

Amine-Modified Multiscale Materials for Reversible CO₂ Capture

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Carbon Capture with Solid Materials

- ▶ Goal: Explore and develop functional multiscale materials to serve as reliable & regenerable sorbents for the capture of CO₂ from industrial processes such as fossil fuel power plants.

Issues:

- Surface Chemistry/Capacity: Can a solid-based system be made that competes with traditional wet amine systems?
- Thermal and Chemical Stability: Can the materials remain durable with high reversible capacity in flue gas conditions over long periods of time?
- Cost: Can these materials be produced and implemented in process systems affordably on a life cycle basis?

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Solid vs. Liquid Capture

Pros:

- Since all functional groups are at the surface, there is effectively no liquid side mass transfer resistance.
- In ideal configuration, there is no downstream purification of CO₂ required after regeneration.
- No liquid handling required.

Cons:

- Not possible to store captured CO₂ and regenerate at preferred times (eg., when power demand is low).
- No possibility for sorbent make up unless moving bed or fluidized bed system is developed.

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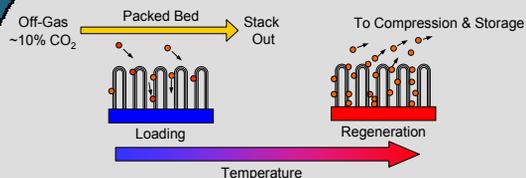
Project Scope

- ▶ Synthesize new materials and new functional approaches
- ▶ Characterize materials in bench scale CO₂ capture apparatus to assess total and working capacity
- ▶ Characterize material structure and mechanism for adsorption (NMR, FTIR, Raman, TGA, electron microscopy)
- ▶ Understand durability of materials under repeated cycling and exposure to potential poisons: SO₂, H₂S, and NO_x.
- ▶ Understand the impact of water vapor on CO₂ capture
- ▶ Develop process concepts and flowsheets for implementation
- ▶ Perform preliminary economic analysis

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Temperature Swing Adsorption



- ▶ Use high surface area materials → inherently high capacity.
- ▶ Large pore volume and surface functionalization useful to reduce mass transfer resistances. This will increase operating capacity.
- ▶ Use material classes that allow facile chemical functionalization.
- ▶ Thermal integration with power plant is critical.

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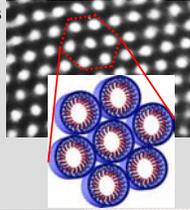
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Functional Multiscale Materials

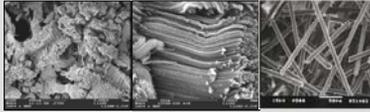
Ordered Mesoporous Oxides & Aerogels

Applications

- Catalysis
- Gas or liquid phase separations
- Chemical storage
- Sensors



Carbon Nanotube Composites, Carbon Fibers



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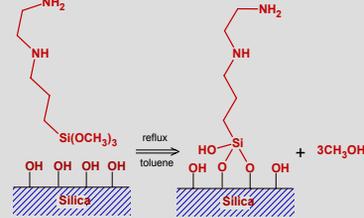
EDA Functionalized Silica

Synthesis

Condensation of an EDA-alkoxysilane and silanols on silica surface.

Substrate: SBA-15 mesoporous silica

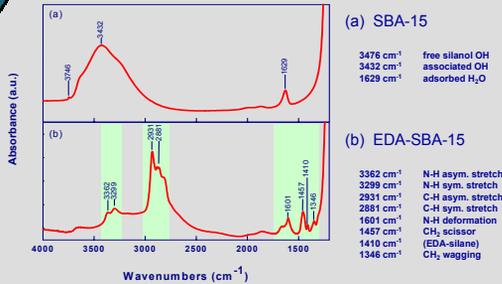
pore diameter 5.5-7.8 nm, surface area 700 m²/g



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FTIR spectra – Before and after grafting EDA ligands



FTIR spectra confirm presence of EDA functional groups in sorbent.

