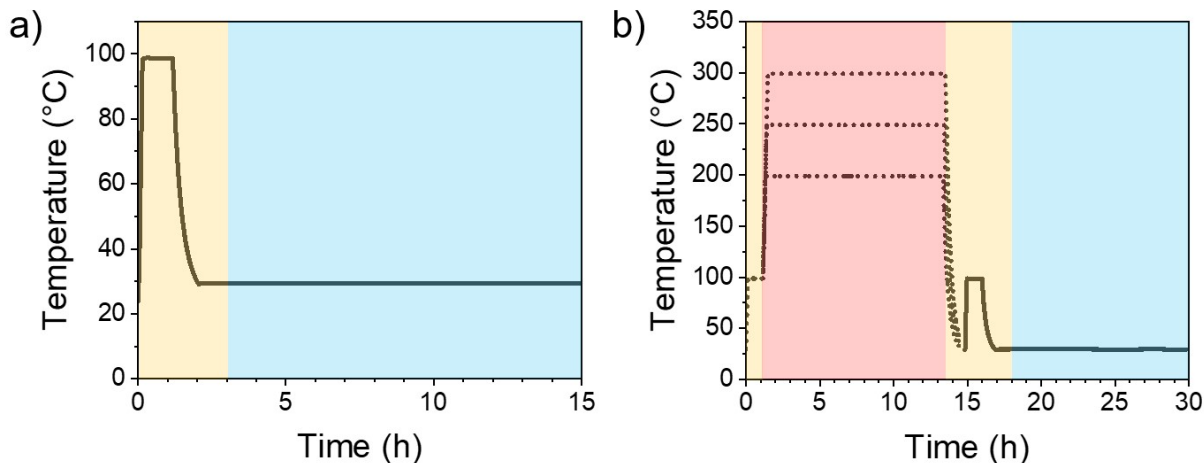


Figure S1. a) TGA temperature profile used for untreated samples. The sample was first degassed under N₂ (yellow) before 410 ppm CO₂ adsorption (blue) at 30 °C. b) TGA temperature profile used for thermally treated samples. The sample was degassed, heated to either 200, 250, or 300 °C in N₂ (red), then degassed again before CO₂ adsorption.

Table S2. TGA profile parameters for degassing, thermal treatment, and adsorption.

Step	Temperature (°C)	Ramp Rate (°C/min)	Time (h)	Gas
Degas	100	10	-	N ₂
Degas	100	-	1	N ₂
Thermal Treatment	200/250/300	10	-	N ₂
Thermal Treatment	200/250/300	-	12	N ₂
Adsorption	30	10	-	N ₂
Adsorption	30	-	1	N ₂
Adsorption	30	-	12	410 ppm CO ₂ in N ₂

The individual CO₂ uptake curves for the data shown in Figure 1a is displayed in Figure S2. The CO₂ uptake capacity and amine efficiency are shown in Figure S3. The standard deviation on the CO₂ capacity is ± 0.01 mol/kg.

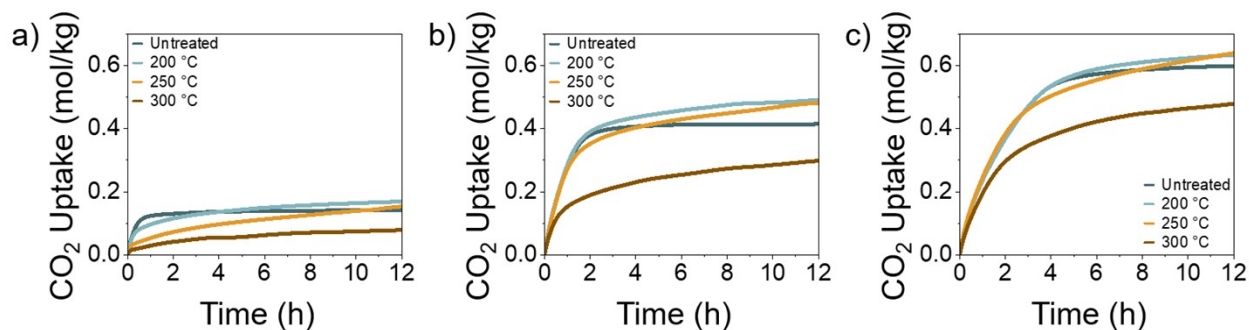


Figure S2. The direct air capture (30 °C, 410 ppm CO₂ in N₂) uptake curve for a) low, b) medium, and c) high loading ethyl diamine grafted SBA-15 exposed to either 200, 250, or 300 °C thermal treatment for 12 hours.

