

Steam Induced Structural Changes of a Poly(ethylenimine) Impregnated γ -Alumina Sorbent for CO₂ Extraction from Ambient Air

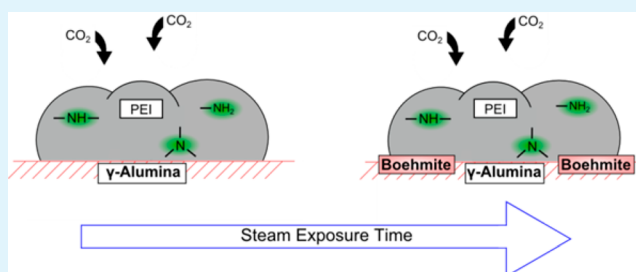
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S Supporting Information

ABSTRACT: Poly(ethylenimine) (PEI) impregnated mesoporous γ -alumina sorbents are utilized for CO₂ adsorption from dry and humid simulated ambient air, and the sorbents are regenerated under an environment of flowing steam for times ranging from 5 min to 24 h of continuous exposure. The sorbents are compared on the basis of equilibrium CO₂ capacities from simulated air at 400 ppm of CO₂, 50% relative humidity, and 30 °C as well as their physicochemical characterization by means of X-ray diffraction (XRD), ²⁷Al NMR spectroscopy, IR spectroscopy, Raman spectroscopy, N₂ physisorption, and elemental analysis. The sorbents retain better than 90% of the initial equilibrium capacity of ~1.7 mmol/g at steam exposure times up to 12 h; however, PEI leaching reduced the capacity of the sorbent to 0.66 mmol/g after 24 h of continuous treatment. It is demonstrated that the γ -alumina support partially hydrates to form a boehmite crystal phase at steam times of 90 min and longer but that this phase transition occurs predominately between 90 min and 12 h of steam treatment, slowing at longer times of 12 and 24 h of treatment. Evidence is presented to suggest that the presence of boehmite on the sorbent surface does not significantly alter the amine efficiency of impregnated PEI. The collected results suggest that γ -alumina/PEI composite materials are promising sorbents for CO₂ capture from ambient air with regeneration in flowing steam.

KEYWORDS: air capture, CO₂ capture, steam stripping, supported amine adsorbents, γ -alumina, boehmite



INTRODUCTION

With the enormous amount of CO₂ emitted each year from fossil fuel combustion, and the growing consensus that it contributes to changes in the global climate,¹ there has been great interest in the development of technologies to reduce such emissions and hence mitigate climate change.^{2–4} Much of the effort to this end has been devoted specifically to reduction or prevention of CO₂ emissions from large, point source emitters such as the flue gas from coal fired power plants. Indeed, one-half to two-thirds of global CO₂ emissions originate from combustion of fossil fuels for electricity generation.⁵ However, emissions from highly dispersed sources such as automobiles, airplanes, and residential fuel combustion, which make up much of the remainder of emissions, remain unaccounted for in scenarios where CO₂ is only removed from power plant flue gas. Thus, there has recently been interest in the extraction of CO₂ from ambient air, or air capture, as a complementary technological strategy to removal of CO₂ from flue gas for the mitigation of climate change.^{6–9}

Among the technologies suggested for CO₂ separation both from flue gases and from ultradilute streams such as air, adsorption with solid sorbents is regarded as being particularly promising due to the potentially low energy requirement compared to the mature liquid absorption technologies.¹⁰ Solid supported amine materials have gained immense popularity as a promising class of solid CO₂ adsorbents, due to their

demonstrated high CO₂ uptake and tolerance to humidity in the CO₂ containing feed stream.^{11–14} These materials have been shown to be particularly attractive for air capture applications, provided that a high degree of primary amines are incorporated.^{15–19} However, the stability of these materials under practical operating conditions remains an area where improvement may be necessary,^{20–27} as any sorbent adopted for large scale operation must have a sufficiently long lifetime, likely requiring efficient operation over many thousands of adsorption cycles.

Due to the strong, chemisorptive nature of the interactions between amines and CO₂, the sorbents typically require a temperature swing for regeneration. Practical regeneration of these sorbents has largely been neglected in laboratory studies, as nearly all large scale CO₂ capture processes require a relatively concentrated CO₂ product, and such is rarely reported in the literature.²⁸ Several regeneration strategies have, however, been proposed including combined temperature vacuum swing adsorption (TVSA),^{18,19,29,30} temperature swing adsorption (TSA) using a concentrated CO₂ purge stream,^{22,23,26,31–34} and steam stripping.^{28,35} Steam stripping could be potentially advantageous compared to the other

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proposed options because steam may be available as waste heat from industry, does not necessarily require external equipment such as large vacuum pumps, and provides both thermal and concentration driving forces for CO₂ desorption from the adsorption sites. Furthermore, a concentrated CO₂ product stream can easily be obtained by compression of the effluent steam/CO₂ mixture that would result from such a process.

Indeed, our group and others have recently demonstrated the use of steam stripping to regenerate several representative supported amine materials. Li et al.²⁸ studied the steam regeneration of all three classes¹¹ of amines supported on a commercial mesoporous silica. In that study, a packed bed of sorbent was subjected to three cycles of CO₂ adsorption followed by exposure to flowing steam for regeneration. Class 1 and 3 sorbents, incorporating poly(ethylenimine) (PEI) into the pores of the support material by physical impregnation or *in situ* polymerization, respectively, adsorbed as much or more CO₂ in cycles 2 and 3 as in cycle 1, indicating that the exposure to flowing steam fully regenerated the CO₂ adsorption sites on the material. On the other hand, a class 2 sorbent, grafted with 3-(aminopropyl)trimethoxysilane (APS), showed a slight reduction in CO₂ capacity in the second two cycles, relative to the first. However, it was not elucidated whether this was due to incomplete regeneration of CO₂ adsorption sites in the material or due to degradation of the material induced by exposure to steam. Recently, Hammache et al.³⁵ extended similar analysis to 8 cycles of CO₂ adsorption followed by steam exposure on both a class 1 PEI impregnated and a hybrid (class 2 and class 1) APS grafted and PEI impregnated commercial mesoporous silica. The authors found that both materials retained at least 88% of their initial CO₂ capacity from simulated flue gas at 10% CO₂, with the capacities on the eighth cycle being 2.8 mmol/g and 2.7 mmol/g, respectively. Importantly, the authors suggest that no significant structural changes occurred to the sorbent as a result of the steam cycling. The materials were also subjected to continuous exposure to steam for 5 h as well as CO₂ free cycling, where the sorbent was exposed to cycles of steam for 30–40 min followed by drying under helium flow. The sorbent exposed to CO₂ free cycling showed greater reduction in CO₂ capacity than that exposed to steam continuously, even though the total steam time during cycling was 3.5 h (1.5 h less than for the continuous sample). Importantly, the authors report that no significant structural changes occurred in the sorbent in these experiments as well. The authors do suggest, however, that PEI may reaggregate in the pores of the sorbent as a result of steam exposure, which may slightly reduce the surface area, pore volume, and CO₂ capacity of the material. Nonetheless, while these studies demonstrate the feasibility of steam to regenerate adsorption sites on supported amine sorbents, they do not provide thorough insight into the stability of such materials over the very long time scales of industrial operation.

