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# Exploring the acid gas sorption properties of oxidatively degraded supported amine sorbents

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**ABSTRACT:** Amine-supported mesoporous oxide materials have proven to be effective acid gas sorbents. While the primary application of these supported amine species has been CO<sub>2</sub> capture, they have also shown to be proficient at adsorbing other damaging flue gas impurities such as SO<sub>x</sub> and NO<sub>x</sub>. The precise nature of the amine (primary, secondary or tertiary) is known to dictate the gas-amine interactions, with tertiary amines of particular interest due to their inability to adsorb dry CO<sub>2</sub>, favoring SO<sub>x</sub> and NO<sub>x</sub> species. The different amine sites also provoke differences in oxidative stability, when exposed to temperatures similar to those used for thermal desorption procedures. Herein we focus on the structural and chemical changes that occur in a range of class 1 (amine-impregnated) and class 2 (amine-grafted) sorbents upon oxidation, and correlate these with their variation in acid gas (CO<sub>2</sub>, NO<sub>2</sub> and SO<sub>2</sub>) uptakes, as a function of the oxidation temperature. These studies suggest that oxidatively degraded or ‘spent’ supported amine materials

may have possible uses as NO<sub>x</sub> or SO<sub>x</sub> sorbents. Specifically despite oxidative degradation these aminopolymer species maintain a reasonable level of NO<sub>2</sub> uptake, despite losing the ability to capture SO<sub>2</sub> or CO<sub>2</sub>, offering unique possibilities in selective NO<sub>2</sub> capture.

## INTRODUCTION

Presently, fossil fuels are the main contributor to the global energy supply, resulting in the accelerated release of carbon dioxide, and increased quantities of anthropogenic CO<sub>2</sub>. The concentration of atmospheric CO<sub>2</sub> has received significant interest in recent decades, due to the strong correlation with environmental issues, such as global warming and numerous health issues, such as respiratory illnesses.<sup>[1,2]</sup> As such there is growing interest in the fields of carbon capture, utilization and sequestration to control CO<sub>2</sub> levels.<sup>[3,4]</sup> The most evolved and widely implemented technology for CO<sub>2</sub> separation from dilute gas streams utilizes liquid amines, such as aqueous monoethanolamine (MEA), which is the prototypical benchmark capture system for post-combustion, or ‘flue-gas’ scrubbing system.<sup>[5]</sup> While liquid amine technology is well understood and extensively employed, its use nonetheless presents challenges. The small amine molecules are volatile and reactive, and as such, a significant quantity of the sorbent is lost throughout the process. Additionally, the solutions are highly corrosive, requiring specialized equipment.<sup>[6]</sup> These issues could be circumvented by employing a solid sorbent.<sup>[7-9]</sup> To date many solid systems, primarily porous materials, have been evaluated as potential CO<sub>2</sub> sorbents, including carbons,<sup>[10,11]</sup> zeolites,<sup>[12]</sup> metal organic frameworks<sup>[13,14]</sup> and supported amine materials.<sup>[15-18]</sup> Supported amine materials have been of great interest as they can capture CO<sub>2</sub> under both flue-gas (10 vol% CO<sub>2</sub>) and direct-air capture (400 ppm CO<sub>2</sub>) conditions.<sup>[19,20]</sup> This is further supported by their lower

regeneration costs accompanied with high amine loadings that create a high density of sites for CO<sub>2</sub> adsorption.<sup>[21,22]</sup>

The use of fossil fuels also results in the production of SO<sub>x</sub> and NO<sub>x</sub> emissions, typically emissions from coal result in concentrations between 0.2 – 0.25 vol% and 0.15 – 0.2 vol% of flue gas, respectively.<sup>[23,24]</sup> While the quantity of these species is much less than CO<sub>2</sub>, they can hinder carbon capture processes, with SO<sub>2</sub> and NO<sub>2</sub> in particular, resulting in the deactivation of amine-based sorbents via irreversible sorption.<sup>[25]</sup> In light of this, processes to selectively remove these species have been implemented, such as scrubbing sulfur gases via CaCO<sub>3</sub>.<sup>[26]</sup> However this limestone process requires temperatures in excess of 800 °C to desorb the SO<sub>2</sub>, and in doing so forms a considerable amount of waste inorganic by-products.<sup>[27]</sup> As such, one could develop a process using supported amines, tailored for the selective reversible adsorption of SO<sub>x</sub> and NO<sub>x</sub> species to pre-scrub flue gas sources before carbon capture occurs.<sup>[28]</sup>

Supported amines have been grouped into four different classes depending on the nature and incorporation method of the amine species. Class 1 “molecular basket” species are the result of oligomeric or polymeric amine species, with varying distributions of primary, secondary or tertiary amines residing within a mesoporous support (typically silica, alumina or carbon).<sup>[29-31]</sup> Examples include poly(allylamine) (PAA, primary amines only), linear poly(ethyleneimine) (L-PEI, secondary amine rich), or branched poly(ethyleneimine) (B-PEI, typically 44% primary, 33% secondary and 22% tertiary amines). These materials have received considerable attention, as they permit high amine loadings (5-10 mmol/g) for improved uptake, and use of higher molecular weight polymers can limit amine evaporation or leaching.<sup>[32]</sup> In contrast, class 2 species have a chemical bond between the support and the amine.<sup>[33-35]</sup> This is typically achieved by anchoring a trialkoxy silane species, such as 3-aminopropyl triethoxysilane to the support, through Si-O-

Si(C<sub>3</sub>H<sub>6</sub>NR<sub>2</sub>) bonds. These species are more resistant to chemical leaching; however, the grafting leads to lower amine loadings (1-2 mmol/g), limiting their ability to capture vast quantities of CO<sub>2</sub>. These silanes are typically relatively expensive, as well. Classes 3 and 4 materials can be viewed as combination of the above two classes. Class 3 is the result of *in situ* polymerization, resulting in an anchored aminopolymer,<sup>[36]</sup> whereas class 4 which contains both anchored and polyamine species within the same structure.<sup>[37]</sup> In all cases, it is possible to tune the nature of the alkylamine by selecting a specific polymer or organosilane.<sup>[38]</sup>

The contrasting behavior of primary, secondary and tertiary amines is of great interest in optimizing selective sorption of acid gases.<sup>[39-42]</sup> It is understood that under 'dry' conditions, primary amines make the more effective supported amine CO<sub>2</sub> sorbents, due to their ability to form strongly bound alkyl ammonium carbamate ionic pairs.<sup>[39-41]</sup> Yet, under anhydrous conditions tertiary amines cannot form these ionic pairs due to the lack of N-H bonds. This means a third species, typically water, is required, leading to the formation of an alkylammonium bicarbonate species.<sup>[42]</sup> As such significant interest has developed in utilizing tertiary amines under dry conditions, to selectively adsorb SO<sub>2</sub>.<sup>[43]</sup> SO<sub>2</sub> has been shown to have a different binding mechanism than CO<sub>2</sub>, whereby a charge-transfer complex is formed by tertiary amines binding to SO<sub>2</sub>; R<sub>3</sub>N--SO<sub>2</sub>.<sup>[44]</sup> Unlike CO<sub>2</sub> sorption, recent literature suggests that secondary amines are more effective than tertiary or primary amines for SO<sub>2</sub> sorption, but the reasons for this are currently not well-understood.<sup>[44]</sup> Similarly the binding mechanism of NO<sub>2</sub> has been hypothesized, but never confirmed, with studies showing that it is able to indiscriminately bind to all types of amines, with similar affinities.<sup>[45]</sup>

