

Biomimetic Sorbents for Selective 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; John To, Graduate Researcher, Chemical Engineering; Chris Lyons, Graduate Researcher, Chemistry, Stanford University.

Abstract

Nitrogen-doped hierarchical mesoporous carbon is synthesized via molecular co-assembly and polymerization of a rationally designed pyrrole derivative via soft-templating with a triblock copolymer in solution, followed by mild carbonization at 350 °C and chemical activation at 500 °C. The nitrogen-rich porous carbon possesses 5.8 wt% N and has a high surface area of 942 m² g⁻¹ with hierarchically distributed pore sizes ranging from sub-nanometer to micrometer. It shows excellent CO₂/N₂ separation properties, including high CO₂ capacity (at 298 K, 1.4 and 4.5 mmol g⁻¹, 0.1 and 1 bar, respectively), record-high CO₂/N₂ selectivity (331:1 at 298 K), mild regeneration conditions, and multi-cycle stability under different operating conditions. These properties suggest its significant potential as an efficient CO₂ sorbent. Furthermore, our design strategy provides a promising approach for the synthesis of other polymeric-based porous materials.

In addition, we have investigated the thermodynamics of CO₂ adsorption/desorption for a set of diamine functionalized SBA-15 sorbents under simulated flue gas conditions (0.15 bar CO₂, 313 K). Enthalpies of CO₂ adsorption (ΔH°_{ads}) of -21.7 and -21.0 kcal mol⁻¹ were obtained for primary diamine (1°-SBA) and secondary diamine (2°-SBA) functionalized material, respectively. Equilibrium constants and ΔG°_{ads} values were estimated using a simple Langmuir adsorption model. Combining ΔG°_{ads} and ΔH°_{ads} values provides a complete thermodynamic picture for the adsorption process.

Introduction

Global annual energy-related CO₂ emissions reached a record high of 31.2 gigatonnes (Gt) in 2012[1], and are expected to rise continuously given the growing energy demands and widespread reliance on fossil fuel energy infrastructure. The mitigation of CO₂ emission has been recognized as a crucial necessity, as CO₂ is a major contributing greenhouse gas correlated to the negative effects of global warming, including sea level rise, significant variation in weather patterns, and threats to human health and wildlife habitats[2]. This has motivated research of post-combustion CO₂ capture and storage (CCS) technologies, targeted at large point source emitters of CO₂ such as coal fired power plants. Absorption with aqueous solutions of amines remains the benchmark approach at scale, but wide spread implementation is currently prohibited by the high energetic cost of sorbent regeneration, chiefly due to water vaporization. Translation of nitrogen based sorbents to porous solid supports is therefore an ongoing area of research.

Background

Carbon Capture

The state-of-the-art technology for CO₂ capture, aqueous amine scrubbing[3], has yet to be proven practical at scale due to considerable energy penalties of regeneration (*ca.* 50 kcal mol⁻¹) [4], chiefly due to the vaporization of liquid water [5-8]. Solid-state post-combustion CO₂ sorbents have certain advantages over traditional aqueous amine systems, such as relatively low regeneration energy requirements [8, 9], tunable pore morphology [10-13], and chemical variability through heteroatom doping or surface functionalization[14].

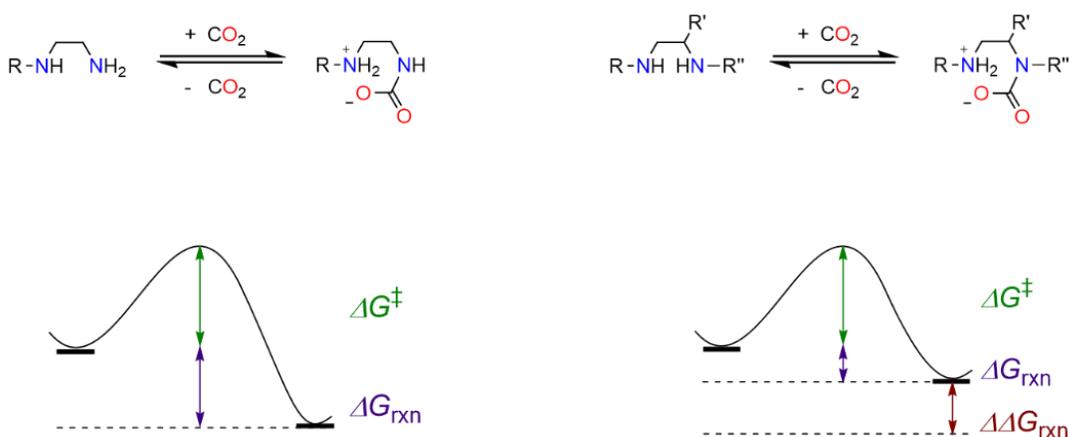
A variety of materials have been investigated for CO₂ capture, including zeolites, metal-organic frameworks (MOFs), porous carbons, porous silicas, and porous polymers[9, 15-20]. Nevertheless, it remains a significant challenge to achieve scalable sorbents that meet all of the requirements for CO₂ capture, *i.e.*, fast kinetics, high CO₂ capacity and selectivity, mild regeneration conditions, and multicycle stability. For example, while chemisorbents like porous solid-supported amines may achieve excellent equilibrium adsorption capacities and CO₂/N₂ selectivities through chemical reactions with CO₂[9, 21, 22], materials often require relatively high regeneration temperatures and long adsorption/desorption cycle times[9]. On the other hand, typical physisorbents, such as activated carbons and MOFs, can be regenerated with minimal energy input, yet have relatively low capacities under post-combustion conditions because of weak CO₂-sorbent interactions and competing adsorption of other flue gas components, like N₂ and H₂O[8, 9]

