Solid Amine CO_2 Adsorbent Degradation: Insights from Experiments and Atomistic Simulations

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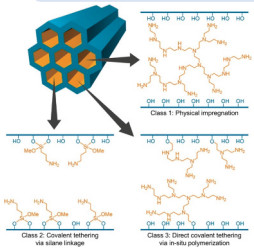
Supported-Amine CO_2 Adsorbents



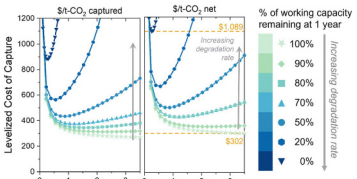
X. Shi, et al. *Angew. Chem. Int. Ed.* (2019) 59, 6984

Supported-amine CO_2 Sorbents for CO_2 Capture

- Lower regeneration energy improves both cost and energy requirements
- Impregnated polyamines exhibit highest mass-based CO_2 uptakes, whereas grafted amines offer tractable system for evaluating composition-performance relationships

Challenges for conventional solid amine CO_2 capture processes

- ✕ Short sorbent lifetime increases cost (target ~$100/ton CO_2)
- ✕ Amine degradation forms products detrimental to the environment and human health (NH_3, CO_2)



H. Holmes, et al. *Energy Environ. Sci.* (2024) 17, 4550

Material R&D Approach

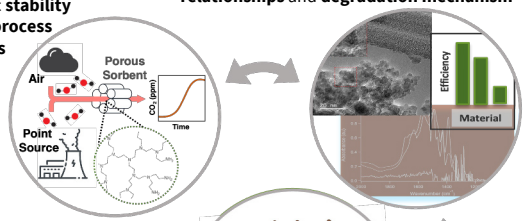
Goal: Develop efficient, robust, and scalable CO_2 capture materials for varying process applications through integrated evaluation of capture performance, sorbent stability, and determination of underlying mechanisms.

Performance Evaluation

Quantification of CO_2 capture **capacity** and cyclic **stability** under **realistic process conditions**

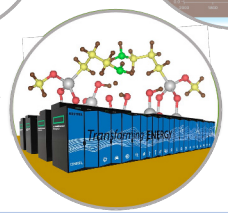
Characterization

Suite of material **characterization** techniques to **establish composition-performance relationships** and **degradation mechanism**



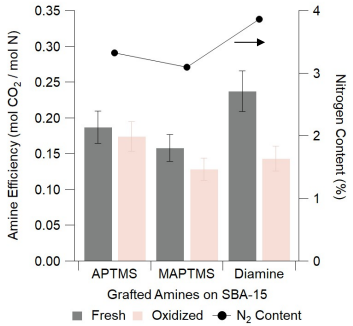
Computational Modeling

Atomistic simulations, leveraging NREL high-performance computing resources, reveal **key steps** and **material attributes controlling CO_2 adsorption/desorption** and **sorbent degradation**



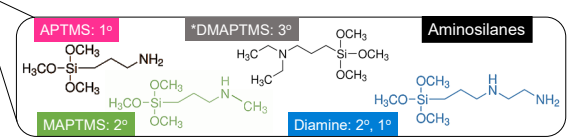
CO_2 Capture Efficiency and Stability

Well-controlled Dry Grafting of Aminosilanes onto Mesoporous SBA-15



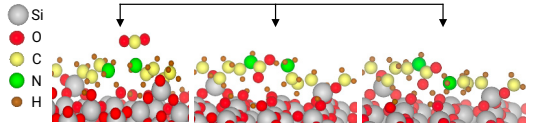
CO_2 Uptake: 400 ppm CO_2, 25 °C
Accelerated oxidative degradation: 18 hr zero air, 120 °C
N content determined via CHN combustion analysis

- Initial amine efficiency: Diamine > 1° ~ 2°
- Decrease in CO_2 uptake after exposure to O_2 at 120°C under zero-air : 1° < 2° < Diamine



*Minimal CO_2 uptake observed on DMAPTMS due to the inability to form carbamates

Adsorption: $CO_2(g) + Amine/SiO_2 \rightarrow CO_2$-bound structures

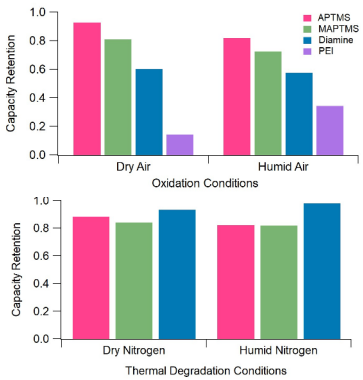


	Physiosorbed	Carbamic acid NH-COOH	Carbamate NH^+-COO^-
APTMS	-37 kJ/mol	-46 kJ/mol	-92 kJ/mol
MAPTMS	-47 kJ/mol	-50 kJ/mol	-100 kJ/mol

Two amines adsorbed to β-Cristobalite (111); VASP (PBE-D3)

- CO_2 binds to grafted 1° and 2° amines as carbamate
- Maximum amine efficiency as carbamate is 0.5 CO_2/N
- Relatively weak binding allows for ease of regeneration

Effects of Degradation Condition, Humidity, and Support Composition

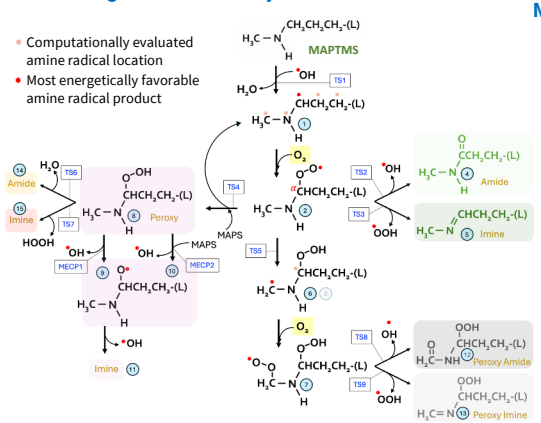


- Degradation conditions: 18hrs, 120°C, zero air or pure nitrogen
- Humidity slightly accelerates oxidative degradation on grafted amines, and improves stability for PEI
- Diamine is most resistant to thermal degradation, particularly in the presence of humidity

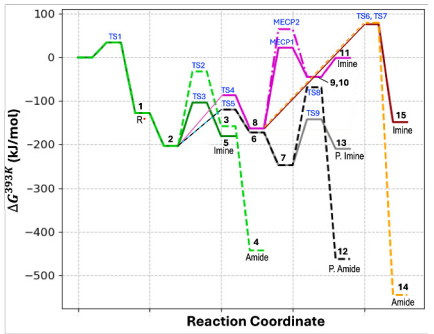
Oxidative Degradation Mechanism

Radical-initiated MAPTMS Oxidative Degradation Pathways

- Computationally evaluated amine radical location
- Most energetically favorable amine radical product



MAPTMS Oxidative Degradation: Free Energy Diagram



Gaussian 16 (m062x, 6-311+g(d,p))
TS = transition state
MECP = minimum energy cross point, approximate TS for spin-crossover reactions

- Facile ($\Delta G^{\ddagger}$ = 34 kJ/mol) radical initiation, followed by formation of the peroxy radical
- Lowest energy subsequent steps proceed via H-shift and/or peroxy radical propagation steps to form imine (C=N) or peroxy imine products
- The highest barrier, and likely rate-controlling, steps during the initiation phase of degradation are the radical propagation steps
- Consistent with spectroscopically observed* degradation products, which contain C=O and C=N bonds

*M. J. Lashaki, S. Khiavi, A. Sayari, *Chem. Soc. Rev.* (2019) 48, 3320

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