

Surface Functionalization of Mesoporous Sorbents for CO₂ Capture

Investigators

Jennifer Wilcox, Assistant Professor, Energy Resources Engineering; T. Daniel P. Stack, Associate Professor, Chemistry; Zhenan Bao, Associate Professor, Chemical Engineering; Jiajun He, Graduate Researcher, Energy Resources Engineering; Reza Haghpanah, Post-Doctoral Researcher, Energy Resources Engineering; John To, Graduate Researcher, Chemical Engineering; J. Brannon Gary, Post-Doctoral Researcher, Chemistry; Chris Lyons, Graduate Researcher, Chemistry, Stanford University

Abstract

Solid sorbent technologies for CO₂ capture have advantages over traditional amine-base absorption approaches performed in water solution including reduced regeneration energies and greater chemical variability of the active sorbent. The majority of the energetic cost of regeneration is water vaporization from the amine-water solution, a cost significantly attenuated, if not absent, in a solid sorbent, and the homogeneous nature needed for efficient CO₂ capture restricts sorbents relative to a heterogeneous implementation. With greater chemical flexibility, the structural and electronic properties of the active sorbent may be varied readily. Mesoporous silicas are attractive materials to create CO₂ sorbents as extensive literature exists for their synthesis and chemical modification. At scale, however, carbon-based mesoporous materials may be advantageous, given its more favorable heat transfer properties. Modular chemical attachment strategies applicable to both silicas and carbons are currently being developed.

In this proposal, we aim to use covalent integration of sorbents in mesoporous silica- and carbon-based materials to achieve highly selective and recyclable materials for efficient CO₂ capture and release. Careful modifications of the electronic and physical structure of the active sorbents will allow control of the kinetics in both directions. Inspiration derives from carbonic anhydrase (CA), a zinc-dependent enzyme that facilitate the conversion of CO₂ and H₂O to carbonic acid at extremely fast rates (i.e. diffusion controlled) in the red blood cells of mammals. The zinc site is tuned in a manner such that the kinetic barriers to CO₂ capture and release are very low relative to the uncatalyzed reaction. It is our aim to apply such design principles to sorbent-based technologies to enhance the mass transfer of CO₂ to an adsorbed phase, in addition to enhancing the kinetics associated with desorption (regeneration) processes.

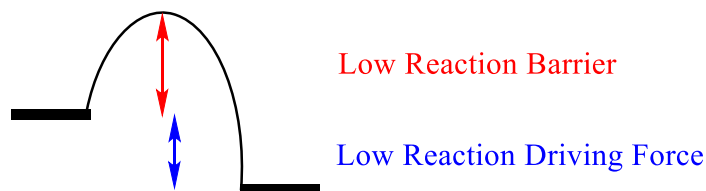
Introduction

The current state-of-the art technology for selective CO₂ capture at scale is amine scrubbing, which is a chemical **absorption**-based technology. Other options for CO₂ capture are solid sorbent **adsorption**-based technologies. There are several benefits associated with using solid sorbents versus aqueous solutions of amines for CO₂ capture, including regeneration savings as large volumes of water do not need to be vaporized, and minimizing the environmental hazards associated with corrosive materials such as monoethanolamine (MEA). Research and development into sorbent-based technologies are expanding as CO₂ capture is anticipated to be a primary component of the CO₂ mitigation portfolio. A challenge with many solid sorbents, such as zeolites and metal-organic frameworks (MOFs), are competitive water binding, as water is present at *ca.* 10-20 mol.% in flue gas.[†] While pre-dehydration of the flue gas is possible, such a process only increases the separation complexity with attendant energy costs. The controlled chemical modification of mesoporous silica- and carbon-based sorbents may circumvent some of these challenges.

Background

The reaction profile of binding CO₂ to a sorbent and its release highlight two key reaction attributes, a finite, but small enthalpy of binding to assure sequestration, and a low forward barrier height. These reaction attributes will create the fastest and most energy efficient sorbent, as the energy required for release of the captured CO₂ will be minimized.

