Stability of Amine-Based Hollow Fiber CO₂ Adsorbents in the Presence of NO and SO₂

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Abstract

Comparative studies of the cyclic stability of primary, secondary, and tertiary amine-grafted silica/polymer composite fiber adsorbents upon exposure to simulated flue gas are reported. A simulated dry flue gas mixture with 200 ppm NO does not cause degradation of the amine grafted fiber adsorbents and all fibers retain their CO₂ capacity in the presence of NO. In contrast, upon exposure to dry flue gas in the presence of 200 ppm SO₂ at 35 °C, the primary amine containing adsorbent, CA-S-APS, shows a CO₂ capacity reduction of 55% over 120 cyclic adsorption-desorption runs. As the initial SO₂ induced degradation occurs in this adsorbent, the amine sites first irreversibly adsorb SO₂ and then begin to gradually adsorb SO₂ reversibly, as evidenced from a quantitative comparison of the amount of adsorbed SO₂ to the amount of desorbed SO₂. The secondary amine containing adsorbent, CA-S-MAPS, exhibits an improved stability and approximately 25% CO₂ capacity loss is observed during cycling in the presence of SO₂. Therefore, the secondary amine based CA-S-MAPS adsorbent demonstrates some degree of tolerance to SO₂ in comparison to the CA-S-APS sample. Under humid conditions, SO₂ imposes

significant detrimental impacts on the two adsorbents, as a result of increased SO₂ adsorption capacities in the presence of moisture. Although the CO₂ uptake is nearly zero in the tertiary amine adsorbent, CA-S-DMAPS, the SO₂ capacity of this adsorbent reaches 0.43 mmol/g under humid conditions and this material has the highest SO₂/N ratio of the fiber adsorbents studied. More importantly, this CA-S-DMAPS sample demonstrates reversible SO₂ adsorption, as indicated from the SO₂ cyclic adsorption experiments. The tertiary amine based fiber adsorbents have good potential for flue gas desulfurization, with advantageous characteristics of high SO₂/N ratio, excellent reversibility, low CO₂ adsorption and relatively low regeneration temperature.

Key words: hollow fiber, adsorbent, amine, cyclic stability, carbon dioxide NO, sulfur dioxide,

1 Introduction

Due to the global concern over the increasing atmospheric CO₂ level, new strategies to decrease CO₂ emissions are sought [1-3]. Post combustion CO₂ capture, as a CO₂ reduction technology that could be retrofitted onto existing large CO₂ emission sources such as coal and gas-fired power plants, has been the focus of intense research in recent years [4-6]. In this regard, environmentally benign, efficient adsorption technologies with low parasitic power plant loads are desired as substitutes for the conventional amine solvent absorption processes traditionally considered for CO₂ capture. Solid adsorbents have been extensively investigated as possible alternatives to amine solvents for CO₂ capture [3, 4, 7-10]. Amine species supported on various solids such as silica are examples of chemisorbents that have high adsorption capacities and desirable selectivity towards CO₂ over N₂. As such, they have emerged as favored candidate materials for post-combustion CO₂ capture [3-5]. However, flue gas impurities such as SO_x and NO_x are known to bind strongly to amines, and thus can degrade the adsorption capacity of solid amine adsorbents as well as amine solutions [11-18]. Although the concentration of SO₂ in flue gas streams, typically 100-500 ppm depending on the coal sources [16, 19, 20], is quite low compared to that of CO₂ (9-18 vol%), this component is more strongly acidic and can irreversibly react with some of the amine adsorption sites [16, 21], causing a dramatic loss of CO₂ capture efficiency in the adsorbent materials. Moreover, with the presence of H₂O and O₂ in flue gas as well, adsorption materials can also be adversely impacted by the formation of H₂SO₄ [22, 23]. Although extensive flue gas desulfurization can reduce SO_x levels to just a few ppm, this treatment is expensive, and operation at more elevated SO_x levels is desirable. In this regard, improved understanding of the long term stability of amine-based solid adsorbents upon

exposure to flue gas with SO_x and NO_x is necessary to assess their potential applications for CO₂ capture.

To date, many studies reporting the stability of various types of amine based solid adsorbents towards common flue gas contaminants such as SO₂, NO and NO₂ have been published [11-14, 16, 21, 24, 25]. In 1994, Diaf et al. [11] reported the adsorption performance of CO₂, SO₂, NO and NO₂ on various amine functionalized polymeric adsorbents. The results revealed that NO₂ led to the oxidation of amine sites and was the most strongly adsorbed component onto the adsorbents compared to CO₂, SO₂ and NO. They also found that tertiary amine functionalized copolymers showed high affinity for SO₂ but did not show measurable CO₂ capacity. In a study conducted by Khatri et al. [16], the strong and irreversible interaction between SO₂ and surface amine groups was found to occur in aminopropyl grafted SBA-15 upon exposure to flowing 2% SO₂/4% H₂O/He, via the formation of sulfates/sulfites. The SO₂ adsorption rate was observed to be slower than that of CO₂ adsorption; however, the adsorbed sulfur compounds could hardly be removed under mild thermal regeneration conditions, thereby effectively permanently blocking active CO₂ adsorption sites. Xu et al. [26] investigated the adsorption performance of poly(ethyleneimine) (PEI) impregnated silica adsorbents in a gas mixture containing 7% CO₂ and 60-70 ppm NO_x. The CO₂ capacity was significantly higher than the NO_x capacity, while very little NO_x was desorbed during regeneration, indicating the irreversible reaction between NO_x and the PEI impregnated silica adsorbents. Hallenbeck et al. [12] conducted a study on the effect of SO₂ on the adsorption capacity of poly(styrene) based CO₂ adsorbents containing primary amines. It was found that SO₂ irreversibly interacted with the adsorbents and the CO₂ adsorption capacity rapidly decreased. The detrimental effects of SO₂ on triamine grafted silica adsorbents were also observed in a study performed by Belmabkhout et al. [24], where the CO₂

capacities of triamine-grafted adsorbents were reduced by over 50% compared to the initial CO₂ capacity upon exposure to pure SO₂. In our previous work [13], we studied the stability of various aminosilane grafted silica adsorbents in the powder form to SO₂, NO and NO₂ by performing thermogravimetric experiments in the presence of various acid gases. The N-methylaminopropyl-grafted silica adsorbents containing secondary amines exhibited the highest affinity for SO₂, with partial reversibility, and the amine efficiency of SO₂/N reached 0.51. We also demonstrated that the degradation of the various aminosilica adsorbents in the presence of NO was not significant, whereas NO₂ dramatically reduced the adsorption capacity of all the adsorbents studied. In a follow-up study, the stability of the supported amines was further evaluated by performing dynamic, multicomponent adsorption experiments in a fixed bed contactor [14]. In agreement with the previously obtained single-component results, SO₂ was found to significantly influence the dynamic CO₂ capacity of the supported amines, while little competitive effect of NO on the CO₂ adsorption was observed. This suggests a decreased affinity of the amine-based adsorbents towards NO as opposed to SO₂.

The aforementioned adsorbents, which contained primary or secondary amine groups, generally possessed higher basicity than adsorbents with tertiary amines, thereby showing stronger affinity with SO₂. More recently, Sayari and co-workers [21] described the use of tertiary amine based solid adsorbents to reversibly adsorb SO₂ under dry or humid conditions, potentially offering a way to purify the gas mixture of SO₂ prior to CO₂ adsorption in a second bed with different adsorbents, which is consistent with the previous report of Diaf [11]. The presence of humidity in the gas mixture dramatically enhanced the SO₂ adsorption capacity, as was also observed for CO₂. Other works by Zhi et al. [27] and Tailor et al. [25] have also demonstrated the positive effects of moisture on SO₂ adsorption in amine grafted adsorbents.

Overall, the above studies involving limited exposure and cycling of amine silica solid adsorbents to nitrogen and sulfur acid gases collectively demonstrated that these adsorbents are liable to be poisoned by NO_2 and SO_2 , with primary and secondary amine-rich adsorbents being at least partially irreversibly poisoned, while NO did not exhibit detrimental impacts on the adsorption properties on the adsorbents. However, the stability of adsorbents during extensive cycling upon exposure to simulated flue gases with acid gas contaminants has rarely reported in the literature.