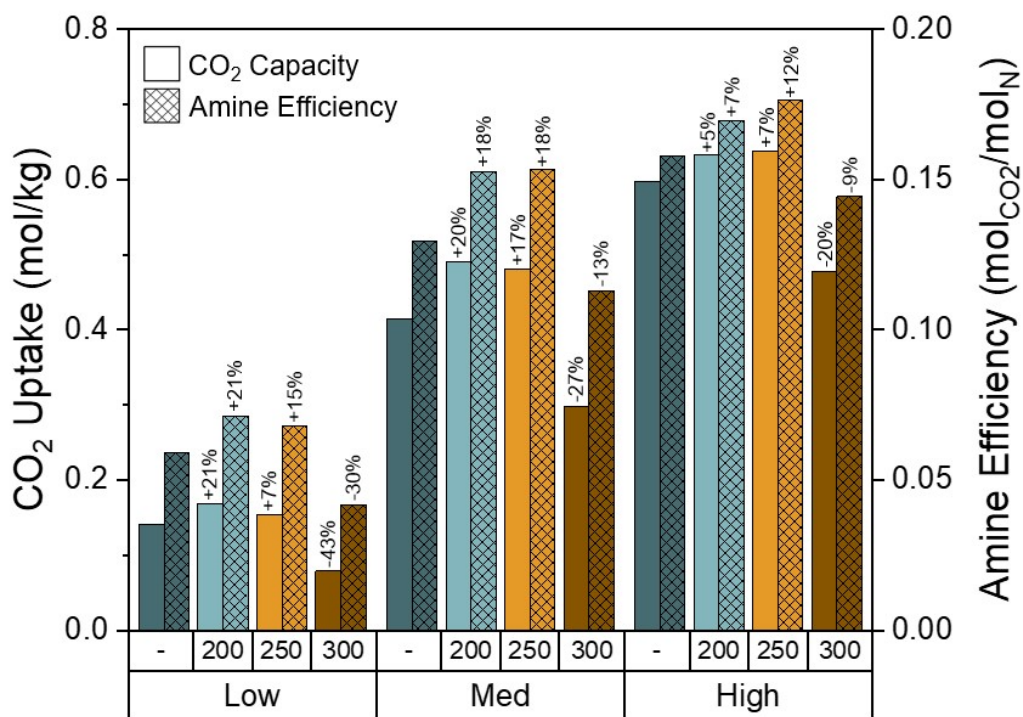


Figure S3. The direct air capture capacity (30 °C, 12 hours, 410 ppm CO₂ in N₂) and amine efficiency for SBA-15 sorbents grafted with low, medium, and high loadings of ethyl diamine. Each loading of sample was exposed to either 200, 250, or 300 °C thermal treatment in N₂ for 12 hours prior to CO₂ uptake and compared against an untreated sample.

The effect of thermal treatment time was investigated on high loading ethyl diamine grafted SBA-15 with a thermal treatment temperature of 200 °C (Figure S4). All treatment times lead to improvements in the CO₂ capacity compared to the untreated sample, with the 30-minute exposure having the largest improvement. While 12 hours is ample time to allow for thermal rearrangements to occur, prolonged exposure at elevated temperatures can lead to greater degradation. No appreciable changes in the uptake rate after the first few minutes were observed between the different treatment times.

