Development of Advanced Solid Sorbents for Direct Air Capture

primary project goal

RTI International, partnered with Creare and Mohammed VI Polytechnic University, is developing two types of advanced adsorbent materials—metal-organic frameworks (MOFs) and phosphorous dendrimers (P-dendrimers)—for direct air capture (DAC) of carbon dioxide (CO_2). The sorbents are being synthesized, characterized, and optimized to achieve high CO_2 capacity at very low CO_2 partial pressures, high swing capacity, improved mass and heat transfer, and long operational life at low cost. The project team is testing two selected sorbents (one MOF adsorbent and one amine-P-dendrimer adsorbent) over 100 adsorption-desorption cycles in a laboratory-scale packed-bed reactor (PBR) and evaluating sorbent performance in the presence of contaminants (e.g., oxygen and water). The best performing sorbent will be evaluated for commercial production cost and scalability. Incorporation of the novel sorbents into a low pressure drop multichannel monolith-type reactor that can capture CO_2 from air at a cost of approximately $70/tonne of CO_2.

technical goals

- Develop MOF- and P-dendrimer-based sorbents for high durable DAC sorbent, to achieve high CO_2 capacity (in excess of 7–9 wt%) at low CO_2 partial pressures observed in air.
- Investigate the mass and heat transfer characteristics of select high CO_2 capacity solid sorbents when incorporated in a multichannel monolith-type reactor configuration.
- Develop computational fluid dynamics (CFD) model of the MOF and P-dendrimer sorbent to help understand the adsorber reactor design and optimize sorbent-absorber integration.
- Demonstrate long-term chemical and mechanical stability of select high CO_2 capacity sorbents (more than 100 cycles). The multicycle performance testing for both sorbents will be used for CFD model validation, including diffusion of gases into the porous sorbent materials.
- Evaluate the impact of sorbent contaminants present in air, such as oxygen (O_2) and water (H_2O), on these advanced solid sorbents at different temperatures and humidity levels.
- Perform a preliminary process design for DAC with a qualitative assessment of sorbent properties affecting the critical process design choices.
- Select sorbents that have high CO_2 capacity, have long-term stability, are low cost (less than $15/kg of sorbent), are contaminant resistant, and can be scaled rapidly in one to two years for future testing.

technical content

The RTI team is developing, studying, and comparing the performance of two novel materials, MOFs and P-dendrimers, for DAC that have the potential of significantly reducing the capital cost of the adsorbent while demonstrating high

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Sorbents

project focus:
Metal-Organic Framework and Phosphorous Dendrimer Sorbents

participant:
Research Triangle Institute

project number:
FE0031954

predecessor projects:
N/A

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partners:
Creare; Mohammed VI Polytechnic University

start date:
10.01.2020

percent complete:
80%

CO_2 working capacity at extremely low CO_2 concentrations (~400 parts per million [ppm]) and high CO_2 selectivity over moisture, oxygen, and nitrogen, which are major constituents of air.

RTI's MOF-Based Sorbent for DAC

RTI's MOF-based sorbent for DAC preliminary data NbOFFIVE-Ni ($[Ni(NbOF_5)(C_4H_4N_2)_2 \cdot 2H_2O]$) are very recently considered as ideal MOF materials for trace CO_2 capture. This MOF displayed square-like channels with contracted pore-aperture sizes ranging from 3.5–3.9 Å (Figure 1) and apparent specific Brunauer–Emmett–Teller (BET) surface area of around 250–300 m^2/g. As stated earlier, these fluorinated MOF platforms show very interesting carbon capture performances, explained by the combined synergetic effect of thermodynamics and kinetics associated with the small pore size of the 1-D channels aligned with a periodic array of fluorine moieties.