In this study, we report the cyclic stability of various types of amine grafted silica/polymer composite fiber adsorbents to flue gas impurities (*i.e.*, NO and SO_2) over 120 consecutive exposure cycles. The composite polymer/silica/amine fiber adsorbents studied in this work are a new type of CO_2 capture platform [28, 29] and hold promise for use as practical structured adsorbers [30]. High adsorption capacity [28], fast adsorption kinetics [31, 32], and low power plant parasitic loads [33] have been associated with this type of structured adsorbent in the past. In our recent study [32], we demonstrated that 40% of the adsorption capacity in PEI impregnated silica fiber adsorbents (Torlon-S-PEI) was retained after 120 cycles upon exposure to 200 ppm SO_2 . Consistent with other reports [13, 14], exposure to NO at 200 ppm over 120 cycles did not lead to a significant degradation of the adsorbents. However, PEI is a mixture of amine groups with varied accessibility and basic strength [3], and it is difficult to study the role of amine type in such materials. In this regard, we have designed a series of monoamine grafted silica fiber adsorbents to systematically determine the effects of amine type on the SO_2 and NO induced degradation of the hollow fiber adsorbents under both dry and humid conditions. The CO_2 capacity over extensive rapid temperature swing adsorption/desorption (RTSA) cyclic operation was utilized as a criterion to assess the resistance of the hollow fiber adsorbents to SO_2

and NO-induced degradation. Furthermore, the effect of primary, secondary and tertiary amines on the SO₂ adsorption capacity in the corresponding grafted fibers was investigated. The thermal reversibility of various types of monoamine grafted fiber adsorbents with respect to SO₂ was explored as well.

2 Experimental section

2.1 Fiber adsorbent preparation and characterization

Dried bare composite cellulose acetate / silica hollow fibers (CA-S) were produced using a non-solvent phase inversion technique commonly referred to as “dry-jet, wet-quench spinning” described in our previous work [28]. Monoamine grafted fiber adsorbents were functionalized by reacting organosilanes of 3-aminopropyltrimethoxysilane (APS), N-methylaminopropyl trimethoxysilane (MAPS) and N,N-dimethylaminopropyl trimethoxysilane (DMAPS) with CA-S fibers that consist of a cellulose acetate (CA) matrix and commercial silica particles (C 803, W.R. Grace), with a silica loading of 57 wt% [28, 29]. Bare CA-S fibers were placed in a custom-designed, jacketed reactor (40 cm length × 3 cm diameter), then mixed with toluene and a desired amount of organosilanes (summarized in **Table 1**). A circulating bath was used to circulate the heating medium through the reactor jacket to maintain the fibers and the reaction mixture near 85 °C. The reaction was carried out for 24 h, and the functionalized fibers were then transferred to another glass tube in which the long, functionalized fibers were washed sequentially with toluene, hexane, and ethanol and then dried under vacuum at 105 °C. The experimental set-up was reported in our previous study [29]. All hybrid hollow fiber adsorbents are represented by a sample designation of Polymer-Silica-Amine (*i.e.*, CA-S-APS, cellulose acetate-silica-aminopropyl) in this work. For example, CA-S-APS represents a cellulose acetate/silica supported fiber adsorbents grafted with primary aminopropyl functional groups.

Nitrogen physisorption measurements were performed using a Micromeritics Tristar II at 77 K. The surface area and pore volume were calculated from the isotherm data using the Brunauer–Emmett–Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively. Infrared spectroscopy was used to characterize the chemical species in the fiber adsorbents after exposure to various gases. Infrared spectra (IR) were recorded on a Bruker Vertex 80V optical bench. KBr pellets of fiber adsorbent samples were prepared by mixing ~1.0 mg fiber powder with 100 mg KBr. Elemental analysis (EA) was used to determine the amine loading of the fiber adsorbents. Analyses were performed by Columbia Analytical Services (Tucson, AZ, U.S.A.)

Table 1. Organosilane materials used to functionalize the fiber adsorbents

Fiber adsorbent	Amine	Structure
CA-S-APS	3-aminopropyltrimethoxysilane
CA-S-MAPS	N-methylaminopropyl trimethoxysilane
CA-S-DMAPS	N,N-dimethylaminopropyl trimethoxysilane

2.2 Cyclic adsorption-desorption experiments

Dynamic cyclic adsorption/desorption tests were carried out using stainless steel fiber modules in a rapid temperature swing adsorption (RTSA) system as shown in **Figure 1**. The testing procedure is illustrated in **Figure 2**. The fresh fiber module was first exposed to simulated dry clean flue gas (14% CO₂, 14% He and 72% N₂) at 40 mL/min for 10 min to estimate the initial CO₂ adsorption capacity $q_{pe,0}$. The effluent composition exiting the fiber adsorbent module was transiently measured by mass spectrometry (Pfeiffer, Omnistar Quadrupole mass spectrometer QMG 220). The fiber adsorbent module was regenerated under N₂ flow at 80 mL/min at 120 °C and then exposed to simulated dry flue gas containing 200 ppm SO₂ /10%

CO₂/ N₂ or 200 ppm NO /10% CO₂/ N₂ for 10 min at 35 °C. After each adsorption step, the fiber module was heated to 120 °C by external heating and held at 120 °C for 15 min under N₂ flow at 80 mL/min to regenerate the fibers. After regeneration, fiber temperature was cooled to 35 °C. After repeating this procedure for 10 cycles in 200ppm SO₂ or NO containing simulated flue gas, the feed stream in the RTSA system was then switched to simulated clean flue gas to evaluate the remaining CO₂ capacity. Then fibers were exposed to flue gas with contaminants again for 10 cycles. Following this procedure, the CO₂ capacity was evaluated after every 10 degradation cycles.

To study the effect of moisture on the adsorption behavior of the hollow fibers, a second series of experiments were conducted where a pre-humidification step was used to ensure the module was saturated with water prior to adsorption tests and then a dry gas stream was fed to prehydrated fiber module. The capacity measurement procedure for the prehydrated fibers was then the same as described for the dry experiments. All CO₂ adsorption measurements were performed at atmospheric pressure and 35 °C. The simulated flue gas flow rate was 40 mL/min. All experiments reported in this work were conducted using a stainless steel module with the inner and outer diameters of 0.18 and 0.25 inch, respectively and module length of 8 inch, housed with 4 fibers (**Figure 1**).

Figure 1. Schematic of the RTSA system and a hollow fiber module.

Figure 2. Experimental procedure of cyclic adsorption-desorption tests. $q_{pe,0}$: the initial CO₂ pseudo-equilibrium adsorption capacity; q_{pe} : the remaining CO₂ pseudo-equilibrium adsorption capacity after 10 degradation test cycles.

2.3 SO₂ adsorption experiments

The SO₂ breakthrough experiments were performed in the RTSA system using a simulated flue gas containing 200 ppm SO₂/10% CO₂ /N₂. In dry SO₂ adsorption experiments, simulated flue gas at a flow rate of 80 mL/min was fed to the fresh fiber module until the SO₂ concentration monitored at the module outlet reached 200 ppm (*i.e.*, complete breakthrough). All experiments were performed at 35 °C and 1 atm. The effluent composition exiting the fiber adsorbent module was transiently measured by mass spectrometry (Pfeiffer, Omnistar Quadrupole mass spectrometer QMG 220). After each adsorption step, the fiber module was heated to 120 °C using external heating and held at 120 °C for 1 hr to regenerate the fibers; at the same time, the feed gas was quickly switched to pure N₂ with a flow rate of 160 mL/min. For SO₂ adsorption under humid conditions, humid N₂ with a relative humidity of 100% at 35 °C was used to prehydrate the fiber module to ensure the module was saturated with water prior to each SO₂ adsorption test. The pseudo-equilibrium capacity of SO₂ adsorption capacity (q_{pe,SO_2}) was estimated from SO₂ breakthrough curves using Eq.1, where C_{0,SO_2} is the SO₂ concentration in simulated flue gas, C_{t,SO_2} is the SO₂ concentration of the effluent gas measured by mass spectrometry, $Q_{flue\ gas}$ is the flue gas flow rate and w is the dry fiber weight.

$$q_{pe,SO_2} = \frac{\int_0^\infty \left(1 - \frac{C_{t,SO_2}}{C_{0,SO_2}}\right) dt C_{0,SO_2} Q_{flue\ gas}}{w} \quad (1)$$

2.4 CO₂ temperature programmed desorption (TPD) experiments

Carbon dioxide temperature-programmed desorption (CO₂-TPD) experiments were carried out on a Micrometrics Autochem 2910 instrument equipped with a thermal conductivity detector (TCD). A sample of approximately 100 mg of fiber was loaded into a U-shape quartz reactor and preheated at 110 °C under helium flow of 50 mL/min for 30 min. The oven temperature was then

cooled down to the adsorption temperature of 40 °C and pure CO₂ was flowed over the sample at 50 mL/min for 60 min. The desorption experiment was started by flowing helium at 50 mL/min and ramping the reactor temperature from 40 °C to 110 °C at a rate of 5 °C/min.