To this end, longer accelerated steam exposure studies have been performed to investigate the possibility of long-term steam induced structural changes to representative sorbents. Li et al.³⁶ found that that exposure to steam for 24 h on sorbents composed of all 3 classes of amines supported on mesocellular foam (MCF), an extra-large pore, thin walled mesoporous silica, caused significant collapse of the silica pore structure, which in turn caused significant loss of CO₂ capacity. Similarly, Chaikittislip et al.³⁷ found that when PEI was supported on SBA-15 mesoporous silica, and the material exposed to steam for 24 h, that a significant loss of the mesopore structure

occurred, causing similarly large reductions in CO₂ capacity. However, when PEI was supported on mesoporous γ -alumina, and the material subjected to the same 24 h of steam exposure, there was much less change in the pore structure observed in the N₂ physisorption data, and the material retained a much greater fraction of its initial CO₂ capacity than did the SBA-15 silica analogue.³⁷ Important to note, however, is that in both of these reports the steam treatment was performed under a static environment in an apparatus similar to a batch reactor. Noteworthy is that the SBA-15 silica, containing much thicker silica walls between pores than the MCF, retained much of its mesopore structure after steam treatment when amines were not present in the pores of the material. Thus, one may surmise that the presence of amines in the silica pore network significantly enhances the degradation of the pore structure, likely due to Si–O–Si bond hydrolysis, which would be catalyzed by the amines. Nonetheless, both of these studies suggest that mesoporous silica, the most common metal-oxide material reported in the literature for use as a support in CO₂ capture sorbent preparation, may be susceptible to hydrolysis in the presence of steam over very long time scales when amine groups are present on the surface. As a result, oxides such as crystalline γ -alumina, which may be less susceptible to hydrolysis and pore collapse, may be more practical supports for sorbents used in a process employing steam stripping as a regeneration technique.³⁷

However, greater resolution into any steam induced structural changes to γ -alumina supported amine sorbents is necessary prior to their large scale deployment. Furthermore, study of such materials under the more practical environment of flowing steam (as opposed to static), similar to the Hammache study, is desired. Here, we report on the findings of an accelerated degradation study of a PEI impregnated (class 1) mesoporous γ -alumina under such conditions. This sorbent is shown to have a high CO₂ capacity under simulated air capture conditions and retains over 90% of this capacity after continuous exposure to steam for up to 12 h. The material was characterized in detail following exposure to flowing steam for various times. It is found that after exposure to steam for times of 90 min and greater, that the γ -alumina partially hydrates to form boehmite, an aluminum oxyhydroxide. The effect of the presence of boehmite in the sorbent on the efficiency of PEI adsorbing CO₂ under simulated air conditions was probed, and the results suggest that the partial phase transition does not significantly affect the PEI amine efficiency. Further subtle structural changes to the sorbent observed in the N₂ physisorption profiles, which suggest possible PEI rearrangement, are discussed as well.

■ EXPERIMENTAL SECTION

Materials. The following materials were used as received from the supplier: methanol (ACS grade, BDH), branched poly(ethylenimine) (PEI) ($M_w \sim 800$, $M_n \sim 600$, Sigma-Aldrich), Versal-250 (V-250) pseudoboehmite (UOP). Nitrogen (UHP), helium (UHP), and a premixed cylinder of 5% CO₂ in helium were purchased from Airgas Inc. A specialty gas mixture of 400 ppm of CO₂ in helium, used in gravimetric CO₂ uptake experiments, was purchased from Matheson Tri-Gas.

Preparation of Poly(ethylenimine) Sorbents. The γ -alumina support used throughout the study was prepared by calcination of the V-250 mesoporous pseudoboehmite. Calcination was performed by increasing the oven temperature from ambient to 550 °C at 5 °C/min and then holding at 550 °C for 12 h, under static air, before cooling to room temperature. Prior to PEI incorporation, the γ -alumina was dried

at 110 °C under vacuum (~20 mTorr) overnight. The dried γ -alumina was then dispersed in methanol in a ratio of 15 mL of methanol to 1 g of dried γ -alumina. Separately, a given amount of PEI was dissolved in 20 mL of methanol. The separate mixtures were equilibrated by stirring for at least 1 h and then were combined by dropwise addition of the PEI/methanol mixture into the γ -alumina/methanol dispersion. The mixtures were then stirred at room temperature for 24 h, before the solvent was removed by rotary evaporation, followed by drying under high vacuum (~20 mTorr) at 100 °C overnight. Prior to testing, sorbents were pelletized by loading 0.5 g of dried sorbent into a cylindrical pellet die of diameter 13 mm and pressing to a pressure between 2500 and 3000 psi. The cylindrical pellets were then crushed and sieved between 150 and 800 μm .

Material Characterization. Organic loadings of the freshly prepared sorbents were determined by thermogravimetric analysis using a Netzsch STA409PG TGA. The organic loading was calculated from the measured weight loss between the temperatures of 120 and 900 °C. For samples containing boehmite, contents of C, H, N, and Al were estimated by elemental analysis performed by Galbraith Laboratories (Knoxville, TN), and the amine loading was determined accordingly. Surface areas and total pore volumes of the sample were estimated from N_2 physisorption data obtained by measurements performed on a Micromeritics Tristar II 3020 apparatus at 77 K. Prior to physisorption analysis, the samples were degassed at 110 °C for at least 10 h. Surface areas were estimated by the BET equation, while total pore volumes were taken to be equal to the total amount of N_2 adsorbed at a P/P_0 of 0.99. Powder XRD patterns were obtained by use of a PANalytical X'pert diffractometer with a Cu-K-alpha X-ray source. FT-IR experiments were performed on a Bruker Vertex 80v optical bench. FT-Raman experiments were performed on an attached Ram II module on the same bench. For FT-IR measurements, ~1 mg of sample was mixed with ~100 mg of KBr and pressed to pellets for analysis. ^{27}Al solid state NMR experiments were performed on a Bruker DSC 400 spectrometer. 2400 scans were taken for each sample with a spinning speed of 12 kHz.