Aside from the differing adsorption behavior, another pivotal factor in the nature of the amine groups is their stability, specifically their reactivity with oxygen, at temperatures necessary for

acid-gas desorption.<sup>[46-50]</sup> It has been reported that secondary amines are the more reactive isolated amine species towards oxygen.<sup>[47-50]</sup> In work by Sayari *et al*, secondary amine (N-methylaminepropyl silane, MAPS) groups were found to form imines, amides and nitron species, through <sup>13</sup>C MAS NMR, upon exposure to carbon-free air at 120 °C for 40 hours.<sup>[34]</sup> In contrast, no significant change was seen for the primary (3-aminopropyl silane, APS) or tertiary (N,N-dimethylaminepropyl silane, DMAPS) amine groups. It is also noted that while isolated primary amine groups were not susceptible to oxidation, they became less stable when in close proximity to secondary amines.<sup>[47-50]</sup> L-PEI (with only secondary amines) and B-PEI (44% primary, 33% secondary and 22% tertiary amines) were compared before and after exposure to oxidizing conditions (110 °C in air for 24 hours). It was found that the combination of different amine sites in B-PEI resulted in lower stability than the (almost) purely secondary-amine L-PEI species, as the CO<sub>2</sub> capacity of B-PEI had dropped by 98% after oxidation, whereas the L-PEI had only dropped by 54%.<sup>[50]</sup> Once oxidatively degraded it is challenging to fully regenerate the supported amine sorbents, meaning they would typically be disposed of for reprocessing. However, if alternative uses could be found for these sorbents then it would mean they could be ‘recycled’ at the end of their carbon capture lifetime, making them highly attractive for large scale applications.<sup>[51]</sup> To this end, there has been a growing interest in propylene linked aminopolymers and dendrimers, which have been reported to show better oxidative stability than ethylene linked polymers during CO<sub>2</sub> adsorption under oxidizing conditions.<sup>[51,52]</sup>

While the influence of oxidative degradation has been well studied on many supported amine species relevant to CO<sub>2</sub> capture,<sup>[51]</sup> scarce few reports exist on how this can influence the sorption properties of different amines for ‘amine-poisoning’ gases such as SO<sub>2</sub> and NO<sub>2</sub>. As such, in this work, we contrast the influence of isolated primary, secondary and tertiary class 2 aminosilane

species, anchored on mesoporous SBA-15, for SO<sub>2</sub>, NO<sub>2</sub> and CO<sub>2</sub> (under both simulated flue-gas and atmospheric conditions) under dry conditions to probe the lifetime of such species for selective acid gas sorption. Similarly we contrast these findings with that of B-PEI, and fully methylated B-PEI impregnated in SBA-15 to understand how different distributions of amine groups can lead to tailored acid gas sorption, and their resilience to oxidative degradation.

## EXPERIMENTAL DETAILS

### Chemicals

All chemicals were obtained from Sigma Aldrich and used without further purification.

### SBA-15 synthesis

SBA-15 was synthesized as per our previous work.<sup>[15]</sup> First, 24.01 g of Pluronic P123 was initially dissolved in 630 mL of H<sub>2</sub>O and 120 mL of concentrated hydrochloric acid (37 wt%) while rapidly stirring at 40 °C to give a clear solution with white foam. Next, 52.68 g of tetraethyl orthosilicate was added dropwise, after which the system was left to stir for 20 hours at 40 °C. The system was then aged under static conditions at 100 °C for 24 hours. The mixture was then filtered and washed with 6 L of deionized water. The white powder was subsequently dried at 75 °C overnight prior to calcination. The powder was calcined by heating to 200 °C at a rate of 1.2 °C/min, holding for 1 hour, and then increasing the temperature to 550 °C at a rate of 1.2 °C/min and holding for 4 hours to yield a white powder.

### Methylating PEI

Branched PEI (800 MW) was methylated following the procedure by Sayari *et al.* First, 1 g of PEI was added to a solution of 12 mL of formaldehyde, 14 mL of formic acid and 0.4 mL of water. The mixture was heated to 120 °C overnight under a nitrogen atmosphere. When cooled, the solvent was removed with a rotary evaporator at 45 °C. This mixture was made basic with 30 mL of a 20 wt% NaOH solution. KOH pellets were then added to the solution until the product was obtained as an oily organic layer. The methylated-PEI was then extracted with diethyl ether and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The orange product was then dried overnight at 110 °C for 12 hours at 10 mbar. The purity of the compound was confirmed through <sup>1</sup>H solution phase NMR using a Bruker DSX-400, with CDCl<sub>3</sub> solvent.

#### PEI Impregnation

Initially, 1.0 g of the above SBA-15 was stirred with 15 mL of methanol at room temperature for 1 hour. A 20 mL solution of methanol containing either 500 mg of 800 MW branched poly(ethyleneimine) (PEI), or 700 mg of methylated poly(ethyleneimine) (Me-PEI) was added to the slurry and stirred for a further 24 hours at room temperature. The solvent was then removed under reduced vacuum at 50 °C to yield a white powder. The sample was then dried at 110 °C for 12 hours at 10 mbar. Samples are labelled as MePEI-SBA or PEI-SBA accordingly.

#### Amine-grafting on silica

First, 1.0 g of the SBA-15 described above was dried overnight at 110 °C under 20 mbar of vacuum. This sample was then mixed in a solution containing 20 mL of dry toluene, 50 µL of deionized water and 3 mmol of either 3-aminopropyl triethoxysilane (APS), 3-methylaminopropyl trimethoxysilane (MAPS) or N,N-dimethylaminopropyl trimethoxysilane (DMAPS). The solution was heated to 70 °C for 24 hours, then filtered with 200 mL of toluene, hexane and ethanol. The



resulting powder was then dried overnight at 110 °C under 10 mbar of vacuum. Samples are labelled as APS/MAPS/DMAPS-SBA accordingly.

#### Organic content

The organic content of the silicate samples was estimated using a Netzsch STA409PG TGA. Weight loss was calculated between 120 to 900 °C, under a combined flow of 90 mL/min of air and a 30 mL/min of nitrogen. The data were collected between 25 and 900 °C heating at a rate of 10 °C/min.

#### Physisorption

Nitrogen physisorption was performed on a Micrometrics Tristar 3020 instrument at 77 K. Samples were degassed for 12 hours at 110 °C prior to analysis. Surface area was calculated using the BET model. Pore volumes and pore-size distributions were calculated using the Bdb-FHH model.<sup>[53]</sup>

#### Acid gas capacity measurements

SO<sub>2</sub>, NO<sub>2</sub> and CO<sub>2</sub> capacities were measured using a TA instruments Q500 TGA. Samples were pretreated under a 100 mL/min flow of helium at 110 °C for 3 hours. The sorbent uptake was then measured from the gain in mass after subsequent exposure to 10% CO<sub>2</sub> in helium, 400 ppm CO<sub>2</sub> in Helium, 200 ppm SO<sub>2</sub> in helium or 200 ppm NO<sub>2</sub> in helium as appropriate, at 35 °C, flowed at 90 mL/min for 6 hours, or until saturation, with a 10 mL/min balance helium flow.