3 Results and discussion

3.1 Fiber adsorbent properties

The CO₂ and He breakthrough curves obtained from an adsorption experiment using a fiber module in clean simulated flue gas (14% CO₂/14% He/N₂) were collected to estimate CO₂ adsorption capacity in the fiber adsorbents (the representative curves are shown in **Figure S1**). The pseudo-equilibrium adsorption capacity, q_{pe} , is defined in this work as a capacity achieved after 500 s of gas exposure, and was calculated by integrating the area bounded by He and CO₂ breakthrough curves over 500 s. Here, He, which is of equal molar percentage with CO₂, acted as the inert tracer to capture the background flow information of the fiber module and CO₂ was the adsorbate of interest. The initial amine loading, CO₂ pseudo-equilibrium capacity, $q_{pe,0}$, and amine efficiency (mmol CO₂/mmol N ratio) for various types of amine adsorbents evaluated under clean dry and prehydrated flue gas conditions are summarized in **Table 2**. Using monoamine grafted fibers (CA-S-APS), the q_{pe} was 0.72 mmol/g under dry conditions and the q_{pe} under humid conditions increased to 1.30 mmol/g. Similarly, the secondary amine containing CA-S-MAPS fibers showed a higher q_{pe} in the presence of moisture as well (0.47 mmol CO₂/g, dry vs. 0.66 mmol /g, humid). In contrast to the primary and secondary amine containing fibers, the tertiary amine adsorbents did not show a measurable CO₂ adsorption capacity under either dry or humid conditions. The reaction mechanism of tertiary amines with CO₂ is different from that of primary and secondary amines, where these latter amines react with CO₂ to form a zwitterion first and then the zwitterion is deprotonated by a free amine base to generate

carbamates [34]. In contrast, for tertiary amines to chemically capture CO₂, carbamate structures are not accessible and the amine must act as a weak base to produce free OH⁻ from water, which could further react with CO₂, eventually forming bicarbonate [35]. On the basis of this mechanism, tertiary amines cannot chemically react with CO₂ without water. In a study performed by Ko et al. [36], a calculated amine efficiency using tertiary amines of 3-(diethylamino) propyl grafted SBA-15 with a flow of pure dry CO₂ was 0.09 mmol CO₂/ mmol N, which likely resulted from physisorption of CO₂. In the CA-S-DMAPS fiber adsorbents studied here, the partial pressure of CO₂ was 0.14 atm. Under these conditions, the physisorption of CO₂ is not dominant. Hence, no CO₂ uptake was measured during the dry adsorption experiment. Under humid conditions, the tertiary amine may in principle react with CO₂ in the presence of moisture; however, the reaction kinetics of tertiary amines are much slower than in the case of primary and secondary amines, as demonstrated in Donaldson's work [35]. As such, in the rapid dynamic adsorption experiments performed in this work, the adsorption step of around 10 min was apparently not sufficiently long enough to yield measureable CO₂ capacities via the purportedly slow reactions between the tertiary amines and CO₂/H₂O.

The amine efficiencies represented by mmol CO₂/mmol N ratio for various types of amine adsorbents are compared in Table 2. The secondary amine adsorbent, CA-S-MAPS, showed much higher amine efficiency than primary amine containing CA-S-APS under dry conditions. Under prehydrated conditions, the water promoted the CO₂ adsorption capacity in CA-S-APS and CA-S-MAPS, thereby increasing amine efficiency. The amine loading plays an important role in determining the amine efficiency of amine functionalized silica adsorbents. A significant pore blockage or pore filling may be caused by the presence of excessive amine groups in the CA-S-APS adsorbent with a high amine loading of 3.9 mmol N/g, where a certain number of

APS groups cannot participate in the CO₂ adsorption under dry conditions. In contrast, the amine loading of CA-S-MAPS with the value of 1.8 mmol N/g is moderate, thus, the majority of amine groups in CA-S-MAPS are accessible to CO₂ molecules. As such, CA-S-APS has a lower amine efficiency than the CA-S-MAPS material (0.18 for CA-S-APS vs 0.26 for CA-S-MAPS) under dry conditions. Under prehydrated conditions, however, the adsorption behavior in fiber adsorbents is much more complicated. In addition to amine loading, the variation of water adsorption capacity influences the amine efficiency as well. Compared to CA-S-MAPS in this work, CA-S-APS, with a higher amine loading, includes more hydrophilic amine groups and likely adsorbs more water than CA-S-MAPS [41]. Therefore, the promoting effects of water on CO₂ adsorption capacity seem to enhance the amine efficiency of CA-S-APS much more significantly than for CA-S-MAPS. Thus, the difference of amine efficiency in the two adsorbents under prehydrated conditions is less pronounced than under dry conditions.

Table 2. Key properties of supported amine hollow fiber adsorbents.

Material	Dry fiber weight g	Amine loading ^a mmol N/g	CO ₂ q _{pe,0} dry mmol/g	CO ₂ q _{pe,0} prehydrated mmol/g	CO ₂ /N ratio dry mmol CO ₂ /mmol N	CO ₂ /N ratio prehydrated mmol CO ₂ /mmol N
CA-S-APS	0.44	3.9	0.72	1.30	0.18	0.33
CA-S-MAPS	0.49	1.8	0.47	0.66	0.26	0.37
CA-S-DMAPS	0.29	1.2	*	*	*	*

a. amine loading was obtained from elemental analysis.

* No measurable capacities from RTSA experiments.

3.2 Effect of SO₂ and NO on cyclic stability of primary and secondary amine grafted fiber adsorbents

In addition to the adsorption capacity, the cyclic stability of any adsorbent is of equal importance to determine its practical potential for application in a post combustion CO₂ capture process. Although many solid adsorbents, including PEI impregnated adsorbents (class 1) [5], amine covalently grafted adsorbents (class 2), zeolites, activated carbon and many others have been developed with the characteristics of high initial adsorption capacity or fast adsorption kinetics, the long-term impacts of SO₂ and NO present in flue gas on their overall adsorption capacities have not been well studied. The stability of monoamine grafted fiber adsorbents, including primary amine and secondary monoamine grafted fiber adsorbents (CA-S-APS and CA-S-MAPS), respectively, was investigated here to determine the stability of different types of amine sites under similar experimental conditions, where the flue gas contained 200 ppm NO or SO₂, respectively. The tertiary amine grafted sorbent was excluded from this set of experiments as it did not show measurable CO₂ uptake in the tests described above.

3.2.1 Cyclic stability of primary amine adsorbent CA-S-APS

The cyclic stability of the CA-S-APS sorbent was evaluated in two simulated dry gas streams containing (i) 200 ppm NO/10% CO₂/N₂ and (ii) 200 ppm SO₂/10% CO₂/N₂, respectively. **Figure 3** compares the normalized CO₂ pseudo-equilibrium capacity q_{pe} , for CA-S-APS over 120 RTSA cycles during exposure to 200 ppm NO and SO₂, respectively. The normalized CO₂ pseudo-equilibrium capacity represented by normalized CO₂ q_{pe} determined by dividing q_{pe} at each cycle by $q_{pe,0}$ (pseudo-equilibrium capacity of fresh fiber module) was used to compare the cyclic stability of the fiber adsorbents under various cyclic conditions. The results demonstrate that fiber adsorbents exhibited excellent stability in the presence of NO. This result is consistent

with previously reported results for amine-based adsorbents [11, 13, 14, 32]. Also, the CO₂ capacity remained nearly constant over 120 cycles, revealing that detectable amine leaching did not occur in these adsorbents, as the amine groups are covalently bonded to the silica surface.

