Degradation and Regeneration of Aminosilica Adsorbents in CO_2 Capture

Keywords: carbon capture, amine degradation, aminosilica adsorbents, adsorbent regeneration

Hypotheses: Aminosilica adsorbents used for post-combustion carbon capture can be partially regenerated through treatment with acid, transesterification, and a Hoffman rearrangement.

Introduction: The most readily available technology to reduce carbon emissions is carbon capture through amine scrubbing followed by geological sequestration. However, amine scrubbing has environmental risks: volatile amines escape into the atmosphere and carcinogenic nitrosamines form from NO_x.[1]

Other technologies exist to capture carbon, but most do not have the fundamental knowledge necessary for pilot testing. Amines covalently tethered to silica supports for adsorption (ASA) use similar chemistry as amine scrubbing to selectively bind CO_2 but avoid the environmental side effects because of a lack of volatility and by binding nitrosamines. The method for attaching amines to silica is common among industry,[2] so scaling up ASA production would be more feasible than other novel adsorbents. Similar to amine solvents, flue gas components, NO_x and O_2, also reduce effectiveness of ASA. NO_x preferentially bind to the amine group[3] while pure O_2 oxidizes ASA to form imines, amides, and carboxylic acids, thus degrading the adsorbent.[4]

Since production of ASA has both environmental and economic costs, reusability is vital for any industrial application. A study by Hallenback and Kitchin explored using NaOH to regenerate adsorbent poisoned with SO_2,[5] but there have been no studies to evaluate the regeneration capacity of amine adsorbents for carbon capture after exposure from NO_x or O_2. <u>I propose investigating the degradation of ASA from NO_x and O_2 and developing regeneration methods to reduce the frequency of adsorbent replacement.</u> More specifically I will

1) Synthesize and characterize the ASA from primary, secondary, and tertiary amines
2) Degrade the ASA using NO_x and O_2 in a packed bed reactor
3) Regenerate NO_x treated ASA using aqueous acetic acid and bromide
4) Regenerate O_2 treated ASA using the Hoffman rearrangement or transesterification

1) Synthesis and Characterization: ASA will be created through condensation of MCM-41 mesoporous silica with a chloroalkoxysilane followed by reaction with ammonia, ethylamine, and diethylamine to form primary, secondary, and tertiary ASA. Since the experimental procedures involve toxic chemicals, a risk assessment will be conducted to determine necessary safety precautions.

Primary ASA degradation from NO_x and O_2 to form nitrosamine (unstable) and amide

Between sections 1, 2, 3, and 4, ASA will be tested for surface area (using Brunauer-Emmett-Teller method[3]), pore size (Barrett-Joyner-Halenda method[3]), elemental analysis (sent for external testing), bonding structure (using C_{13}NMR and Fourier Transform Infrared Spectroscopy[4,5]), and CO_2 capacity and kinetics (in a packed bed reactor with live analysis of exiting gas composition[5]).
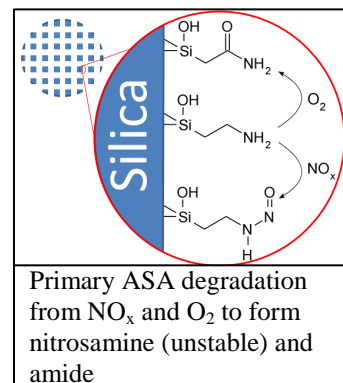
2) Degradation: The characterized ASA will be placed in packed bed reactors with a mixture of gas containing N_2, CO_2, H_2O, and either NO_x or O_2. The NO_x experiments will be conducted at 50°C, the standard adsorbing temperature, while the O_2 experiments will run at 150°C, the desorption temperature. The ASA will be considered degraded when the exiting concentration of pollutant approaches the inlet concentration. The degraded ASAs will then be characterized.

I expect that ASA will initially react with NO_x and O_2 in a similar manner with amine solvents: NO_x will form nitrosamines and nitramines, and O_2 will oxidize the α-carbon.

Furthermore, primary ASA should show a decrease in nitrogen content after exposure to NO_x since primary nitrosamines degrade into N_2. A mixture of alcohols, amides, imides, and acids should result from the O_2 exposure at elevate temperatures.[4] These all decrease the capacity of the amine solvent.[3–5]

3) Regeneration-NO_x: To remove nitrosamine and nitramine functional groups, the denitrosation procedure for aliphatic nitrosamines described by Dix et al.[6] will be followed. If more stringent conditions are necessary, testing an ASA embedded with 2-amino acetic acid would indicate whether oxidative degradation improves amine denitrosation.[6] Regeneration from NO_x may not work well for primary amines since they degrade into N_2. Secondary and tertiary amines treated with NO_x should increase in capacity as the original amines reform.

4) Regeneration-O_2: For primary amines, a Hoffman rearrangement can produce an amine from the degraded amide using mild reagents.[7] Secondary and tertiary amines would require too strong reducing agents and cause significant damage to the silica. For these, transesterification with ethanol amine will be employed to recover lost activity. Due to the variety of products formed, regeneration from O_2 exposure may be more difficult than denitrosation.

Further Analysis: The effluent from the regeneration steps will be tested for silica to determine the extent of support degradation. Assays requiring acidic treatments will use adsorbent with t-butyl groups near the organosilane bond to protect from hydrolysis. For the methods that show marginal improvement, conditions for regeneration will be altered to improve effectiveness. For these optimized methods, repeated degradation and regeneration cycles will assess durability.

Expected Results: These results will indicate the most suitable ASA given different capture conditions. For example, when NO_x are removed before carbon capture, primary amines may be most beneficial since the Hoffman rearrangement can easily reform amines from O_2 oxidation. Furthermore, the findings may also correlate well with other solid amine adsorbents, so a general trend in regeneration can be seen regardless of the type of amine adsorbent.

Broader Impacts: Reducing CO_2 emissions will help stabilize our planet's temperature to prevent negative effects of climate change like desertification and a rising sea level which would decrease food supply and increase land scarcity. ASA can isolate CO_2 to reduce emissions and slow climate change. The degradation studies in this project will further characterize ASA, and the regeneration methods developed will help make using ASA more economical. Since amine based adsorbents can capture CO_2 with reduced emissions of toxic amines and carcinogens, this work will also help reduce the negative environmental impact of carbon capture.

I will disseminate my results through conferences and publications so other researchers can improve upon and apply the findings towards further development and application. I will mentor undergraduate students and encourage them to develop their own projects so that they gain valuable research skills before graduate school. Since solving climate change requires international cooperation, I plan to collaborate with foreign institutions specializing in carbon capture like the Norwegian Technical University to accelerate the application of CO_2 capture.

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