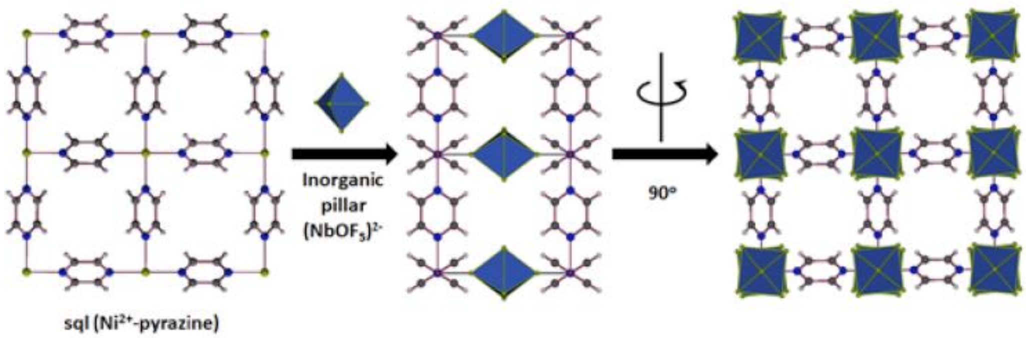

Figure 1: Structural representation of the NbOFFIVE-1-Ni (left), the 2-periodic square grid layer constructed by linking Ni(II) with pyrazine ligands, (middle), pillaring of square-grid layers by the (NbOF5)2- inorganic pillars, (right), square-shaped channels in the resultant 3-periodic pcu-MOF, NbOFFIVE-1-Ni.

RTI's partner Mohammed VI Polytechnic University has studied the CO_2 adsorption performance of NbOFFIVE-1-Ni at different conditions and has shown that this MOF exhibit 5.7 and 9.6 wt% at 400 ppm and 10 vol% CO_2, respectively (Figure 2), which surpasses the performance of the SIFSIX family and the Mg-MOF-74, one of the best MOFs for low-pressure CO_2 adsorption. In addition, RTI has prepared and tested this MOF in thermogravimetric analysis (TGA) at 1,000 ppm CO_2 and in RTI's lab-scale PBR at 500 ppm CO_2. Fluorinated MOF, NbOFFIVE-1-Ni, exhibits the highest CO_2 gravimetric uptake (ca. 7.2 wt% at 1,000 ppm CO_2 and 6.5 wt% at 500 ppm CO_2) for a physical adsorbent at low partial pressures of CO_2.

The contracted square channels decorated with proximal fluorine moieties were believed to confer this MOF with the observed exceptional CO_2/nitrogen (N_2) selectivity. Moreover, NbOFFIVE-1-Ni presented an exceptional chemical stability especially toward water; hence, NbOFFIVE-1- Ni stands as the best physical adsorbent material for CO_2 capture from atmospheric air with a CO_2 gravimetric uptake (at 400 ppm), 300% higher than the reference physical adsorbent, namely SAPO- 34(Sr^{2+}). The RTI team will further evaluate the performance of NbOFFIVE-1-Ni as an advanced sorbent for DAC, in particular, the long-term cycling and the effect of contaminants.

The competition of CO_2 adsorption with water vapor is a significant challenge for physisorbent materials in CO_2 capture, either from DAC or from flue gas. However, fluorinated MOFs with high uniform charge density and small pore sizes such as MFFIVE-1-Ni will enhance the affinity of MOFs for water molecules in the highly confined pore system without affecting CO_2 adsorption. For example, these characteristics permitted water and CO_2 to adsorb at distinct sites. In particular, water will preferentially adsorb to the open metal coordination sites, and CO_2 will preferentially adsorb via interactions with the fluorine moieties.