Upon exposure to SO₂, the CO₂ capacity, q_{pe} , dropped approximately 55% after 70 cycles, reducing from 0.72 mmol/g to 0.31 mmol/g. As shown in **Figure 3**, the CO₂ capacity decreased rapidly over the first 70 cycles, reflecting that the primary amine grafted fiber adsorbents were not stable upon exposure to a gas stream containing 200 ppm SO₂. This is expected, as the SO₂ can bind to the amine groups to form thermally stable sulfite/sulfate compounds, which are difficult to remove by thermal regeneration [12, 13]. However, no measureable CO₂ capacity loss was found after 70 cycles. Based on these experimental results, it is concluded that the SO₂ does deactivate the primary amine adsorbent by reacting with the amine sites, but that some residual CO₂ capacity is maintained and a new pseudo-steady-state adsorption capacity, which is around 0.31 mmol/g, was achieved after an initial deactivation period.

Figure 3. Cyclic stability of the CA-S-APS fiber adsorbent upon exposure to dry flue gas with 200 ppm NO or 200 ppm SO₂. CO₂ capacities are normalized to the adsorbent's initial CO₂ adsorption capacity, $q_{pe,0}$.

The lower plateau CO₂ capacity in the SO₂ deactivated amine adsorbents has been seen in other studies as well [12, 13]; however, no further discussion was included to clarify what contributes to this capacity. This issue is explored more deeply here. **Figure 4** shows the SO₂ desorption profile during regeneration of the CA-S-APS fiber adsorbents at various points during the 120 cycle experiments. During the 1st cycle, an insignificant desorbed SO₂ peak with a maximum SO₂ concentration of 15 ppm was observed, reflecting that the majority of the SO₂

adsorbed during the adsorption step was irreversibly captured by the adsorbent. As the temperature swing cyclic operation proceeded from the 1st cycle to 70th cycle, the concentration of desorbed SO₂ gradually increased. From 70th cycle to 110th cycle, the amount of SO₂ released in the regeneration step, $q_{de,so2}$, was nearly the same, as exhibited by the similar SO₂ desorption profiles. By converting the area under the SO₂ desorption profile, $q_{de,so2}$ was estimated to be approximately 0.0084 ± 0.0004 mmol SO₂ /g per cycle, which is nearly equal to the total amount of adsorbed SO₂, $q_{ad,so2}$, (0.0089 mmol SO₂/g) at each adsorption-desorption cycle. As 200 ppm SO₂ did not break through the fiber module at each adsorption step of around 10 min, the $q_{ad,so2}$ at one cycle was approximated using the equation below:

$$q_{ad,so2} = \frac{Q_{flue\ gas} C_{0,SO2} t_{ad}}{w} \quad (2)$$

In this equation, $Q_{flue\ gas}$ is the flue gas flow rate, $C_{0,so2}$ is the SO₂ concentration of the simulated flue gas and t_{ad} is the adsorption time at one cycle.

This result indicates that the partially degraded fiber adsorbents became reversible SO₂ adsorbents after the initial degradation. This trend reveals that as the degradation proceeds in the CA-S-APS fiber adsorbent, the degradation may render the average binding energy of SO₂ with the adsorption sites much weaker. Alternately, we hypothesize that there exists a distribution of sites with different SO₂ binding strengths, which may be associated with the variation of amine spacing in silica supports [37], and after the first strongly binding sites are filled, all that remain are weaker SO₂ binding sites that can reversibly adsorb and desorb. After extensive cyclic operation, only reversible active adsorption sites for SO₂ remain and no further SO₂ induced degradation occurs in fiber adsorbents. This observation explains why a plateau capacity was found using the CA-S-APS sorbent after exposure to 200 ppm SO₂ for 70 cycles (see **Figure 3**).

Figure 4. SO₂ desorption profile at various cycles in CA-S-APS upon exposure to 200 ppm SO₂. Desorption temperature: 120 °C.

As discussed briefly in our previous study of PEI-impregnated fiber adsorbents [32], this plateau capacity likely comes from the CO₂ adsorption of remaining isolated amine groups, along with adsorption as physisorbed CO₂ in the porous silica or polymer structure as well. The number of isolated amine sites should rise progressively with the degradation of the adsorbents in the initial stages of exposure to SO₂. These isolated amine sites have been suggested to exhibit much weaker interactions with CO₂ and demonstrate easily thermally reversible reactions with CO₂ [38]. Early studies reported that in the absence of neighboring amine groups, hydrogen bonded carbamic acid could form between one isolated amine group and surface hydroxyl group of silica [39, 40]. Assuming that SO₂ reacts with an amine in a similar way [11], isolated amines are hypothesized to bind SO₂ weakly as well, and may have some thermal reversibility. The hypothesized physisorbed CO₂ is suggested to be due to the free Si-OH groups that remain on the porous silica surface, which have some weak, physical adsorption capability for CO₂ by hydrogen bonding [32]. We have noticed that the tertiary amine fiber adsorbent did not have any CO₂ adsorption capacity, indicating the amount of physisorbed CO₂ on fibers under a pseudo-equilibrium state is negligible. Likewise, the contribution of physisorbed CO₂ to the plateau capacity of the degraded samples is negligible as well.

3.2.2 Cyclic stability of secondary amine adsorbent CA-S-MAPS

The secondary amine adsorbent, CA-S-MAPS, was evaluated for its cyclic stability in NO or SO₂ containing simulated flue gases, respectively, under the same experimental conditions as

described for the CA-S-APS sample above. The CO₂ capacities remained nearly the same after exposure to NO, as shown in **Figure 5**. In contrast to the primary amine grafted fiber adsorbent, the secondary amine grafted fiber adsorbents exhibited a less significant degradation upon exposure to 200 ppm SO₂. Only 25% capacity loss was observed over 120 cyclic operations. The CO₂ pseudo-equilibrium capacity was reduced from 0.47 mmol/g to 0.35 mmol/g. **Figure 6** presents the SO₂ desorption profiles for the CA-S-MAPS adsorbent, showing nearly no changes from the 1st cycle to the 100th cycle. In other words, the released SO₂ amount during each cycle did not change significantly in the CA-S-MAPS adsorbent, indicating the average binding energy of SO₂ with adsorption sites remained nearly unchanged during cycling operation, unlike what was observed in the case of the CA-S-APS material. The maximum SO₂ concentration observed from the desorbed SO₂ peak reached around 40 ppm in the CA-S-MAPS adsorbent. The moderate capacity loss in the CA-S-MAPS adsorbent after exposure to SO₂ reveals that the secondary amines studied here have much more adsorption reversibility upon exposure to SO₂ than the similar primary amines. Indeed, the secondary amine based powder samples reported in previous studies [13, 14] were shown to be more reversible upon exposure to SO₂ as well.

To further understand the degradation behavior of the CA-S-MAPS adsorbent in SO₂ containing simulated flue gas, the amount of SO₂ released in the regeneration step, $q_{de,so2}$, was compared to the total amount of adsorbed SO₂, $q_{ad,so2}$. The $q_{de,so2}$ was estimated to be approximately 0.0098 ± 0.0005 mmol SO₂ /g in each adsorption-desorption cycle. The total amount of adsorbed SO₂, $q_{ad,so2}$, was around 0.011 mmol SO₂/g per cycle. Apparently, the value of $q_{de,so2}$ in CA-S-MAPS fiber adsorbents is slightly lower than that of the adsorbed SO₂ amount $q_{ad,so2}$ at each cycle, suggesting a small amount of SO₂ irreversibly bonded to fiber adsorbents over the 120 consecutive adsorption-desorption cycles. Correspondingly, the cyclic capacities

revealed around 25 % CO₂ capacity loss in the CA-S-MAPS fibers, with no plateau CO₂ capacity observed. This capacity loss is suggested to be mainly due to the deactivation of secondary amine groups as a result of non-desorbed SO₂, which was strongly bonded to the fiber adsorbents. The other possible reason for this capacity loss could be due to the presence of some propylamine impurities in MAPS silane [41, 42]. Correspondingly, the deactivation of primary amine impurities upon exposure to SO₂ would lead to the loss of capacity as well. Meanwhile, an insufficiently high desorption temperature may also contribute to the incomplete regeneration of fiber adsorbents. As compared to CO₂, SO₂ is a much stronger acid gas and may need a higher temperature to be desorbed. All desorption experiments in this work were conducted at 120 °C. To determine if this temperature was an appropriate desorption temperature for SO₂, the influence of the desorption temperature on SO₂ desorption profiles was further investigated. The amount of desorbed SO₂ significantly increased when the desorption temperature increased from 110 °C to 120 °C. However, with a further increase of desorption temperature from 120 °C to 130 °C, the desorbed SO₂ was nearly the same (**Figure S2**). Thus, 120 °C may be an optimum desorption temperature for the thermal regeneration of SO₂ adsorbed to these aminosilica adsorbents, as a further increase of the desorption temperature did not offer additional advantage.