#### Sample degradation

To evaluate the oxidative stability of the materials described above, 500 mg of the adsorbent was packed into a Pyrex tube, 1 cm in diameter, with a frit at the center to allow for flow of gas through the sample without loss of the adsorbent. To remove residual water from the system, the bed was first heated to 110 °C and nitrogen was passed through the bed at 20 mL/min for 1 h. The temperature was then set to the desired oxidation temperature, and the flow was switched to air oxygen at 20 mL/min. The air flow was stopped after 24 h, and the material was recovered for post-oxidation chemical analysis.

### <sup>13</sup>C MAS NMR

<sup>13</sup>C cross-polarization magic angle spinning (CP-MAS) solid-state nuclear magnetic resonance (NMR) measurements were carried out on a Bruker DSX-300 spectrometer. The samples were spun at a frequency of 10 kHz, and 18 000 scans were taken.

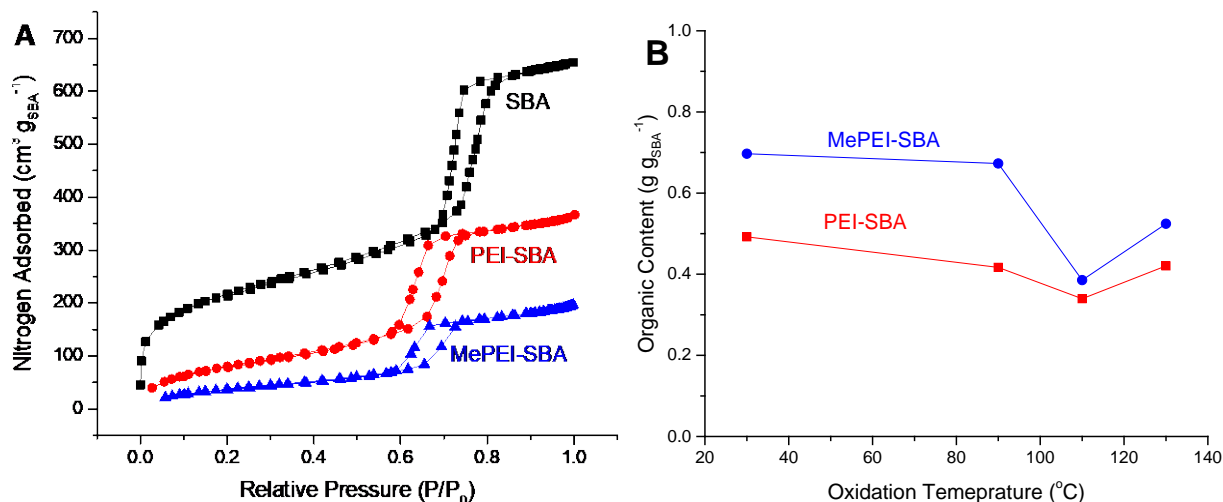
## RESULTS AND DISCUSSION

### **Physicochemical properties of Class 1 sorbents**

The integrity of the bare SBA-15 (referred to here on as SBA) support was confirmed using nitrogen physisorption (Figure 1 and S1). This showed a surface area of 793 m<sup>2</sup> g<sup>-1</sup> and a pore volume of 1.00 cm<sup>3</sup> g<sup>-1</sup>; a narrow pore distribution was observed using the BdB-FHH method, showing an average pore diameter of 81 Å, all consistent with the previous literature.<sup>[15,19,20]</sup> SBA-15 was then impregnated with both branched 800 MW PEI (henceforth known as PEI-SBA), and fully methylated branched 800 MW PEI (henceforth known as MePEI-SBA). The latter was

synthesized as stated above, and its phase purity was confirmed through  $^1\text{H}$  NMR (Figure S2), showing excellent agreement with previous work by Sayari *et al.*<sup>[24]</sup>

When discussing the physicochemical properties, we present our findings per gram of SBA ( $\text{g}_{\text{SBA}}^{-1}$ ), to normalize the sorbent to equivalent quantities to allow more insightful structural comparisons. In both cases the average pore size for the three samples (SBA, PEI-SBA and MePEI-SBA), shows a significant decrease (from 81 Å to 63 Å) (Figure 1 and S1). A dramatic decrease in surface area and pore volume were also seen on impregnation, confirming that the polymers are occupying the mesopores of SBA. It is noted that the addition of MePEI decreases the surface area and pore volume more than PEI. This is partially attributed to the greater organic content of MePEI-SBA ( $0.70 \text{ g}_{\text{SBA}}^{-1}$ ) over PEI-SBA ( $0.49 \text{ g}_{\text{SBA}}^{-1}$ ) (Figure S1B), which was necessary to ensure approximately equivalent amounts of amines in the two systems. Here MePEI-SBA has an amine content of  $12.2 \text{ mmol g}_{\text{SBA}}^{-1}$  and PEI-SBA has an amine content of  $11.4 \text{ mmol g}_{\text{SBA}}^{-1}$ . However this difference may also be due to a difference in topology between the two systems.<sup>[19,39]</sup> It is understood that PEI binds to SBA-15 through hydrogen-bonding interactions between silanol species and primary amines.<sup>[39]</sup> As there are no primary amines in MePEI, the hydrogen bonding interactions will be more limited. Also, methylating all the amines likely makes the system more hydrophobic than materials made with conventional PEI. The combination of these two factors will likely result in MePEI adopting a different morphology to PEI in the pores, contributing to the physicochemical differences observed.

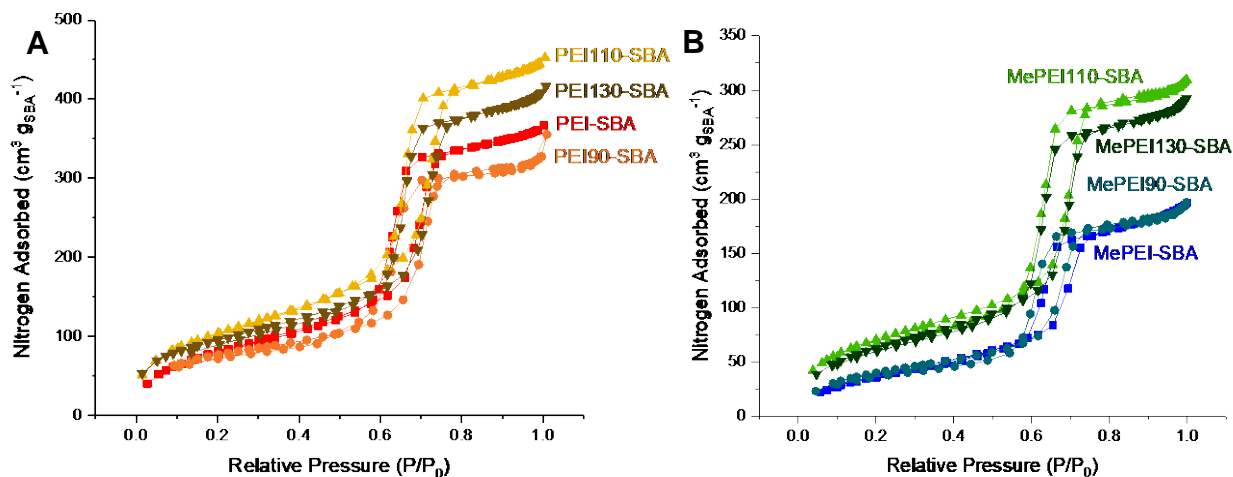


**Figure 1.** A) N<sub>2</sub> physisorption isotherms contrasting SBA, PEI-SBA and MePEI-SBA, showing a significant N<sub>2</sub> uptake on impregnation of the aminopolymers, and B) Showing the variation in organic content after oxidation treatment as a function of oxidation temperature of the PEI-SBA and MePEI-SBA series.