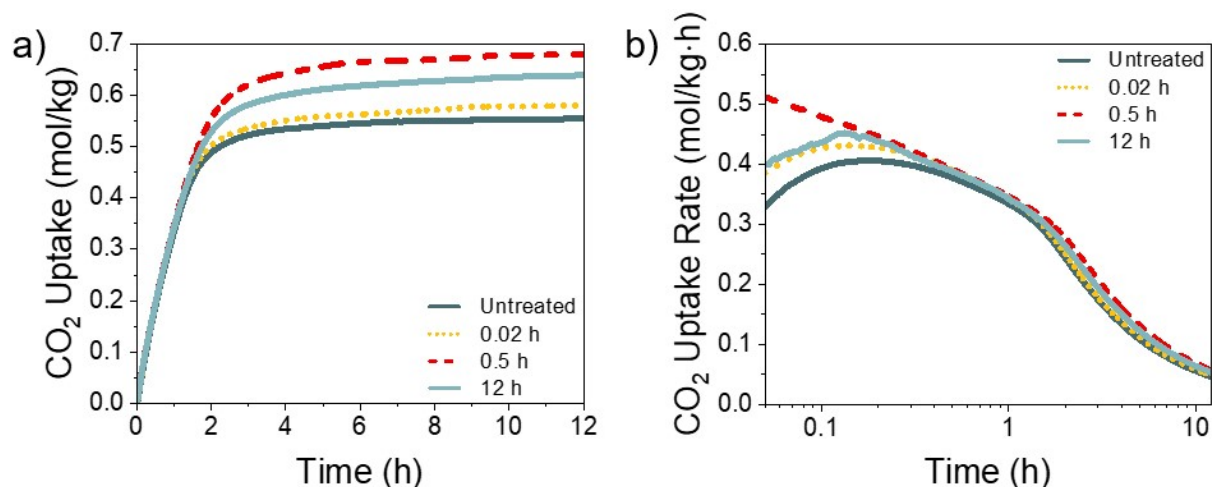


Figure S4. The effect of thermal treatment time of the direct air capture (30 °C, 410 ppm CO₂ in N₂) uptake curve for high loading ethyl diamine grafted SBA-15 treated at 200 °C for various lengths of time. The corresponding instantaneous CO₂ uptake rate over the course of the adsorption steps.

The grafting of amines with structural variations was also investigated. The CO₂ uptake performance of a primary amine, 3-aminopropyl trimethoxysilane (propyl monoamine), and a diamine with a hexyl carbon spacer, (6-aminohexyl)aminopropyl trimethoxysilane (hexyl diamine), are shown in Figure S5. Interestingly, the CO₂ capacity does not exhibit the same decrease at 300 °C as seen in with the ethyl diamine grafted materials, suggesting that these amine structures may be more resistant to degradation from the thermal treatments.

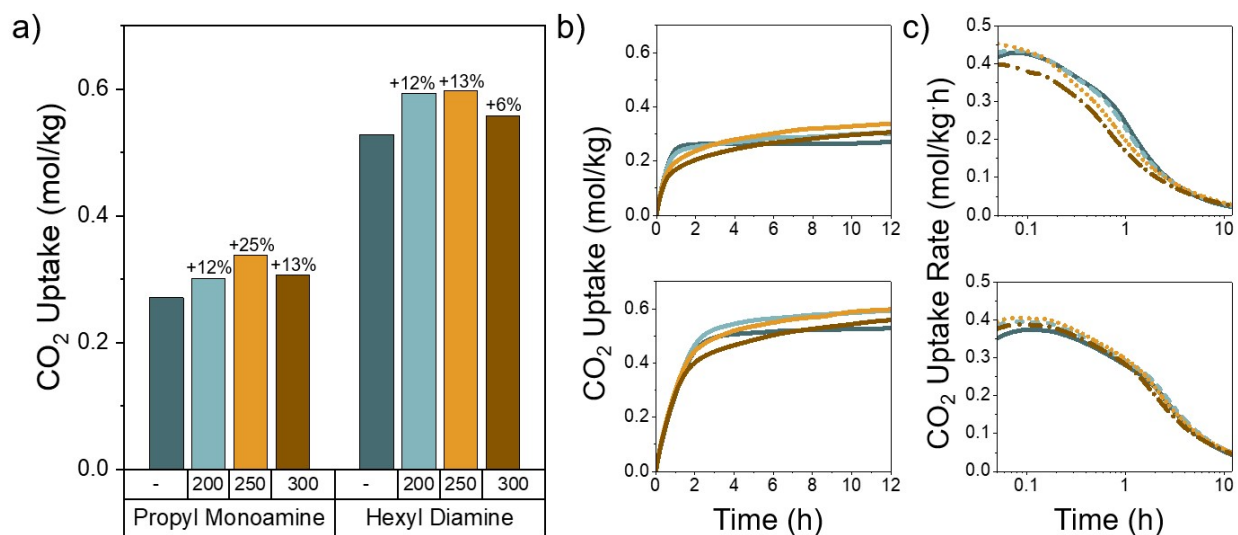


Figure S5. The direct air capture (30 °C, 410 ppm CO₂ in N₂) uptake curve for a) propyl monoamine and hexyl diamine grafted SBA-15 sorbents exposed to either 200, 250, or 300 °C thermal treatment for 12 hours. b) The uptake curves for propyl monoamine (top) and hexyl diamine (bottom) grafted SBA-15. c) The corresponding instantaneous CO₂ uptake rate over the course of the adsorption step for propyl monoamine (top) and hexyl diamine (bottom) grafted SBA-15. The colors represent the different thermal treatments, dark blue – untreated, blue – 200 °C, orange – 250 °C, and brown – 300 °C.

Ethyl diamine was grafted onto commercially available alumina (Al_2O_3), silica (SiO_2), and titania (TiO_2) supports and exposed to thermal treatments (Figure S6). The CO_2 capacity trends for each support are similar to the SBA-15 grafted sorbents. However, the alumina grafted materials exhibit a much more dramatic loss in capacity with thermal treatment temperature that could be related to acidity of the alumina surface hydroxyls compared to silica or titania.