Unlike CA-S-APS adsorbents, the CO₂ capacity in CA-S-MAPS fibers exhibited a decreasing trend even after 120 cycles as shown in **Figure 5**. Based on the hypothesis that the plateau capacity in deactivated CA-S-APS was from the CO₂ adsorption of remaining isolated amine groups and adsorption as physisorbed CO₂ in the porous fibers, a stabilized capacity was not expected in a slightly deactivated CA-S-MAPS adsorbent. Such an adsorbent still had a relatively high amine density, allowing SO₂ to react with two neighboring amine groups to form stable deactivated compounds. If adsorption cycles are to proceed further beyond 120 cycles, the

CO₂ capacity would be expected to stabilize at a certain value when the majority of amine groups in CA-S-MAPS adsorbents are deactivated and only isolated amine groups remain in the adsorbent.

Figure 5. Cyclic stability of the CA-S-MAPS adsorbent upon exposure to dry flue gas with 200 ppm NO or 200 ppm SO₂. CO₂ capacities are normalized to the adsorbent's initial CO₂ adsorption capacity $q_{pe,0}$.

Figure 6. SO₂ desorption profile at various cycles from the CA-S-MAPS sorbent upon exposure to flue gas containing 200 ppm SO₂. Desorption temperature: 120 °C.

In summary, under normal RTSA operation conditions, the majority of SO₂ was desorbed from the secondary amine adsorbent, CA-S-MAPS. In contrast, only a small amount of SO₂ was released from the primary amine adsorbent, CA-S-APS, at the earlier stages of cycling operations. When the SO₂ induced deactivation further proceeded at the expense of additional amine groups in the CA-S-APS after many cycles, the remaining adsorption sites were observed to adsorb SO₂ reversibly and a plateau capacity was found after 70 cycles.

3.2.3 Comparison of cyclic stability of CA-S-APS with CA-S-MAPS in SO₂

Figure 7. Comparison of CO₂ q_{pe} in CA-S-APS and CA-S-MAPS adsorbents upon exposure to dry flue gas with 200 ppm SO₂.

The CO₂ pseudo-equilibrium capacity of CA-S-APS over 120 cycles upon exposure to SO₂ is compared to that of CA-S-MAPS in **Figure 7**. It can be clearly observed that the secondary amine fiber material is more resistant to SO₂ deactivation than the primary amine based fibers, particularly at the initial stage of cyclic operation. This result is consistent with observations

from secondary amine-based solid adsorbents [11, 13]. During the first 30 cycles, CA-S-APS exhibited a much more rapid reduction of CO_2 q_{pe} than CA-S-MAPS. Then over 30 cycles, the capacity of CA-S-APS showed a similar decreasing trend to CA-S-MAPS. The different degrees of SO_2 degradation in CA-S-APS and CA-S-MAPS samples is likely associated with the variation of adsorption sites with different SO_2 binding energy in these fiber adsorbents. CA-S-APS, with a high amine loading, may include more SO_2 -susceptible high-energy binding sites than CA-S-MAPS, both due to the amine type and amine loading. Therefore, the SO_2 degradation of CA-S-APS is much more dramatic than CA-S-MAPS at the initial stage of cyclic operation. On the other hand, the different degrees of SO_2 degradation in CA-S-APS and CA-S-MAPS samples is likely associated with the SO_2 reaction mechanism in each material. The SO_2 reaction with amine groups occurs with the formation of electron donor-acceptor complexes between the acid and base [43]. The stability of such complexes is related to the amine basicity [44]. The stronger electron donating property of the methyl group is supposed to make MAPS a stronger base than the primary amine containing APS [45], but MAPS also has a higher steric hindrance than APS. As a consequence, APS and MAPS have a similar basicity, with a pK_b of about 4 [45]. Considering the higher steric hindrance in MAPS, it is expected that SO_2 less effectively accesses the lone electron pair in the MAPS groups [45], perhaps leading to a lower affinity of SO_2 with MAPS than APS (*i.e.*, the bulkier groups in MAPS than APS kinetically limit the formation of much stable amine- SO_2 compounds), which might be confirmed by the measurement of the isosteric heat of adsorption of SO_2 on the materials in the future [37]. Future investigation is needed to explore the SO_2 reaction mechanism with a variety amine types, from a molecular perspective. Different from the acid gas component SO_2 , the NO did not cause the degradation of the amine-grafted fiber adsorbents even at high concentrations (~ 200 ppm).

However, it should be noted that NO₂ likely deactivates amine silica fiber adsorbents based on the previous reports that NO₂ does deactivate amine based adsorbents [11, 13, 14, 26, 46].

3.2 CO₂ TPD experiments

CO₂-TPD measurements were performed to gain an insight into the adsorption-desorption behavior at the different adsorption sites that are present in the CA-S-APS and CA-S-MAPS fibers. The corresponding profiles are presented in **Figure 8**. For the fresh CA-S-APS adsorbent, the CO₂ desorption profile exhibited a wide asymmetric peak with the peak temperature at around 60 °C. In the deactivated sample, this peak shifted to a lower temperature of 50 °C. This indicates that only lower binding energy sites in the deactivated adsorbents were available to adsorb CO₂ and the strong binding energy sites had been deactivated by SO₂ exposure. As the adsorption sites with stronger interactions disappeared progressively due to the irreversible adsorption of SO₂, weaker adsorption sites started to adsorb CO₂. In the deactivated CA-S-APS adsorbent, the low temperature desorption peak tended to be more symmetric and the interaction energy was weakened, as evidenced by the lower desorption peak temperature. This observation again confirms that the remaining active sites in the deactivated sample only bind CO₂ weakly.

The TPD-CO₂ desorption profiles of fresh CA-S-MAPS included only one symmetric peak in the temperature range from 40 °C to 100 °C, with a peak temperature of 54 °C. In the deactivated fibers, the peak temperature remained unchanged and the peak intensity was simply reduced. This indicates that the interaction energy between secondary amine adsorption sites and CO₂ did not have measurable changes after limited degradation in SO₂, and simply that the amount of CO₂ adsorbed was reduced, as illustrated by the reduction of the peak intensity. This is not consistent with the hypothesis that deactivation occurs due to irreversible adsorption on primary

amine impurities, and more likely, a progressive deactivation of secondary amine sites occurs over cycling.

Figure 8. CO₂-TPD profiles of the CA-S-APS and deactivated CA-S-APS sorbents (a) CA-S-MAPS and deactivated CA-S-MAPS (b).

3.3 Material characterization

The textural properties of both the fresh and deactivated fiber adsorbents after exposure to dry flue gas with SO₂ over 120 cycles were evaluated. The surface area and pore volume were derived from the adsorption and desorption isotherms of N₂ at 77K. The pore volume and surface area shown in **Table 3** did not show significant changes after degradation of CA-S-APS and CA-S-MAPS by exposure to acid gases.

FTIR spectra were collected from fresh fibers and deactivated samples to identify the possible differences after SO₂ degradation. On the deactivated CA-S-APS sample, the asymmetric COO⁻ stretching band from the carbamate ion at 1565 cm⁻¹ [38-40, 47-50], which is generated from the preadsorbed CO₂ species (perhaps from exposure to air) [51], was weakened, indicating that available amine groups required to capture CO₂ were reduced in the deactivated fibers (**Figure 9 a**). Meanwhile, the other characteristic peaks at 1487 cm⁻¹ corresponding to the ammonium ion bending mode from ammonium carbamate [39, 52, 53] observed in the fresh CA-S-APS samples, disappeared in the spectra of the deactivated sample. Ammonium carbamate ion pairs, which are formed through the reaction of CO₂ with neighboring amine sites, are the dominant adsorbed CO₂ species in the adsorbents with the strongest CO₂-amine bonds [39, 52]. The loss of this peak further confirms that the CA-S-APS fibers were deactivated upon exposure

to SO₂, leading to the significant reduction of amine density. Therefore, only remaining relatively isolated amines bind CO₂ weakly.

The silica support exhibited a strong broad IR absorption band in the region of 1000~ 1300 cm⁻¹. The formation of sulfate/sulfite compounds, which show IR peaks in the same region [16, 54, 55], could not be discerned from the IR spectra, whereas the presence of these compounds was clearly revealed in the spectra of recycled PEI, which was washed from PEI impregnated fibers after exposure to SO₂ (**Figure S3**). The spectra of the deactivated CA-S-MAPS sample in **Figure 9 (b)** did not show a visible difference compared to that of the fresh fibers, revealing that no significant amine density reduction occurred in this material over 120 adsorption-desorption cycles. More detailed spectroscopic evidence is required to fully understand the reaction mechanism of SO₂ with the supported amines.