Nitrogen-Doped Porous Carbon Materials

Ordered N-doped mesoporous carbons have attracted considerable attention in the application of CO₂ capture owing to their high surface area, tunable pore structure, narrow pore size distribution, high N weight percentages, and mechanical, thermal, and electric properties. Typically, N-doped mesoporous carbons are prepared by a nanocasting method using a sacrificial template like porous silica. Nitrogen functionality can be incorporated by impregnation with nitrogen-containing organic molecules, followed by carbonization and removal of the silica template, or through post-synthesis treatment of mesoporous carbon using acetonitrile or ammonia chemical vapor deposition. These multiple-step processes are costly and time consuming. Other methods include the co-assembly of a nitrogen-containing monomer, melamine resin, urea-phenol-formaldehyde resin, or dicyandiamide with a structural directing agent; however, the resulting porous polymers usually exhibit poor thermal stability. The decomposition process is further promoted by the high oxygen content within the triblock polymer. Development of reliable and facile strategies to synthesize N-doped mesoporous carbons without the use of a hard template is highly desirable. Carbons made by carbonization of polypyrrole possess graphitic structures and have high thermal conductivity that is desirable for heat transfer during adsorption and/or thermal regeneration. In this work, we report the successful synthesis of nitrogen-doped porous carbon using a modified-pyrrole monomer as the nitrogen source, which displays high CO₂ capacity, high CO₂/N₂ selectivity, and facile regeneration.

CO₂ Sorption Thermodynamics

A diverse range of solid CO₂ sorbents have been studied, but emphasis is typically placed on maximizing the equilibrium CO₂ capacities of materials. The thermodynamics of the adsorption/desorption process and, specifically, how the structure of sorbent molecules dictate the freeenergy of both CO₂ adsorption and desorption reactions are not well understood. Mesoporous silicas are attractive solid supports due to their high surface areas, well-defined molecular-scale pore structures, and established synthetic and covalent modification procedures. By chemically altering the structure of amine sorbents and incorporating said sorbents onto the surface of ordered mesoporous silica, we have gained chemical level insights about the CO₂ capture process and how amine structural perturbation effects the thermodynamics of the adsorption process (Scheme 1).



Scheme 1. Changes to reaction free-energy with amine structural perturbation.

Results

Nitrogen-Doped Mesoporous Carbon

A series of N-doped mesoporous activated carbons (SU-MAC-500, 600 and 800) have been synthesized, with surface areas ranging from 942 to 2369 m² g⁻¹, abundant ultra-small microporosity (Figure 1), and various types of nitrogen functionalities (Figure 2). CO₂ sorption capacity measurements were performed by pure gas adsorption, yielding values as high as 1.4 mmol g⁻¹ and 4.5 mmol g⁻¹ at 0.1 and 1 bar CO₂, respectively (298 K) (Figure 3). More importantly, the N-doped carbons show unprecedented CO₂/N₂ selectivity of 331:1 at 298 K.