CO_2 Adsorption. Humid CO_2 adsorption capacities were measured in packed bed experiments, while dry capacities were measured gravimetrically on a TGA. All CO_2 capacities reported in this paper were measured at a CO_2 concentration of 400 ppm. Packed bed experiments were performed in a flow adsorption system (see Figure S1 for schematic) using 1 g of pelletized sorbent. A Li-COR Li-840A $\text{CO}_2/\text{H}_2\text{O}$ IR gas analyzer was used to follow real time CO_2 and H_2O gas phase concentrations. Prior to CO_2 adsorption experiments the samples were pretreated under flowing N_2 and heated to 110 °C until less than 0.01 mmol/min of H_2O and CO_2 was observed in the effluent downstream of the sorbent bed. CO_2 adsorption was then performed by exposing the sample bed to a flow of simulated air at 30 °C, 400 ppm of CO_2 balanced by N_2 , and 50% relative humidity (at 30 °C). Humidity was controlled by passing the CO_2/N_2 mixture through a sparger containing DI H_2O immersed in a temperature controlled fluid bath. CO_2 adsorption experiments were terminated when the concentration of CO_2 in the effluent stream was at least 99% of that in the inlet stream. In this way, the reported CO_2 capacities are pseudoequilibrium values. Adsorption capacities were estimated by integrating the resulting CO_2 breakthrough curves and were measured both before and after steam exposure.

Dry adsorption capacities were measured gravimetrically on a TA Instruments Q500 TGA. The samples were pretreated by heating to 110 °C and holding at this temperature for 3 h under helium flow. The samples were then cooled to 30 °C and allowed to thermally equilibrate at this temperature for 60 min. Subsequently, the gas flow was switched from helium to a premixed gas containing 400 ppm of CO_2/He and allowed to equilibrate for 12 h.

Steam Exposure. To investigate steam induced structural changes to the γ -alumina supported PEI sorbents, samples were exposed to flowing steam for various times. Steam exposure experiments were performed in the same flow adsorption system as was used to measure humid CO_2 capacities. A schematic of the system is reported in Figure S1 of the Supporting Information. Samples were exposed to steam following an initial measurement of equilibrium adsorption capacity

(see above). Prior to steam treatment, the samples were pretreated under N_2 flow at 110 °C, during which upstream lines and the packed bed reactor jacket were heated to ~115 °C. Steam was then introduced at ~5 g/min and allowed to contact the samples continuously for times of 5 min, 90 min, 12 h, and 24 h in distinct experiments. In a separate experiment, one sample was exposed to steam flow in a cyclic fashion. Here, the sorbent was exposed to cycles of preheating to 110 °C under N_2 flow, followed by exposure to flowing steam for 5 min, and then finally to partial cooling and drying under N_2 flow. During the cooling/drying step N_2 was immediately introduced into the packed bed after the steam was turned off. Heating of the reactor jacket and upstream system lines were turned off, and N_2 was allowed to flow until the packed bed reached a temperature of 30 °C. A total of 18 cycles of these three steps were completed, such that the total steam exposure time was 90 min. Preceding and following all steam exposure experiments, pseudoequilibrium CO_2 capacities of the materials were estimated by flowing simulated air over the sample and subsequently integrating the resulting breakthrough curve, as described above.

RESULTS AND DISCUSSION

Fresh Sorbent Characterization. Figures 1 and 2 show the XRD patterns and N_2 physisorption profiles of the calcined

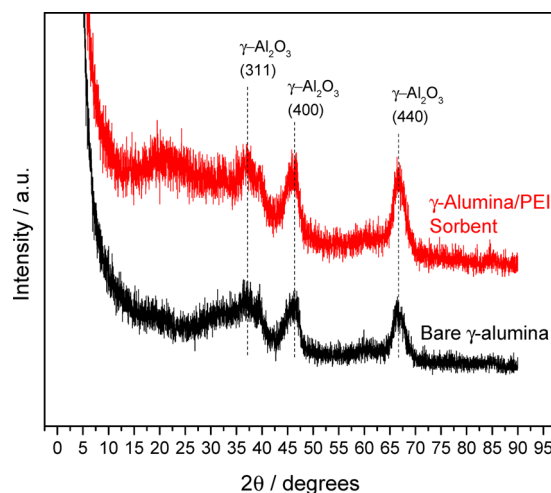


Figure 1. XRD patterns of γ -alumina support before and after PEI incorporation.

γ -alumina support before and after impregnation with 30 wt % of poly(ethylenimine) (PEI). The diffraction patterns of the bare support and impregnated sorbent show characteristic γ -alumina peaks³⁸ at 2θ of 37, 46.5, and 66.5 as well as a broad peak between 2θ of 15–30 that is attributed to diffraction arising from average intermolecular distances of Al and O atoms in amorphous regions of the alumina sample.³⁹ γ -Alumina is poorly crystalline, and so it may be expected that such regions would exist in the sample. The amorphous peak is more prominent and slightly shifted to higher 2θ in the PEI impregnated sample. This change, while subtle, may be due to coordination of aminopolymer to surface atoms, slightly disrupting the γ -alumina structure at this interface. Nonetheless, the prominence of the γ -alumina peaks in the diffraction pattern before and after PEI impregnation suggests the alumina remained predominantly in the γ form. Table 1 shows the BET surface area (m^2/g) and total pore volume (cm^3/g) of the materials, the latter calculated by total adsorbed N_2 at a partial pressure of 0.99. The values here are normalized by the mass of Al_2O_3 . The physisorption profiles of the bare γ -alumina show

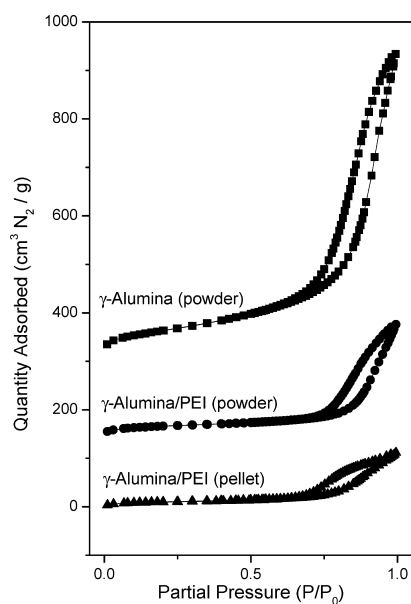


Figure 2. N₂ physisorption profiles at 77 K of γ -alumina before and after PEI incorporation in powder and pellet form. Profiles are offset by 150 cm³/g.

Table 1. Physical Characteristics of γ -Alumina Support before and after PEI Incorporation in Powder and Pellet Form

sample	BET SA (per g Al ₂ O ₃) (m ² /g)	total PV ^a (cm ³ /g)	amine loading ^b (per g sorbent) (mmol N/g)
γ -alumina	243	1.04	n/a
γ -alumina pellets	244	0.69	n/a
PEI impregnated sorbent	97	0.53	8.4
pelletized sorbent	58	0.26	8.5

^aValues estimated from total N₂ sorption at $P/P_0 = 0.99$. ^bValues estimated from TGA.

significant N₂ uptake at partial pressures greater than 0.8, indicative of large mesopores and macropores. The existence of hysteresis on the desorption branch of the isotherm confirms the presence of mesopores in the material. After impregnation with PEI, the surface area and total pore volume of the material decreased substantially. The reduction in pore volume between the bare γ -alumina support and that impregnated with PEI was calculated to be 0.50 cm³/g Al₂O₃, which is very close to the expected occupied volume of PEI of 0.49 cm³/g Al₂O₃.