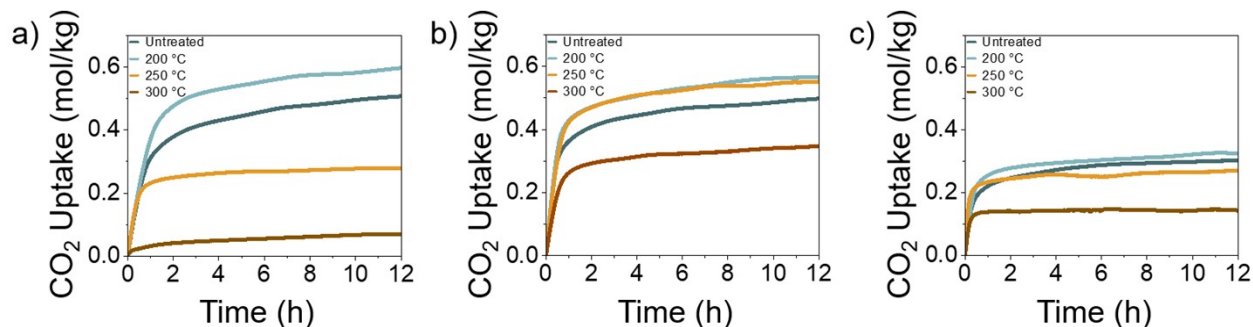


Figure S6. The direct air capture (30 °C, 410 ppm CO_2 in N_2) uptake curve for ethyl diamine grafted onto commercially available a) Al_2O_3 , b) SiO_2 , and c) TiO_2 supports exposed to either 200, 250, or 300 °C thermal treatment for 12 hours.

The use of a higher concentration feed was investigated with the high loading ethyl diamine grafted SBA-15. The uptake results using 4% CO_2 are shown in Figure S7. A similar trend in CO_2 capacity change with thermal treatment temperature is observed.

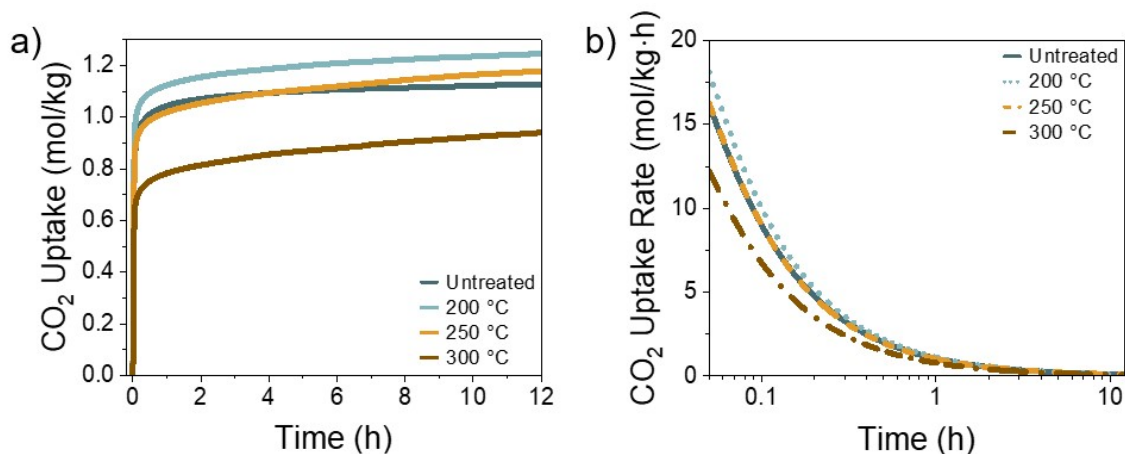


Figure S7. The 4% CO_2 in N_2 uptake curve for a) high loading ethyl diamine grafted SBA-15 exposed to either 200, 250, or 300 °C thermal treatment for 12 hours. The CO_2 uptake was measured at 30 °C. b) The corresponding instantaneous CO_2 uptake rate over the course of the adsorption step.

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments were conducted on a Nicolet iS50 spectrometer using the Praying Mantis accessory and high temperature reaction chamber with CaF₂ windows. Data was collected in the OMNIC software in the range of 1111–4000cm⁻¹ with resolution set to 4 and collecting 32 scans for each spectrum. A background with KBr in the sample cup was collected and subtracted from each spectrum.

Figure S8 shows a schematic of when the DRIFTS scans in Figure 2 were taken as a function of experiment time, along with the reactor parameters in Table S3. The solid lines represent the spectra, with the dashed lines representing the baseline used for subtraction. The spectra in Figure 2a were taken after the second degas step in Figure S8; untreated sample shown by 1-1B and thermally treated samples shown by 2-2B. The spectra in Figure 2b were taken at the points represented by 3-3B (untreated) and 4-4B (thermally treated). The full spectra for the high loading ethyl diamine SBA-15 before and after thermal treatment and the CO₂ binding spectra are shown in Figure S9.