Table 3. Structural properties of the fresh and deactivated fibers

Material	Surface area	Pore volume
	m ² /g	mL/g
CA-S-APS	41	0.23
CA-S-APS_De	38	0.23
CA-S-MAPS	55	0.36
CA-S-MAPS_De	54	0.31

Figure 9. FT-IR spectra of CA-S-APS (a) and CA-S-MAPS (b) fiber adsorbents before and after exposure to SO₂ .

3.4 Effect of pre-adsorbed water and SO₂ on primary and secondary amine grafted fiber adsorbent

The tolerance of primary and secondary amine fiber adsorbents to H₂O/SO₂ was further examined by flowing simulated flue gas with 200 ppm SO₂ over prehydrated fiber adsorbents (a prehumidification step was used to ensure the module was saturated with water before exposure to dry simulated flue gas with SO₂). The normalized CO₂ cyclic capacities in the prehydrated fibers were compared to those of the dry fibers over 100 RTSA cycles upon exposure to simulated flue gas containing 200 ppm SO₂ (**Figure 10**). The loss of capacity occurred much more rapidly in the CA-S-APS fibers than the secondary amine grafted CA-S-MAPS fibers under both dry and prehydrated conditions. The pseudo-equilibrium capacity, q_{pe} , in the prehydrated CA-S-APS fibers suffered extensive CO₂ capacity loss over 100 cycles, reducing from 1.30 mmol/g to 0.39 mmol/g (approximately 70% capacity loss). In contrast to the primary amine CA-S-APS adsorbent, the prehydrated secondary amine CA-S-MAPS adsorbent exhibited less capacity loss, which was around 38%, with the q_{pe} dropping from 0.66 mmol/g to 0.41 mmol/g.

Figure 10. Comparison of the cyclic CO₂ capacity of dry fibers vs. prehydrated fibers in simulated flue gas cycling with 200 ppm SO₂. CO₂ capacities are normalized to the adsorbents' initial CO₂ adsorption capacity $q_{pe,0}$ before degradation.

It should also be noted that for both primary and secondary amines, the prehydrated fibers were much more susceptible to deactivation upon exposure to SO₂ than the dry fibers throughout the entire cycling test. The severe capacity reduction in the prehydrated state was most likely due to the increased reaction ratio of SO₂/N under prehydrated conditions, assuming the major

reaction between SO₂ and the primary or secondary amine sites followed the pathways shown in Eq. 3 and Eq. 4. More detailed studies are required to clarify the reaction mechanism between SO₂/H₂O and amine groups. This argument is based on the observations in the literature that CO₂/N ratios approach 0.5 under dry conditions and 1 under wet conditions, with extrapolation to the SO₂ case [3, 5].

3.5 Breakthrough experiments of SO₂ under dry vs prehydrated conditions

The breakthrough experiments of SO₂ were conducted with exposure to the simulated flue gas containing 200 ppm SO₂/10% CO₂ /N₂ at 35 °C and 1 atm to evaluate the pseudo-equilibrium capacity of SO₂, q_{pe,so2}, in various types of amine fiber adsorbents. The q_{pe,so2} was defined as the amount of SO₂ adsorbed by the adsorbents during a certain time period when the effluent concentration of SO₂ was nearly the same as the inlet value (~200 ppm). At this point, the adsorption nearly approached the equilibrium state.

A set of representative SO₂ breakthrough curves for the CA-S-APS adsorbents under dry and prehydrated conditions is shown in **Figure 11**. The breakthrough and pseudo-equilibrium adsorption time using 200 ppm SO₂ increased significantly in the presence of water. Similar results were observed in secondary amine fibers CA-S-MAPS and tertiary amine fibers C-S-DMAPS, data for which are included in the supporting information as **Figure S4**. Correspondingly, the capacities in all three types of adsorbents under prehydrated conditions dramatically increased compared to those under dry conditions (**Table 4**), indicating that the presence of H₂O improved the amine efficiency for SO₂ adsorption. This result further explains

the aforementioned observation that prehydrated fibers exhibited a rapid deactivation in CO₂ cycling tests as a result of the enhancement by water on the SO₂ uptake.

Figure 11. Effect of pre-adsorbed water on SO₂ breakthrough curves in CA-S-APS fiber adsorbents.

Table 4 summarizes the SO₂ adsorption capacities and SO₂/N ratio of various types of monoamine grafted fibers under both dry and prehydrated conditions. The SO₂ capacity for the CA-S-APS sample was 0.15 mmol/g in the dry fiber and 0.28 mmol/g in the prehydrated fibers. The secondary amine CA-S-MAPS exhibited the highest SO₂ capacity of 0.34 mmol/g (dry) and 0.55 mmol/g (prehydrated), despite the fact that the amine loading was much lower than for the primary amine fiber adsorbent, CA-S-APS. The tertiary amine CA-S-DMAPS did not have a CO₂ capacity under either dry or prehydrated conditions. However, the SO₂ capacity in this type of adsorbent can reach 0.29 mmol/g (dry) and 0.43 mmol/g (prehydrated). Correspondingly, tertiary amine exhibited the highest SO₂/N ratio among three types of fibers (**Table 4**). It should be noted that the variation of amine loading in the three fiber adsorbents studied in this work perhaps affects the SO₂/N ratio. Based on a previous report [13], the amine loading plays an important role in determining the amine efficiency (SO₂/N ratio) in the case of SO₂ adsorption on aminosilica adsorbents in powder form.

Table 4. SO₂ capacity, $q_{pe,so2}$, and SO₂/N ratio in all adsorbents under dry and prehydrated conditions

Material	$q_{pe,so2}$	$q_{pe,so2}$	SO ₂ /N ratio	SO ₂ /N ratio
	dry	prehydrated	dry	prehydrated
	mmol/g	mmol/g	mmol SO ₂ /mmol N	mmol SO ₂ /mmol N

CA-S-APS	0.15	0.28	0.04	0.07
CA-S-MAPS	0.34	0.55	0.19	0.31
CA-S-DMAPS	0.29	0.43	0.24	0.36

3.6 Cyclic SO₂ adsorption experiments in fiber adsorbents

To understand the SO₂ adsorption-desorption reversibility on primary, secondary and tertiary amine-grafted fiber adsorbents, a series of experiments were carried out to test the SO₂ adsorption capacities over three consecutive cycles upon exposure to 200 ppm SO₂/10% CO₂/N₂ under dry conditions. **Figure 12** presents the normalized cyclic SO₂ adsorption performance of the primary, secondary and tertiary amine-grafted hollow fibers. The initial dry SO₂ adsorption capacities, $q_{pe, so2}$, were 0.15 mmol/g, 0.34 mmol/g and 0.29 mmol/g for the primary, secondary and tertiary amine-grafted fibers, respectively. After three SO₂ adsorption-desorption cycles, the $q_{pe, so2}$ was reduced by 20%, 10% and 5%, respectively. The tertiary amine based adsorbent demonstrated the highest reversibility to SO₂ as compared to other two adsorbents.

The 1st cycle SO₂ desorption profiles for three aminosilica adsorbents are presented in **Figure 13**. It can be noted that the amount of desorbed SO₂ from the primary amine based adsorbent, CA-S-APS, was much lower than from the CA-S-MAPS and CA-S-DMAPS materials. As discussed previously, this fact is likely due to the basicity difference of the three amines. As the primary amines of CA-S-APS have strong basicity with low steric hindrance [45], a much higher affinity towards SO₂ may be expected from the CA-S-APS fibers. Accordingly, a much more rapid SO₂ capacity loss was observed. The magnitude of the desorbed SO₂, represented by $q_{d,so2}$, was estimated by converting the area under the SO₂ desorption profile. It was found that less than 5% of the adsorbed SO₂ (~ 0.02 mmol/g) was desorbed from the CA-S-APS fibers at 120 °C. In contrast, the secondary amine CA-S-MAPS material demonstrated good cycling regenerability

and around 88% of the adsorbed SO₂ (~0.30 mmol/g) was desorbed. This result further confirms that the secondary amine fibers have better SO₂ reversibility than the primary amine based fibers though SO₂ capacity of the secondary amine fibers is high. For the tertiary amine based sample, CA-S-DMAPS, the q_{d,so_2} (~ 0.28 mmol/g) was nearly equal to the q_{pe,so_2} (~ 0.29 mmol/g), revealing excellent SO₂ reversibility [11, 21, 25].