The PEI-SBA and MePEI-SBA systems were oxidized in a controlled environment, to mimic oxidative degeneration of the sorbents. By simulating increased temperatures and air exposure we sought insights into sorbent lifetime and stability on desorption. Both systems were oxidized for 24 hours at 90, 110 and 130 °C to create a series of sorbents, labelled as (MePEI/PEI)(90/110/130)-SBA to indicate the original sorbent and the oxidation temperature. In all cases, the organic content was monitored via TGA, both before and after the oxidation treatment (Figure S3).

Both the PEI-SBA and MePEI-SBA series show similar trends (Figure S3). A gentle decrease in organic content, after oxidation at 90 °C is followed by a more rapid decrease at 110 °C. Previous work suggests that the primary modes of oxidative degradation are the formation of imines, amides and conjugated amides.<sup>[30]</sup> Of these, only imine formation reduces the organic content. Yet this does not occur at tertiary amines, and even quantitative imine formation in PEI-SBA

cannot account for all the organic content lost. Therefore it is likely that the decrease in organic content is due to aminopolymer evaporation, leaching or cracking.<sup>[32]</sup> A greater proportion of the organic content is lost in MePEI-SBA (45 % from fresh to 110 °C) than PEI-SBA (31 % from fresh to 110 °C, Table 1). Recent SANS and theoretical work suggests that initially aminopolymers form strong interactions with the pore wall through primary amine groups, creating a monolayer along the pore walls.<sup>[19,39]</sup> After the monolayer formation, polymer-polymer interactions dominate as the polymer forms ‘plugs’ in the mesopores, similar to the bulk (non-encapsulated) polymer.<sup>[19,39]</sup> This helps rationalize why a greater decrease is observed in the MePEI-SBA, than PEI-SBA. As MePEI-SBA has no primary amines, the polymer-support interactions will be much weaker, leading to a greater amount of polymer mobility and possibly leaching. In both cases an increase in organic content is seen from 110 to 130 °C, which is likely due to oxygen addition to the aminopolymers, or fragments thereof, in forming amide or other oxygen-containing species above 110 °C.<sup>[30]</sup>



**Figure 2.** N<sub>2</sub> physisorption isotherms of A) PEI impregnated SBA-15 (PEI-SBA), and B) Methylated PEI impregnated SBA-15 (MePEI-SBA), after oxidative treatment at the specified temperatures.

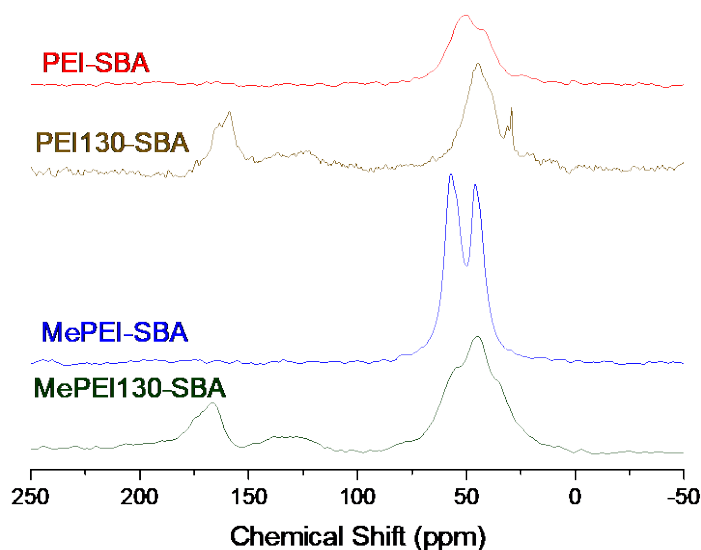
A similar trend is also seen in the physisorption data (Figure 2 and S4), as both the pore volume and surface of the 110 °C treated samples are significantly higher than the fresh systems (Table 1). This is in line with the theory that the pores are now less occluded due to loss of aminopolymer. Going from the 110 °C oxidation to 130 °C, in both systems, a reduction in both pore volume and surface area are observed, likely due to the increased molecular weight of the oxidized aminopolymers. We note subtle shifts in average pore diameter with increasing temperatures for the oxidation process, with larger pores reappearing in both the 110 °C and 130 °C treated materials, likely due to aminopolymer leaching.

**Table 1:** Summarizing the physicochemical properties of the bare support and of both series of class 1, amine-impregnated sorbents, both fresh and after oxidation treatment.

System	Organic Content / (g g <sub>SBA</sub> <sup>-1</sup> )	Surface Area / (m <sup>2</sup> g <sub>SBA</sub> <sup>-1</sup> )	Pore Volume / (cm <sup>3</sup> g <sub>SBA</sub> <sup>-1</sup> )	Pore Distribution / Å	Average Pore Diameter / Å
SBA	N/A	793	1.00	70 – 102	81
PEI-SBA	0.49	305	0.65	53-70	63
PEI90-SBA	0.42	267	0.60	53-75	63
PEI110-SBA	0.34	382	0.77	58-77	71
PEI130-SBA	0.42	345	0.70	58-72	64
MePEI-SBA	0.70	148	0.36	58-78	64
MePEI90-SBA	0.67	151	0.38	53-67	58
MePEI110-SBA	0.39	269	0.57	57-74	63
MePEI130-SBA	0.52	234	0.54	57-75	63

The chemical environment of the both the fresh aminopolymer systems, and the systems oxidized at 130 °C were probed using <sup>13</sup>C magic angle spinning solid state NMR (Figure 3). The fresh PEI-SBA and MePEI-SBA samples exclusively show peaks in the 35 to 70 ppm region, representing aliphatic amine species.<sup>[33,34,50,52]</sup> On oxidation, peaks appear in the 180 to 150 ppm

and 150 to 115 ppm ranges in both PEI130-SBA and MePEI130-SBA. The former set of peaks have been previously attributed to C=O stretches from amide groups,<sup>[30,33,34,50]</sup> showing that oxygen has clearly reacted with the amines present, in both species. The peaks at 150 to 115 ppm are attributed to C=C, and C-N bonds from hetrocycles and aromatic species.<sup>[33]</sup> It is interesting to note that these species were not seen by Sayari *et al* using their solvent extraction method.<sup>[50]</sup> However, such species may have coked onto the surface, or were not separated during to the solvent extraction protocol used. In this study we cannot clearly resolve any signals that are readily attributed to imine species (~ 45 ppm), as these would overlap with the signals from the sp<sup>3</sup> carbons in the fresh aminopolymers.<sup>[50]</sup> However the main signal in PEI-SBA shifts from 50 ppm to 45 ppm on oxidation, which could suggest imine formation. A less dramatic change is observed in this region or the MePEI-SBA systems, as imine species are unable to form from tertiary amines (Figure 3). However there is still significant evidence for the formation of oxidative products in the MePEI-SBA system, showing significant degradation and amide formation.<sup>[51]</sup>



**Figure 3.** Solid state magic angle spinning cross polarisation <sup>13</sup>C NMR of both fresh aminopolymers, and after oxidation treatment at 130 °C.

