DOI: 10.1002/anie.201207495

CO_2 Capture

Enhancing Amine-Supported Materials for Ambient Air Capture**

Julian P. Sculley and Hong-Cai Zhou*

CO_2 capture · direct air capture · porous materials

The current level of global atmospheric CO_2 is about 392 ppm and rising as we continue to burn fossil fuels.[1] There has thankfully been a significant amount of funding directed towards research into carbon capture and sequestration (CCS) technologies with several major programs worldwide. Most of these efforts have focused on postcombustion capture from large single-point sources like power plants, for several reasons including that they account for about one-third of all global emissions (about 12 gigatons of CO_2 per year). Fortunately significant advances in this area have been made and systems to stem the flow of CO_2 are being deployed at several locations worldwide.[2] In reality, however, removing these emissions from the equation will not reduce global levels of CO_2; it will, at best, modify the trajectory we are currently on.

Along with these advances a smaller group of researchers have also focused on various direct air capture (DAC) technologies.[3] Such technologies are complimentary to flue gas capture as they operate based on the same principles and could be used in both scenarios. Over the years there has been some debate regarding the costs and feasibility of removing CO_2 from air, including a detailed report by the American Physical Society.[4] These reports have generally focused on chemical absorption processes frequently using solutions of sodium hydroxide or amines generally at high operational costs.

A growing number of researchers are taking interest in using solid sorbents for DAC, in part because these have the potential to work at lower regeneration energies than chemical sorbents in solutions. These adsorbents are typically solid-supported amine materials. An initial report by Kulkarni and Sholl detailing the use of such sorbents at several potential U.S. sites indicates that it may be much more economically favorable than previously thought with estimations around \$100 per ton of CO_2.[5] It is highly likely that DAC may never compete on equal economic footing with postcombustion capture technologies, but it certainly has many advantages, such as proximity to storage sites, reduced pipeline transport costs, and the possibility of addressing CO_2 mitigation from all sources, that the higher price tag per ton of CO_2 may actually be attractive. DAC systems can also be powered by renewable energy sources and/or used to generate CO_2 for productive purpose (feeding greenhouses, or algae installations for biofuel production), thus qualifying them as truly “carbon-negative technologies”. A key factor to driving down the cost per ton of captured CO_2 will be to increase working capacities at ultradilute concentrations of CO_2. With the goal of increased capacities and reduced regeneration energies in mind, several groups have investigated the effects of amine loading, composition, and altering the silica support, with the general conclusion that a balance of several factors must be achieved to reach optimal values.[6]

Within this avenue of research, Jones and co-workers have also optimized a variety of materials in systematic fashion, reaching some of the highest CO_2 capacities reported to date.[8] They recently addressed a very fundamental and exciting, previously unexplored variable which showed extraordinary enhancements in CO_2 uptake capacities, material stability, and desorption kinetics.[7] They investigated the effects of acidity/basicity of the support by stoichiometrically incorporating Zr ions (0–14 mol%) into the SBA-15 support itself (Figure 1). The materials were loaded with 30 wt% poly(ethyleneimine) (PEI), and their CO_2 adsorption performance was then tested by thermogravimetric analysis under ambient air (400 ppm CO_2) and a flue gas simulant (10% CO_2 in Ar). PEI/Zr7-SBA-15 loaded with 7 mol% Zr ions was four times more effective than pristine PEI/SBA-15 in terms of the loading capacity (0.19 to 0.85 mmol g^{-1}) and amine efficiency (0.026 to 0.10 mol CO_2 per mol N) at 400 ppm CO_2 (Figure 2). Similar improvements (0.65 to 1.56 mmol g^{-1}) were also

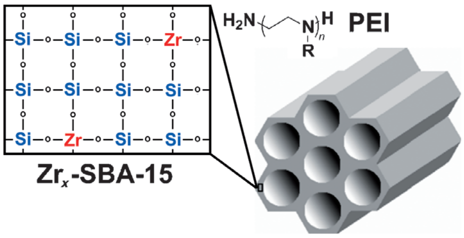

Figure 1. Representation of an SBA-15 support with incorporated zirconium ions which is loaded with poly(ethyleneimine) (PEI).

---

[*] J. P. Sculley, Prof. Dr. H.-C. Zhou
Department of Chemistry, Texas A&M University
College Station, TX 77843 (USA)
E-mail: zhou@chem.tamu.edu
Homepage: http://www.chem.tamu.edu/rgroup/zhou/

[**] Funding was provided by U.S. Department of Energy (DOE DE-SC0001015).