The cyclic stability of CA-S-DMAPS was further assessed under prehydrated conditions. The SO₂ capacities in consecutive three cycles under prehydrated conditions were 0.43 mmol/g, 0.41 mmol/g, and 0.41 mmol/g, respectively, again demonstrating good stability. From the reaction mechanism perspective, the tertiary amines may interact with SO₂ through the formation of a noncovalent adduct rather than via an acid-base reaction [21], suggesting a low adsorption enthalpy. Thus, complete desorption of SO₂ from the tertiary amines can be easily achieved under dry or humid conditions. In other words, a high regeneration temperature is not required to desorb SO₂ from the tertiary amine based adsorbents, contrary to the limestone sulfur removal process [21, 56, 57]. These results imply that tertiary amine grafted fibers are a promising thermally regenerable candidate adsorbents to capture SO₂.

Figure 12. Cyclic SO₂ adsorption in a variety of monoamine grafted fiber adsorbents under dry conditions. SO₂ capacities are normalized to the adsorbents' initial SO₂ adsorption capacity before degradation.

Figure 13. Desorption profile of SO₂ in various types of amine adsorbents at 1st dry adsorption-desorption cycle. Desorption temperature: 120 °C. Y axis is the mole percentage of SO₂ in effluent gas from fiber module outlet measured by mass spectrometry.

4 Conclusions

This study explored the cyclic stabilities of a variety of amine-based hollow fiber adsorbents upon exposure to simulated flue gas containing NO or SO₂. All the fiber adsorbents displayed excellent stability upon exposure to NO, exhibiting a nearly constant CO₂ capacity over 120 cycles. However, the CO₂ capacity in the primary amine based adsorbents, CA-S-APS, dropped rapidly in the presence of SO₂ before stabilizing with a minimal plateau capacity. The secondary amine adsorbent, CA-S-MAPS, exhibited a much better SO₂ reversibility, thereby demonstrating better performance after exposure to SO₂ than the CA-S-APS fibers. As directly evidenced from the SO₂ desorption profiles, the majority of the adsorbed SO₂ was released from the CA-S-MAPS sample during the desorption step, whereas only a trace amount of SO₂ was desorbed from the CA-S-APS material over the initial degradation stage due to a much stronger binding energy associated with the primary amines/SO₂ interaction. Moisture had a positive effect on SO₂ adsorption in all the fiber adsorbents, as expected, indicating that SO₂ with an acidic nature may follow the same reaction pathway as CO₂ in terms of the reaction with amines/water. Reversible SO₂ adsorption occurred in tertiary amine containing fibers under dry and prehydrated conditions, as exhibited with almost constant adsorption capacity in three consecutive cycles.

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6 References

- [1] Aaron D, Tsouris C. Separation of CO₂ from flue Gas: a review. *Sep Sci Technol* 2005; 40: 321-348.
- [2] D'Alessandro DM, Smit B, Long JR. Carbon dioxide capture: prospects for new materials. *Angew Chem Int Ed* 2010;49: 6058-6082.

- [3] Choi S, Drese JH, Jones CW. Adsorbent materials for carbon dioxide capture from large anthropogenic point sources. *ChemSusChem* 2009; 2: 796-854.
- [4] Samanta A, Zhao A, Shimizu GKH, Sarkar P, Gupta R. Post-combustion CO₂ capture using solid sorbents: a review. *Ind Eng Chem Res* 2011; 51: 1438-1463.
- [5] Bollini P, Didas SA, Jones CW. Amine-oxide hybrid materials for acid gas separations. *J. Mater. Chem.* 2011; 21: 15100-15120.
- [6] Fauth DJ, Gray ML, Pennline HW, Krutka HM, Sjoström S, Ault AM. Investigation of porous silica supported mixed-amine sorbents for post-combustion CO₂ capture. *Energy Fuels* 2012; 26: 2483-2496.
- [7] Xu X, Song C, Andresen JM, Miller BG, Scaroni AW. Novel polyethylenimine-modified mesoporous molecular sieve of MCM-41 type as high-capacity adsorbent for CO₂ capture. *Energy Fuels* 2002; 16: 1463-1469.
- [8] Hicks JC, Drese JH, Fauth DJ, Gray ML, Qi G, Jones CW. Designing adsorbents for CO₂ capture from flue gas-hyperbranched aminosilicas capable of capturing CO₂ reversibly. *J Am Chem Soc* 2008; 130: 2902-2903.
- [9] Liu Y, Ye Q, Shen M, Shi J, Chen J, Pan H, Shi Y. Carbon dioxide capture by functionalized solid amine sorbents with simulated flue gas conditions. *Environ Sci Technol* 2011; 45: 5710-5716.
- [10] Sung S, Suh MP. Highly efficient carbon dioxide capture with a porous organic polymer impregnated with polyethylenimine. *J Mater Chem A* 2014; 2: 13245-13249.
- [11] Diaf A, Garcia JL, Beckman EJ. Thermally reversible polymeric sorbents for acid gases: CO₂, SO₂, and NO_x. *J Appl Polym Sci* 1994; 53: 857-875.
- [12] Hallenbeck AP, Kitchin JP. Effects of O₂ and SO₂ on the capture capacity of a primary-amine based polymeric CO₂ sorbent. *Ind Eng Chem Res* 2013; 52: 10788-10794.
- [13] Rezaei F, Jones CW. Stability of supported amine adsorbents to SO₂ and NO_x in postcombustion CO₂ capture. 1. single-component adsorption. *Ind Eng Chem Res* 2013; 52: 12192-12201.
- [14] Rezaei F, Jones CW. Stability of supported amine adsorbents to SO₂ and NO_x in postcombustion CO₂ capture. 2. multicomponent adsorption. *Ind Eng Chem Res* 2014; 53: 12103-12110.
- [15] Levasseur B, Ebrahim AM, Bandosz TJ. Interactions of NO₂ with amine-functionalized SBA-15: effects of synthesis route. *Langmuir* 2012; 28: 5703-5714.
- [16] Khatri RA, Chuang SSC, Soong Y, Gray M. Thermal and chemical stability of regenerable solid amine sorbent for CO₂ capture. *Energy Fuels* 2006; 20: 1514-1520.
- [17] Uyanga IJ, Idem RO. Studies of SO₂ and O₂ induced degradation of aqueous mea during CO₂ capture from power plant flue gas streams. *Ind Eng Chem Res* 2007; 46: 2558-2566.
- [18] Bonenfant D, Mimeault M, Hausler R. Estimation of the CO₂ absorption capacities in aqueous 2-(2-aminoethylamino)ethanol and its blends with MDEA and TEA in the presence of SO₂. *Ind Eng Chem Res.* 2007; 46: 8968-8971.
- [19] Lin KYA, Petit C, Park AHA. Effect of SO₂ on CO₂ capture using liquid-like nanoparticle organic hybrid materials. *Energy Fuels* 2013; 27: 4167-4174.
- [20] NETL advanced carbon dioxide capture R&D program: technology update; 2013 May, Department of Energy, 2013.
- [21] Tailor R, Abboud M, Sayari A. Supported polytertiary amines: highly efficient and selective SO₂ adsorbents. *Environ Sci Technol* 2014; 48: 2025-2034.