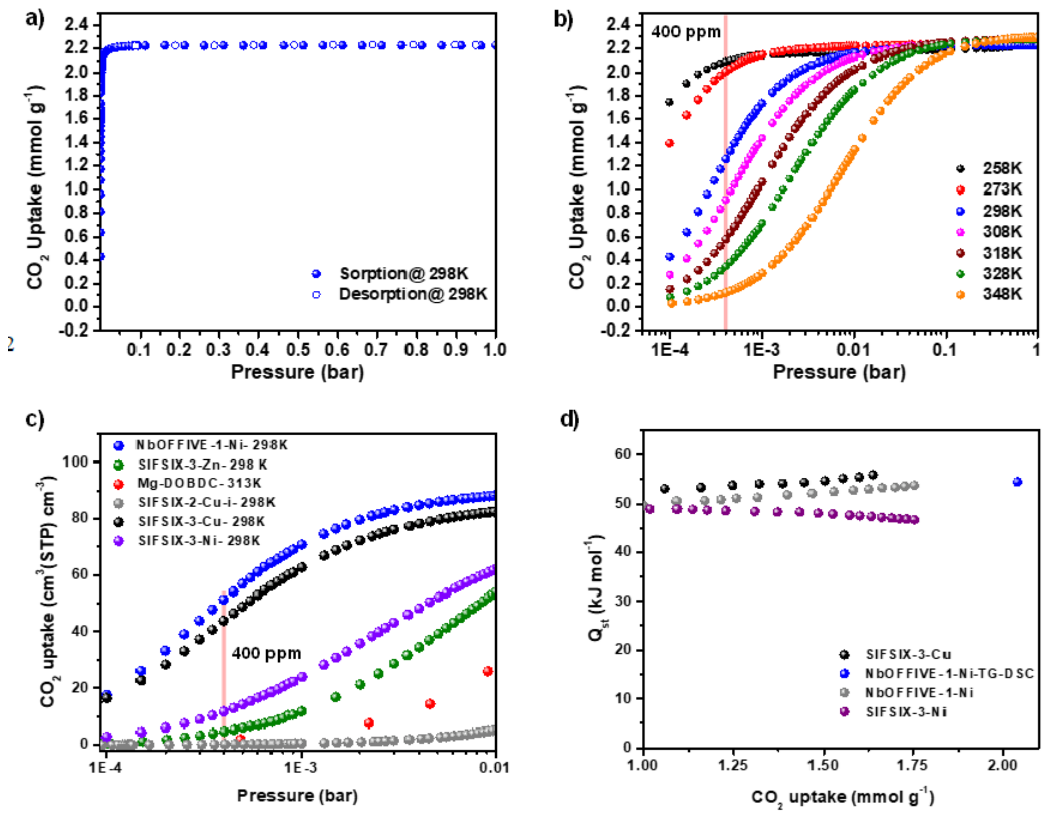

Figure 2: (a) CO_2 adsorption isotherm for NbOFFIVE-1-Ni up to 1 bar and 298 K. (b) CO_2 adsorption isotherms for NbOFFIVE-1-Ni at different temperatures. (c) Comparison of the CO_2 uptake at low pressures between the NbOFFIVE-1-Ni and the SIFSIX family and the Mg-MOF-74, one of the best MOFs for low-pressure CO_2 adsorption. (d) CO_2 heat of adsorption for NbOFFIVE-1-Ni as compared to SIFSIX-3-Ni and SIFSIX-3-Cu, determined using multiple CO_2 adsorption isotherms and TG-DSC measurements.

RTI's P-Dendrimer-Based Sorbent for DAC

Under a U.S. Department of Energy/National Energy Technology Laboratory (DOE/NETL)-funded project (DE-FE0026432), RTI developed a novel water stable solid sorbent that was produced in 91% yield by crosslinking polyethyleneimines (PEIs) with polyaldehyde P-dendrimers (Figure 3), capturing on average 13.1 wt% CO_2 from simulated flue gas over 350 cycles (700 continuous hours running with no degradation or loss of CO_2 observed). The sorbent shows excellent thermal and chemical stabilities when operating under simulated flue-gas conditions with rapid kinetics for both adsorption and regeneration. This sorbent was also tested, after two years stored in the bench at 25°C, for CO_2 capture at 500 ppm of CO_2 in RTI's PBR. For the adsorption condition, the sorbent was exposed to 150 standard cubic centimeter (sccm) of 500 ppm-CO_2 in air at 25°C in the presence of 40% relative humidity (RH). The sorbent regeneration was performed by heating the sorbent to 80°C with 40% RH while monitoring the CO_2 desorbed from the sorbent at the reactor outlet. The CO_2 loading was determined from both the adsorption and regeneration steps for comparison. This adsorbent has demonstrated a CO_2 capacity of 7.45 wt% with 100% regeneration (80°C) and no degradation or capacity loss over eight cycles.

