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Stability of amine-based hollow fiber CO_2 adsorbents in the presence of NO and SO_2

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HIGHLIGHTS

- SO_2-deactivated primary amine fibers reversibly adsorb additional SO_2.
- Secondary amine fibers exhibit better SO_2 tolerance than primary amine fibers.
- Tertiary amine grafted fibers have good SO_2 reversibility under dry or humid conditions.
- NO does not affect the CO_2 capacity of the fibers over 120 adsorption–desorption cycles.

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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 CO_2 capacity in the presence of NO. In contrast, upon exposure to dry flue gas in the presence of 200 ppm SO_2 at 35 °C, the primary amine containing adsorbent, CA–S–APS, shows a CO_2 capacity reduction of 55% over 120 cyclic adsorption–desorption runs. As the initial SO_2 induced degradation occurs in this adsorbent, the amine sites first irreversibly adsorb SO_2 and then begin to gradually adsorb SO_2 reversibly, as evidenced from a quantitative comparison of the amount of adsorbed SO_2 to the amount of desorbed SO_2. The secondary amine containing adsorbent, CA–S–MAPS, exhibits an improved stability and approximately 25% CO_2 capacity loss is observed during cycling in the presence of SO_2. Therefore, the secondary amine based CA–S–MAPS adsorbent demonstrates some degree of tolerance to SO_2 in comparison to the CA–S–APS sample. Under humid conditions, SO_2 imposes significant detrimental impacts on the two adsorbents, as a result of increased SO_2 adsorption capacities in the presence of moisture. Although the CO_2 uptake is nearly zero in the tertiary amine adsorbent, CA–S–DMAPS, the SO_2 capacity of this adsorbent reaches 0.43 mmol/g under humid conditions and this material has the highest SO_2/N ratio of the fiber adsorbents studied. More importantly, this CA–S–DMAPS sample demonstrates reversible SO_2 adsorption, as indicated from the SO_2 cyclic adsorption experiments. The tertiary amine based fiber adsorbents have good potential for flue gas desulfurization, with advantageous characteristics of high SO_2/N ratio, excellent reversibility, low CO_2 adsorption and relatively low regeneration temperature.

1. Introduction

Due to the global concern over the increasing atmospheric CO_2 level, new strategies to decrease CO_2 emissions are sought [1–3]. Post combustion CO_2 capture, as a CO_2 reduction technology that could be retrofitted onto existing large CO_2 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 CO_2 capture.

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Solid adsorbents have been extensively investigated as possible alternatives to amine solvents for CO_2 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 toward CO_2 over N_2. As such, they have emerged as favored candidate materials for post-combustion CO_2 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 SO_2 in flue gas streams, typically 100–500 ppm depending on the coal sources [16,19,20], is quite low compared to that of CO_2 (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 CO_2 capture efficiency in the adsorbent materials. Moreover, with the presence of H_2O and O_2 in flue gas as well, adsorption materials can also be adversely impacted by the formation of H_2SO_4 [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 CO_2 capture.

To date, many studies reporting the stability of various types of amine based solid adsorbents toward common flue gas contaminants such as SO_2, NO and NO_2 have been published [11–14,16,21,24,25]. In 1994, Diaf et al. [11] reported the adsorption performance of CO_2, SO_2, NO and NO_2 on various amine functionalized polymeric adsorbents. The results revealed that NO_2 led to the oxidation of amine sites and was the most strongly adsorbed component onto the adsorbents compared to CO_2, SO_2 and NO. They also found that tertiary amine functionalized copolymers showed high affinity for SO_2 but did not show measurable CO_2 capacity. In a study conducted by Khatri et al. [16], the strong and irreversible interaction between SO_2 and surface amine groups was found to occur in aminopropyl grafted SBA-15 upon exposure to flowing 2% SO_2/4% H_2O/He, via the formation of sulfates/sulfites. The SO_2 adsorption rate was observed to be slower than that of CO_2 adsorption; however, the adsorbed sulfur compounds could hardly be removed under mild thermal regeneration conditions, thereby effectively permanently blocking active CO_2 adsorption sites. Xu et al. [26] investigated the adsorption performance of poly(ethyleneimine) (PEI) impregnated silica adsorbents in a gas mixture containing 7% CO_2 and 60–70 ppm NO_x. The CO_2 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 and Kitchin [12] conducted a study on the effect of SO_2 on the adsorption capacity of poly(styrene) based CO_2 adsorbents containing primary amines. It was found that SO_2 irreversibly interacted with the adsorbents and the CO_2 adsorption capacity rapidly decreased. The detrimental effects of SO_2 on triamine grafted silica adsorbents were also observed in a study performed by Belmabkhout and Sayari [24], where the CO_2 capacities of triamine-grafted adsorbents were reduced by over 50% compared to the initial CO_2 capacity upon exposure to pure SO_2. In our previous work [13], we studied the stability of various aminosilane grafted silica adsorbents in the powder form to SO_2, NO and NO_2 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 SO_2, with partial reversibility, and the amine efficiency of SO_2/N reached 0.51. We also demonstrated that the degradation of the various aminosilica adsorbents in the presence of NO was not significant, whereas NO_2 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, SO_2 was found to significantly influence the dynamic CO_2 capacity of the supported amines, while little competitive effect of NO on the CO_2 adsorption was observed. This suggests a decreased affinity of the amine-based adsorbents toward NO as opposed to SO_2.

The aforementioned adsorbents, which contained primary or secondary amine groups, generally possessed higher basicity than adsorbents with tertiary amines, thereby showing stronger affinity with SO_2. More recently, Sayari and co-workers [21] described the use of tertiary amine based solid adsorbents to reversibly adsorb SO_2 under dry or humid conditions, potentially offering a way to purify the gas mixture of SO_2 prior to CO_2 adsorption in a second bed with different adsorbents, which is consistent with the previous report of Diaf et al. [11]. The presence of humidity in the gas mixture dramatically enhanced the SO_2 adsorption capacity, as was also observed for CO_2. Other works by Zhi et al. [27] and Tailor et al. [25] have also demonstrated the positive effects of moisture on SO_2 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 SO_2 adsorption capacity in the corresponding grafted fibers was investigated. The thermal reversibility of various types of monoamine grafted fiber adsorbents with respect to SO_2 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