Table 2. Textural Properties and CO₂ Capacities of Samples after Exposure to Steam

sample	BET SA (per gram sorbent) (m ² /g)	total PV ^a (cm ³ /g)	amine loading ^b (mmol N/g)	CO ₂ capacity ^c (mmol CO ₂ /g)	amine efficiency (mol CO ₂ /mol N)
fresh sorbent	38	0.17	7.81	1.71	0.22
5 minute steam	37	0.17	7.95	1.96	0.25
1.5 h steam	46	0.17	8.33	1.73	0.21
1.5 h steam - cycled	70	0.21	7.13	1.79	0.25
12 h steam	53	0.19	7.61	1.5	0.20
24 h steam	177	0.45	2.34	0.66	0.28

^aValues estimated from total N₂ sorption at $P/P_0 = 0.99$. ^bValues estimated from elemental analysis. ^cValues estimated from humid adsorption experiments in the flow adsorption system at 50% RH, 30 °C, and 400 ppm of CO₂.

(calculated assuming a liquid density of 1.05 g/mL for PEI), indicating successful impregnation of the PEI into the pores of the γ -alumina.⁴⁰ Since samples exposed to steam were in the form of pellets, the BET surface area and pore volume of the pelletized material are reported in Table 1 as well. The surface area of bare γ -alumina remained unchanged after pelletization, but the total pore volume decreased significantly, by 0.35 cm³/g Al₂O₃. After pelletization of the PEI impregnated sorbents a reduction of 39 m²/g Al₂O₃ and 0.27 cm³/g Al₂O₃ was observed in the BET surface area and total pore volume, respectively.

Effect of Steam Exposure on CO₂ Capacity. Table 2 and Figure 3 show the results of the steam exposure experiments.

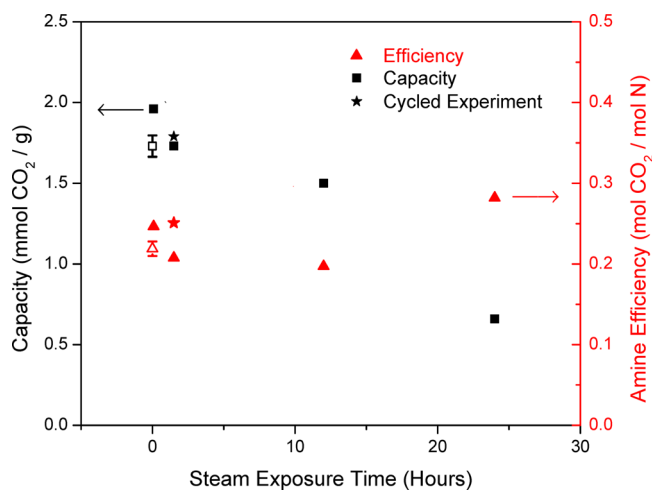


Figure 3. CO₂ capacities of sorbents after exposure to steam for various times. Capacities measured in the flow adsorption system at 30 °C, 50% RH, and 400 ppm of CO₂/N₂. Open symbols are fresh sorbent capacity and efficiency values, while closed symbols are those after exposure to steam. Error bars on fresh sample capacity and efficiency are standard deviations calculated from initial capacity measurements on all samples.

Figure 3 shows pseudoequilibrium CO₂ capacities and amine efficiencies of the materials as a function of time exposed to steam. The data points furthest to left on the plot, and containing error bars, correspond to the capacity and efficiency of the material prior to steam exposure, measured to be 1.71 mmol/g and 0.22 mol N/mol CO₂, respectively. The shortest steam exposure time was 5 min, chosen to represent a typical exposure time of one desorption cycle in a hypothetical large scale process. After exposure to steam flow for 5 min, the CO₂ capacity of the material increased to 1.96 mmol/g. Because the sample was thoroughly dried following exposure to steam, and

adsorption experiments were performed at 50% relative humidity, differences in the amount of physisorbed water left from steaming between experiments are likely negligible and hence are likely not responsible for this observed increase in capacity. While we have not thoroughly investigated the nature of this increase, we hypothesize that it may be due to the combined effect of a reduction in surface acidity as a result of surface hydration via steam treatment *prior* to reagglomeration of PEI inside the sorbent pores. As discussed below, the N_2 physisorption data suggest that PEI shifts inside the pores of the support at steam times of 90 min and greater but not after the 5 min exposure. However, the ^{27}Al NMR data suggest a reduction in tetrahedral aluminum sites after 5 min of steaming, which may indicate a decrease in surface acidity.⁴¹ These two combined phenomena may lead to the increase in capacity that is observed. After 90 min of continuous steam exposure the capacity of the material was nearly unchanged compared to that of the fresh sample. The sorbent was also exposed to steam in a cyclic fashion, where the material was subjected to 18 cycles of 5 min steam exposure followed by partial drying under inert N_2 flow (for a total of 90 min of cumulative steam time). The capacity of the material after this cyclic treatment was slightly higher than that of the fresh sample, though within the expected experimental error limits of the adsorption system. The slight increase in surface area and decrease in amine loading, as evidenced in Table 2, suggests that a small degree of amine leaching may have occurred during this testing, though a reduction in CO_2 capacity was not observed. Further decreases in the capacity after exposure to steam for 12 h (1.62 mmol/g) and 24 h (0.66 mmol/g) were observed. The significant decrease in CO_2 capacity of the sample exposed to steam for 24 h is attributed to leaching of PEI out of the pores of the γ -alumina support. As can be seen from the data in Table 2, the amine loading of the sample decreased from ~ 8 mmol N/g to ~ 2 mmol N/g after this extensive steam treatment. Each of the other samples did not show such a decrease in amine loading. The amine efficiency of each of the samples ranged between 0.21 to 0.28 mol CO_2 /mol N, with the highest value being that of the sample exposed to steam for 24 h. This result is somewhat unexpected, since at moderate amine loadings amine efficiency typically increases with amine loading.¹¹ The slight increase here may be due to a reduction in surface acidity associated with hydration and subsequent formation of boehmite on the γ -alumina surface, as discussed in detail below.

Hammache et al.³⁵ reported that PEI leaching did not occur in their similar studies using mesoporous silica as a support, though the longest steam exposure time tested was 5 h in that study. Nonetheless, our data suggest that PEI leaching can occur over significantly longer time scales of steam exposure to γ -alumina supported PEI. Worth noting, however, is that it is difficult to extrapolate degrees of amine leaching from these laboratory studies to what might occur in industrial scale operation of a sorbent. Factors such as contactor configuration, sorbent cycle steps, and steam flow rate and quality remain unexplored and may play an important role in promoting or reducing PEI leaching. Furthermore, extended continuous steam exposure is clearly impractical in a large scale operation and is meant here to accelerate degradative mechanisms.