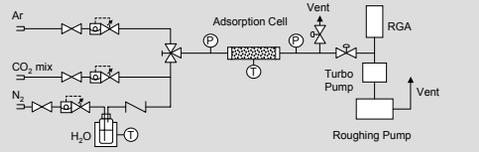
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CO₂ Sorption Bench



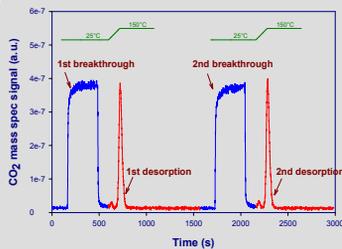
- CO₂ levels of 1-50% possible
- SO₂ examined using mixes
- CO₂ level measured with RGA
- ΔP & Isotherms easily measured



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Breakthrough Testing



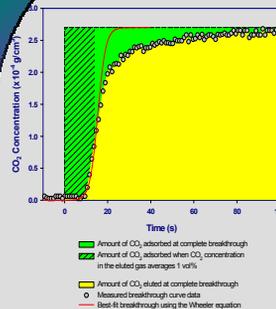
Type of Measurements:
Adsorption capacity
Adsorption kinetics
Desorption temperature

Known concentration of CO₂/N₂ mix was flowed through sorbent bed, followed by a TPD to release adsorbed CO₂.

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Total vs. Working Capacity



EDA-SBA-15 sorbent 0.229 g
Feed gas: 15 vol% CO₂ and balance N₂ at 25°C
Flow rate: 40 sccm

Wheeler Eqn (Wood, 2002)

$$t_b = \frac{w_c}{C_0 Q} \left[w - \frac{\rho_B Q}{\kappa_v} \ln \left(\frac{C_0 - C}{C} \right) \right]$$

Capacity and Rate Coefficient Data:

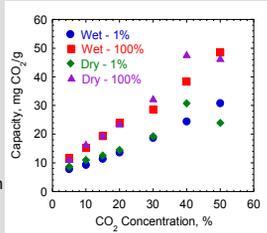
$w_c = 12.1$ mg/g (Wheeler equation)
 $\kappa_v = 414.2$ min⁻¹ (Wheeler equation)
 $w_c = 19.3$ mg/g (by integration at complete breakthrough)
 $w_o = 10.2$ mg/g (by integration at 1% breakthrough)

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Performance – Dry vs. Wet

- ▶ 100% indicates capacity to full breakthrough. 1% indicates working capacity for total equivalent slip of 1% CO₂.
- ▶ Data pertain to CO₂ in N₂.
- ▶ Wet corresponds to 2% H₂O in gas mixture.
- ▶ Little difference in capacity when water is added to the stream indicates good selectivity.

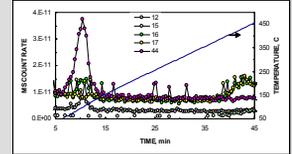
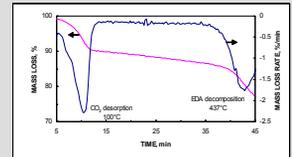


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TGA-MS Analysis: Thermal Stability

- ▶ Mass loss indicates significant desorption events.
- ▶ Mass spectrometry indicates what comes off sorbent.
- ▶ In He, EDA decomposes above 400°C.
- ▶ In air, EDA decomposes above 200°C.



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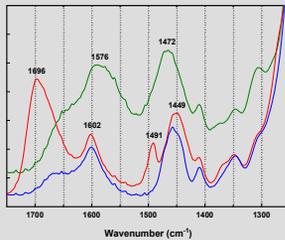
FTIR - Reaction with CO₂

Free amine groups are abundant in regenerated sorbent.
1602 cm⁻¹ N-H deformation vibrations
1449 cm⁻¹ CH₂ deformation vibrations

Upon exposure to CO₂ at room temperature, the sorbent forms an intramolecular carbamate ammonium salt.
1576 cm⁻¹ NH₂⁺ deformation vibrations

When exposed to CO₂ at higher temperature, the carbamate partially converts to ethylene urea.
1696 cm⁻¹ C=O stretch (Amide I band)
1491 cm⁻¹ Amide II band

IR band assignments are tentative. Experiments to confirm urea formation in progress.