[†] flue gas from a coal-fired utility boiler can reach up to 12 mol% depending upon coal rank and up to 18 mol.% in the case of natural gas combustion



Beyond the active sorbent, the overall pore structure and surface area are important in the materials design. The pore architecture, size, and tortuosity will need to be adjusted to minimize the mass diffusion limitations. Since the synthesis and chemical modification of ordered mesoporous silica structures is more fully documented, our initial efforts have focused on developing appropriate chemical attachment chemistries in mesoporous silicas with the full intent of transferring such chemistry to carbon materials, given their favorable heat transfer properties.

Both structure and pore surface chemistry will be tuned within the sorbents of the proposed study. Based on the size of the discrete complexes to be used (*ca.* 1 nm), the ideal pore size of the mesoporous carbon supports (MCS) would be 3-6 nm to assure facile diffusion of the gases to and from the adsorbing complexes. We want to select chemistry that will allow tunable pore size so that we can synthesize several pore sizes to test the optimal conditions. Moreover, to maximize the usable surface area and reduce dead end pores, an ordered MCS is desired.

Ideal sorbent characteristics include:

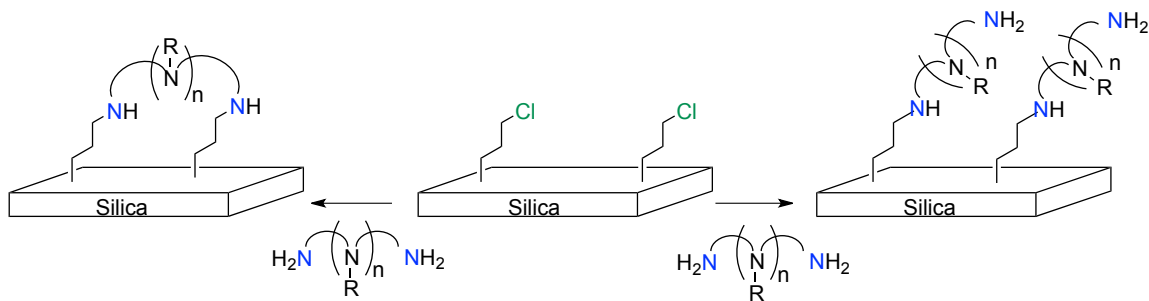
- high CO₂ selectivity,
- fast adsorption kinetics (low reaction barrier),
- low heat of adsorption (low thermodynamic driving force),
- steep adsorption isotherm, and
- high working capacity

Preliminary Results

1) Synthesis of Polyamines on Mesoporous Silica Materials

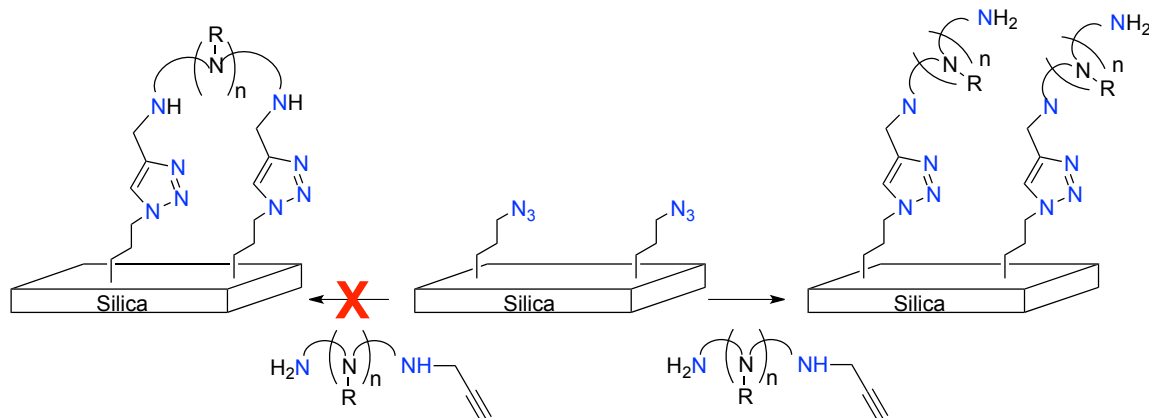
a) Alkyl Halide Displacement with Polyamines