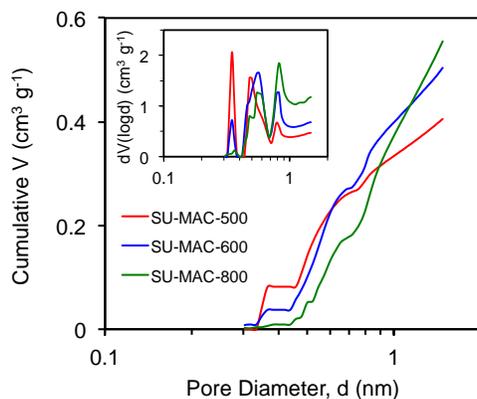


Figure 1: Cumulative pore volumes and pore size distributions (PSDs, inset) based upon the CO₂ adsorption isotherms at 273 K.

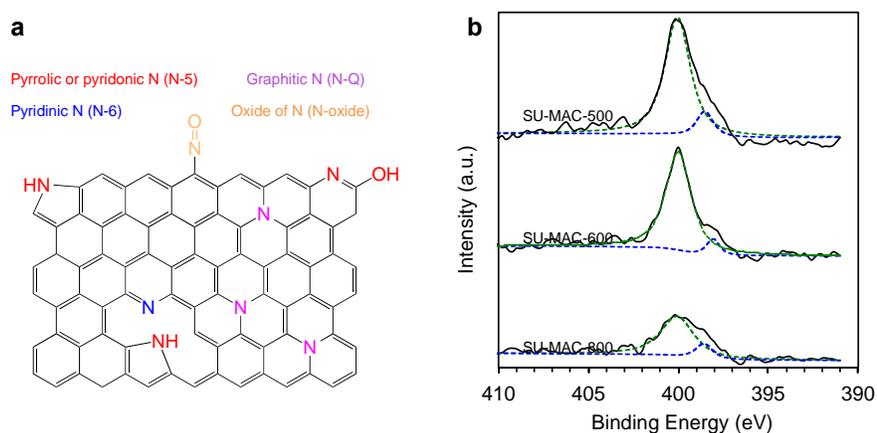


Figure 2: (a) Schematic of proposed nitrogen functionalities in SU-MAC materials, including N-5, N-6, N-Q and N-oxides and (b) N1s X-ray photoelectron spectra (XPS) of SU-MAC materials (398.1 eV: N-6, 400.0 eV: N-5, 403.4 eV: N-oxide).

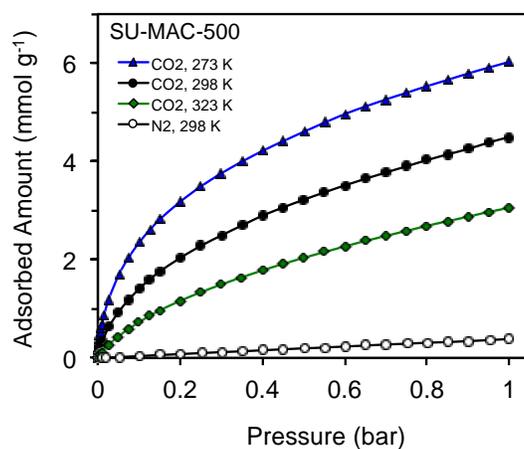


Figure 3: Gas adsorption performance of SU-MAC-500: CO₂ at 273 K, 298 K and 323 K, and N₂ at 298 K

Thermodynamics of CO₂ Capture on Mesoporous Silica

The CO₂ adsorption profiles for synthesized SBA-15 mesoporous silica, functionalized with similar monolayer loadings of either primary (1°-SBA) or secondary (2°-SBA) diaminosilane were measured under simulated flue gas conditions (Figure 4). A sudden mass increase is observed for both materials upon introduction of CO₂ at time 0. After 60 minutes, equilibrium amine efficiency values (θ , moles CO₂ / moles amine) of 0.59 and 0.38 are achieved for 1°-SBA and 2°-SBA, respectively. While the amine efficiencies of 1°-SBA and 2°-SBA differ significantly, comparable enthalpies of adsorption (ΔH°_{ads}) were determined for both materials at -21.7 kcal mol⁻¹ and -21.0 kcal mol⁻¹, respectively.

