Amine-Appended Metal-Organic Frameworks as Switch-Like Adsorbents for Energy-Efficient Carbon Capture

primary project goal

Lawrence Berkeley National Laboratory (LBNL), as part of the Discovery of Carbon Capture Substances and Systems (DOCCSS) Initiative, has developed a novel amine-based solid sorbent for capture of carbon dioxide (CO_2) from flue gas. The sorbent consists of a metal-organic framework (MOF) coated with alkyl amines with high affinity for CO_2. The amine-appended solid sorbents capture CO_2 in a cooperative manner through a chain reaction. The cooperative adsorption mechanism allows the sorbents to exhibit step-shaped adsorption isotherms, which allow for larger working capacities with only moderate temperature swings in contrast to the large temperature swings required by traditional amine-based sorbents. The MOF is inexpensive, as well as chemically and thermally robust. The research team identified, synthesized, and characterized amine-MOF pairs using existing and new computationally designed MOF and amine structures. The synthesized sorbent materials were tested using simulated flue gas to determine CO_2 adsorption and desorption kinetics, tolerance to flue gas impurities, and cycling performance, as well as to identify the most promising sorbents with realistic potential for industrial implementation in carbon capture. DOCCSS is a partnership coupling unique skill sets and perspectives of national laboratories, industry, and academic institutions, working collaboratively to facilitate discovery, synthesis, performance assessment, and functionalization of new carbon capture materials, and to accelerate the rate at which transformational processes for carbon capture are commercialized.

technical goals

- Identify, synthesize, and characterize amine-MOF pairs using existing and new computationally designed MOF and amine structures.
- Test the synthesized sorbent materials using simulated flue gas to determine CO_2 adsorption and desorption kinetics, tolerance to impurities, and cycling performance.
- Identify the most promising sorbents with realistic potential for implementation in carbon capture.
- Field-test the MOF sorbent using actual coal-derived flue gas.

technical content

LBNL combined computational and experimental programs to synthesize and characterize amine-appended MOF sorbents for energy-efficient carbon capture. An example of the structure of an MOF with appended amines is shown in Figure 1. These MOF materials show switch-like CO_2 adsorption behavior and can be tuned to optimize working capacities under mild regeneration conditions. They exhibit step-change isotherms enabled by a cooperative CO_2 adsorption

program area:
Point Source Carbon Capture

ending scale:
Bench Scale

application:
Post Combustion Power Generation PSC

key technology:
Sorbents

project focus:
Amine-Appended Metal-Organic Framework Sorbent

participant:
Lawrence Berkeley National Laboratory

project number:
FWP-FP00006194

predecessor projects:
N/A

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partners:
Mosaic Materials; Svante; Electricore Inc.

start date:
08.31.2017

percent complete:
100%

mechanism, as shown in Figure 2. This step-change isotherm allows for larger sorbent working capacities with minor temperature swings, as opposed to the large temperature swings required by traditional amine-based sorbents. The step-change isotherm shows very little hysteresis upon desorption of CO_2, and the step shifts rapidly to higher pressure with increasing temperature. Balancing CO_2 capture performance and cost is done through vigorous optimization efforts of the amine molecules and pore geometries, combining computational modeling, characterization of molecules, and experiments to evaluate CO_2 capture performance.

Diamine-appended MOFs were identified and synthesized, targeting materials showing step-change or switch-like reversible CO_2 adsorption isotherms. Computational modeling was used to identify promising amine-MOF pairs. The computational analysis and measurements of CO_2 adsorption behavior provide insight to identify second-generation materials with desired properties. The research team identified, synthesized, and characterized amine-MOF pairs using existing and new computationally designed MOF and amine structures. The synthesized sorbent materials were tested using simulated flue gas to determine CO_2 adsorption and desorption kinetics, tolerance to flue gas impurities, and cycling performance, as well as to identify the most promising sorbents with realistic potential for industrial implementation in carbon capture.