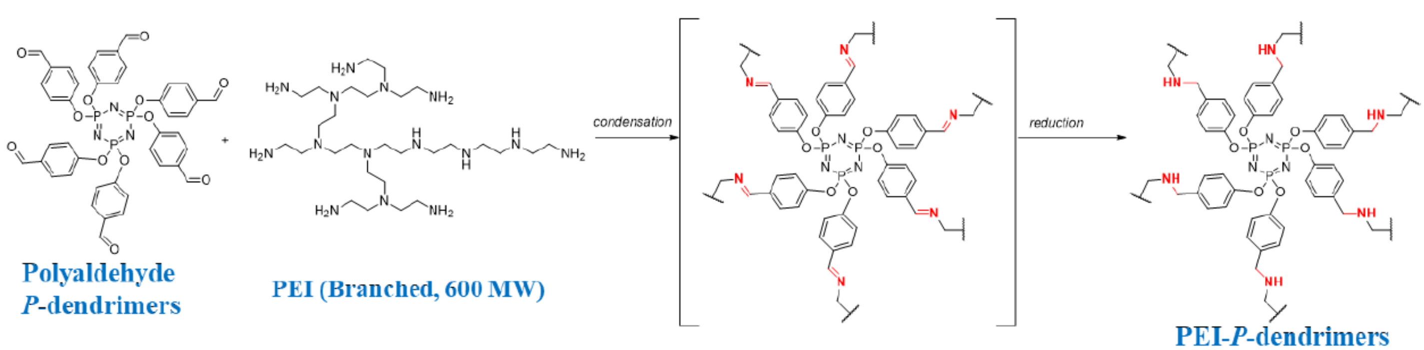

Figure 1: Synthesis of PEI-P-dendrimer.

The RTI team will prepare new sorbents with different textural properties and functionalized by grafting three polyamines: short chain ethylenediamine, 600 MW PEI, and 10,000 MW PEI and a polyaldehyde P-dendrimer crosslinker. To improve the capacity of the sorbent for DAC, RTI will optimize the material's pore size, pore volume, and surface area through a neutral templating cycle route and disrupt the hydrogen bonding between dendrimers for improved CO_2 uptake.

technology advantages

- High-capacity, fast kinetics, robust cycling, facile/cheap synthesis procedures, and easy scalability.
- Low-cost sorbents.
- Selective binding for CO_2.
- Ultra-microporous fluorinated MOFs offer fast sorption kinetics to enable selective capture of CO_2 over both N_2 and H_2O (low % RH), effective for trace CO_2 capture under both dry and humid conditions.
- The P-dendrimer amine-based sorbents perform very well under DAC conditions regardless of concentration of water vapor in air.

R&D challenges

- Improve performance under the presence of contaminants.
- Demonstrate the scale-up of selected candidate sorbents.

status

MOF synthesis and characterization of three different MOFs were accomplished in collaboration with Mohammed VI Polytechnic University. The CO_2 capture and kinetics under optimal conditions were determined and one MOF was evaluated using TGA and PBR for CO_2 capture uptake under relevant DAC conditions. The P-dendrimer amine sorbents were prepared using different amines ranging from short (ethylene diamine) to branched (polyethyleneimine) and tested in the PBR to determine their CO_2 capture uptake under the optimal conditions. The best performing amine sorbent is currently being evaluated for chemical stability under multi-cycle performance and under different RH. Long-term multi-cycle testing, air-gas contaminant evaluation, and sorbent scale-up and cost evaluation are currently being conducted.

available reports/technical papers/presentations

Mustapha Soukri, "Development of Advanced Solid Sorbents for Direct Air Capture," Project kickoff meeting presentation, Pittsburgh, PA, November 2020. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11053&filename=Development+of+Advanced+Solid+Sorbents+for+Direct+Air+Capture.pdf*.

Mustapha Soukri, "Development of Advanced Solid Sorbents for Direct Air Capture," Direct Air Capture kickoff meeting presentation, Pittsburgh, PA, February 2021. *https://www.netl.doe.gov/projects/plp-download.aspx?id=11052&filename=Development+of+Advanced+Solid+Sorbents+for+Direct+Air+Capture.pdf*.

Mustapha Soukri, "Development of Advanced Solid Sorbents for Direct Air Capture," NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Soukri.pdf*