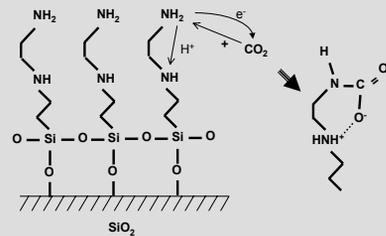


— Regenerated sorbent
— After CO₂ adsorption at 25°C
— After reaction with CO₂ at 135°C

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Mechanism (Ethylene Diamine)

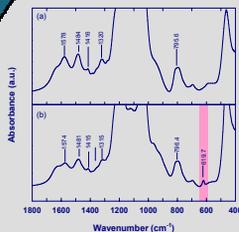


Stability of Zwitterionic compound (intramolecular carbamate) governs ease of regeneration and working capacity

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FTIR – Effect of SO₂ exposure



(a) Sample exposed to ambient air
1578 cm⁻¹ NH₂⁺ deformation
1484 cm⁻¹ unassigned
1416 cm⁻¹ unassigned
1320 cm⁻¹ CH₂ wagging
795.6 cm⁻¹ Si-O-Si sym. stretch

(b) Sample exposed to 500ppm SO₂, 21% CO₂, and balance N₂
Band structure same as (a) except for one new band:
619.7 cm⁻¹ SO₂ bending in -NH-SO₂ complex¹

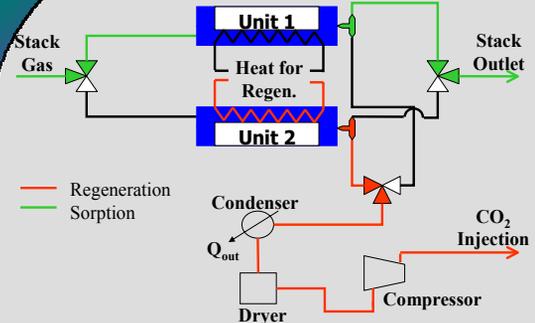
¹Vasiljev et al. (1995) Thin Solid Film, 261, 296-298

It is believed that SO₂ reacts with secondary amine to form a charge-transfer complex. Determination of the fate of the SO₂ adduct upon heating is likely reversible based on Diaz, Garcia, and Beckman (1994).

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Parallel Bed: Thermal Swing



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Economics

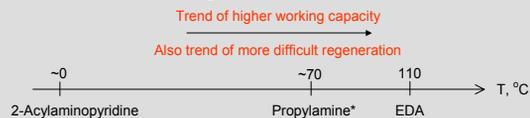
- ▶ It is essential to perform economic analysis in tandem with technical discovery and development in order to guide work in direction of commercial viability.
- ▶ Preliminary economics suggest approach could be attractive with future expected improvements.
- ▶ Preliminary model is based on adaptation of carbon adsorber model available from EPA for VOC capture.
- ▶ Expecting posting of a new solid-based capture model from NETL soon.

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Future Work

- ▶ Continue to develop additional amine-modified materials.
 - Fill in operating temperature gaps in order to make applicable to many streams.
- ▶ Complete economic analysis and use as a basis for R&D targets.
- ▶ Look at steam regeneration.



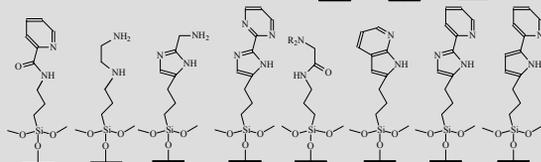
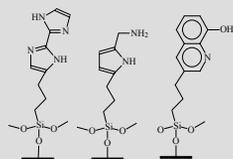
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*Published work by NETL

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Various Approaches Possible

- Target ligands result in facile proton transfer during H uptake
- Multifunctional ligands also attractive.
- Polymeric and dendrimeric functionality are being examined



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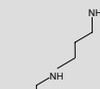
Immediate Targets



Propyl Amine
(verify comparison to NETL literature)



Piperazine
(determine impact of ligand rigidity and amine degree)



Propylene Diamine
(determine impact of carbamate ring size)



Aminomethyl Imidazole
(examine cyclic compounds with potential multifunction)

Various Polymeric Species
(multifunctional approach)

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