## Physicochemical properties of Class 2 sorbents

To observe the influence of different amines (primary, secondary and tertiary) in isolation, a range of class 2 sorbent species were also prepared, and oxidized at 130 °C. The fresh samples were prepared to ensure similar they had similar amine loadings (2.4 – 2.7 mmol g<sub>SBA</sub><sup>-1</sup>).

**Table 2:** Summarizing the physicochemical properties of the bare support and the three different class 2 sorbents, both before and after oxidation treatment at 130 °C.

System	Organic Content / (g g <sub>SBA</sub> <sup>-1</sup> )	Surface Area / (m <sup>2</sup> g <sub>SBA</sub> <sup>-1</sup> )	Pore Volume / (cm <sup>3</sup> g <sub>SBA</sub> <sup>-1</sup> )	Pore Distribution / Å	Average Pore Diameter / Å
SBA	N/A	793	1.00	70 – 102	81
APS-SBA	0.12	391	0.81	64 – 83	71
APS130-SBA	0.13	286	0.62	65 – 85	72
MAPS-SBA	0.16	470	0.76	63 – 86	72
MAPS130-SBA	0.15	408	0.74	63 – 88	71
DMAPS-SBA	0.17	459	0.95	64 – 86	70
DMAPS130-SBA	0.16	439	0.76	63 – 79	70

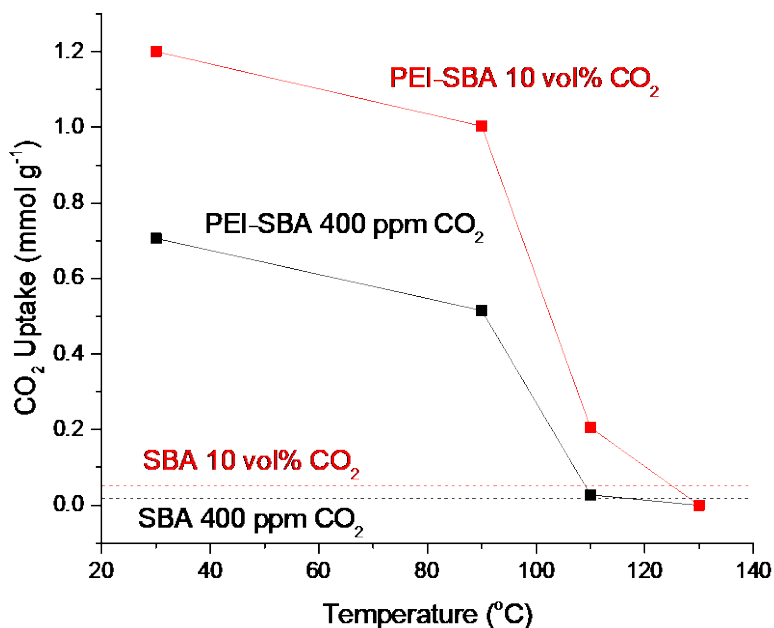
In all cases, the fresh class 2 sorbents (APS/MAPS/DMAPS-SBA) showed a lower surface area and pore volume than the bare SBA support (Table 2, Figure S5 and S6), indicating that the organosilane moieties had been successfully anchored into the mesopores. As a result, the average pore diameter was in all cases reduced from the 81 Å in the bare SBA to 71 ± 1 Å in the class 2 species. After oxidation at 130 °C the organic content of the class 2 species showed minor variations of ± 10 %. However, this is expected, as the modest amine loadings used means the mass resolution is not sufficient to conclusively determine whether the species has oxidized or not.



As expected, no significant amine loss or leaching was observed, due to the strong chemical bond anchoring the organosilane to the surface. Nitrogen physisorption shows that the oxidation of the class 2 sorbents at 130 °C results in notable decreases in both pore volume and surface area (Table 2, Figure S5). This is attributed to subtle chemical transformation of the amines, as previously seen,<sup>[46-50]</sup> which modify surface-amine interactions, changing the morphology of the tethered amines, possibly by forcing them off the pore walls. We note that we did not perform analogous <sup>13</sup>C NMR studies of the oxidatively degraded class 2 materials, as this is already well documented.<sup>[33]</sup>

### **Acid gas adsorption**

The supported amine sorbents were tested for the uptake of various acid gases, including 10 vol% CO<sub>2</sub> (mimicking flue gas), 400 ppm CO<sub>2</sub> (mimicking atmospheric CO<sub>2</sub>), 200 ppm SO<sub>2</sub> and 200 ppm NO<sub>2</sub>. The latter two gases were chosen to evaluate the potential for using supported amines for impurity adsorption.<sup>[25,43-45]</sup> In this section we normalize our results per gram of sorbent (g<sup>-1</sup>); this is due to the difficulties in contrasting systems of different classes, with different amine loadings, thus this format allows for a more reasonable comparison of the uptake of the sorbents.

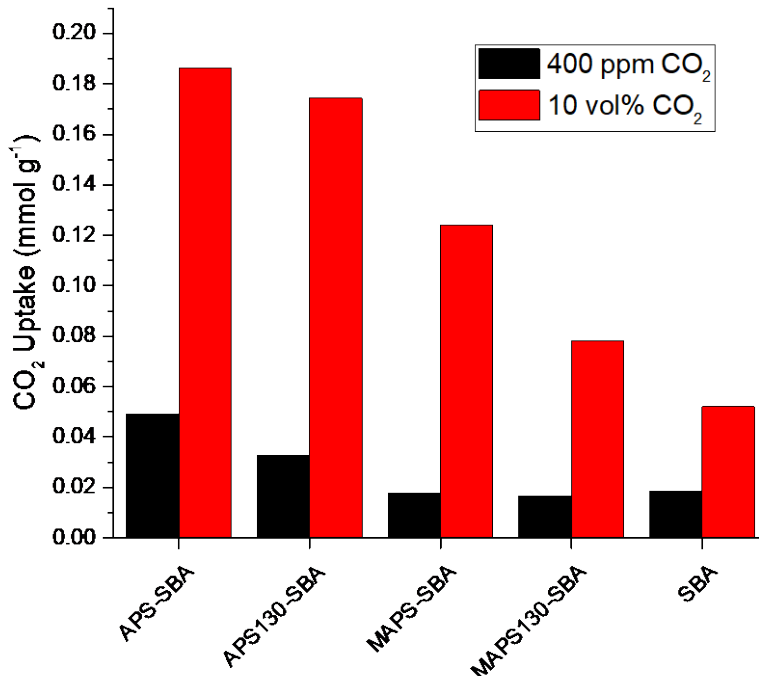


**Figure 4.** Variation in CO<sub>2</sub> uptake of the PEI impregnated SBA-15 series as a variation of oxidation treatment temperature for both 10 vol% and 400 ppm CO<sub>2</sub> feedstocks, contrasted with the bare SBA-15 support. Measurements were performed at 35 °C, flown at 90 ml/min for 6 hours, with a 10 ml/min balance helium flow.