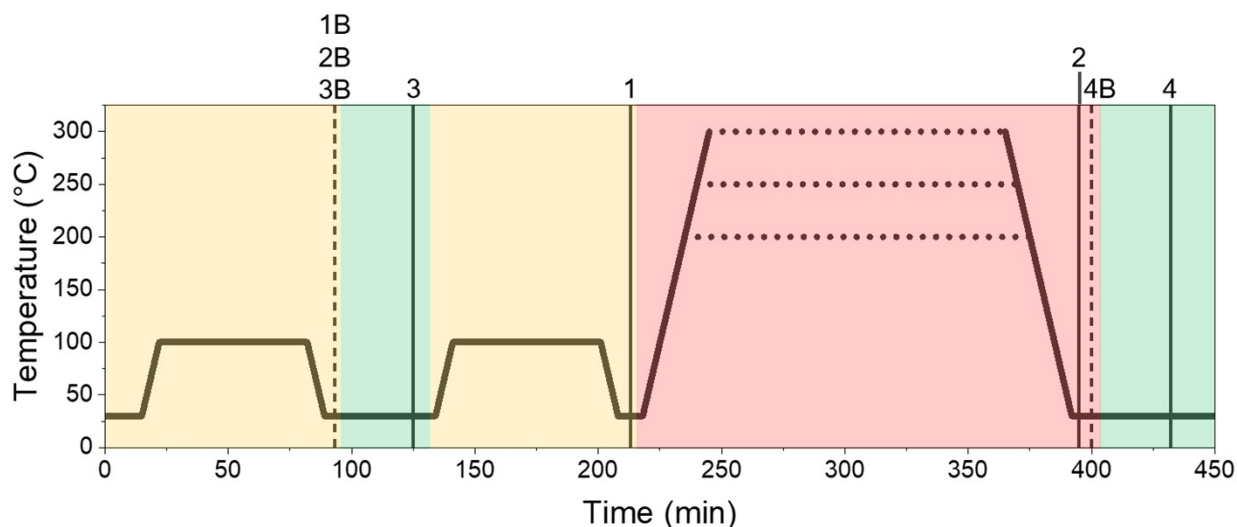


Figure S8. The temperature profile used during DRIFTS measurements of high loading ethyl diamine SBA-15. The sample was first degassed under N₂ (yellow) before adsorption in a 1% CO₂/He atmosphere (green) at 30 °C. The samples were thermally treated at either 200, 250, or 300 °C in N₂ (red) before a second CO₂ adsorption step. The solid vertical lines represent the IR scans associated with measurements and the dashed vertical lines correspond to the baseline spectra subtracted from them. The measurement lines are labeled with their corresponding baselines (e.g., line 1 with baseline 1B).

Table S3. Reactor parameters for degassing, adsorption, and thermal treatment for the in-situ DRIFTS measurement. The total gas flow was kept constant at 100 mL/min.

Step	Temperature (°C)	Ramp Rate (°C/min)	Time (h)	Gas
Degas	100	10	-	N ₂
Degas	100	-	1	N ₂
Adsorption	30	10	-	N ₂
Adsorption	30	-	0.5	1% CO ₂ in He
Thermal Treatment	200/250/300	10	-	N ₂
Thermal Treatment	200/250/300	-	2	N ₂

