Supporting Information

Designing Adsorbents for CO_2 Capture From Flue Gas - Hyperbranched Aminosilicas Capable of Capturing CO_2 Reversibly

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Materials. The following chemicals were commercially available and used as received: Pluronic 123 (Aldrich), HCl (Fisher), 3-aminopropyltrimethoxysilane (APTMS, Aldrich), tetraethyl orthosilicate (TEOS, Aldrich), glacial acetic acid (Fisher), anhydrous toluene (Acros), sodium hydroxide pellets (VWR), N-(3-(trimethoxysilyl)propyl)ethane-1,2-diamine (AEAPTMS, Aldrich), methanol (Aldrich), ethanol (VWR) 2-chloroethylamine hydrochloride (Aldrich), tetraethylenepentamine (TEPA, Aldrich), high MW polyethylenimine (PEI, MW ~ 750,000, Aldrich) and low MW polyethylenimine (PEI, MN ~ 600, MW ~ 800, Aldrich). Anhydrous toluene and anhydrous hexanes were further treated by a packed bed solvent purification system utilizing columns of copper oxide catalyst and alumina.[1]

Synthesis of SBA-15 Support. Approximately 12.0 g of Pluronic 123 was weighed and added to a 1000 mL Erlenmeyer flask. To the polymer, 369 g of deionized (D.I.) water and 67 g of HCl was added. This solution was stirred for about 3 hours (or until the polymer dissolved). Once the Pluronic 123 dissolved, 26.4 g of TEOS was added and stirred for 3 minutes. The solution was stirred in the oven for 20 hours at 35 °C. A white precipitate was formed during this time period. At this point, the solution was not stirred and heated to 80 °C for 24 hours. The solution was quenched by adding ~ 400 mL of D.I. water. The precipitate was filtered and washed with D.I. water. The white solid was dried in the sample oven overnight. Some of the as-synthesized SBA-15 (uncalcined, SBA-UN) was used as a support for TEPA shown below (SBA-UNTEPA). The calcination performed involved heating at 1.2 ° C/min to 200 °C and held for 1 hour. Finally, the last ramp was done at 1.2 °C/min to 550 °C and held for 6 hours. The calcined SBA was subsequently dried at 200 °C under vacuum for 3 hours.[2-4]

Synthesis of Aziridine. Aziridine was synthesized in a manner similar to reported procedures with minor changes.[5] A solution of 135 g of D.I. H_2O and 23.14 g of NaOH was prepared. To this solution, 23.60 g of 2-chloroethylamine hydrochloride was added and heated to 50 °C for 2 hours. The product was then distilled at 530 mmHg. The amount of product collected was 6.99 g (80% yield). The aziridine was immediately cooled to 0°C. ^{1}H NMR (400 MHz, D_2O) δ 1.56 (s). ^{13}C NMR (400 MHz, CD_2Cl_2): δ 18.1. Health Hazards: Aziridine is toxic if swallowed, inhaled or absorbed through the skin. Aziridine is a carcinogen. Aziridine is a reproductive hazard.

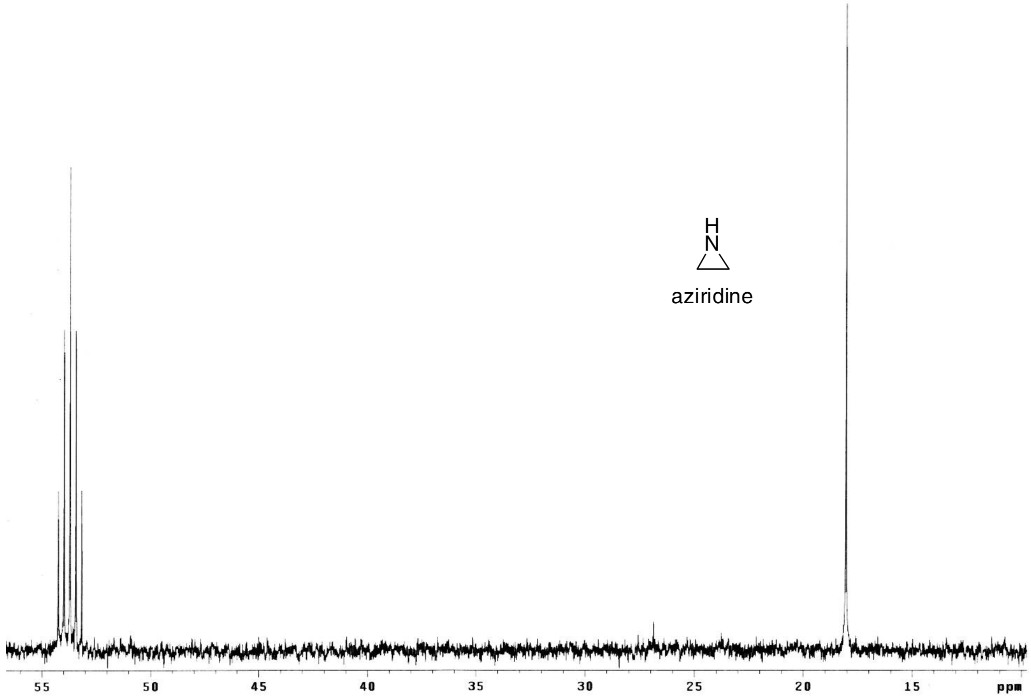

Figure S1. Solution ^{13} C NMR of aziridine.