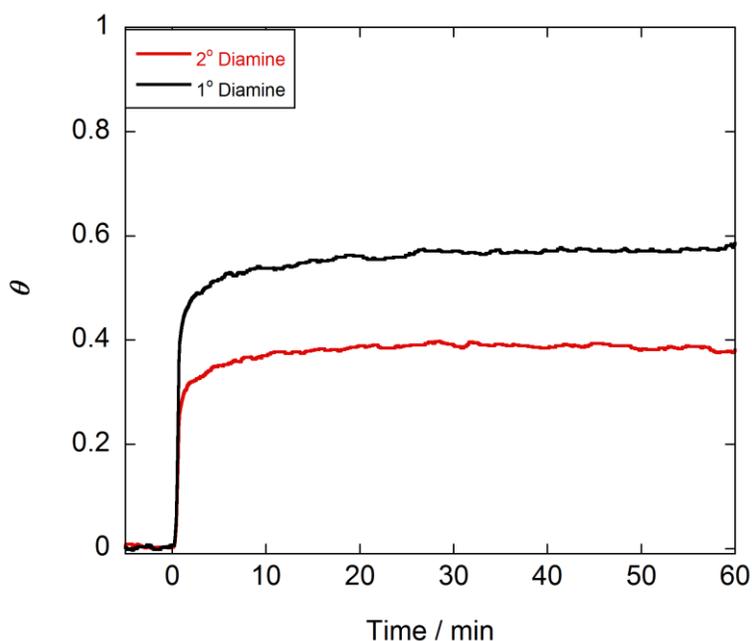


Figure 4. CO₂ adsorption profile for 1°-SBA (black) and 2°-SBA (red). Ads conditions: 0.15 bar CO₂, 0.85 bar N₂, 313 K, 100 mL min⁻¹.

To further probe the CO₂ adsorption mechanism, adsorption isotherms were measured for diamine-SBA materials at 313 K in the pressure range 0.01 – 1.0 bar of CO₂. Across all pressures, 1°-SBA displays higher θ values, suggesting that the driving force for CO₂ adsorption is differentiated by amine structure. Fitting the data to a simple Langmuir adsorption model provides estimates of the equilibrium constants for CO₂ adsorption (K_{ads}) at 313 K of 2.9 and 1.2 for 1°-SBA and 2°-SBA, respectively. From these values, the standard free-energy of CO₂ adsorption (ΔG°_{ads}) can be determined and correlated to ΔH°_{ads} to provide a complete thermodynamic treatment of the adsorption reaction.

Table 1. Thermodynamic quantities for CO₂ adsorption on 1°-SBA and 2°-SBA.

Sample	K_{ads}	ΔG° (kcal mol ⁻¹)	ΔH° (kcal mol ⁻¹)	ΔS° (cal mol ⁻¹ K ⁻¹)
1°-SBA	2.91	-0.66	-21.7	-67.2
2°-SBA	1.22	-0.12	-21.0	-66.7

Progress

We have demonstrated the design and synthesis of N-doped mesoporous carbons through a soft template approach, using a rationally designed N-containing monomer. The porous conjugated polymer-derived carbons possess high specific surface areas, large pore volumes, and hierarchical structures ranging from macro, meso, to microporous. More importantly, the low-temperature carbonization and activation steps lead to abundant ultra-small pores and strong CO₂ binding nitrogen sites, which are essential in enhancing the CO₂-sorbent interactions and selectivity. The hierarchical porous carbon achieved a record-high CO₂/N₂ selectivity of 331:1 at ambient temperature, which is an order of magnitude higher than those reported for micro and mesoporous carbons. Furthermore, very high specific CO₂ adsorption capacity was achieved (1.4 and 4.5 mmol g⁻¹ at 298 K, 0.1 and 1 bar CO₂, respectively). This material can be fully regenerated under mild conditions. It also exhibited high performance and excellent stability under humid conditions and when exposed to acid impurities. The design concepts in this work open up exciting possibilities for further development and improvement of CO₂ capture performance.

In addition, we have shown that structural perturbations of diamine sorbents immobilized on SBA-15 lead to changes in the thermodynamics of the adsorption process. The driving force of adsorption is differentiated by amine structure, providing a potential strategy to tune sorbent molecular structure to improve the efficiency of CO₂ adsorption/desorption cycling.

Future Plans

As the nitrogen functionalities play an important role in CO₂ adsorption, we plan to investigate further the interaction between CO₂ and the nitrogen sites in SU-MAC materials. This would provide useful insights in sorbent design for enhanced CO₂ capture capacity and selectivity. Furthermore, due to the high surface area and abundance of micropores of SU-MAC, materials have potential application to CO₂ capture from natural gas or syngas, which require higher pressures compared to post-combustion CO₂ capture. High-pressure adsorption experiments are currently under way.

To further assess the role that amine structure plays in CO₂ adsorption/desorption performance, we are currently expanding our set of materials to include a range of diamine and monoamine molecular species. Furthermore, to probe the effect amine surface distribution has on the CO₂ capture process, we are currently investigating materials with sub-monolayer coverages to provide isolated adsorption sites.