- [22] Yang FH, Yang RT. Ab initio molecular orbital study of the mechanism of SO₂ oxidation catalyzed by carbon. *Carbon* 2003; 41: 2149-2158.
- [23] Mochida I, Korai Y, Shirahama M, Kawano S, Hada T, Seo Y et al. Removal of SO_x and NO_x over activated carbon fibers. *Carbon* 2000; 38: 227-239.
- [24] Belmabkhout Y, Sayari A. Isothermal versus non-isothermal adsorption–desorption cycling of triamine-grafted pore-expanded MCM-41 mesoporous silica for CO₂ capture from flue gas. *Energy Fuels* 2010; 24: 5273-5280.
- [25] Tailor R, Ahmadalinezhad A, Sayari A. Selective removal of SO₂ over tertiary amine-containing materials. *Chem Eng J* 2014; 240: 462-468.
- [26] Xu X, Song C, Miller BG, Scaroni AW. Adsorption separation of carbon dioxide from flue gas of natural gas-fired boiler by a novel nanoporous “molecular basket” adsorbent. *Fuel Process Technol* 2005; 86: 1457-1472.
- [27] Zhi Y, Zhou Y, Su W, Sun Y, Zhou L. Selective adsorption of SO₂ from flue gas on triethanolamine-modified large pore SBA-15. *Ind Eng Chem Res* 2011; 50: 8698-8702.
- [28] Labreche Y, Lively RP, Rezaei F, Chen G, Jones CW, Koros WJ. Post-spinning infusion of poly(ethyleneimine) into polymer/silica hollow fiber sorbents for carbon dioxide capture. *Chem Eng J* 2013; 221: 166-175.
- [29] Rezaei F, Lively RP, Labreche Y, Chen G, Fan Y, Koros WJ et al. Aminosilane-grafted polymer/silica hollow fiber adsorbents for CO₂ capture from flue gas. *ACS Appl Mater & Interfaces* 2013; 5: 3921-3931.
- [30] Lively RP, Chance RR, Kelley BT, Deckman HW, Drese JH, Jones CW et al. Hollow fiber adsorbents for CO₂ removal from flue gas. *Ind Eng Chem Res* 2009; 48: 7314-7324.
- [31] Fan Y, Lively RP, Labreche Y, Rezaei F, Koros WJ, Jones CW. Evaluation of CO₂ adsorption dynamics of polymer/silica supported poly(ethylenimine) hollow fiber sorbents in rapid temperature swing adsorption. *Int J Greenhouse Gas Control* 2014; 21: 61-71.
- [32] Fan Y, Labreche Y, Lively RP, Jones CW, Koros WJ. Dynamic CO₂ adsorption performance of internally cooled silica-supported poly(ethylenimine) hollow fiber sorbents. *AIChE J.* 2014; 60: 3878-3887.
- [33] Lively RP, Chance RR, Koros WJ. Enabling low-cost CO₂ capture via heat integration. *Ind Eng Chem Res.* 2010; 49: 7550-7562.
- [34] Caplow M. Kinetics of carbamate formation and breakdown. *J Am Chem Soc* 1968; 90: 6795-6803.
- [35] Donaldson TL, Nguyen YN. Carbon dioxide reaction kinetics and transport in aqueous amine membranes. *Ind Eng Chem Fundam* 1980; 19: 260-266.
- [36] Ko YG, Shin SS, Choi US. Primary, secondary, and tertiary amines for CO₂ capture: designing for mesoporous CO₂ adsorbents. *J. Colloid Interface Sci.* 2011; 361: 594-602.
- [37] Alkhabbaz MA, Bollini P, Foo GS, Sievers C, Jones CW. Important roles of enthalpic and entropic contributions to CO₂ capture from simulated flue gas and ambient air using mesoporous silica grafted amines. *J. Am. Chem. Soc.* 2014; 136: 13170-13173.
- [38] Srikanth CS, Chuang SSC. Infrared study of strongly and weakly adsorbed CO₂ on fresh and oxidatively degraded amine sorbents. *J Phys Chem C* 2013; 117: 9196-9205.
- [39] Bacsik ZN, Ahlsten N, Ziadi A, Zhao G, Garcia-Bennett AE, Martín-Matute BN et al. Mechanisms and kinetics for sorption of CO₂ on bicontinuous mesoporous silica modified with n-propylamine. *Langmuir* 2011; 27: 11118-11128.

- [40] Danon A, Stair PC, Weitz E. FTIR study of CO₂ adsorption on amine-grafted SBA-15: elucidation of adsorbed species. *J Phys Chem C* 2011; 115: 11540-11549.
- [41] Didas SA, Kulkarni AR, Sholl DS, Jones CW. Role of amine structure on carbon dioxide adsorption from ultradilute gas streams such as ambient air. *ChemSusChem* 2012; 5: 2058-2064.
- [42] Sayari A, Belmabkhout Y, Da'na E. CO₂ deactivation of supported amines: does the nature of amine matter? *Langmuir* 2012; 28: 4241-4247.
- [43] Oh JJ, Hillig KW, Kuczkowski RL. Structure of the dimethylamine-sulfur dioxide complex. *J Phys Chem* 1991; 95: 7211-7216.
- [44] Miller DD, Chuang SSC. Experimental and theoretical investigation of SO₂ adsorption over the 1,3-phenylenediamine/SiO₂ system. *J Phys Chem C* 2015.
- [45] Zelenak V, Halamova D, Gaberova L, Bloch E, Llewellyn P. Amine-modified SBA-12 mesoporous silica for carbon dioxide capture: effect of amine basicity on sorption properties. *Microporous Mesoporous Mater* 2008; 116: 358-364.
- [46] Diaf A, Beckman EJ. Thermally reversible polymeric sorbents for acid gases, iv. affinity tuning for the selective dry sorption of NO_x. *React Polym* 1995; 25: 89-96.
- [47] Roeges NPG. A guide to the complete interpretation of infrared spectra of organic structures. *J.Chem Educ* 1995; 72: A93.
- [48] Wang X, Schwartz V, Clark JC, Ma X, Overbury SH, Xu X et al. Infrared study of CO₂ sorption over “molecular basket” sorbent consisting of polyethylenimine-modified mesoporous molecular sieve. *J Phys Chem C* 2009; 113: 7260-7268.
- [49] Hiyoshi N, Yogo K, Yashima T. Adsorption characteristics of carbon dioxide on organically functionalized SBA-15. *Microporous Mesoporous Mater* 2005; 84: 357-365.
- [50] Bacsik ZN, Atluri R, Garcia-Bennett AE, Hedin N. Temperature-induced uptake of CO₂ and formation of carbamates in mesocaged silica modified with n-propylamines. *Langmuir* 2010; 26: 10013-10024.
- [51] Choi S, Drese JH, Eisenberger PM, Jones CW. Application of amine-tethered solid sorbents for direct CO₂ capture from the ambient air. *Environ Sci Technol* 2011; 45: 2420-2427.
- [52] Didas SA, Sakwa-Novak MA, Foo GS, Sievers C, Jones CW. Effect of amine surface coverage on the co-adsorption of CO₂ and water: Spectral deconvolution of adsorbed species. *J Phys Chem Lett* 2014; 5: 4194-4200.
- [53] Knöfel C, Martin C, Hornebecq V, Llewellyn PL. Study of carbon dioxide adsorption on mesoporous aminopropylsilane-functionalized silica and titania combining microcalorimetry and in situ infrared spectroscopy. *J Phys Chem C* 2009; 113: 21726-21734.
- [54] Faguy PW, Marinković NS, Adžić RR. An in situ infrared study on the effect of pH on anion adsorption at Pt(111) electrodes from acid sulfate solutions. *Langmuir* 1996; 12: 243-247.
- [55] Wu W, Han B, Gao H, Liu Z, Jiang T, Huang J. Desulfurization of flue gas: SO₂ absorption by an ionic liquid. *Angew Chem Int Ed* 2004; 43: 2415-2417.
- [56] Srivastava RK, Jozewicz W, Singer C. SO₂ scrubbing technologies: a review. *Environ Prog* 2001; 20: 219-228.
- [57] Ryu HJ, Grace JR, Lim CJ. Simultaneous CO₂/ SO₂ capture characteristics of three limestones in a fluidized-bed reactor. *Energy Fuels* 2006; 20: 1621-1628.

List of Figure Captions

Figure 1. Schematic of the RTSA system and a hollow fiber module.

Figure 2. Experimental procedure of cyclic adsorption-desorption tests. $q_{pe,0}$: the initial CO₂ pseudo-equilibrium adsorption capacity; q_{pe} : the remaining CO₂ pseudo-equilibrium adsorption capacity after 10 degradation test cycles.

Figure 3. Cyclic stability of the CA-S-APS fiber adsorbent upon exposure to dry flue gas with 200 ppm NO or 200 ppm SO₂. CO₂ capacities are normalized to the adsorbent's initial CO₂ adsorption capacity, $q_{pe,0}$.

Figure 4. SO₂ desorption profile at various cycles in CA-S-APS upon exposure to 200 ppm SO₂. Desorption temperature: 120 °C.

Figure 5. Cyclic stability of the CA-S-MAPS adsorbent upon exposure to dry flue gas with 200 ppm NO or 200 ppm SO₂. CO₂ capacities are normalized to the adsorbent's initial CO₂ adsorption capacity $q_{pe,0}$.

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