Reaction of Aziridine with SBA-15 (SBA-HA). The reaction of aziridine with silica was performed similarly to previous reports.[6] The hyperbranched aminosilica (SBA-HA, Figure S2) was synthesized by adding 2.04 g of aziridine to 1.10 g SBA-15 in anhydrous toluene. A small amount of glacial acetic acid was added to catalyze the reaction with the SBA-15 surface. The mixture was stirred overnight at room temperature in a glass pressure vessel. The resulting solid was filtered and washed with copious amounts of toluene then dried at 50 °C under high vacuum. The loading of the material was determined by elemental analysis (EA) as 7.0 mmol N/g.[7]

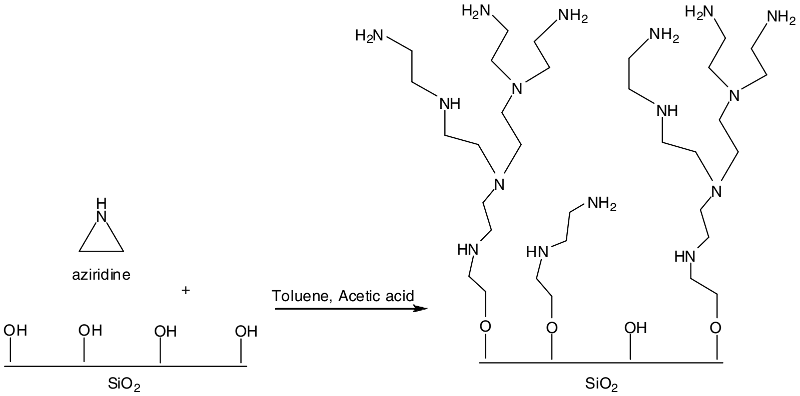

Figure S2. Synthesis and hypothesized structure of the hyperbranched aminosilica (SBA-HA).

Synthesis of Traditional Aminosilica (SBA-NH$_2$). Excess 3-aminopropyltrimethoxysilane, APTMS, (2.0 g) was added to 2 g of SBA-15 in anhydrous toluene. The mixture was allowed to stir for 24 h at room temperature under argon. The resulting solid (SBA-NH$_2$) was filtered, washed with toluene, dried under vacuum at 50 °C overnight, and then stored in a drybox. The organic loading of the material was determined by EA as 1.90 mmol N/g.

Synthesis of Diamine-Functionalized Silica (SBA-Diamine). Excess N-(3-(trimethoxysilyl)propyl)ethane-1,2-diamine, APAETMS, (1.0 g) was added to 1 g of SBA-15 in anhydrous toluene. The mixture was allowed to stir for 24 h at room temperature under argon. The resulting solid (SBA-NH-NH$_2$) was filtered, washed with toluene, dried under vacuum at 50 °C overnight, and then stored in a drybox. The organic loading of the material was determined by EA as 2.50 mmol N/g.

Synthesis of PEI-Impregnated SBA-15 (SBA/PEI (MW 750,000) and SBA/PEI (MW 800)). This material was synthesized similarly to literature procedures using SBA-15 rather than MCM-41.[8, 9] The desired amount of PEI (either high molecular weight ~750,000 or low molecular weight ~800) to create a material with 50 wt % PEI was dissolved in methanol and stirred for 15 minutes. Subsequently, 1 gram of SBA-15 was added and stirred for an additional 30 minutes. The methanol was removed under vacuum. The resulting SBA/PEI was dried for 16 hours at 70 °C and 10 mTorr.

Synthesis of As-Prepared SBA-15 with Occluded Organic Template (SBA-UCTEPA). Materials prepared by methods similar to Zhu et al.[10] Tetraethylenepentamine (TEPA, 0.2 g, 1.06 mmol) was dissolved in ethanol (10 g) and stirred for 30 min at room temperature. Uncalcined SBA-15 (0.2 g) was added and the mixture was refluxed under stirring for 2 hr. The mixture was transferred to a beaker and heated at 80°C until the solvent evaporated. The remaining solid was heated at 100°C for 1 hr.

Polymer Cleavage from the Silica Support. HAS (0.15 g) was added to a concentrated base solution (50 mL, 25wt% potassium hydroxide in D.I. water) and stirred at 40°C for 24 hours. Saturated brine solution (20 mL) was added and three separate extractions were performed with 100 mL portions of dichloromethane. The organic phases were combined and the solvent evaporated under vacuum. A solution of methanol and tetrahydrofuran (60mL, 1:1 vol ratio) was added to the dried residue and stirred for 24 hours. The mixture was centrifuged for 20 minutes at 8500 rpm to settle out insoluble salts. The solvent was evaporated from the decanted liquid under vacuum to recover the polymer.

Characterization Methods. The XRD patterns were collected on a PAN analytical X'Pert Pro powder X-ray diffractometer using Cu Kα radiation and a PW3011 proportional detector with a parallel plate collimator. Cross-polarization magic angle spinning (CP-MAS) NMR spectra were collected on a Bruker DSX 300-MHz instrument. Approximately 300 mg of the sample was packed in a 7-mm zirconia rotor and spun at 5 kHz. Typical ^{13}C CP-MAS parameters were 3000 scans, a 90° pulse length of 4 μs, and recycle times of 4 s. Typical ^{29}Si CP-MAS parameters were 5000 scans, a 90° pulse length of 5 μs, and recycle times of 5 s. FT-Raman spectra were obtained on a Bruker FRA-106 with a resolution of 2-4 cm^{-1}. At least 512 scans were collected. Thermogravimetric analysis (TGA) was performed on a Netzsch STA409. Samples were heated under air and nitrogen from 30 °C to 900 °C at a rate of 10 °C/min. The organic loading was determined from the weight loss between 200 °C to 700 °C. Nitrogen physisorption measurements were conducted on a Micromeritics ASAP 2010 at 77 K. The SBA-15 sample was pretreated by heating under vacuum at 200 °C for 24 h. The HAS sample was pretreated by heating at 100 °C under vacuum for 24 hours. CO$_2$ adsorption experiments were performed with a Pfeiffer Vacuum QMS 200 Prisma Quadrupole Mass Spectrometer for residual gas analysis in ultra high vacuum. The molecular weights of the polymers were determined by aqueous size exclusion chromatography (ASEC) at 25°C. The ASEC system was comprised of a Shimadzu LC-20AD pump, a Shimadzu

RID-10A RI detector, a Shimadzu SPD-20A UV detector, a Shimadzu CTO-20A column oven, and Viscotek TSK Viscogel PW_{XL} Guard, G3000, G4000 and G6000 columns mounted in series. The mobile phase consisted of 0.5M $NaNO_3$ and the flow rate was maintained at 0.5 mL/min. Poly(ethylene glycol) narrow standards were used to calibrate the ASEC by the universal calibration method. Mark-Houwink parameters for PEI were obtained from the literature.[8] Inversely gated ^{13}C NMR spectra of commercial, low molecular weight (vendor claimed Mw = 800) PEI and the polymer cleaved from the HAS material were obtained in D_2O following literature methods.[9] For the cleaved polymer, Cr(III) acac was added as a relaxant, along with deuterated DMSO and the spectrum was obtained at 50ºC.