Publications and Patents

None to report.

Contacts

Jennifer Wilcox: wilcoxj@stanford.edu

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

Zhenan Bao: zbao@stanford.edu

Jiajun He: jiajunhe@stanford.edu

John To: johnto@stanford.edu

Chris Lyons: ctlyons@stanford.edu

References

1. IEA, *World Energy Outlook*, 2012, International Energy Agency: Paris, France.
2. IPCC, *Climate Change 2007: Synthesis Report*, 2007, IPCC: Geneva, Switzerland.
3. Rochelle, G.T., *Amine Scrubbing for CO₂ Capture*. *Science*, 2009. **325**(5948): p. 1652-1654.
4. Song, H.J., et al., *Simplified Estimation of Regeneration Energy of 30 wt % Sodium Glycinate Solution for Carbon Dioxide Absorption*. *Industrial & Engineering Chemistry Research*, 2008. **47**(24): p. 9925-9930.
5. Wilcox, J., *Carbon Capture*. *Carbon Capture*, 2012: p. 1-323.
6. IPCC, *IPCC Special Report on Carbon Dioxide Capture and Storage*, 2005, Cambridge University Press: Cambridge.
7. Haszeldine, R.S., *Carbon Capture and Storage: How Green Can Black Be?* *Science*, 2009. **325**(5948): p. 1647-1652.
8. D'alessandro, D.M., B. Smit, and J.R. Long, *Carbon Dioxide Capture: Prospects for New Materials*. *Angewandte Chemie-International Edition*, 2010. **49**(35): p. 6058-6082.
9. Choi, S., J.H. Drese, and C.W. Jones, *Adsorbent Materials for Carbon Dioxide Capture from Large Anthropogenic Point Sources*. *Chemsuschem*, 2009. **2**(9): p. 796-854.
10. Wan, Y., Y. Shi, and D. Zhao, *Supramolecular Aggregates as Templates: Ordered Mesoporous Polymers and Carbons†*. *Chemistry of Materials*, 2007. **20**(3): p. 932-945.
11. Meng, Y., et al., *Ordered mesoporous polymers and homologous carbon frameworks: amphiphilic surfactant templating and direct transformation*. *Angewandte Chemie*, 2005. **117**(43): p. 7215-7221.
12. Zhang, F., et al., *A facile aqueous route to synthesize highly ordered mesoporous polymers and carbon frameworks with Ia 3 d bicontinuous cubic structure*. *Journal of the American Chemical Society*, 2005. **127**(39): p. 13508-13509.
13. Epps, T.H., et al., *Network phases in ABC triblock copolymers*. *Macromolecules*, 2004. **37**(19): p. 7085-7088.
14. Wu, Z. and D. Zhao, *Ordered mesoporous materials as adsorbents*. *Chemical Communications*, 2011. **47**(12): p. 3332-3338.
15. Xu, X.C., et al., *Novel polyethylenimine-modified mesoporous molecular sieve of MCM-41 type as high-capacity adsorbent for CO₂ capture*. *Energy & Fuels*, 2002. **16**(6): p. 1463-1469.
16. Morris, R.E. and P.S. Wheatley, *Gas Storage in Nanoporous Materials*. *Angewandte Chemie International Edition*, 2008. **47**(27): p. 4966-4981.
17. Hedin, N., L.J. Chen, and A. Laaksonen, *Sorbents for CO₂ capture from flue gas- aspects from materials and theoretical chemistry*. *Nanoscale*, 2010. **2**(10): p. 1819-1841.
18. MacDowell, N., et al., *An overview of CO₂ capture technologies*. *Energy & Environmental Science*, 2010. **3**(11): p. 1645-1669.
19. Wang, Q.A., et al., *CO₂ capture by solid adsorbents and their applications: current status and new trends*. *Energy & Environmental Science*, 2011. **4**(1): p. 42-55.

20. Banerjee, R., et al., *High-throughput synthesis of zeolitic imidazolate frameworks and application to CO₂ capture*. *Science*, 2008. **319**(5865): p. 939-943.
21. Chen, Z.H., et al., *Activated carbons and amine-modified materials for carbon dioxide capture - a review*. *Frontiers of Environmental Science & Engineering*, 2013. **7**(3): p. 326-340.
22. Hicks, J.C., et al., *Designing Adsorbents for CO₂ Capture from Flue Gas-Hyperbranched Aminosilicas Capable of Capturing CO₂ Reversibly*. *Journal of the American Chemical Society*, 2008. **130**(10): p. 2902-2903.