XRD Experiments. To probe the potential for structural changes to the γ -alumina itself as a result of steaming, the materials were characterized with XRD following steam treatment. Mixtures of aluminum oxides, such as γ -alumina, and water at elevated temperatures are known to be

thermodynamically unstable,^{42–44} though the dynamics of phase transition are reported to be on the order of hours⁴⁴ for liquid water, and days⁴³ for water vapor. Figure 4 shows the

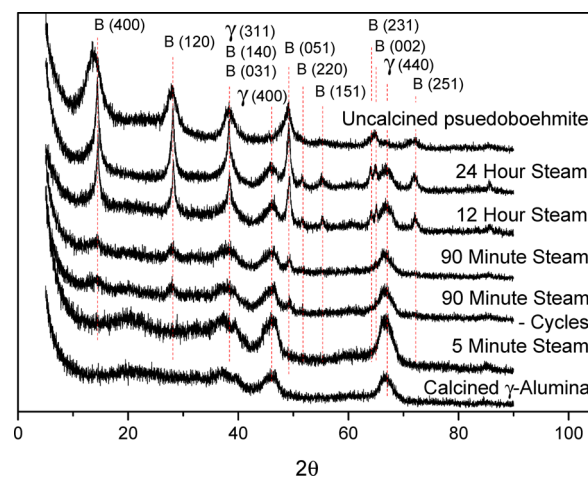


Figure 4. XRD patterns of the sorbents after exposure to steam for various times. Diffraction peaks are labeled according to species (B for boehmite and γ for γ -alumina) with the corresponding species Miller index.

XRD patterns of the materials after the steam exposure experiments as well as the pattern of the V250 pseudoboehmite precursor that was used in the preparation of the γ -alumina support used in this study. Relatively intense X-ray peaks associated with boehmite at 2θ of 14.5, 28.2, 38.3, and 49 degrees are observed on the samples exposed to steam for 90 min or longer, while additional less intense peaks at 2θ of 51.5, 55, 65, 72 degrees can be observed in the samples exposed to steam for 12 and 24 h. The boehmite peaks in the patterns of the samples exposed to steam for 12 and 24 h are quite intense compared to those on the samples exposed to steam for 90 min, indicating that further boehmite crystallization occurred with increasing steam exposure time. In each of the samples, the peaks at 46.5 and 66.5 degrees associated with γ -alumina are still present, indicating that on these time scales, full phase transition of the materials did not occur. This is further confirmed by ^{27}Al MAS NMR experiments as discussed below. Notable is that the patterns of the samples exposed to steam for 90 min continuously and in cyclic fashion are nearly identical, in terms of relative intensities and the presence of boehmite peaks. This indicates that the cycling did not significantly change the dynamics or extent of boehmite formation on these materials compared to continuous exposure.

^{27}Al MAS NMR Experiments. To further investigate and quantify the phase transition from γ -alumina to boehmite during steam treatment, ^{27}Al MAS NMR experiments were performed to probe the nature of aluminum atoms present in the samples. It is well established that γ -alumina contains aluminum atoms that are both tetrahedrally and octahedrally coordinated, with $\sim 30\%$ of the Al atoms present in tetrahedral form.^{45,46} Boehmite, on the other hand, does not contain tetrahedral Al atoms.⁴⁶ By comparing relative amounts of tetrahedral and octahedral atoms, as determined by peak integration of ^{27}Al NMR results, it is possible to estimate the amount of boehmite present in a sample.⁴⁴ Figure 5 shows the ^{27}Al MAS NMR results for each of the samples. For all of the samples, both the tetrahedral peak (67 ppm) and octahedral

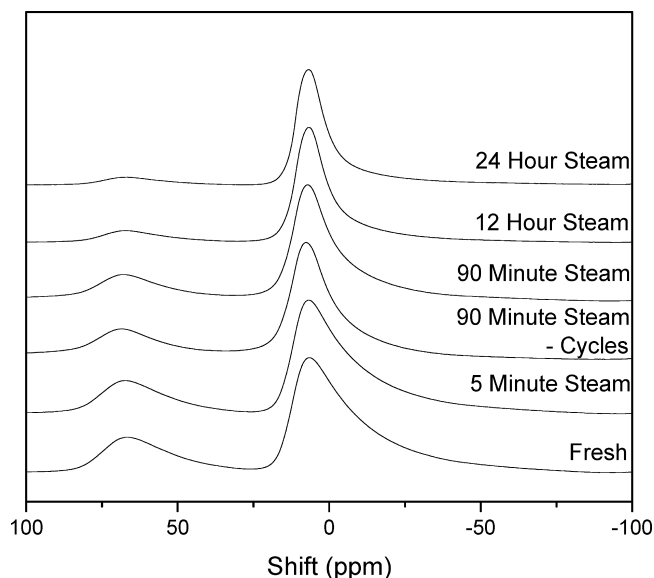


Figure 5. ^{27}Al NMR spectra of samples after exposure to steam for various times. Tetrahedral aluminum peak at ~ 67 ppm and octahedral aluminum peak at ~ 7 ppm.

peak (6.6 ppm) are observed, though in different relative intensities. It is clear that the relative intensity of the tetrahedral peak decreases for samples exposed to steam for 90 min or longer compared to the fresh sample, consistent with the results from the XRD experiments.

The peaks corresponding to tetrahedral and octahedral aluminum were integrated, and the ratio of the integrated area of the tetrahedral peak to those of the tetrahedral plus the octahedral peaks (percentage tetrahedral atoms) are shown in Figure 6.

The fresh sample contained 24% tetrahedral atoms, slightly less than the $\sim 30\%$ that is normally reported. The samples exposed to steam for times between 5 and 90 min, including the cycled experiment, appear to show a reduction in the

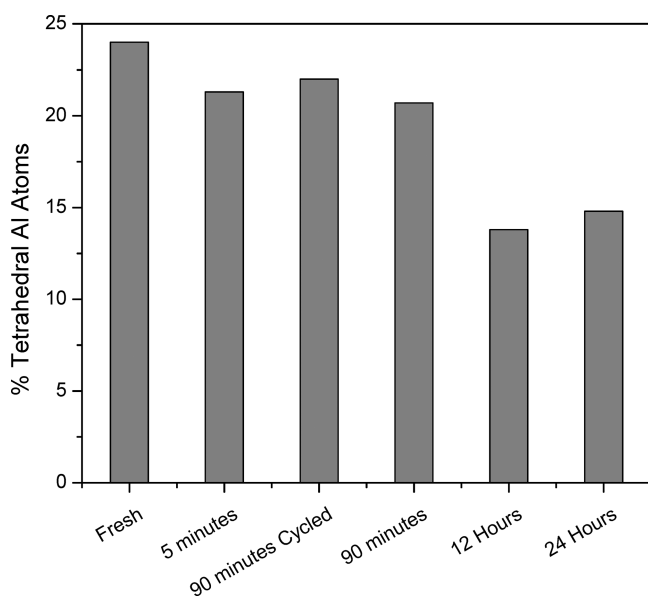


Figure 6. Percentage tetrahedral atoms; estimated by integration of ^{27}Al NMR peaks associated with tetrahedral and octahedral atoms and taking the ratio of tetrahedral to total aluminum.