Adsorption Capacity Measurements in a Fixed Bed Flow System. CO_2 capture capacities were determined by analysis via Mass Spectrometry (MS). A Pfeiffer Vacuum QMS 200 Prisma Quadrupole Mass Spectrometer for residual gas analysis in ultra high vacuum was selected for the analyses of all simulated flue gas experiments. In a typical experiment, approximately 70 – 100 mg of the sorbent was dispersed in 200 – 300 mg of sieved sand (250 – 425 micron). The dispersed sorbent was placed in a pyrex tubular reactor (1/4 in O.D.) and was pretreated with pure argon with a flow rate of 20 ml/min. The temperature was maintained at 130 ^{o}C under atmospheric pressure for three hours. During this pretreatment period, the reaction gas consisting of 10% Carbon Dioxide/Argon was humidified (~ 1.6 % water) and directed to the mass spectrometer to form the baseline carbon dioxide concentration required for these tests. The gas flow was maintained at 20 ml/min with a temperature of either 25 ^{o}C or 75 ^{o}C at atmospheric pressure. Then the reaction gas stream was switched to the reactor and the amount of carbon dioxide captured by the sorbent was tracked by the mass spectrometer. After approximately 200 minutes the gas stream was switched back to the pretreatment conditions and the reactor temperature was increased to 130 ^{o}C for three hours to desorb CO_2 from the sorbent. The CO_2 desorption procedure on previously reported materials was preformed as reported.

Background Adsorption Capacity Measurements. Fixed bed flow systems have typically generated higher CO_2 capacities compared to TGA experiments. In our flow system, the reason for this difference in capacities was dilution of the 10 % CO_2/Ar with the stagnant Ar remaining in the tubing when the gases were switched in the fixed bed flow system, which caused an overestimation of the adsorption capacity if this dilution was not taken into account via blank experiments. When the argon line was switched to the 10 % CO_2/Ar stream, the difference in concentration between the two sides created a gradient which caused dilution of the gases. This result indicated that a background must be subtracted from the adsorption data in order to generate quantitative results. For instance, several control experiments were performed where pure Ar (flowrate of 20 mL/min) was passed through the tubing and adsorption column containing sand and unmodified SBA-15. Subsequently, the gas was switched to 10 % CO_2/Ar (humidified – flowing through bubblers) and the response was analyzed (Figure S3). The dilution of the 10 % CO_2/Ar in the stagnant Ar was then quantified and referred to as a background (Figure S4).[10]

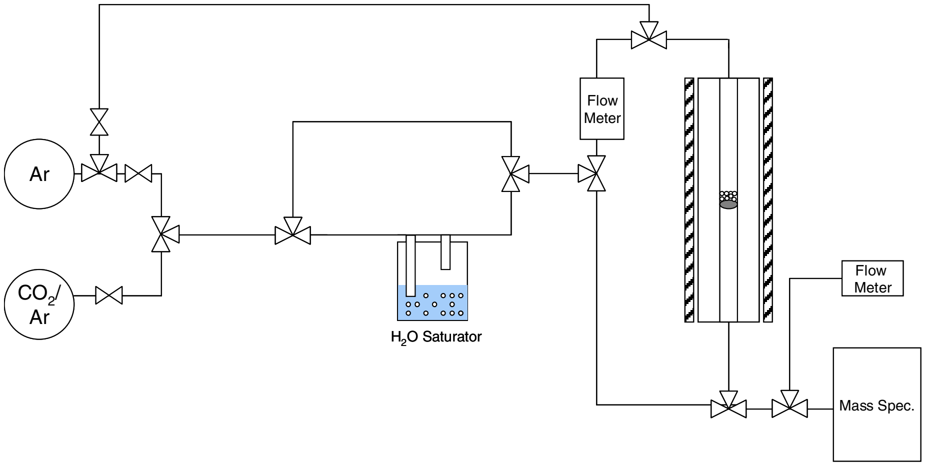

Figure S3. Diagram of the fixed bed flow system.

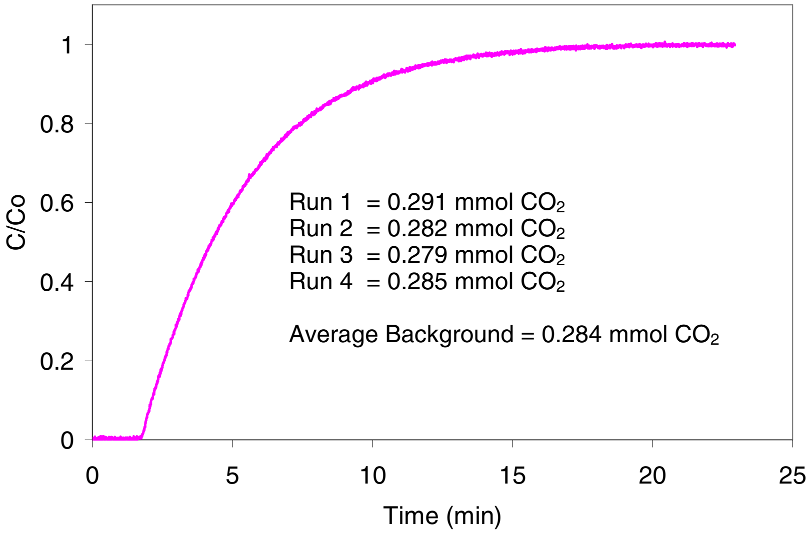

Figure S4. Typical background response of CO_2 concentration due to dilution of the 10% CO_2/Ar in the stagnant Ar. Various runs were performed to assess reproducibility.