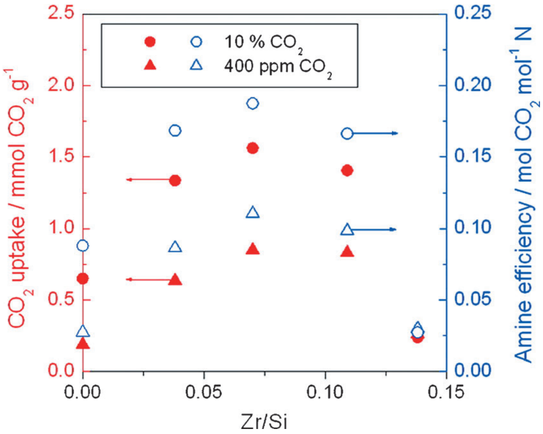

Figure 2. CO_2 adsorption capacities in flue gas and ambient air (solid symbols) and amine efficiencies (open symbols) of PEI/Zr-SBA-15 materials as a function of the Zr/Si molar ratio of the support.[7] Reprinted with permission from the American Chemical Society.

observed with simulated flue gas. Amine efficiency, the molar ratio of CO_2 adsorbed per amino group, is an important metric in this area of research as it gives an indication of how many amino groups in a material are accessible enough to capture CO_2. Typically these are dependent on the type of amine and free pore volume, although other factors also play a role. The authors conclude that this increased efficiency in Zr-doped silicas was due to beneficial interactions between the Zr-containing oxide surface and the amines. These interactions are most likely the stabilization of PEI by the Zr ions which thus limits the undesired degradation/aggregation of PEI. Shifts in FTIR spectra and increased decomposition temperatures of the Zr-doped material compared to SBA-15, as well as control experiments with bare Zr7-SBA-15 validated this hypothesis. The effects of amine stabilization were also observed during cycle testing in which the Zr-loaded materials showed only negligible losses, while the pristine material showed adsorption capacity decreases of 34 % over four cycles.

In order for any material to be considered for large-scale DAC, it must have high working capacities and also low regeneration energies, two values that typically scale in opposite directions. Strong sorbent–sorbate interactions typically result in high capacities at ultradilute conditions, but also require more energy input to release the CO_2 molecules during regeneration. The Zr-impregnated materials clearly have improved capacities and interestingly also seem to have favorable regeneration energies as shown by the FTIR difference spectra. CO_2 release was monitored by exposing the Zr-loaded and pristine PEI/SBA-15 to CO_2 and then pulling vacuum over the course of one hour. The faster and more complete release of CO_2 from the Zr-doped material is indicative of lower binding energies because more CO_2 was released under the same desorption conditions. More complete release may also be a factor in the improved cyclabilty of PEI/Zr7-SBA-15.

Reductions in capture costs will be directly correlated with higher working capacities (particularly over multiple cycles) and decreased regeneration energies. Long-term thermal and chemical stability, primarily to contaminants, and improved resistance to oxidative degradation will help mitigate operational and maintenance costs. Improving these factors will involve some more innovative chemistry and complex multivariable analysis as parameters such as amine loading, pore volume, identity of the amine and silicate support, and now, surface composition of the support are systematically altered. Much work still needs to be done, but with the investigations Jones and co-workers have been presenting over the last several years, further breakthroughs are sure to come. There are still many significant scientific and policy challenges to overcome for DAC to become an economically viable technology, but can we really afford to wait?

Received: September 16, 2012

---

[1] *National Oceanic and Atmospheric Administration. Trends in Atmospheric Carbon Dioxide*, http://www.esrl.noaa.gov/gmd/ccgg/trends/global.html, Accessed August 30, 2012.

[2] a) N. MacDowell, N. Florin, A. Buchard, J. Hallett, A. Galindo, G. Jackson, C. S. Adjiman, C. K. Williams, N. Shah, P. Fennell, *Energy Environ. Sci.* **2010**, *3*, 1645–1669; b) P. Markewitz, W. Kuckshinrichs, W. Leitner, J. Linssen, P. Zapp, R. Bongartz, A. Schreiber, T. E. Muller, *Energy Environ. Sci.* **2012**, *5*, 7281–7305.

[3] C. W. Jones, *Annu. Rev. Chem. Biomol. Eng.* **2011**, *2*, 31–52.

[4] R. H. Socolow, et al., *A Technology Assessment for the APS Panel on Public Affairs*, American Physical Society, June 1, **2011**.

[5] A. R. Kulkarni, D. S. Sholl, *Ind. Eng. Chem. Res.* **2012**, *51*, 8631–8645.

[6] a) J. H. Drese, S. Choi, R. P. Lively, W. J. Koros, D. J. Fauth, M. L. Gray, C. W. Jones, *Adv. Funct. Mater.* **2009**, *19*, 3821–3832; b) Y. Belmabkhout, R. Serna-Guerrero, A. Sayari, *Chem. Eng. Sci.* **2010**, *65*, 3695–3698; c) S. Choi, M. L. Gray, C. W. Jones, *ChemSusChem* **2011**, *4*, 628–635; d) S. A. Didas, A. R. Kulkarni, D. S. Sholl, C. W. Jones, *ChemSusChem* **2012**, *5*, 2058–2064.

[7] Y. Kuwahara, D.-Y. Kang, J. R. Copeland, N. A. Brunelli, S. A. Didas, P. Bollini, C. Sievers, T. Kamegawa, H. Yamashita, C. W. Jones, *J. Am. Chem. Soc.* **2012**, *134*, 10757–10760.

[8] a) S. Choi, J. H. Drese, P. M. Eisenberger, C. W. Jones, *Environ. Sci. Technol.* **2011**, *45*, 2420–2427; b) J. H. Drese, S. Choi, S. A. Didas, P. Bollini, M. L. Gray, C. W. Jones, *Microporous Mesoporous Mater.* **2012**, *151*, 231–240; c) W. Chaikittisilp, R. Khunsupat, T. T. Chen, C. W. Jones, *Ind. Eng. Chem. Res.* **2011**, *50*, 14203–14210.