The MePEI-SBA series showed no notable CO<sub>2</sub> uptake at 35 °C under dry conditions (as expected), however PEI-SBA and PEI90-SBA both showed significant uptake, with fresh PEI-SBA showing amine efficiencies of 0.21 and 0.12 for the 10 vol% and 400 ppm CO<sub>2</sub> feeds, respectively (Table S1, Figure 4). The reduction in CO<sub>2</sub> uptake with more dilute feedstocks is likely due to less frequent CO<sub>2</sub>-amine interactions.<sup>[19,20]</sup> Further, less sites can initiate the stronger CO<sub>2</sub>-amine interactions required to selectively capture CO<sub>2</sub> at low concentrations (> 60 kJ mol<sup>-1</sup>).<sup>[15,40]</sup> The CO<sub>2</sub> uptake for 400 ppm CO<sub>2</sub> between PEI-SBA and PEI90-SBA decreased by 29 % (from 0.71 mmol g<sup>-1</sup> to 0.52 mmol g<sup>-1</sup>); however, the organic content only decreased by 15 % (from 0.48 g g<sub>SBA</sub><sup>-1</sup> to 0.41 g g<sub>SBA</sub><sup>-1</sup>). Given this disparity, it is likely that the aminopolymer lost or

degraded was the more effective species for adsorbing 400 ppm CO<sub>2</sub>, which we previously suggested, through microcalorimetry, was the ‘bulk’ or ‘plug’ PEI molecules.<sup>[15,19]</sup> In contrast, the CO<sub>2</sub> uptake for 10 vol% CO<sub>2</sub> decreased by roughly 16 % (from 1.20 mmol g<sup>-1</sup> to 1.00 mmol g<sup>-1</sup>), in line with the organic content lost (Table 1). The higher concentration of CO<sub>2</sub> is less challenging to adsorb, and therefore a wider range of amine sites (both monolayer and ‘bulk’ aminopolymer) can likely capture it.<sup>[19,20]</sup> The lower uptake of PEI90-SBA for both concentrations of CO<sub>2</sub> is therefore attributed specifically to the leaching, deactivation or rearrangement of ‘bulk’ aminopolymer, as seen by TGA (Figure S3, Table 1), leading to less amine sites available to bind 400 ppm CO<sub>2</sub>.

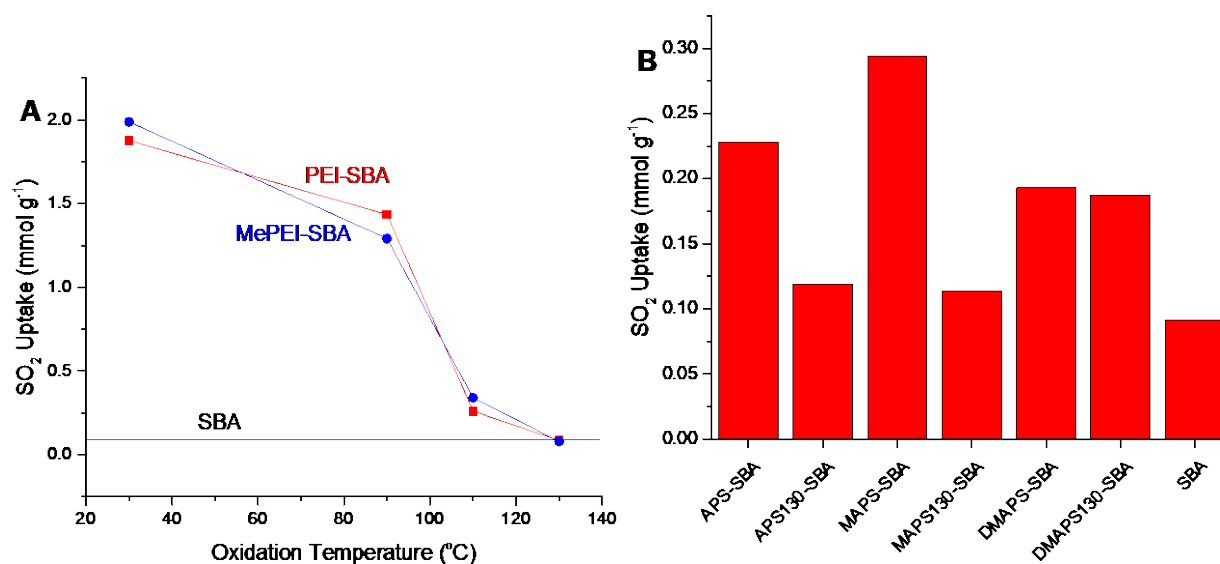
Increasing the oxidation temperature to 110 °C results in a dramatic decrease in CO<sub>2</sub> capacity at both CO<sub>2</sub> concentrations (Figure 4, Table S1), and is similar to the bare SBA support, suggesting that the aminopolymer is now significantly less effective at adsorbing CO<sub>2</sub>. This rapid decline in performance is attributed not only to the aminopolymer leaching, but also the oxidation of the amine species into amides and heterocycles, as seen by the <sup>13</sup>C solid state NMR (Figure 3), and suggested by the theoretical amine efficiencies (Table S1).<sup>[30,33,34,50]</sup> This is likely initiated by the secondary amines being in close proximity to other amines, as previously discussed.<sup>[46-50]</sup> PEI130-SBA shows the same uptake as the bare SBA support. This suggests that almost all of the amines have been oxidized, to the point where they cannot chemisorb CO<sub>2</sub>.



**Figure 5.** Showing the variation in CO<sub>2</sub> uptake of class 2 sorbents, both fresh and after 130 °C oxidation treatment, contrasted with the bare SBA-15 support. Measurements were performed at 35 °C, flowed at 90 mL/min with either 400 ppm CO<sub>2</sub>, or 10 vol% CO<sub>2</sub> (as labelled) for 6 hours, with a 10 mL/min balance helium flow.

For the class 2 sorbents we see a clear trend whereby the primary amines (APS) are superior CO<sub>2</sub> sorbents than secondary amines (MAPS) for both 400 ppm and 10 vol% CO<sub>2</sub> feedstocks (Figure 5, Table S1).<sup>[15-20]</sup> Isolated tertiary amine (DMAPS) species showed little CO<sub>2</sub> uptake for either feedstock, again due to the ‘dry’ conditions. Once oxidized at 130 °C the MAPS-SBA system loses a significant amount of its CO<sub>2</sub> uptake for the 10 vol% feedstock. In contrast the primary (APS) system seems more resilient to oxidation at 130 °C, with the uptake decreasing only slightly for the 10 vol% CO<sub>2</sub>. This is in good agreement with the previous literature, whereby isolated

secondary amines are more readily oxidized, with isolated primary amines being comparatively stable.<sup>[46-50]</sup> Neither the MAPS-SBA or MAPS130-SBA species are effective for adsorbing 400 ppm CO<sub>2</sub>, as they show similar uptakes to the bare SBA. However, for 400 ppm CO<sub>2</sub> the APS system shows a notable decrease in CO<sub>2</sub> capacity when oxidized at 130 °C. This is likely because any site that can effectively interact with CO<sub>2</sub> at such low concentrations will require a high binding energy (in the region of 60 – 80 kJ mol<sup>-1</sup>).<sup>[15,40]</sup> However, these sites that interact strongly with CO<sub>2</sub> appear to also react with oxygen under these conditions. Overall, these findings show that after oxidation at 130 °Cm the class 2 materials can still uptake significant amounts of 10 vol% CO<sub>2</sub>, confirming that the isolated amines are generally more stable than aminopolymers under the employed degradation conditions.<sup>[50]</sup> This is most likely due to a lack of diamine structures and/or amine reorganization in class 2 materials.