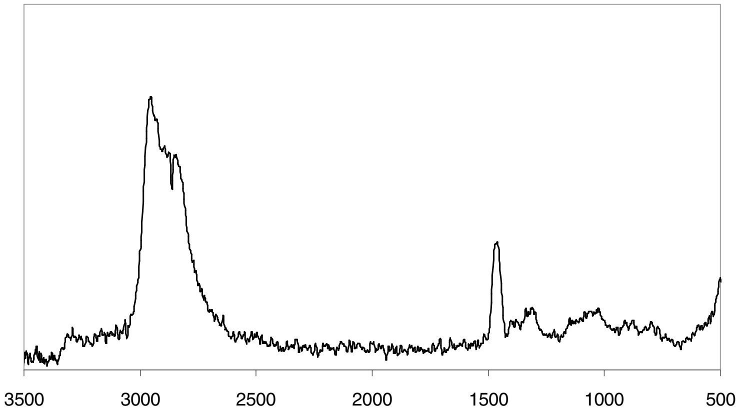

Figure S5. FT-Raman spectroscopy of SBA-HA. The FT-Raman spectrum of the hyperbranched aminosilica sorbent showed two distinct peaks associated with the formation of a hyperbranched aminosilica. The C-H aliphatic transition was seen between 3000 – 2750 cm^{-1}, while the CH_2 transition was seen at 1457 cm^{-1}, indicating the addition of organic groups on the silica surface.

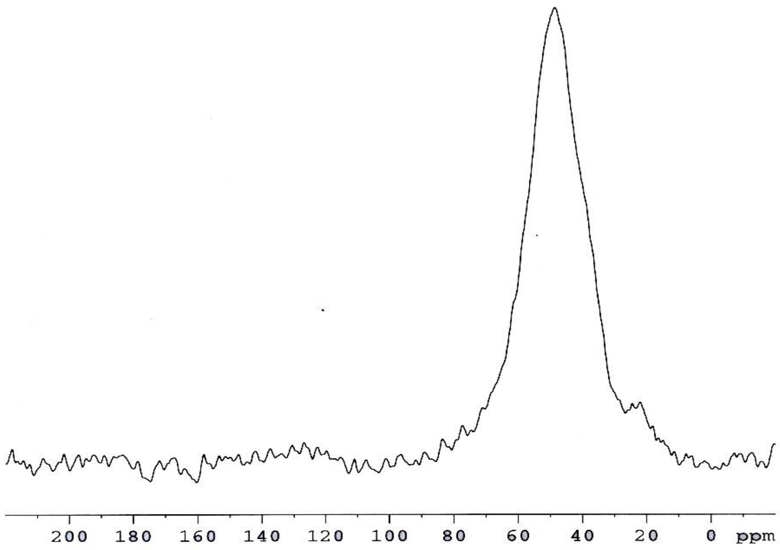

Figure S6. Solid state CPMAS ^{13}C NMR of SBA-HA. The spectrum shows the presence of a broad peak between 20 and 70 ppm. The broad peak included carbon resonances from the different types of carbons present in the hyperbranched aminosilica material. For instance, a broad peak was expected since multiple types of CH_2 groups were present in the material, which overlapped each other between the 30 – 60 ppm (Si-O-*C*H_2-, Si-O-CH_2-*C*H_2-NH_2, Si-O-CH_2-CH_2-NH-*C*H_2-, Si-O-CH_2-CH_2-N-(CH_2-)*C*H_2-, etc.)

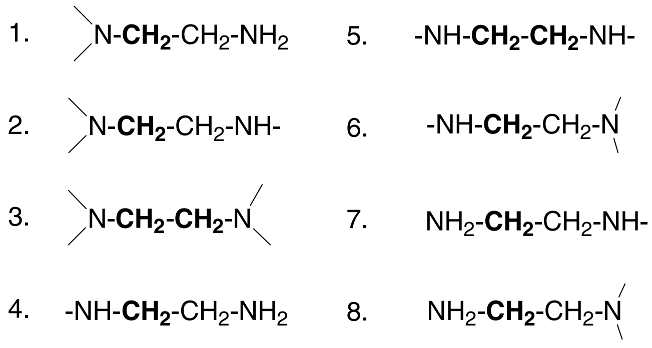

Figure S7: Schematic representation of 8 different carbon species in PEI samples.[9] ^{13}C NMR chemical shifts in order are: 57.5, 54.5, 52.5, 52, 49, 47, 41 and 39 ppm.[9]

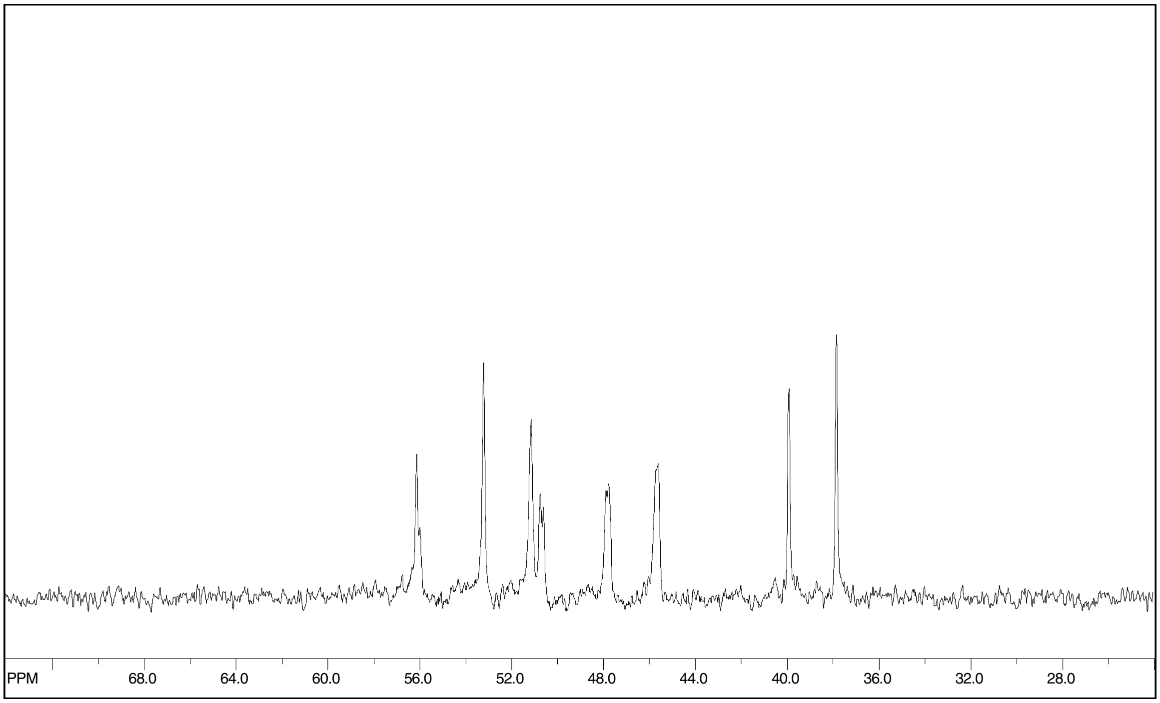

Figure S8: ^{13}C inversely gated NMR spectrum of commercial, low molecular weight PEI (Mw = 800). Primary:secondary:tertiary amine ratios are determined as shown in Figure S7 to be 44:33:23. Note chemical shifts are slightly different from the literature, deviating by 1ppm or less.[9]

