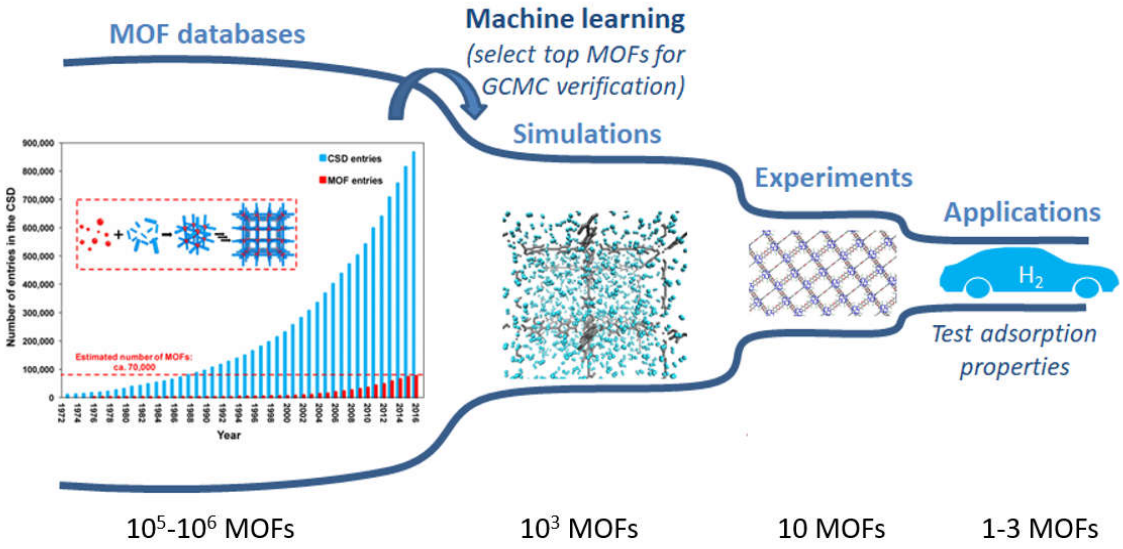
Theory-Guided Design and Discovery of Materials for Reversible Methane and Hydrogen Storage



P.I.: Omar K. Farha

Co-P.I.: Randall Q. Snurr

Northwestern University

Co-P.I.: Taner Yildirim, NIST

May 1, 2020

Project ID: ST209

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline and Budget

- Project Start Date: Jan, 2020
- Project End Date: Jan, 2023 (subject to annual evaluation by DOE)
- Total Project Budget: $1,125,000
  - Total Recipient Share: $225,000
  - Total Federal Share: $900,000
  - Total DOE Funds Spent*: $80,547 *(This is an estimate only. Due to the delays in revising, receiving and setting up the award an exact number cannot be provided at this time, and next report will reflect the exact spendings.)*

* As of 3/31/2020

Barriers

- A. System Weight and Volume
- B. System Cost
- C. Efficiency
- D. Durability/Operability
- G. Materials of Construction

Partners

Collaborations:

- Taner Yildirim, NIST Fellow

National Institute of Standards and Technology

Relevance

Objectives:

- Perform high-throughput computational discovery: A key advantage of MOFs is structural predictability that can be leveraged to rapidly search in silico for optimal materials by expanding current databases of predicted MOFs to include various topologies (i.e. 85 topologies) as well as new building blocks from commercially available sources.
- Screen database of 100,000 MOFs for hydrogen uptake using machine learning algorithm and GCMC for fast screening and identify materials with total capacity (up to 100 bar) that can reach the storage capacity of hydrogen tank at 700 bar
- Synthesize and characterize the top candidate MOFs generated in silico for hydrogen storage while keeping in mind stability (thermal, chemical and mechanical stability), scalability and cost.
- Study catechol and bipyridine/phenanthroline containing MOFs in which open metal sites can be created upon removal of solvent molecules, for storage of molecular hydrogen at and near room temperature.

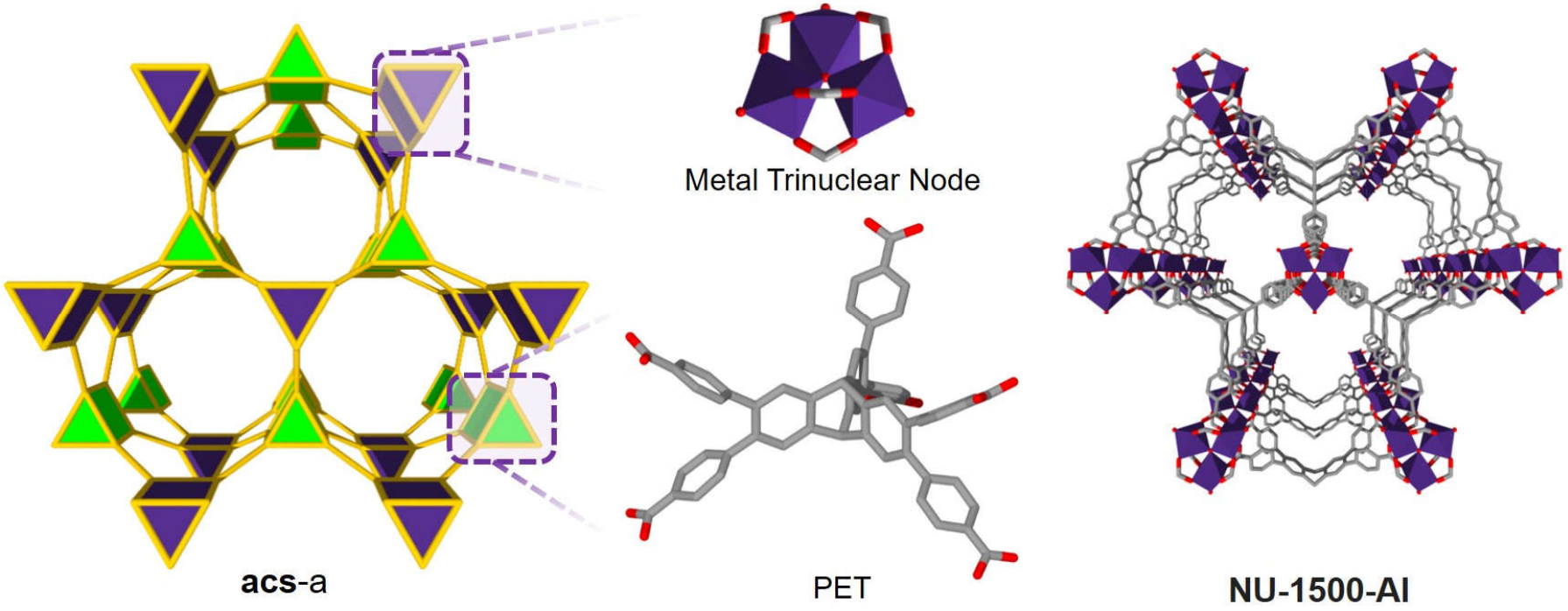
Approach/Milestone

Milestone Q1.1: Synthesis and characterization of MOFs for hydrogen storage based on physical adsorption （Accomplished）

- Synthesis, characterization and N2 isotherm collection for NU-1500 and its isoreticular analogues. Collection of high-pressure hydrogen isotherms of different temperatures for PSA/TSA application to maximize working capacity. (100%)
- Subtask 1.1.1 Synthesis and characterization of NU-1500 (100%)
- Subtask 1.1.2 High pressure isotherm collections on NU-1500 (100%)
- Subtask 1.1.3 Design and synthesis of linkers for extended NU-1500 family of MOFs (100%)
- Subtask 1.1.4 Synthesis of extended series of MOFs as well as their isoreticular series with different metals (100%)
- Subtask 1.1.5 High pressure isotherm collections on extended and isoreticular NU-1500 series (100%)

Accomplishments and Progress

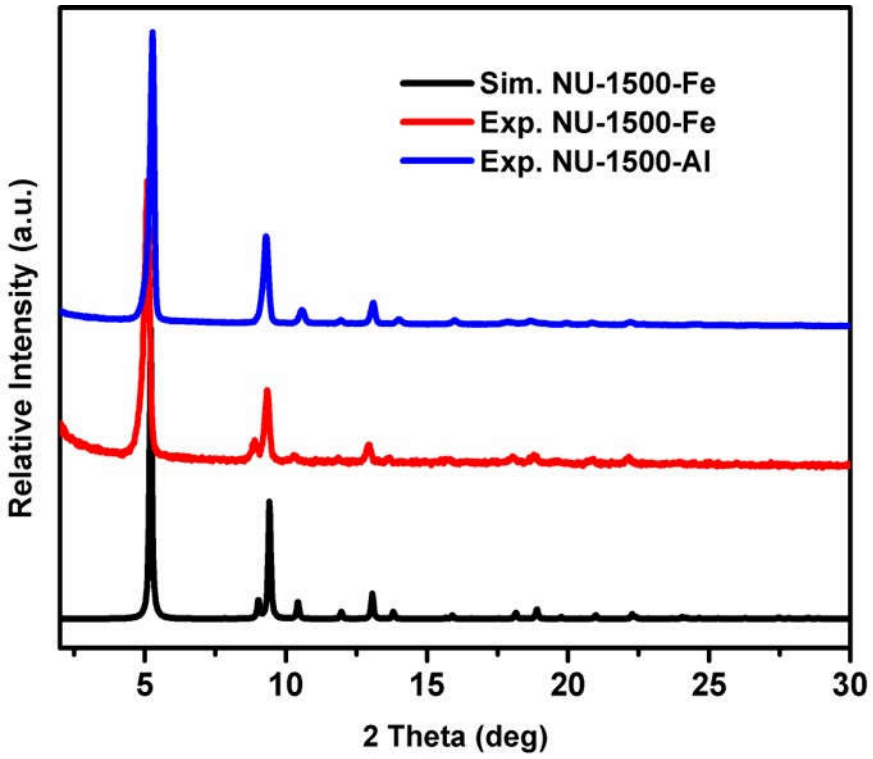
Structural illustration of NU-1500-Al

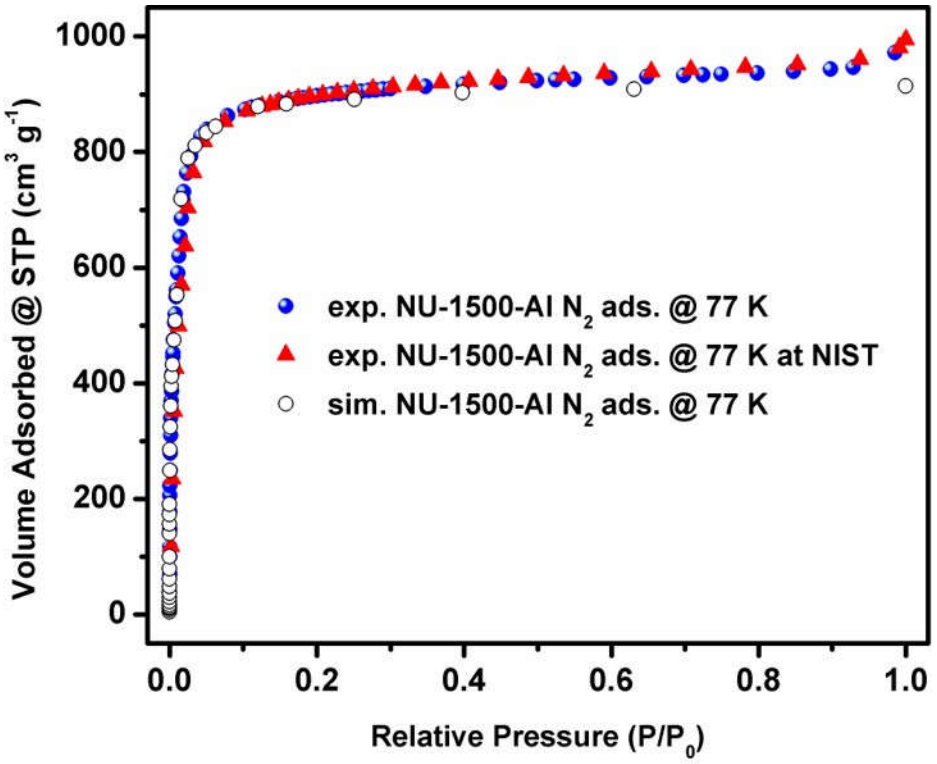


An isoreticular Al-based analogue of NU-1500-Fe was synthesized and showed high surface area.

Accomplishments and Progress (cont.)

PXRD patterns and N_2 adsorption isotherms of NU-1500-Al

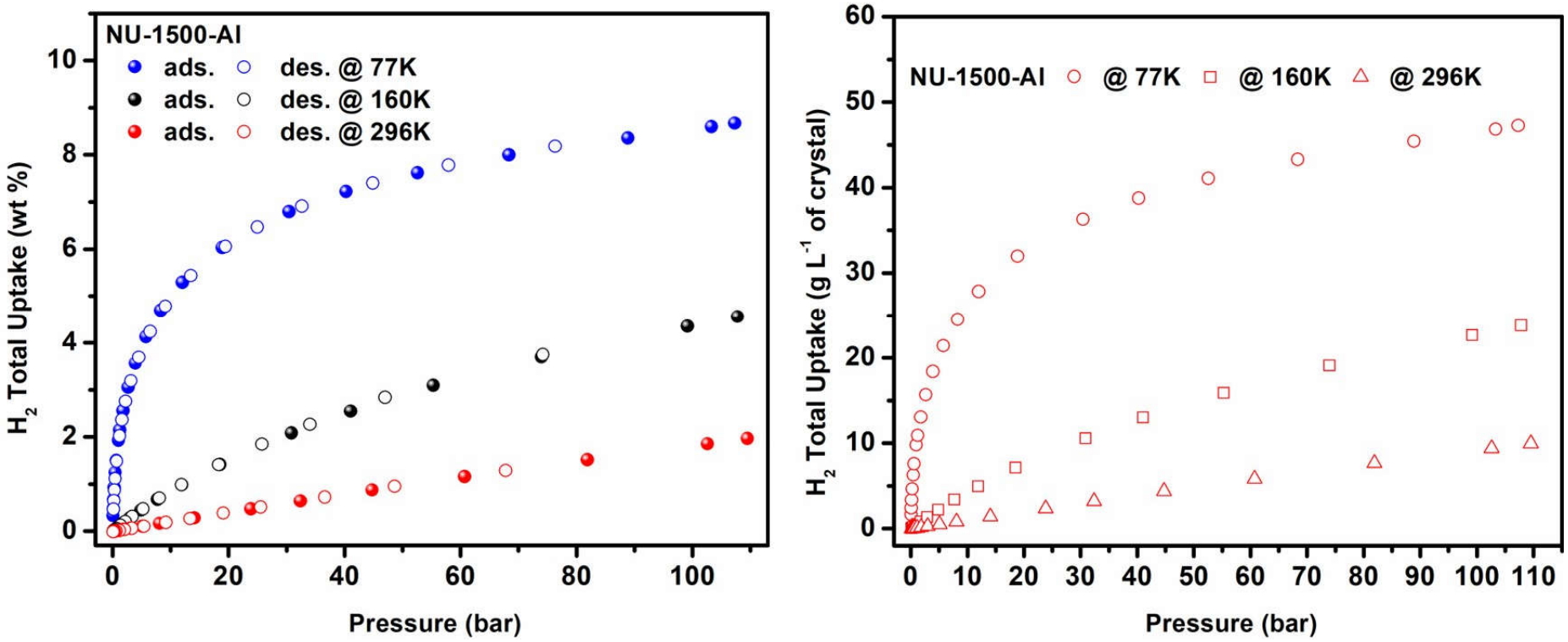




- BET area of 3560 $m^2\ g^{-1}$—satisfying the four BET consistency criteria
- Experimental total pore volume of 1.46 $cm^3\ g^{-1}$

Accomplishments and Progress (cont.)

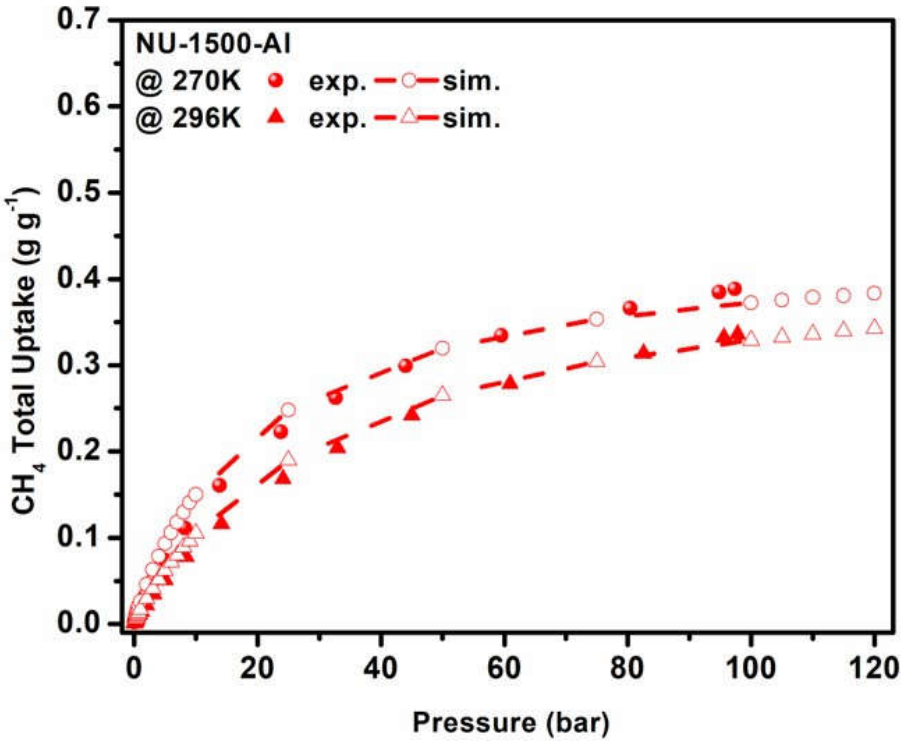
High-pressure H_2 sorption of NU-1500-Al collected at NIST

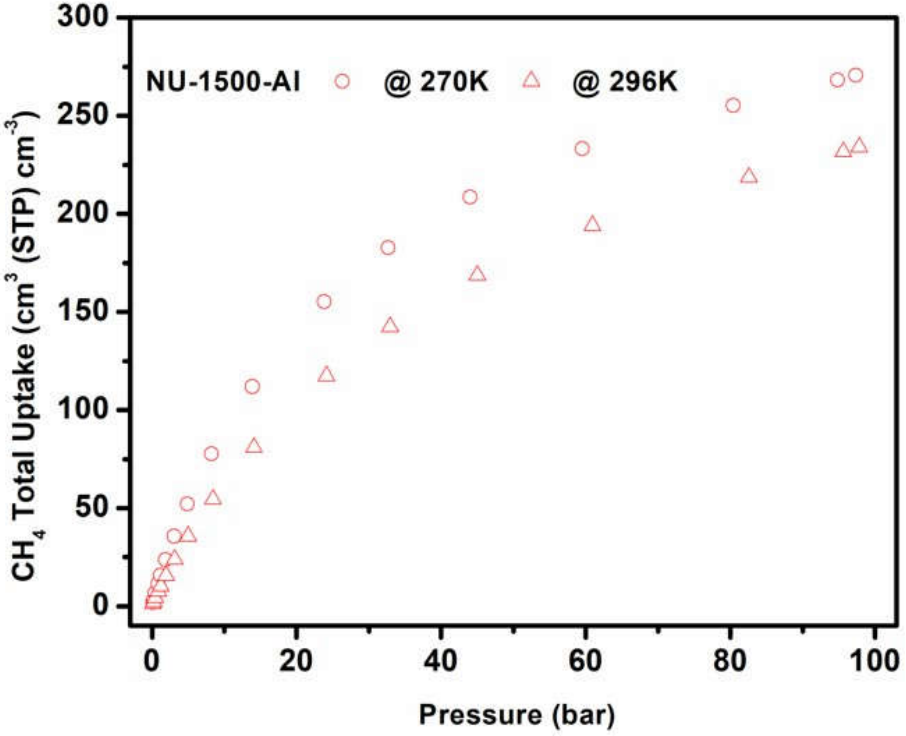


- NU-1500-Al adsorbed ~8.6 wt% (46.8 g L^{-1}) of H_2 at 100 bar and 77 K
- Deliverable capacity of 8.2 wt% (44.6 g L^{-1}): Ads at 77 K/100 bar → Des at 160 K/5 bar

Accomplishments and Progress (cont.)

High-pressure CH_4 sorption of NU-1500-Al

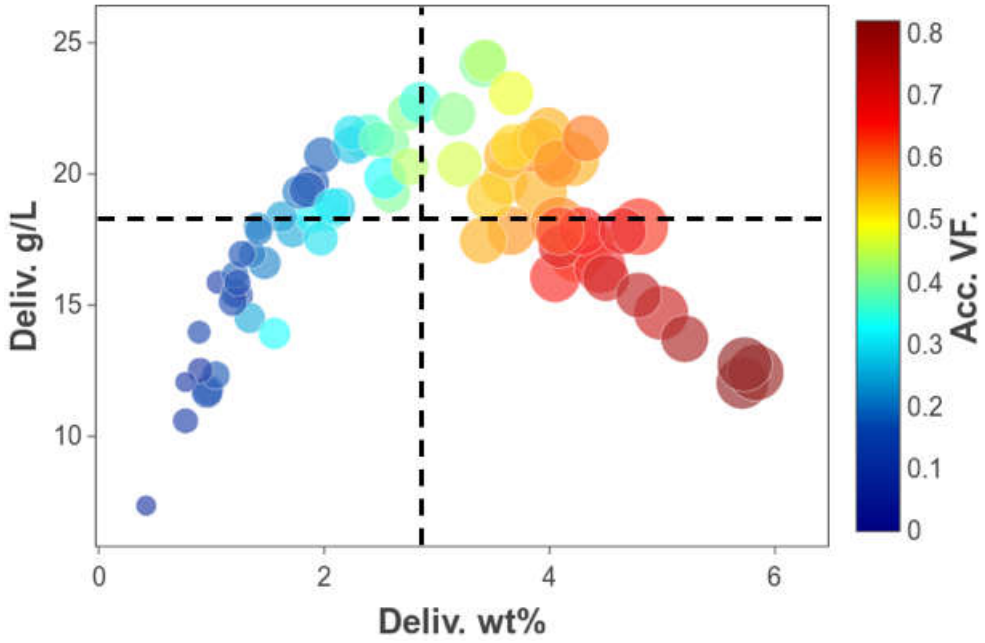




- NU-1500-Al adsorbed ~0.34 g g^{-1} (237 cm^3 (STP) cm^{-3}) and ~0.39 g g^{-1} (273 cm^3 (STP) cm^{-3}) of CH_4 at 296 K and 270 K 1t 100 bar, respectively
- Deliverable capacities of 0.29 g g^{-1} (202 cm^3 (STP) cm^{-3}) and ~0.32 g g^{-1} (224 cm^3 (STP) cm^{-3}) between 5 bar and 100 bar.

Accomplishments and Progress (cont.)

Correlation between the gravimetric (x-axis), volumetric (y-axis) deliverable capacities of H_2, accessible void fraction (color bar) and gravimetric surface area (dot size) for the top MOFs at 296 K with pressure swing from 100 bar to 5 bar, from computational screening.



A total of 20 MOFs were able to meet both Year 1 targets (2.8 wt% and 18 g/L) simultaneously at this working condition. More are expected for the pressure-temperature swing from (233 K, 100 bar) to (296 K, 5 bar).

Accomplishments and Progress (cont.)

Responses to Previous Year Reviewers' Comments

This project was not reviewed last year

Collaboration and Coordination

- Northwestern University (Omar Farha, Randy Snurr)
  - Lead institution
  - Computational modelling, material discovery, synthesis and initial gas storage property screening

- National Institute of Standards and Technology (NIST, