

Effects of O₂ and SO₂ on the capture capacity of a primary-amine based polymeric CO₂ sorbent

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Abstract

Post combustion CO₂ capture is most commonly carried out using an amine solution that results in a high parasitic energy cost in the stripper unit due to the need to heat the water which comprises a majority of the amine solution. It is also well known that amine solvents suffer from stability issues due to amine leaching and poisoning by flue gas impurities. Solid sorbents provide an alternative to solvent systems that would potentially reduce the energy penalty of carbon capture. However, the cost of using a particular sorbent is greatly affected by the usable lifetime of the sorbent. This work investigated the stability of a primary amine-functionalized ion exchange resin in the presence of O₂ and SO₂, both of which are constituents of flue gas that have been shown to cause degradation of various amines in solvent processes. The CO₂ capture capacity was measured over multiple capture cycles under continuous exposure to two simulated flue gas streams, one containing 12 vol% CO₂, 4% O₂, 84% N₂, and the other containing 12.5 vol% CO₂, 4% O₂, 431 ppm SO₂, balance N₂ using a custom-built packed bed

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reactor. The resin maintained its CO₂ capture capacity of 1.31 mol/kg over 17 capture cycles in the presence of O₂ without SO₂. However, the CO₂ capture capacity of the resin decreased rapidly under exposure to SO₂ by an amount of 1.3 mol/kg over 9 capture cycles. Elemental analysis revealed the resin adsorbed 1.0 mol/kg of SO₂. Thermal regeneration was determined to not be possible. The poisoned resin was, however, partially regenerated with exposure to 1.5M NaOH for 3 days resulting in a 43% removal of sulfur, determined through elemental analysis, and a 35% recovery of CO₂ capture capacity. Evidence was also found for amine loss upon prolonged (7 days) continuous exposure to high temperatures (120 °C) in air. It is concluded that desulfurization of the flue gas stream prior to CO₂ capture will greatly improve the economic viability of using this solid sorbent in a post-combustion CO₂ capture process.

Introduction

It is widely agreed upon that anthropogenic CO₂ emissions are a contributing factor to global climate change.¹ The combustion of fossil fuels such as coal, oil, and natural gas for energy is responsible for a significant fraction of CO₂ emissions.² Specifically, 39% of the total U.S. CO₂ emissions in 2009 were due to electricity generation.³ One potential approach to mitigating the impact of these emissions on climate change is post combustion carbon capture and sequestration, which would allow the current energy infrastructure to remain largely intact while continued research into alternative fuels and energy production is done.

Methods

The CO₂ capture capacity of OC 1065 was measured under a variety of controlled conditions in a custom-built packed bed reactor apparatus.⁴ The apparatus is equipped to control, and measure key variables such as reactor temperature, flow rate, CO₂ concentration, and pressure drop via a Labview acquisition module. The CO₂ concentration in the reactor effluent is measured simultaneously using both a (Valtronics 2015SP3) OEM CO₂ analyzer and a high resolution mass

spectrometer (Hiden HPR-20). Quantitative measurement of the CO₂ concentration from the mass spectrometer intensity is done through a calibration procedure done prior to every experiment with 3 gases of known concentrations, typically 0%, 100% CO₂ as well as the test gas, typically either 10 or 12 vol% CO₂.

$$V_{CO_2} = \int (Qb_{CO_2} - Q(t) \cdot C_{CO_2}(t)) dt \quad (1)$$

Results and Discussion

Estimating available amine sites

In our previous work the maximum theoretical amine loading was deduced from energy-dispersive x-ray spectroscopy measurements to be 6.7 mol N/kg.⁴ However, elemental analysis provides another, complementary estimate of the amine loading of the resin. In this work the value of 7.9% N averaged over 4 measurements (Table 1) represents an amine loading of 5.9 ± 0.1 mol N/kg. However, since only a fraction of the total amine sites are accessible to reaction with CO₂, the more critical value is the number of accessible amine sites. This value can be estimated from the sulfate loading on the resin following saturation with sulfuric acid which based on the average of 3 measurements (Table 2) was 2.7 mol H₂SO₄/kg. Assuming a 1:1 molar stoichiometry the amine loading available to reaction is 2.7 mol/kg. This suggests that the measured CO₂ capture capacity of the resin at 50 °C from a pure CO₂ stream, 2.5 mol/kg, is approaching the capacity limit of this sorbent.

Table 1: Mass-based Elemental analysis of OC 1065 as received and dried (precision: $\pm 0.30\%$).

Sample	%C	%H	%N	%O	%S
1	81.79	8.25	8.00	3.48	0.00
2	82.09	8.36	7.97	4.13	0.00
3	81.11	8.26	7.94	4.19	0.00
4	81.28	7.85	7.77	3.15	0.00

Table 2: Mass-based Elemental analysis of OC 1065 following saturation with 1.5M H₂SO₄ aqueous solution (precision: $\pm 0.30\%$).

Sample	%C	%H	%N	%O	%S
1	64.31	7.12	6.03	15.22	6.59
2	63.66	7.08	6.08	16.60	7.00
3	63.15	6.87	6.13	15.16	6.47

Effect of O₂ in flue gas on OC 1065

The tolerance of OC 1065 to O₂ was studied by conducting 17 continuous cycles of adsorption and desorption with a test gas of 12 vol% CO₂, 4% O₂, 84% N₂. This gas was passed continuously through the loaded reactor during the entire course of the experiment and adsorption and desorption occurred via a thermal swing between 50 °C and 127 °C. Each cycle lasted 2 hours and 12 minutes. All capacity calculations are calculated using the baseline concentration of 12% CO₂ for the entire experiment.

Conclusions

The tolerance of a primary amine-functionalized ion exchange resin (OC 1065) to O₂ and SO₂ was evaluated in this work. The CO₂ capture capacity remained stable over 17 capture cycles under continuous exposure to a 12% CO₂, 4% O₂, 84% N₂ gas stream indicating that irreversible oxidation did not significantly occur over this timescale. The resin was, however, poisoned quickly by continuous exposure to a 12.5% CO₂, 4% O₂, 431 ppm SO₂, 84% N₂ gas stream resulting in an adsorption of 0.98 mol/kg of SO₂ and a decrease in CO₂ capture capacity of 1.31 mol/kg after only 9 temperature swing regeneration cycles. The poisoned resin was not thermally regenerable. Treating the poisoned resin with NaOH resulted in a 43% SO₂ removal and 35% reclamation of CO₂ capture capacity under 10 vol% CO₂ and 50 °C capture conditions. The difficulty in fully regenerating the poisoned resin is most likely due to an irreversible reaction between SO₂ and the amine due to the stronger acidity of SO₂ in comparison with CO₂. That the poisoned resin is partially regenerable could indicate that SO₂ is adsorbing on the resin through more than one

mechanism, one of which, is reversible. Additionally evidence was found for amine oxidation during extended exposure to a hot (120 °C) oxygen-rich environment.

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Supporting Information Available: All of the data files used in this work, including the representative data of the total volumetric flowrate and the data used in the BET analysis, as well as all of the analysis used in generating the figures is available in the Supporting Information. This information is available free of charge via the Internet at <http://pubs.acs.org>.

References

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