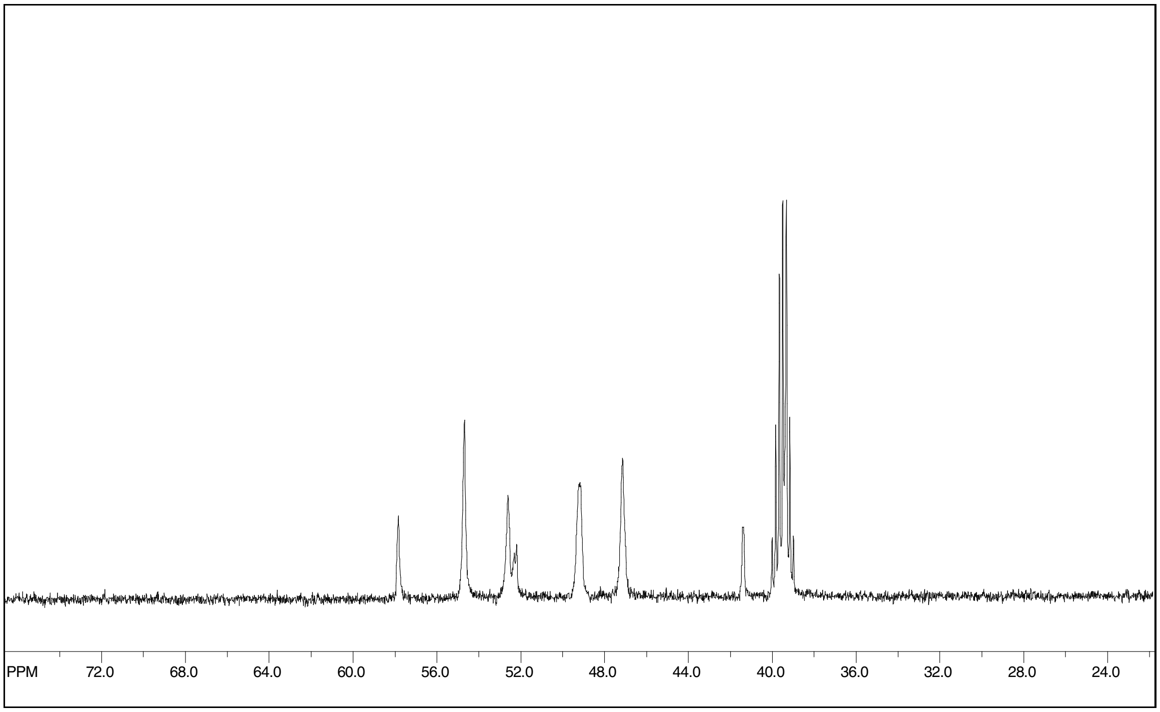

Figure S9: Inversely-gated ^{13}C NMR spectrum of polymer cleaved from HAS samples in D_2O with added DMSO. Primary:secondary:tertiary amine ratios are determined as shown in Figure S7 to be 28:47:25. Note chemical shifts are slightly different from the literature and the above commercial sample, dlikely due to the influence of DMSO.

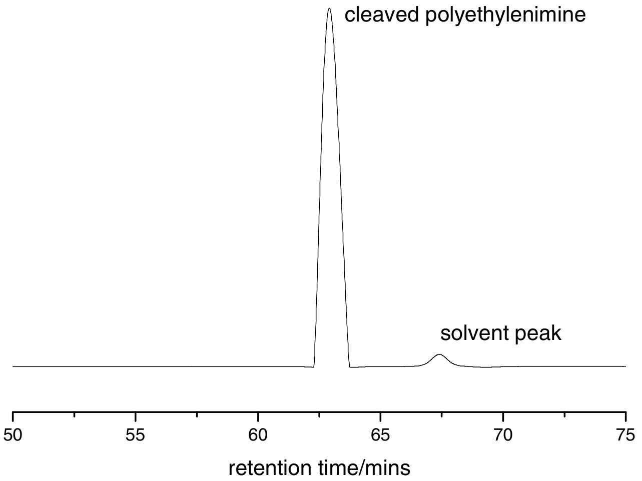

Figure S10: Aqueous size exclusion chromatography (ASEC) suggested the molecular weight of the cleaved polymer from HAS was 840 Daltons, with a PDI of 1.01. Similarly, the two commercial PEI samples, low molecular weight commercial PEI (vendor molecular weight 800 g/mol) and high molecular weight, commercial PEI (vendor molecular weight 750,000 g/mol) were determined by GPC to have Mws = 540 and 802,840, respectively, along with PDIs of 1.01 and 1.96 respectively.

Table S1. Nitrogen Physisorption Results for the Amino-functionalized Sorbents

Nitrogen Physisorption Results

Sample	BET SA (m^2/g)	BJH PD (A°)	Pore Vol (cc/g)
SBA-15 Calcined	802.3	65	0.71
SBA-HA	168.9	44	0.246
SBA-UN	53.8	62	0.101
SBA-UCTEPA	N/A	N/A	N/A
SBA-NH_2	346.4	57	0.412
SBA/PEI (750,000 MW)	27.1	N/A	0.027
SBA/PEI (800 Mw)	0.2	N/A	N/A
SBA-Diamine	251.6	54	0.353

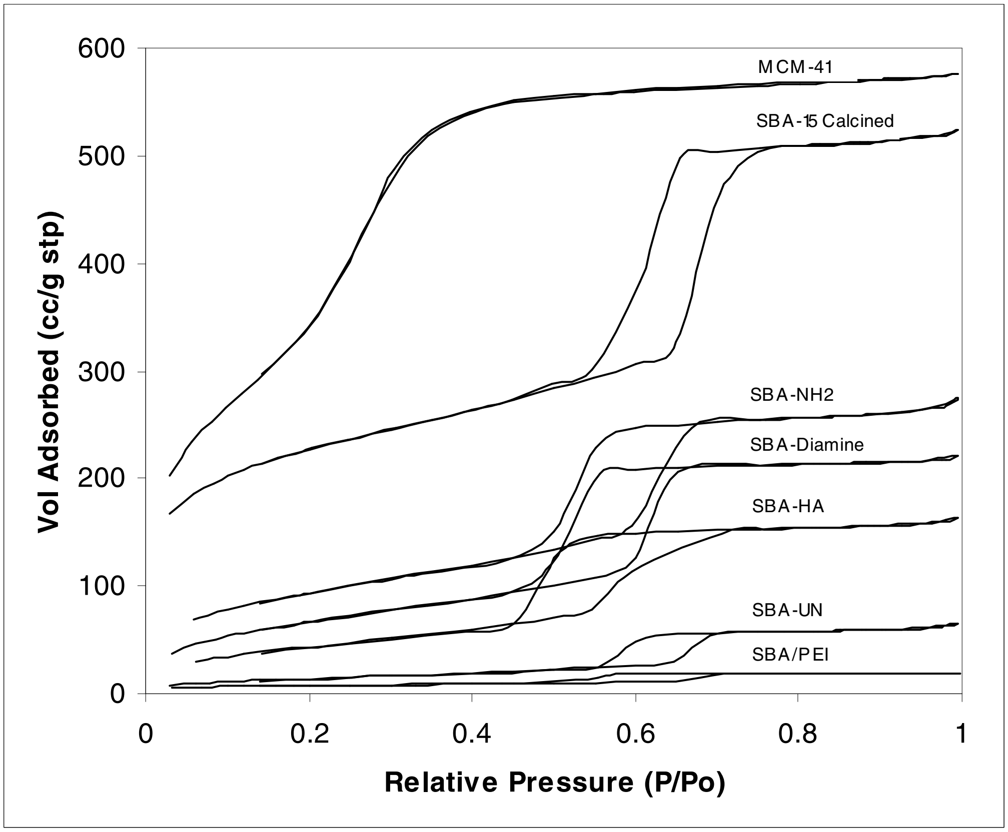

Figure S11. Nitrogen physisorption isotherms for the amino-functionalized sorbents.

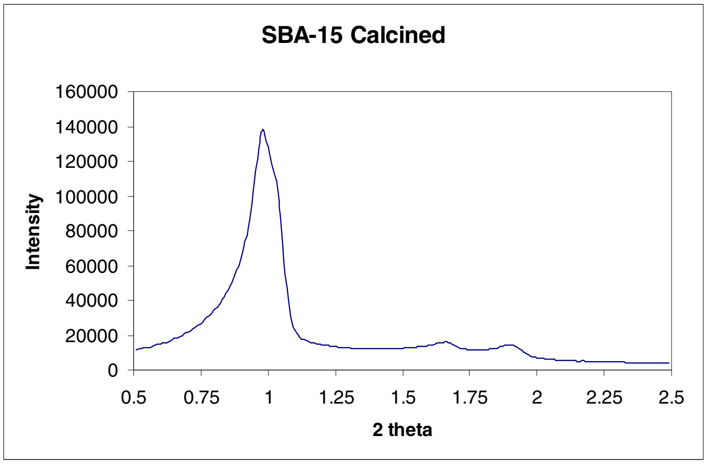

Figure S12. Powder XRD pattern for calcined SBA-15.

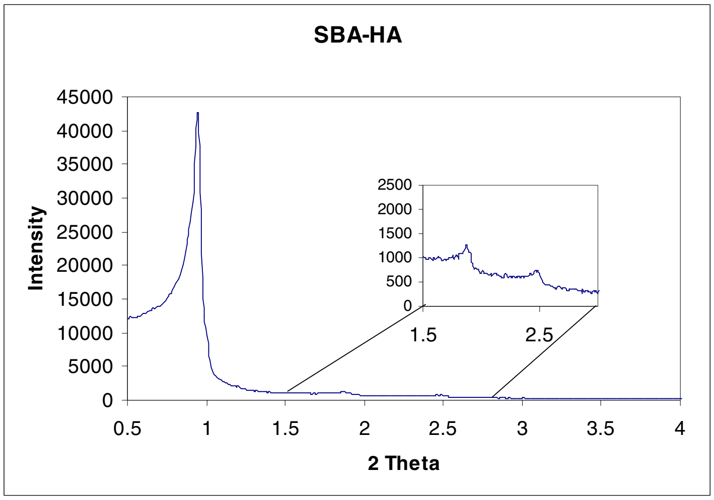

Figure S12. Powder XRD pattern for HAS (SBA-HA).

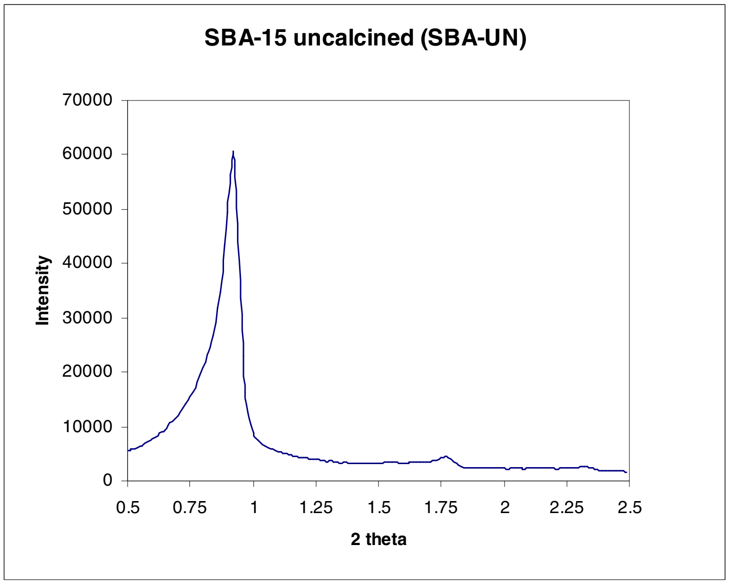

Figure S13. Powder XRD pattern for uncalcined SBA-15 (SBA-UN).

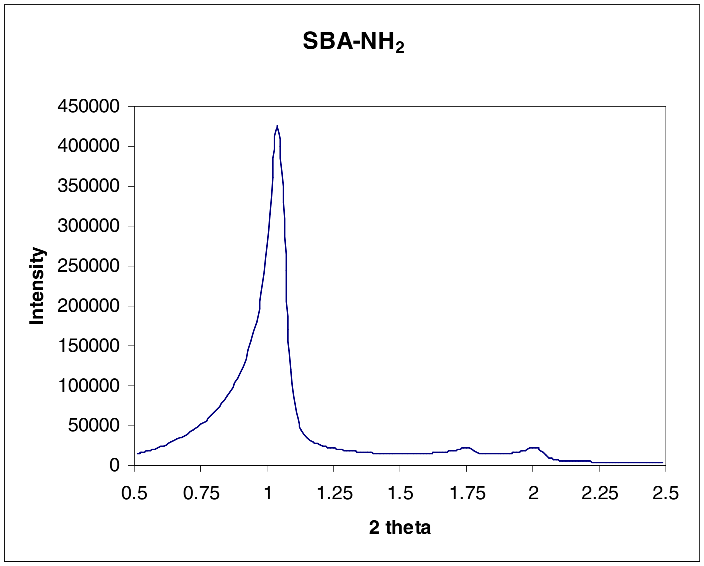

Figure S14. Powder XRD pattern for 3-APTMS grafted SBA-15 (SBA-NH_2).

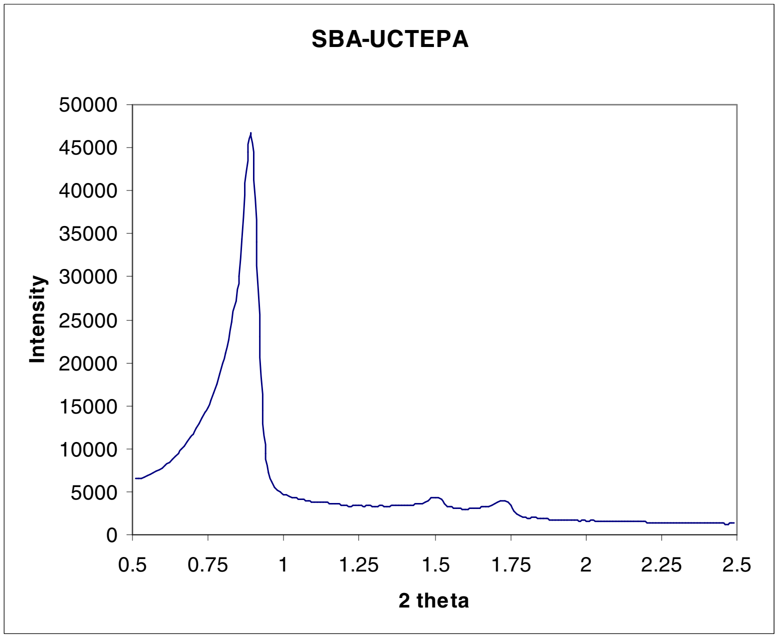

Figure S15. Powder XRD pattern for uncalcined SBA-15 loaded with TEPA (SBA-UCTEPA).

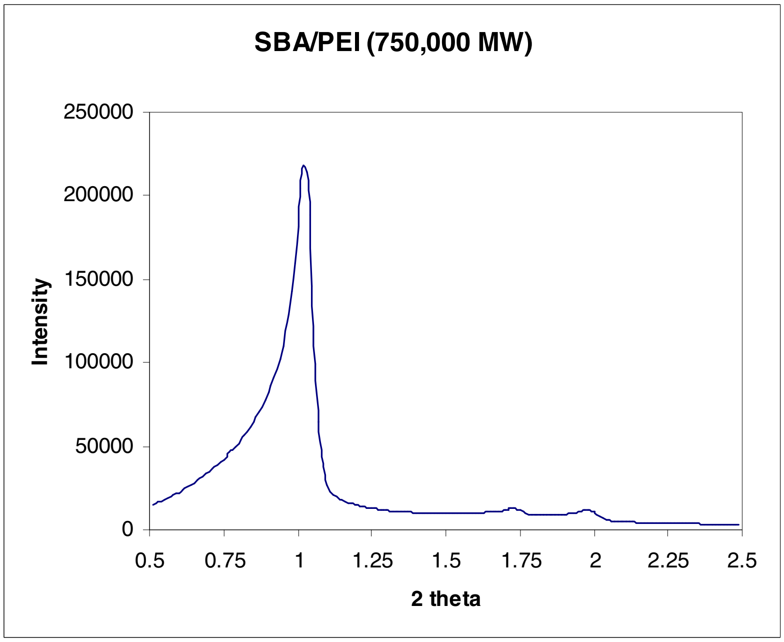

Figure S16. Powder XRD pattern for calcined SBA-15 loaded with 750,000 Mw PEI.

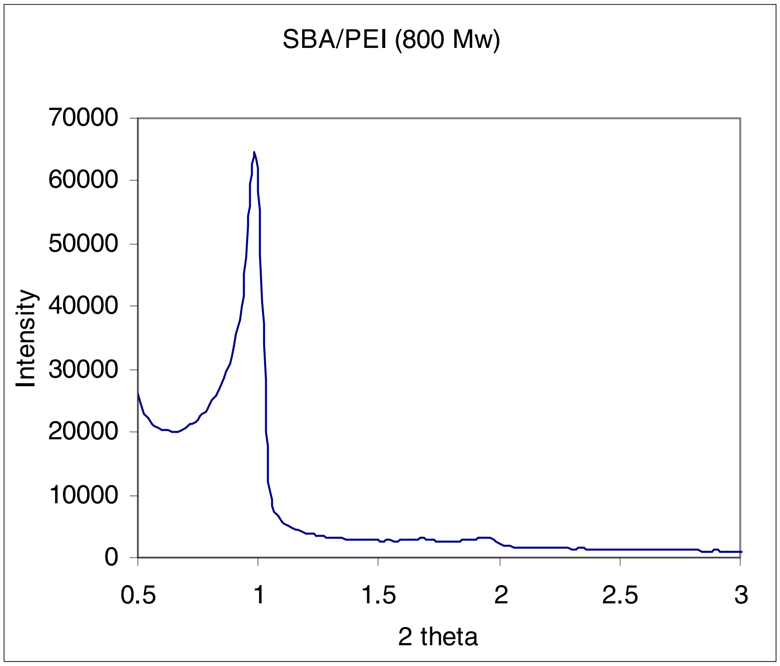

Figure S17. Powder XRD Pattern for calcined SBA-15 loaded with 800 Mw PEI.