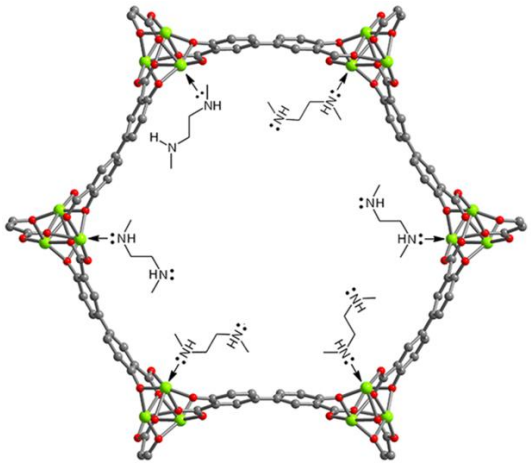

Figure 1: Example of an MOF with appended amines.

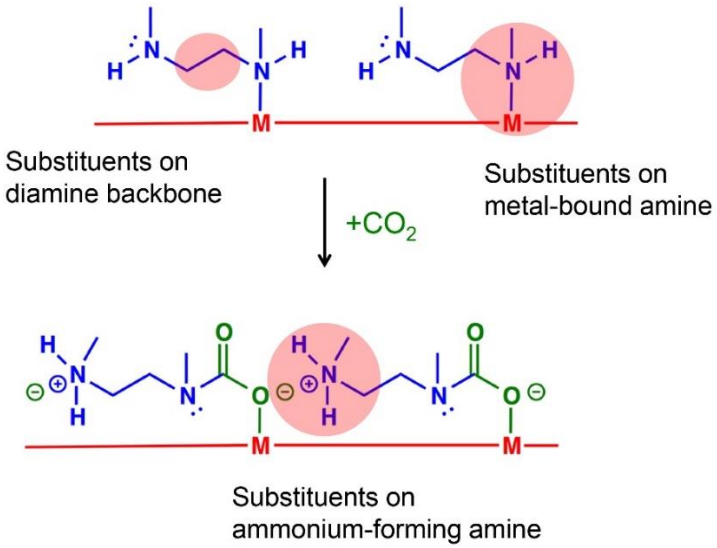

Figure 2: Cooperative CO_2 adsorption.

This project included a combined effort among several entities. LBNL was responsible for materials discovery, synthesis, and characterization. Mosaic Materials developed materials production protocols and scaled-up research and development (R&D). Sorbent production scaled-up and optimized efforts include the evaluation of four distinct steps: synthesis of the MOF, purification of the MOF to remove impurities, amination where the purified MOF is impregnated with amines, and activation where the solvent is removed. Svante and Electricore integrated the diamine-appended MOFs

in a cost-effective CO_2 capture system through system development efforts. Svante performed testing of the sorbent in powder form and in a structured-bed form in their capture test units to confirm performance.

The overall effort included testing first-generation (Gen1) materials, continued development to synthesize improved diamine-appended MOF (Gen2) materials, and evaluated long-term stability, impurity effects, and alternate regeneration strategies to recover greater CO_2 capacity, culminating in field-testing using actual coal-derived flue gas.

technology advantages

- High tunability of amine-appended framework materials.
- Large working capacity due to stepped CO_2 adsorption.
- High CO_2 selectivity over nitrogen, oxygen, and water.

R&D challenges

- Large-scale and economic production of materials.
- Integration within an appropriate separation platform.
- Durability and chemical stability of these MOFs under actual flue gas.
- Reducing the regeneration cost in temperature swing.
- Steam stability and volatilization—tetraamines can significantly improve material stability due to their bidentate binding mode.
- Sulfur dioxide (SO_2)-induced degradation—extended cycling tests in the presence of these contaminants via an automated breakthrough system.
- Improving adsorbent resistance to steam stripping—identification of an adsorbent, which is better aligned with the steam regeneration methods of the VeloxoTherm™ process.
- Increasing volumetric density—investigation of alternative adsorbent forming methods, which increases sorbent density with minimal impact on capacity.
- Improving space-time yield of adsorbent synthesis—increasing the amount of adsorbent made per time and reactor volume will help lower the costs of adsorbent manufacturing.

status

LBNL identified and synthesized a Gen1 material with a 2.4 mmol CO_2/gram working capacity with a 60°C temperature swing. Mosaic Materials successfully synthesized 1 kilogram of Gen1 material that met CO_2 performance metrics and was delivered for testing at the Svante test unit.