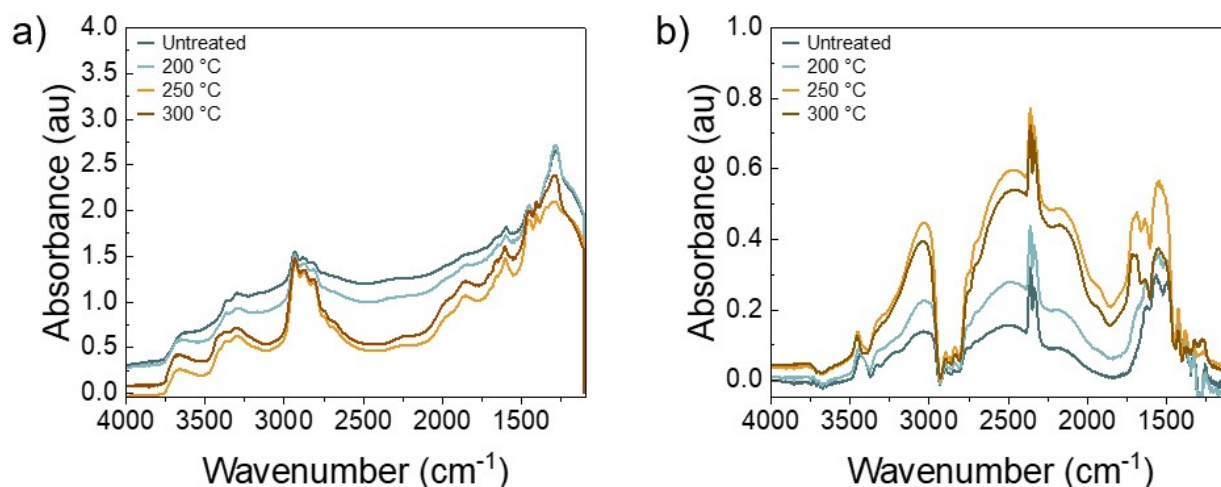


Figure S9. a) Full DRIFTS spectra of high loading ethyl diamine grafted SBA-15 sorbents untreated and exposed to thermal treatments (separate samples). Spectra measured in an N₂ environment. b) Full DRIFTS CO₂ binding spectra for high loading ethyl diamine grafted SBA-15 sorbents untreated and exposed to thermal treatments. Spectra measured in a 1% CO₂/He environment.

The peak assignments from the DRIFTS spectra in Figure 2 are listed in Tables S4 and S5.

Table S4. DRIFTS peak assignments for high loading ethyl diamine grafted SBA-15 measured in a N_2 environment.

Frequency (cm^{-1})	Assignment	Group
3425	$\nu O-H$	Silanol
3370	$\nu_{asym} N-H$	Aminosilane
3300	$\nu_{sym} N-H$	Aminosilane
2935	$\nu_{asym} C-H$	Aminosilane
2875	$\nu_{sym} C-H$	Aminosilane
2810	$\nu_{sym} C-H$	Aminosilane

Table S5. DRIFTS peak assignments for high loading ethyl diamine grafted SBA-15 measured in a 1% CO_2/He environment.

Frequency (cm^{-1})	Assignment	Group
1715	$\nu C=O$	Carbamic acid
1690	$\nu C=O$	Carbamic acid
1630	$\delta_{asym} NH_3^+$	Ammonium ion
1537	$\delta_{asym} NH_3^+$	Ammonium ion

Solid-state Nuclear Magnetic Resonance Spectroscopy

Solid-state nuclear magnetic resonance (SS NMR) spectroscopy was conducted on a 400 MHz Bruker Neo spectrometer operating at Larmor frequencies of 100.6 and 79.48 MHz for ^{13}C and ^{29}Si , respectively. Samples were packed into 4 mm ZrO_2 rotors for magic angle spinning (MAS) measurements within an Ar glovebox and spun at 10 kHz within a 4 mm Revolution HX probe. Spectra were acquired with $^{13}\text{C}\{^1\text{H}\}$ and $^{29}\text{Si}\{^1\text{H}\}$ cross-polarization MAS with a ramped contact pulse on the ^1H channel and with spinal64 ^1H decoupling ($\nu_{rf,H} = 43$ kHz) during acquisition. The Hartmann-Hahn match condition was optimized while spinning at 10 kHz using glycine and kaolinite as standards for ^{13}C and ^{29}Si , respectively. For $^{13}\text{C}\{^1\text{H}\}$ CP/MAS, a ^1H excitation pulse of 3.19 μs ($\nu_{rf,H} = 78$ kHz) was used with a power of $\nu_{rf,H} = 67$ kHz for the contact pulse length of 0.75 ms with the ^{13}C contact pulse matched at $\nu_{rf,H} = 56$ kHz. ^{13}C - ^1H heteronuclear correlation (HETCOR) experiments used the same cross-polarization parameters as the $^{13}\text{C}\{^1\text{H}\}$ CP/MAS, except using a short contact time of 0.1 ms to probe the nearest neighbor protons. The HETCOR spectrum was acquired with 32 points in the indirect dimension and using $\nu_{rf,H} = 100$ kHz of FSLG for homonuclear decoupling. For $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS, a ^1H excitation pulse length of 3.72 μs ($\nu_{rf,H} = 67$ kHz) was used with a power of $\nu_{rf,H} = 36$ kHz for the contact pulse length of 1 ms with the ^{29}Si contact pulse matched at $\nu_{rf,Si} = 22$ kHz. A 3.5 s recycle delay was used for all experiments with the number of scans varying from 6144 to 8192 for the CP/MAS experiments and 256 scans per transient for the HETCOR experiments. ^{13}C and ^{29}Si chemical shifts were externally referenced to adamantane ^{13}C $\delta_{iso} = 38.48$ ppm and the mineral kaolinite ^{29}Si $\delta_{iso} = -92$ ppm, respectively.