relative amount of tetrahedral aluminum present in the samples. Interestingly, the sample exposed to steam for 5 min shows this reduction in tetrahedral aluminum content, but no peaks associated with boehmite are observed in the XRD patterns of the sample. This may be due to isolated tetrahedral aluminum atoms that are converted to octahedral coordination upon hydration,⁴⁷ but that have not been able to form large enough boehmite crystals to be observed in the XRD pattern. Further reduction in the tetrahedral aluminum content is observed for the samples exposed to steam for 12 and 24 h. Importantly, both of these samples show essentially equal quantities of tetrahedral aluminum atoms, which suggests that significant additional boehmite formation may not occur in hours 12–24 of steam treatment. Again, this is consistent with the XRD patterns of the samples, where the relative intensities of boehmite peaks are very similar for the 12 and 24 h steamed samples. These data suggest a nonlinear dependence of steam exposure time on the rate of boehmite formation under the steam conditions and time scales tested, with significant boehmite formation occurring between hours 1.5 and 12 of steam treatment and very little boehmite formation occurring after 12 h of steam treatment. It is hypothesized that this could be due to a difference in the rate of boehmite formation of surface aluminum atoms compared to those buried deeper inside the walls of the pore structure of the material. Aluminum atoms at the surface may undergo a rapid phase transition to boehmite at time scales between 1.5 and 12 h, while those inside the pore walls take much longer to form crystalline boehmite under the conditions tested.

Sorbent Textural Properties. To probe changes to the textural properties of the sorbents, the N_2 physisorption profiles of the sorbents after exposure to steam were measured and are shown in Figure 7, while the total pore volumes and BET surface areas are reported in Table 2. The BET surface areas and total pore volumes of each of the samples remain nearly unchanged, aside from the 24 h steamed sample, which showed an increase in both due to PEI leaching. The physisorption profiles for fresh sample and that exposed to steam for 5 min are nearly identical, suggesting that short exposure times do not significantly change the porous characteristics of the sample. The profiles for the samples exposed to steam for 90 min, including the sample exposed to cyclic steam treatment, and 12 h show qualitative differences in the hysteresis region of the isotherm, which is associated with capillary condensation and evaporation from mesopores.

The changes to the isotherms for the two 90 min samples and the 12 h sample in the hysteresis region suggest some change to the mesoporous character of these samples, induced by steam exposure. To clearly illustrate these qualitative observations, Figure 8 (top) shows the physisorption profiles of the fresh and 90 min samples overlaid. In the profiles for each of these samples, relative to the profile of the fresh sample, the N_2 adsorption at a given partial pressure in the region of capillary condensation is higher. This may be indicative of an effective decrease in the mesopore size. On the desorption branch of the isotherm, the onset of significant N_2 evaporation occurs at lower partial pressures for the steamed samples compared to the fresh sample. While it is much more difficult to draw direct inferences in qualitative changes to the desorption branch of a N_2 physisorption isotherm to a material property (as compared to changes in the adsorption branch), the desorption branch is thought of as being controlled by network characteristics of the mesoporous material.⁴⁸ However,

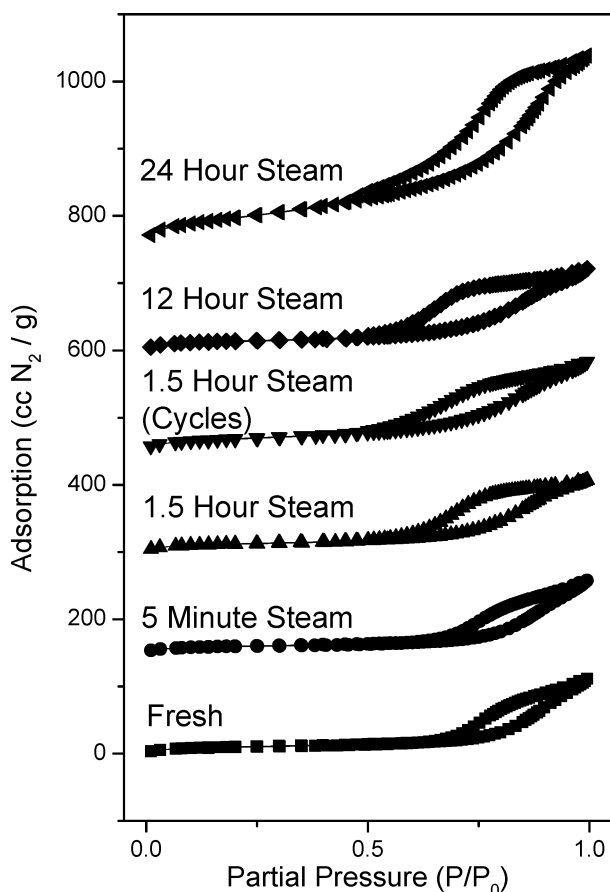


Figure 7. N₂ physisorption profiles at 77 K of samples exposed to steam for various times. Profiles offset by 150 cm³/g.

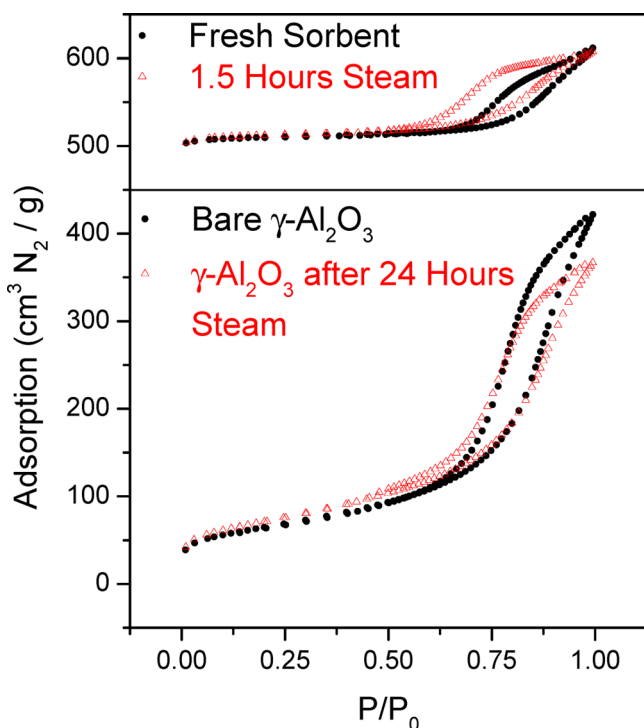


Figure 8. N₂ physisorption profiles of PEI containing sorbent (top) and bare γ -alumina support (bottom) before and after steam treatment. Sorbent profiles offset 500 cm³/g.

it is unclear whether these changes are due to rearrangement of the aminopolymer in the pores of the support as a result of extended exposure to steam, or if the changes are a result of the phase change to boehmite that is observed in each of these samples.