**Figure 6.** A) Influence of oxidation temperature on SO<sub>2</sub> uptake with SBA impregnated with either PEI or methylated PEI, contrasted with the uptake of the bare SBA-support. B) Variation in SO<sub>2</sub> uptake of class 2 sorbents, both fresh and after 130 °C oxidation treatment, contrasted with the

bare SBA-15 support. All measurements were performed at 35 °C, in gas flow at 90 mL/min with 200 ppm SO<sub>2</sub> until saturation, with a 10 mL/min balance helium flow.

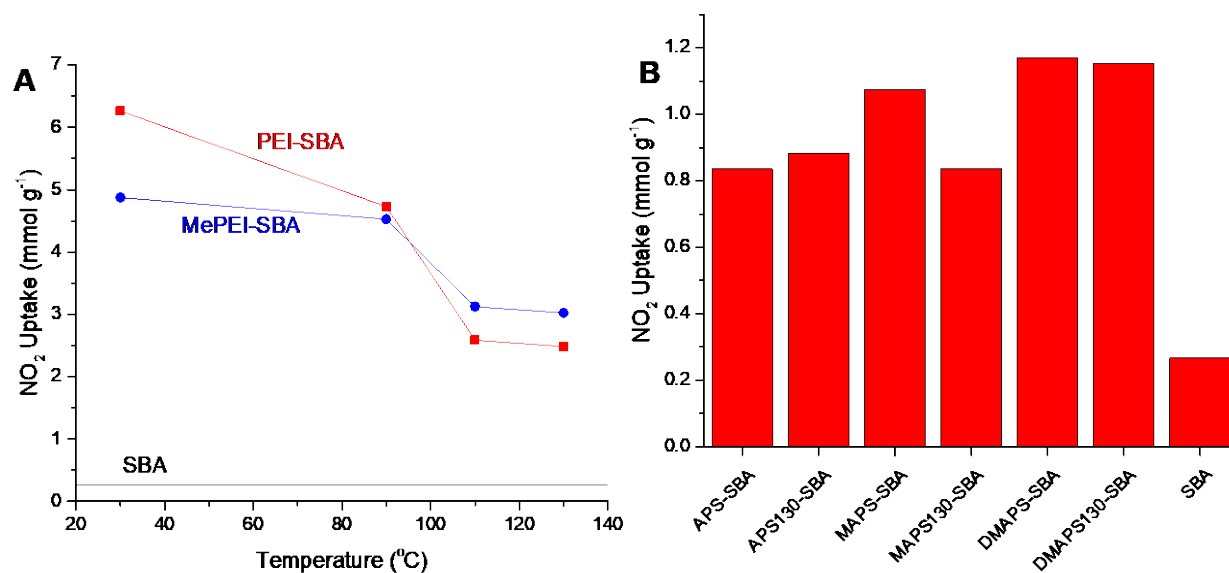
While CO<sub>2</sub> adsorption is a good probe for the stability of certain amines, SO<sub>2</sub> and NO<sub>2</sub> can probe a wider range of available amine sites.<sup>[23,24,43-45]</sup> SO<sub>2</sub> is known to favor secondary amine sites,<sup>[23,24]</sup> whereas NO<sub>2</sub> binds almost indiscriminately to amines.<sup>[23]</sup> The combination of these probe molecules, and CO<sub>2</sub>, will provide a more holistic view of the impact of oxidative degradation within these aminopolymers.

The oxidized PEI-SBA and MePEI-SBA series show very similar behavior in the uptake of SO<sub>2</sub> (Figure 6A, Table S2). Both show a gentle decrease in uptake after oxidation at 90 °C, and then a rapid decrease in uptake after oxidation at 110 °C. Both systems show very similar uptake to the bare SBA system after oxidation at 130 °C. The initial SO<sub>2</sub> uptake is marginally greater in the MePEI-SBA system (1.99 mmol g<sup>-1</sup>) than the PEI-SBA system (1.88 mmol g<sup>-1</sup>). This is likely due to the slightly higher amine loading in the MePEI-SBA system than the PEI-SBA system (12.1 mmol g<sub>SBA</sub><sup>-1</sup> and 11.3 mmol g<sub>SBA</sub><sup>-1</sup> respectively). This translates into a much higher amine efficiency for MePEI-SBA (0.54 versus 0.33 for PEI-SBA, Table S2), suggesting the tertiary amines present are able to adsorb the SO<sub>2</sub> better than the mixture of primary/secondary/tertiary amines in the PEI-SBA.. This result shows that while the MePEI system cannot adsorb CO<sub>2</sub> in dry conditions, it is still equally as effective at adsorbing dry SO<sub>2</sub> as branched PEI. Therefore, one could satisfactorily use MePEI-SBA as a system to selectively adsorb dry SO<sub>2</sub>.<sup>[24]</sup>

As the oxidation temperature increases to 90 °C the SO<sub>2</sub> uptake of both the MePEI-SBA and PEI-SBA systems decrease (Figure 6A, Table S2), with the MePEI-SBA SO<sub>2</sub> uptake decreasing

at a faster rate. This is likely due to the greater aminopolymer loss in MePEI-SBA, likely through evaporatipn or cracking, as seen through TGA (Figure S3 and Table 1). Again the two sorbents show very similar SO<sub>2</sub> uptakes (PEI90-SBA, 1.44 mmol g<sup>-1</sup>; MePEI-90-SBA, 1.29 mmol g<sup>-1</sup>). On oxidation at 110 °C very little uptake is seen, again due to the oxidation of the amines, in both aminopolymers. This suggests there is little difference in stability between the fully methylated MePEI and the standard branched PEI for degradation by oxidation at this temperature. At 130 °C both systems have the same capacity as the SBA support, suggesting that few of the oxidized amine sites can chemisorb SO<sub>2</sub>.

Contrasting this with the class 2 species (Figure 6B, Table S2) shows that the complete deactivation of the amines is not necessarily a strong function of proximity, as once oxidized, the APS130-SBA and MAPS130-SBA systems show a similar level of SO<sub>2</sub> uptake to SBA. However DMAPS-SBA and DMAPS130-SBA show similar SO<sub>2</sub> uptakes, far in excess of SBA. This suggests that while primary and secondary amines do deactivate in isolation, isolated tertiary amines are more resilient and do not degrade as readily, unlike tertiary amines in close proximity, such as MePEI. Again, the fresh sorbents follow the literature precedent that secondary amines are best suited to adsorbing SO<sub>2</sub>. However, this is also accompanied by more facile oxidative deactivation.<sup>[46-50]</sup>



**Figure 7.** A) Influence of the temperature of the oxidation treatment on NO<sub>2</sub> uptake with SBA impregnated with either PEI or methylated PEI, contrasted with the uptake of bare SBA-support. B) Variation in NO<sub>2</sub> uptake of class 2 sorbents, both fresh and after 130 °C oxidation treatment, contrasted with the bare SBA-15 support. All measurements were performed at 35 °C, flow at 90 mL/min with 200 ppm NO<sub>2</sub> until saturation, with a 10 mL/min balance helium flow.