A screening database was created to discover new MOFs with similar open metal site distance distributions to the Gen1 material, with three candidate materials of interest identified with potential for greater than 3.0 mmol/gram CO_2 uptake. One of these Gen2 materials showed a 3.6 mmol/gram working capacity with a 45°C temperature swing and an approximate regeneration energy of 2.2 MJ/kg CO_2. This Gen2 material was stable for more than 1,000 humid adsorption/desorption cycles under simulated coal-derived flue gas conditions. LBNL's work to develop a transformational technology based upon an amine-appended MOF for post-combustion CO_2 capture led to the following accomplishments:

- Synthesized and characterized a series of amine-appended MOF materials for CO_2 capture from coal flue gas—Gen1 material [chemical structure: dmpn–Mg_2(dobpdc)].
- Provided chemical insight that cannot be easily obtained using spectroscopy via density functional theory (DFT).
- Developed methods to screen through large databases for diamine-appended MOFs and accelerated the discovery of new MOF-diamine combinations.
- Demonstrated the ability to produce kilogram-scale quantities of a promising class of sorbent materials, particularly well-suited to applications in carbon capture.
- Developed the economic analysis of the production methods, which shows a path to delivering sorbent at a cost target of less than $50/kg.

- Evaluated the laminated Gen1 material in a VeloxoTherm rapid cycle temperature swing adsorption (RC-TSA) to measure key performance indicators (KPIs) and lifetime stability for coal applications. The KPI was estimated to be ca. 2 tonne-per-day/m^3 for the hot CO_2 (dry or wet) regeneration.
- Observed long regeneration times (about five to 10 times longer than the desired target [i.e., moderate KPI]). Identified that this was due to the slow heat transfer of heating the bed via a hot CO_2 purge, and pivoted toward using a steam purge, which provided much more rapid heating.
- Observed low CO_2 capacity in Gen1 laminate, which was determined to be due to the temperature rise in the bed during adsorption, as the unit is not actively cooled.
- Discovered and characterized a Gen2 material, Candidate 9, that possesses a higher CO_2 step temperature, making it more tolerant to heat rises in the bed and which exhibits unprecedented robust steam stability.
- Concluded that the Candidate 9 Gen2 MOF is superior to the Gen1 MOF material from the perspective of initial steam durability and may be suitable for preparing laminates to be tested in the VeloxoTherm process with direct steam exposure.

available reports/technical papers/presentations

Long, J., Neaton, J., and Haranczyk, M. “Amine-Appended Metal-Organic Frameworks as Switch-Like Adsorbents for Energy-Efficient Carbon Capture,” Final Briefing, Pittsburgh, PA, May 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11827&filename=Amine-+Appended+Metal-Organic+Frameworks+as+Switc-Like+Adsorbents+for+Energy-Efficient+Carbon+Capture.pdf*.

Long, J., Neaton, J., and Haranczyk, M. “Amine-Appended Metal-Organic Frameworks as Switch-Like Adsorbents for Energy-Efficient Carbon Capture,” Presented at 2020 NETL Project Review Meeting - Carbon Capture, Pittsburgh, PA, October 2020. *https://netl.doe.gov/sites/default/files/netl-file/20VPRCC_Long.pdf*

Long, J., Neaton, J., and Haranczyk, M. “Amine-Appended Metal-Organic Frameworks as Switch-Like Adsorbents for Energy-Efficient Carbon Capture,” Presented at 2019 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/J-Long-LBNL-Amine-Appended-MOF.pdf*

Long, J., Neaton, J., and Haranczyk, M. “Amine-Appended Metal-Organic Frameworks as Switch-Like Adsorbents for Energy-Efficient Carbon Capture,” Presented at 2018 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/J-Long-LBNL-Amine-Appended-MOFs.pdf*

Long, J., Neaton, J., and Haranczyk, M. “Amine-Appended Metal-Organic Frameworks as Switch-Like Adsorbents for Energy-Efficient Carbon Capture,” Presented at 2017 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2017. *https://netl.doe.gov/sites/default/files/event-proceedings/2017/co2%20capture/4-Thursday/J-Long-LBNL-Metal-Organic-Frameworks.pdf*