Figure 8 (bottom) shows the physisorption profiles of the bare alumina before and after exposure to steam for 24 h. The surface area of the material increased slightly after exposure to steam, while the pore volume of the sample exposed to steam decreased. The increase in surface area is expected to be due to formation of small boehmite particles on the large γ -alumina surface.⁴⁴ The XRD pattern of the material, shown in Figure S2 (Supporting Information), confirms that boehmite did begin to form. Interestingly, the intensity of the boehmite peaks in the bare γ -alumina sample exposed to steam for 24 h is less intense than those of the PEI impregnated sorbent exposed to steam for the same amount of time and even is less intense than the PEI impregnated sample exposed to steam for 12 h. This suggests that the presence of the PEI on the surface may facilitate the phase transition in some manner. The hysteresis region of the two samples is qualitatively very similar and does not appear to show the differences observed in the PEI impregnated sorbents discussed above. It is suggested, then, that the changes observed in the profiles of the composite sorbents are likely not due to the formation of boehmite but are more likely attributable to physical rearrangement of the aminopolymer due to exposure to steam. Worth noting is that Hammache et al.³⁵ suggested a steam induced polymer rearrangement as well, though they invoked this due to their observed reductions in surface areas and pore volumes of the sorbents after steam treatment.

FT-IR and FT-Raman Spectra. To probe whether the steam treatment induced any chemical change to the PEI, FT-IR and FT-Raman spectra were collected and are reported here in Figures 9 and 10, respectively. Previous studies on steam treatment of all three classes of amines supported on silica, and exposed to an environment of static steam for 24 h, showed no change in the FT-IR or FT-Raman spectra when oxygen was

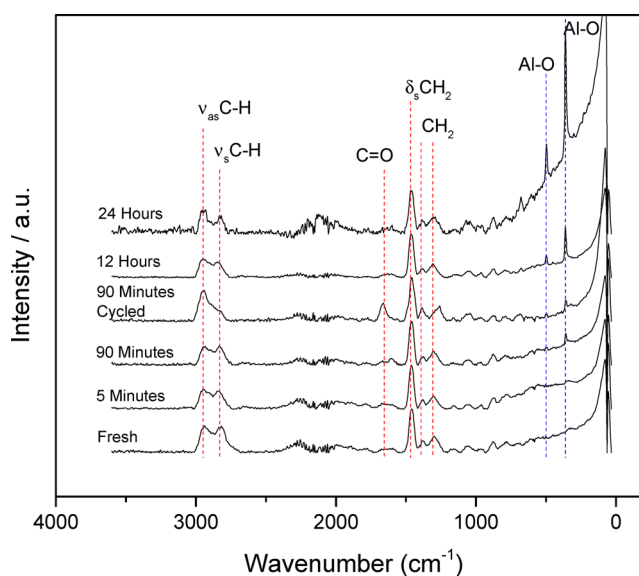


Figure 9. FT-Raman spectra of samples exposed to steam for various times. Red assignments are associated with organic moieties, while blue assignments are associated with boehmite.

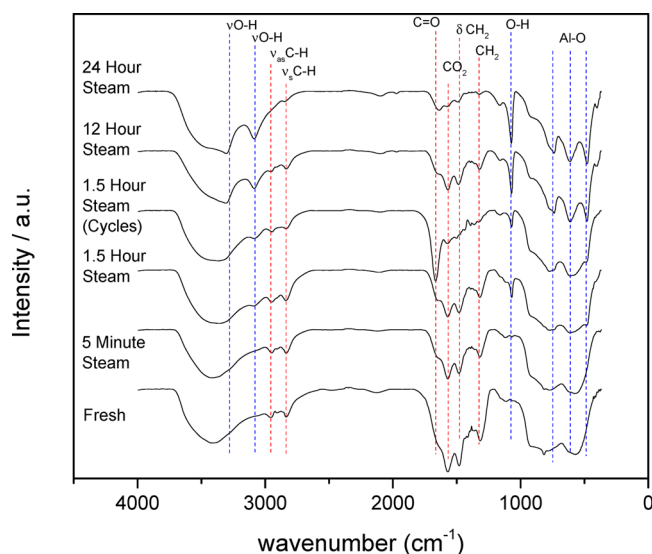


Figure 10. FT-IR spectra of samples exposed to steam for various times. Red assignments are associated with organic moieties, while blue assignments are associated with boehmite.

not present in the system.³⁶ As such, since oxygen was not expected to be present in the experiments reported here, no change was expected to be observed in the spectra for peaks associated with PEI.

Both the FT-Raman and FT-IR spectra for each sample show the expected peaks associated with PEI as well as the emergence of some new peaks associated with boehmite. The cycled sample shows a strong peak in both the FT-IR and the FT-Raman at 1667 cm^{-1} associated with the carbonyl stretch of an amide group, which is likely due to oxidation of the PEI. This oxidation is attributed to an error in sample handling after completion of testing and not to the steam treatment itself, as the sample was left in the heated reactor overnight in the absence of an inert purge flow passing over it. This is explained further in the Supporting Information. In the FT-Raman spectra, peaks observed at 1460 , 1390 , and 1300 cm^{-1} are associated with methylene motions.⁴⁹ In the FT-IR spectra, peaks associated with methylene motions are observed at 1480 and 1310 cm^{-1} . An additional strong peak in the IR spectra at 1565 cm^{-1} is due to chemisorbed CO_2 from the ambient environment.^{50–54} Symmetric and antisymmetric C–H stretches from PEI are observed at 2950 and 2830 cm^{-1} in both the FT-Raman and FT-IR spectra.⁴⁹ At steam times of 90

min and greater, peaks in the FT-Raman at 495 and 360 cm^{-1} associated with Al–O stretches in boehmite begin to become observable. Similarly, in the FT-IR spectra, an O–H stretching peak at 1070 cm^{-1} is observed for steam times of 90 min and greater. At steam times of 12 and 24 h, O–H stretches associated with boehmite at 3300 and 3080 cm^{-1} are observed in the FT-IR spectra, and the low wavenumber ($<1000\text{ cm}^{-1}$) fingerprint region of the spectra shows the characteristic shape of boehmite.³⁸ As expected, there is no evidence in the spectra to suggest any degradation of the PEI, aside from the oxidation observed due to improper handling of the cycled sample. Small changes in the FT-Raman spectrum of the cycled sample in the region of the symmetric C–H stretch (2830 cm^{-1}) and one methylene motion (1460 cm^{-1}) have been observed in the spectra of other oxidized PEI samples supported on γ -alumina as well.²⁰

Effect of Boehmite on CO_2 Adsorption Capacity. Since significant boehmite formation appears to occur in early time scales of steam treatment (relative to hundreds or thousands of hours of exposure in a large scale operation), and since boehmite formation is observed in the sample exposed to cyclic steam exposure, it can be inferred that a partial phase transition to boehmite may occur during large scale operation of the sorbents. Furthermore, it has recently been shown that the composition of the mesoporous oxide support can have significant effects on the amine efficiency of PEI in CO_2 adsorption applications.^{55,56} Thus, it is important to understand any impact this partial phase change may have on the properties of the sorbent and its CO_2 capture performance.