To further probe the thermal stability of the grafted ethyl diamine functionality, we gathered solid-state NMR spectra on high loading ethyl diamine grafted SBA-15 before and after thermal treatment at 250 °C (Figure S10). The ^{13}C NMR spectra shows four major peaks at 11, 24, 42, and ~53 ppm corresponding to the propyl and ethyl carbons as depicted in Figure S10a.² The intensity of the carbons coordinated to amines (C3-C5) decreases slightly following the thermal treatment, in agreement with the loss of amines. The SBA-15 surface coordination is shown in the $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS spectrum (Figure S10b), displaying four peaks corresponding to Si atoms with different degrees of coordination. They are termed Q_3 (~ -100 ppm), Q_4 (~ -110 ppm), T_2 (~ -60 ppm), and T_3 (~ -65 ppm). Q_4 is fully coordinated framework $\text{Si}(\text{O}-\text{Si})_4$, and Q_3 are single silanols $\text{Si}(\text{O}-\text{Si})_3(\text{O}-\text{R})$. Similarly, T_3 is triply coordinated surface-grafted $\text{Si}(\text{O}-\text{Si})_3(\text{R})$ and T_2 is doubly coordinated surface-grafted $\text{Si}(\text{O}-\text{Si})_2(\text{OH})(\text{R})$. After thermal treatment, there is a small

decrease of Q_3 (unreacted surface Si) and T_2 (partially reacted grafted silane) surface sites, suggesting a removal of hydroxyls and slight condensation of the Si surface.

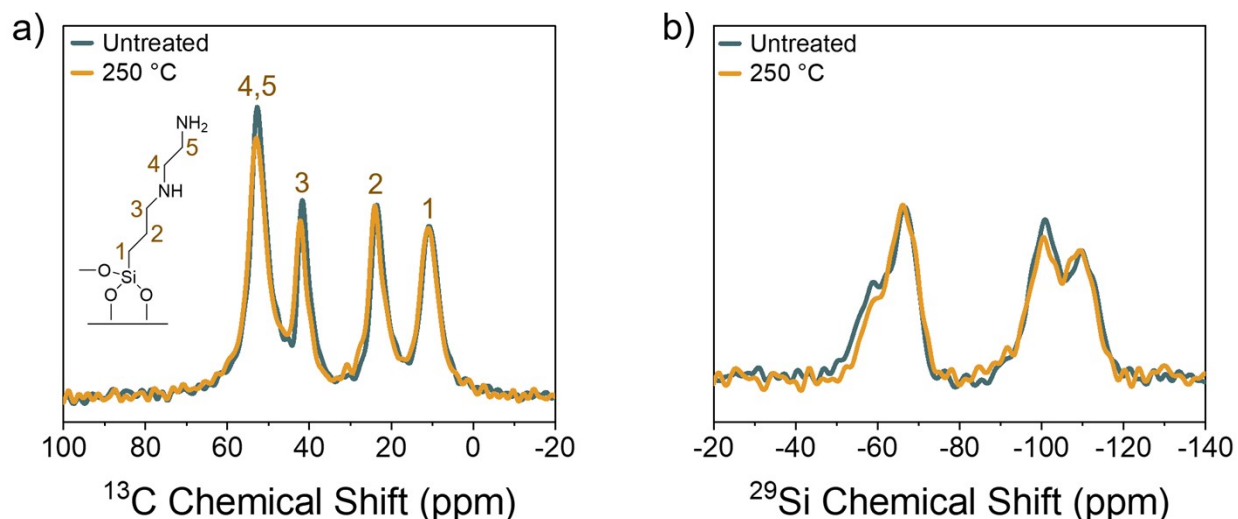


Figure S10. a) ^1H - ^{13}C and b) ^1H - ^{29}Si CP/MAS SS NMR spectra of an untreated and high loading ethyl diamine grafted SBA-15 treated at 250 °C.

To gain more insight into the chemical changes from thermal treatment, ^{13}C - ^1H HETCOR is used to indirectly probe the proton environment on high loading ethyl diamine grafted SBA-15 samples. Similar to the ^{13}C CP/MAS spectra, the differences due to the thermal treatment, as observed in the HETCOR (Figure S11), are minor. They show a growing intensity for ^1H at ~ 3.5 ppm where it is most apparent between the C4 and C3 sites and the small peak correlated to the C1 site. The ^1H spectrum from taking the projection of the indirect dimension (Figure S12) more clearly shows this increase by the rise of a shoulder peak between 3.5–4.5 ppm after thermal treatment. This increased peak intensity points to an increase in hydrogen bonded -OH groups that are undergoing some chemical exchange between silanols and surface bound water.³ This increase in hydrogen bonded -OH groups is in agreement with the observed rise of -OH stretching intensity observed by DRIFTS.

