Effects of O_2 and SO_2 on the capture capacity of a primary-amine based polymeric CO_2 sorbent

Alexander P. Hallenbeck[†] and John R. Kitchin[*,†,‡]

National Energy Technology Laboratory-Regional University Alliance (NETL-RUA), Pittsburgh, Pennsylvania 15236, and Department of Chemical Engineering, Carnegie Mellon University, 5000 Forbes, Ave, Pittsburgh, PA 15213

E-mail: jkitchin@cmu.edu

Abstract

Post combustion CO_2 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 O_2 and SO_2, both of which are constituents of flue gas that have been shown to cause degradation of various amines in solvent processes. The CO_2 capture capacity was measured over multiple capture cycles under continuous exposure to two simulated flue gas streams, one containing 12 vol% CO_2, 4% O_2, 84% N_2, and the other containing 12.5 vol% CO_2, 4% O_2, 431 ppm SO_2, balance N_2 using a custom-built packed

_____

[*]To whom correspondence should be addressed
[†]National Energy Technology Laboratory-Regional University Alliance (NETL-RUA)
[‡]Carnegie Mellon University

bed reactor. The resin maintained its CO_2 capture capacity of 1.31 mol/kg over 17 capture cycles in the presence of O_2 without SO_2. However, the CO_2 capture capacity of the resin decreased rapidly under exposure to SO_2 by an amount of 1.3 mol/kg over 9 capture cycles. Elemental analysis revealed the resin adsorbed 1.0 mol/kg of SO_2. 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 CO_2 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 CO_2 capture will greatly improve the economic viability of using this solid sorbent in a post-combustion CO_2 capture process.

Introduction

It is widely agreed upon that anthropogenic CO_2 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 CO_2 emissions.[2] Specifically, 39% of the total U.S. CO_2 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 CO_2 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, CO_2 concentration, and pressure drop via a Labview acquisition module. The CO_2 concentration in the reactor effluent is measured si-

multaneously using both a (Valtronics 2015SP3) OEM CO_2 analyzer and a high resolution mass spectrometer (Hiden HPR-20). Quantitative measurement of the CO_2 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% CO_2 as well as the test gas, typically either 10 or 12 vol% CO_2.

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

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 CO_2, 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 H_2SO_4/kg. Assuming a 1:1 molar stoichiometry the amine loading available to reaction is 2.7 mol/kg. This suggests that the measured CO_2 capture capacity of the resin at 50 { }C from a pure CO_2 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: ± 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 H_2SO_4 aqueous solution (precision: ± 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 O_2 in flue gas on OC 1065

The tolerance of OC 1065 to O_2 was studied by conducting 17 continuous cycles of adsorption and desorption with a test gas of 12 vol% CO_2, 4% O_2, 84% N_2. 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% CO_2 for the entire experiment.

Conclusions

The tolerance of a primary amine-functionalized ion exchange resin (OC 1065) to O_2 and SO_2 was evaluated in this work. The CO_2 capture capacity remained stable over 17 capture cycles under continuous exposure to a 12% CO_2, 4% O_2, 84% N_2 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% CO_2, 4% O_2, 431 ppm SO_2, 84% N_2 gas stream resulting in an adsorption of 0.98 mol/kg of SO_2 and a decrease in CO_2 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% SO_2 removal and 35% reclamation of CO_2 capture capacity under 10 vol% CO_2 and 50 °C capture conditions. The difficulty in fully regenerating the poisoned resin is most likely due to an irreversible reaction between SO_2 and the amine due to the stronger acidity of SO_2 in comparison with CO_2. That the poisoned resin is partially regenerable could indicate that SO_2 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.

Acknowledgement

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

(1) Prepared by Working Group III of the IPCC , *IPCC Special Report on Carbon Dioxide Capture and Storage*; 2005 (accessed January 2013).

(2) International Energy Agency, *CO_2 Emissions from Fuel Combustion - Highlights*; 2012 (accessed May 2013).

(3) US-EPA, *Inventory of U.S. Greenhouse Gas Emissions and Sinks:1990-2009*; 2011 (accessed January 2013).

(4) Alesi, W. R.; Kitchin, J. R. Evaluation of a Primary Amine-Functionalized Ion-Exchange Resin for CO_2 Capture. *Ind. Eng. Chem. Res.* **2012**, *51*, 6907.