To this end, the effect of the presence of boehmite on the mesoporous support of the sorbent on the amine efficiency of PEI was directly probed. Two analogous sets of materials were prepared at 4 weight loadings of PEI: 10%, 20%, 30%, and 40%. In one set, PEI was impregnated into freshly calcined γ -alumina, similar to the sorbents discussed previously. In the other set, PEI was impregnated into γ -alumina that had been previously exposed to steam for 24 h and had partially hydrated to boehmite. By preparing the samples in this fashion, the textural properties of each sorbent at a given weight loading were very similar. Worth noting is that the pore volume of the boehmite/alumina sample was completely filled at 40 wt % PEI, while a small pore volume remained for the alumina sample at 40 wt % of PEI. The BET surface areas and total pore volumes of the samples are shown in Table 3, and the physisorption profiles of the PEI impregnated materials are reported in Figure S4 (Supporting Information). Because the textural properties of the sample sets were very similar at each PEI loading, it is

Table 3. Textural Properties, CO_2 Capacities, and Amine Efficiencies of Materials Used To Evaluate the Effect of Boehmite on the Amine Efficiency of PEI

sample	BET SA (per g sorbent) (m^2/g)	total PV ^a (cm^3/g)	amine loading ^b (per g sorbent) (mmol N/g)	CO_2 capacity ^c ($\text{mmol CO}_2/\text{g}$)	amine efficiency ($\text{mol CO}_2/\text{mol N}$)
alumina 10%	131	0.39	3.1	0.24	0.08
alumina 20%	73	0.27	4.7	0.61	0.13
alumina 30%	19	0.12	7.1	0.95	0.13
alumina 40%	4.7	0.04	8.8	1.23	0.14
boehmite/alumina 10%	138	0.43	2.3	0.26	0.11
boehmite/alumina 20%	80	0.34	4.7	0.47	0.11
boehmite/alumina 30%	27	0.16	6.7	0.89	0.14
boehmite/alumina 40%	0.1	0.01	9.3	1.12	0.12

^aValues estimated from total N_2 sorption at $P/P_0 = 0.99$. ^bValues estimated from TGA. ^cValues estimated from dry adsorption experiments at 400 ppm of CO_2/He in via TGA.

expected that the primary difference between each sample set is the presence of boehmite on one and not the other. Pseudoequilibrium adsorption capacities were estimated for these samples by use of a TGA, using dry CO₂ adsorption at 400 ppm of CO₂ in helium. The results of the study are shown in Figure 11, in which the calculated amine efficiency of the PEI is plotted as a function of the weight percent of PEI in the sorbent.

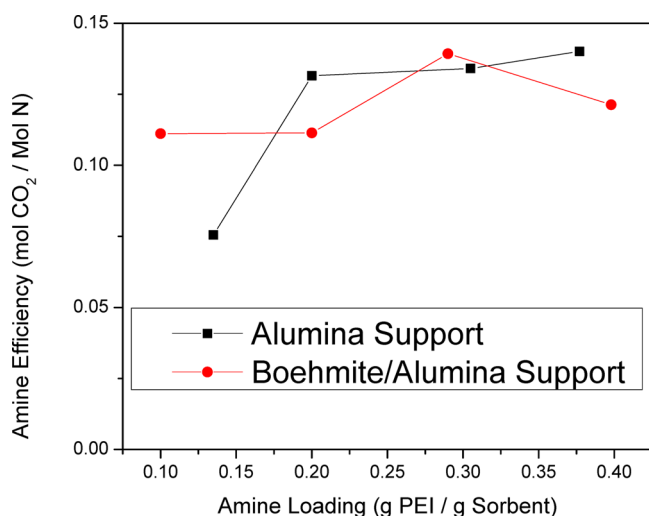


Figure 11. Amine efficiency as a function of amine loading of sorbents composed of PEI supported on either pure γ -alumina or γ -alumina partially hydrated to boehmite.

Both sample sets show a general trend of increasing amine efficiency with increasing weight loading of PEI, a trend that is expected at moderate levels of PEI incorporation and is typically associated with an increased amine proximity,¹¹ which is thought to be a necessary condition for CO₂ adsorption in the absence of water. The slight decrease of amine efficiency at 40 wt % for the boehmite/alumina sample is likely due to complete pore filling with PEI, which induces severe CO₂ diffusion limitations. No other obvious trend is evident from these data, leading to the conclusion that the presence of boehmite on the support does not significantly alter the ability of the PEI to adsorb CO₂, at least from a thermodynamic standpoint. Worth noting is that at 30 wt % of PEI, the amine efficiencies of the samples are nearly identical. Because the sorbents discussed previously in the study were prepared at a weight loading of 30 wt % PEI, these data suggest that the formation of boehmite may not have played a direct role in altering the CO₂ capacity of the material in the steam treatment experiments.

CONCLUSIONS

The CO₂ adsorption properties of PEI-impregnated alumina sorbents after exposure to flowing steam for various times were evaluated here. The as-synthesized sorbent was shown to have a high equilibrium CO₂ capacity of ~ 1.7 mmol/g at simulated air conditions. It was found that the γ -alumina support partially hydrated to form boehmite, an aluminum oxyhydroxide, at steam exposure times of 90 min and greater, including in a sample exposed to cyclic steam exposure. XRD and ²⁷Al NMR experiments suggested that significant boehmite formation occurred between 90 min and 12 h of steam exposure, but then the phase transformation slowed after 12 h of steam exposure.

It was shown that the presence of boehmite in the sorbent did not significantly affect the equilibrium CO₂ capacity of the PEI at simulated air capture conditions. Significant PEI leaching occurred in only the sample exposed to flowing steam for 24 continuous hours and was primarily responsible for the observed reduction of CO₂ capacity for that sample, whereas the PEI content of the other sorbents remained unchanged. Subtle changes observed in the N₂ physisorption data for samples exposed to steam for times of 90 min and 12 h were attributed to PEI rearrangement inside the pores of the support material during steam cycling.

ASSOCIATED CONTENT

Supporting Information

Diagram of flow adsorption/steam stripping system. XRD pattern of bare γ -alumina before and after exposure to steam for 24 h. Discussion of oxidation of cycled sample. N₂ physisorption profiles of sorbents with and without boehmite at various PEI loadings. Comparison of sorbent composition after steam treatment for various times. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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