The controlled loading and distribution of active sorbent groups into a mesoporous structure capable of binding CO₂ is the goal of this project. A focus for our initial work began with the modification of previously reported mesoporous silica materials (SBA-15) containing chloropropyl groups on the surface.[1] Importantly, these materials have ordered mesoporous structures, high surface areas (> 900 m² g⁻¹), and high loadings of the chloropropyl functionality (1.2 mmol g⁻¹). Functionalizing these materials initially focused on the displacement of the chlorides with polyamines. We hypothesized that high concentrations of polyamines would yield a single polyamine per chloropropyl functionality on the surface, thereby maximizing amine coverage in the pores. Chemical titrations and CO₂ adsorption profiles of these prepared materials suggest multiple points of attachment of the polyamines presumably through the primary amine to the surface, reducing the absorption CO₂ capacity.



b) Development of Click Chemistry Strategies

Better control of the covalent attachment of polyamines to the surface is possible through a copper catalyzed cycloaddition reaction between an organoazide on the surface and an asymmetrically derivatized polyamine containing a terminal alkyne.



Importantly, we had previously shown that it is possible to control the loading of functional groups in the pores through a direct synthesis approach.[2] The subsequent cycloaddition coupling of terminal alkynes to the surface allows for controlled amounts of polyamines on the mesoporous silica. Such control at sub-monolayer coverages has been illusive for CO₂ adsorption studies. With this strategy, we can systematically investigate how active sorbent loading affects both the kinetics of formation and regeneration.

2) Mesoporous Carbon Structures

a) Azide Derivatized Mesoporous Carbon

Recent advances in the functionalization of glassy carbon surfaces has a dramatic implication for transfer of polyamine amines to carbon surfaces.[3] Using gaseous iodine azide, carbon surfaces have been derivatized with a monolayer of azides, which react with terminal alkynes under the catalytic cycloaddition reaction conditions. Azide derivatization of mesoporous carbon powders are under current investigation. Controlled loading of polyamine to carbon materials should be possible.

b) Mesoporous Carbon Synthesis

Synthesis of mesoporous carbon structures is ideal for sorbent based systems due to the higher heat conductivity inherent in carbon based materials. Towards this goal, we have synthesized a variety of carbon-based materials using polymer templates with pyrrole precursors. Current efforts are focused upon controlled surface area and pore structures of these materials to combine with the surface chemistry outlined above.

Progress

The development of two types of surface bonded polyamine has been accomplished and evaluated for CO₂ adsorption. Through the cycloaddition reaction, we have the ability to control the loading of polyamines on silica-based sorbents. This strategy allows us to achieve controlled chemical modification of silica surfaces and study the effect on CO₂ adsorption. We have also been able to synthesize a series of new mesoporous carbon materials and are studying the surface properties of these materials. These materials will allow us to expand our studies to mesoporous carbon frameworks.

Future Plans

The team will continue to work toward the design and synthesis of controlled mesoporous carbons with enhanced surface area and surface functionalization using amine-based functional groups for optimal CO₂ adsorption. As many of these polyamines have the ability to chelate zinc, it will be added to these amine-materials so that CO₂ reactivity similar to carbonic anhydrase can be realized. Capacity estimates of

these materials will be made using a Rubotherm microbalance and kinetics will be measured using a zero-column breakthrough apparatus under realistic flue gas conditions.

Publication and Patents

None to report at this time

References

1. Corriu, R.J.P., et al., *Direct synthesis of functionalized mesoporous silica by non-ionic assembly routes. Quantitative chemical transformations within the materials leading to strongly chelated transition metal ions*. Chemistry of Materials, 2004. **16**(1): p. 159-166.
2. Nakazawa, J., B.J. Smith, and T.D.P. Stack, *Discrete Complexes Immobilized onto Click-SBA-15 Silica: Controllable Loadings and the Impact of Surface Coverage on Catalysis*. Journal of the American Chemical Society, 2012. **134**(5): p. 2750-2759.
3. Stenehjem, E.D., et al., *Gas-Phase Azide Functionalization of Carbon*. Journal of the American Chemical Society, 2013. **135**(3): p. 1110-1116.

Contacts

Jennifer Wilcox: wilcoxj@stanford.edu

T. Daniel P. Stack: stack@stanford.edu

Zhenan Bao: zbao@stanford.edu

Jiajun He: jiajunhe@stanford.edu

Reza Haghpanah: rezahagh@stanford.edu

John To: johnto@stanford.edu

J. Brannon Gary: jbgary@stanford.edu

Chris Lyons: ctlyons@stanford.edu