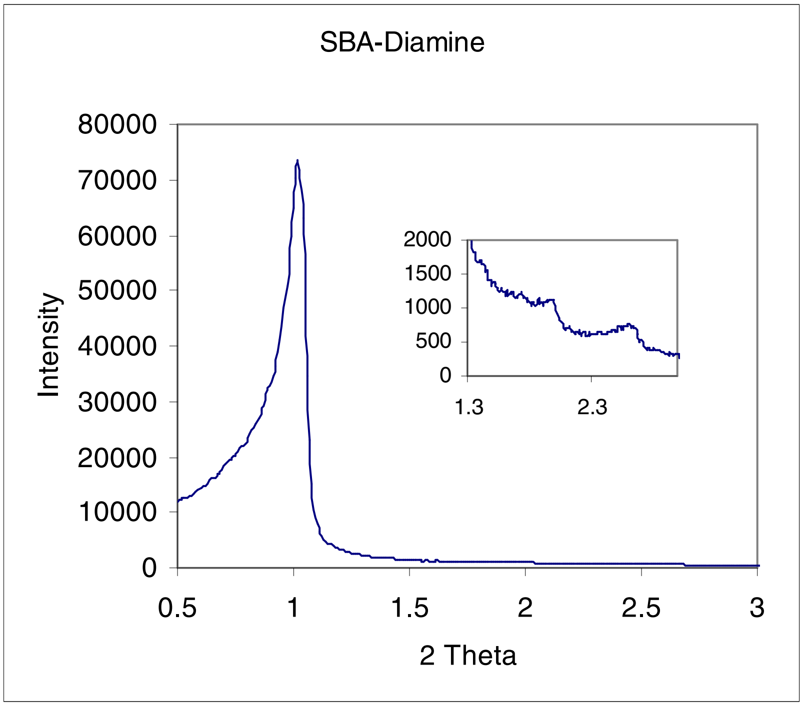

Figure S18. Powder XRD pattern for calcined SBA-15 loaded AEAPTMS (SBA-Diamine).

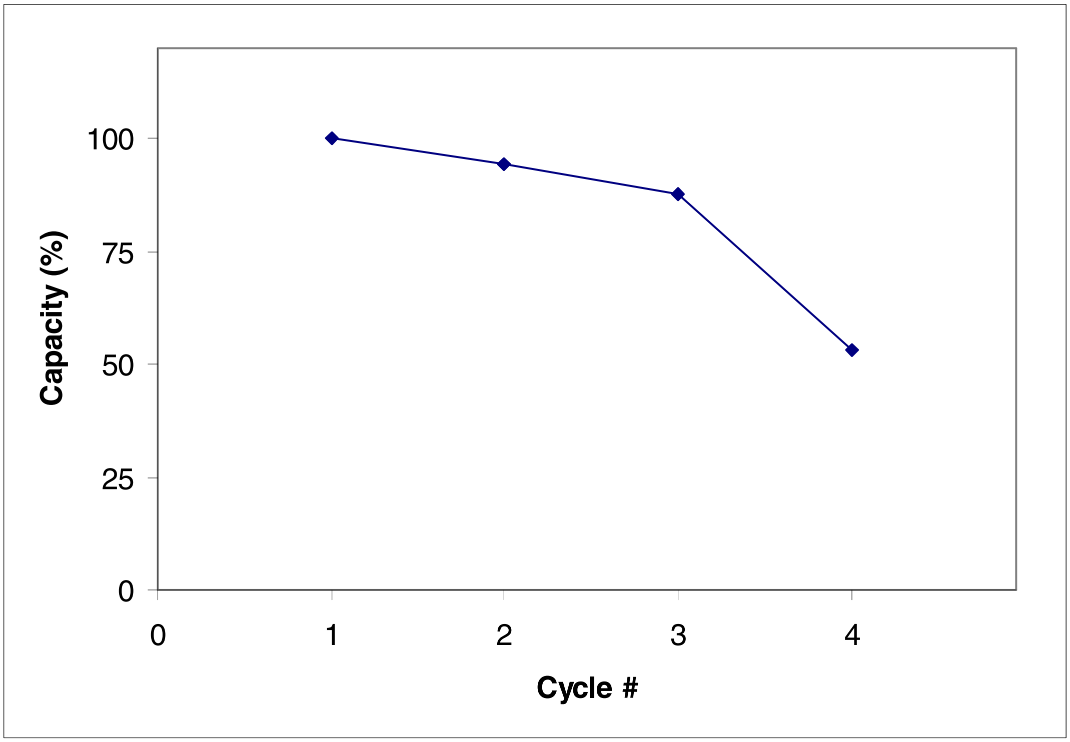

Figure S19 Decrease in capacity of SBA-UNTEPA over successive adsorption-desorption cycles. Points are normalized to the initial value determined for this material in cycle 1 (2.27 mmol CO_2/g). Visually, leaching was observed in later cycles by the discoloration of the material. After 4 cycles the capacities were not measurable due to decomposition of the material.

References

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(5) This synthesis has been performed multiple times. However, the amine loadings depend on multiple factors: quantities of SBA-15, quantities of aziridine, temperature, time, etc. In our hands, we have obtained loadings via TGA between 5 - 9 mmol N/g material.

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(10) It is unclear from previous reports whether or not dilution effects were taken into consideration. We feel it is very important to subtract these backgrounds from the experimental runs in order to obtain the most accurate CO_2 capacity number.