NO<sub>2</sub> sorption shows different trends to both CO<sub>2</sub> and SO<sub>2</sub>. NO<sub>2</sub> is known to adsorb more readily onto supported amines than both SO<sub>2</sub> and CO<sub>2</sub>, hence larger uptake values are seen (Figure 7A, Table S2).<sup>[23]</sup> It can also be seen that the vast majority of the NO<sub>2</sub> uptake comes from the aminopolymer, and not the SBA support, given the NO<sub>2</sub> uptake values of the fresh aminopolymers (PEI-SBA 6.26 mmol g<sup>-1</sup> and MePEI-SBA 4.88 mmol g<sup>-1</sup>) are significantly higher than the bare support (SBA 0.27 mmol g<sup>-1</sup>). PEI-SBA does adsorb more NO<sub>2</sub> than MePEI-SBA, but it also has a lower amine efficiency (1.10 compared to 1.33). Given that this is a significantly higher uptake than both SO<sub>2</sub> and CO<sub>2</sub> (Table S2) it is likely that amine blockage and diffusion limitations play a



more significant role in hindering CO<sub>2</sub> and SO<sub>2</sub> uptake. However, this observation may also be attributable to differences in amine-NO<sub>2</sub> binding mechanism for different amine types.<sup>[19,20]</sup> The PEI-SBA is likely to be the less restrictive of the two, as the favorable polymer-wall interactions will limit the ‘plug’ morphology.<sup>[15,19]</sup> In contrast, the MePEI-SBA may favor polymer-polymer interactions, due to the lack of primary amines, causing the polymer to ‘plug’ in the pore, restricting diffusion through the polymer, and hindering access to the available amine sites.<sup>[19,20]</sup>

Again we note that the tertiary amines are able to adsorb NO<sub>2</sub>, and therefore could be useful as selective NO<sub>2</sub> sorbents under ‘dry’ conditions. The NO<sub>2</sub> capacity of both MePEI-SBA and PEI-SBA decreases after oxidation at 90 °C, (Figure 7A, Table S2) and decreases more rapidly once oxidized at 110 °C. The decrease is more pronounced in the PEI-SBA series. This agrees with our hypothesis of the amine sites in PEI-SBA being more available. If the NO<sub>2</sub> uptake of MePEI-SBA is indeed hindered by diffusion due to its ‘plug’ morphology, then loss of some of the MePEI (through cracking or evaporation) will make other amine sites accessible, causing less of a change in NO<sub>2</sub> uptake. However, if the sites in PEI-SBA are generally more available, then removing any aminopolymer will only remove accessible, active amine species, causing a more rapid decay in NO<sub>2</sub> uptake.

Unlike the other acid gases tested, when the aminopolymers are oxidized at 130 °C they still retain a significant amount of NO<sub>2</sub> adsorption (Figure 7A, Table S2). It has already been established that very few unoxidized amines remain after oxidation at 130 °C, as seen by the loss of SO<sub>2</sub> and CO<sub>2</sub> uptake. Given this, we conclude that the oxidatively degraded amines (likely amides, imines etc.) in the aminopolymers, are active NO<sub>2</sub> sorbents, despite not being able to adsorb significant amounts of CO<sub>2</sub> or SO<sub>2</sub>. This suggests that such species could be highly selective NO<sub>2</sub> sorbents, and have potential in NO<sub>2</sub> capture. This could allow ‘used’ (degraded) PEI-based

sorbents that can no longer adsorb CO<sub>2</sub> to be recycled for effective NO<sub>2</sub> scrubbing. The behavior of the isolated class 2 species suggest that tertiary amines have a higher equilibrium capacity for NO<sub>2</sub> uptake (Figure 7B, Table S2). However the more revealing fact is that the APS130-SBA and DMAPS130-SBA show only a slight deviation from the NO<sub>2</sub> uptake values of the fresh systems. In contrast, the MAPS130-SBA shows a significant decrease from the fresh system. Therefore while NO<sub>2</sub> is less selective about the type of amine it binds to, the oxidation products of isolated secondary amines, specifically, are not as effective for NO<sub>2</sub> binding. However the oxidation products from tertiary and primary amines are still able to effectively adsorb NO<sub>2</sub>. It is therefore likely that the more noticeable reduction in NO<sub>2</sub> uptake in PEI-SBA over MePEI-SBA is due to the oxidized secondary amines in PEI-SBA being less effective for NO<sub>2</sub> capture. However, it should be noted that in all cases the degraded class 2 sorbents still significantly outperformed the bare SBA support, and therefore the oxidized secondary amines are only comparatively less effective than the other supported amine species tested here.

## CONCLUSION

In this study we have demonstrated how extended oxidative degradation, mimicking aerobic thermal desorption conditions, can play a determining role in sorbent lifetime and uptake capacity of a range of acid gases. We have contrasted the oxidative degradation behavior of two encapsulated aminopolymers, varying only in their amine types, with analogous isolated grafted amines. We probed their capacity for adsorbing CO<sub>2</sub>, and common impurities such as SO<sub>2</sub> and NO<sub>2</sub>, which have previously been shown to rapidly degrade supported amine sorbents. By controlling the distribution of primary, secondary and tertiary amines in both class 1 and 2

sorbents, we are able to consider the behavior of each amine in the oxidation process. It was shown that CO<sub>2</sub> and SO<sub>2</sub> sorption are severely affected by oxidative degradation, with the resulting most oxidized supported amines losing all uptake capacity. In contrast, isolated class 2 species were found to be notably more stable for adsorbing mimicked flue gas (10 vol% CO<sub>2</sub>); however, with the exception of isolated tertiary amines (DMAPS-SBA), they were unable to adsorb significantly more SO<sub>2</sub> than the bare SBA support after oxidation above 110 °C. Therefore tertiary amines may be stable and selective SO<sub>2</sub> sorbents, prior to oxidative degradation. In stark contrast, all systems were able to adsorb notable quantities of NO<sub>2</sub>, even once oxidized at 130 °C. This finding suggests that the oxidized products of these supported amines could show promise as a novel sorbent for the selective adsorption of NO<sub>2</sub>. This opens unique avenues for recycling used (oxidized) supported amine sorbents. Thus, once supported amines are unable to adsorb CO<sub>2</sub> effectively they can instead be used to pre-remove NO<sub>2</sub> from CO<sub>2</sub> sources to preserve active supported amine sorbents for CO<sub>2</sub> removal.

## ASSOCIATED CONTENT

### **Supporting Information.**

The following files are available free of charge.

A PDF file containing pore-size distributions and TGA analysis for all the samples used in this work, <sup>1</sup>H NMR spectra of MePEI and numerical values for CO<sub>2</sub> (400 ppm and 10 vol%), SO<sub>2</sub> (200 ppm) and NO<sub>2</sub> (200 ppm) uptake with theoretical amine efficiencies.

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## Author Contributions

The manuscript was written through contributions of all authors.

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