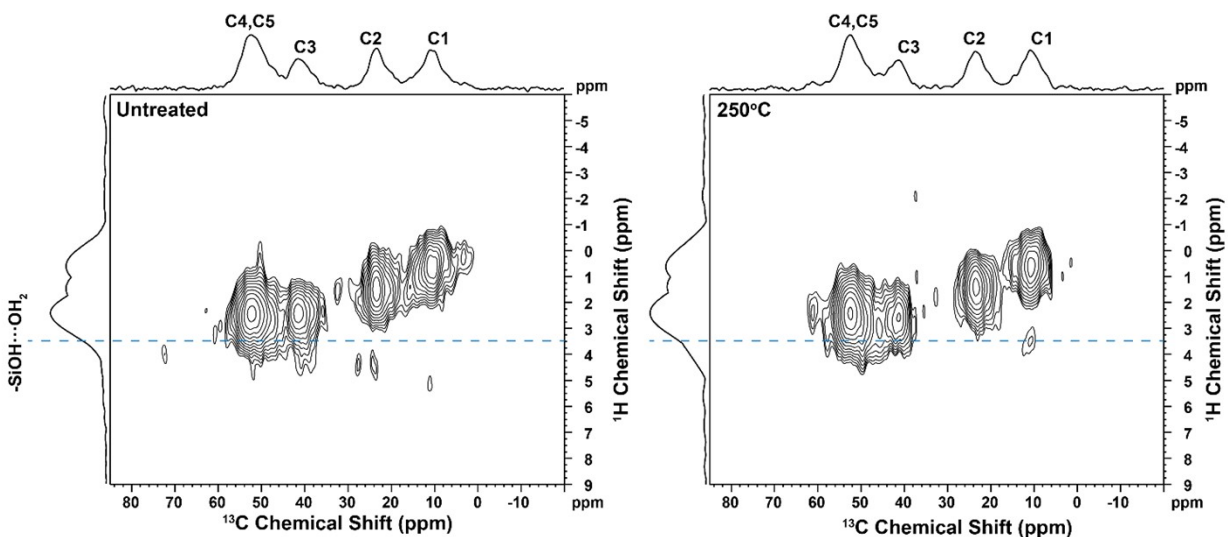


Figure S11. ^1H - ^{13}C HETCOR NMR spectra of high loading ethyl diamine grafted SBA-15 untreated (left) and after 250 °C thermal treatment (right). The ^1H chemical shift for hydrogen bonded -OH groups is noted by a dashed line at 3.5 ppm as a reference.

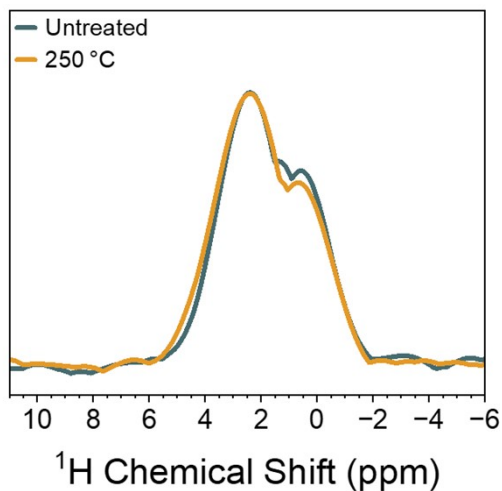


Figure S12. ^1H spectra from the projection of the indirect dimension of the ^1H - ^{13}C HETCOR experiments.

Comparison Data

Table S6 highlights various amine-based sorbents supported on SBA-15 silica studied for DAC. Class I (physical impregnation), Class II (chemical grafting), and Class III (in-situ polymerization) materials are listed for comparison.

Table S6. Comparison of amine/SBA-15 sorbents under dry conditions. CO₂ capacity was measured at 25-30 °C with 400-410 ppm CO₂ feed gas.

Amine	Class	Amine Loading (mol N/kg)	CO ₂ Capacity (mol/kg)	Reference
PEI ¹	I	9.23	1.05	4
APTMS ²	II	3.67	0.43	5
Poly(Z-L-lysine)	III	5.18	0.60	6
APTMS ² (low)	II	2.38	0.14	This work
APTMS ² (med)	II	3.20	0.41	This work
APTMS ² (high)	II	3.78	0.60	This work

¹PEI: poly(ethyleneimine)

²APTMS: 3-aminopropyltrimethoxysilane

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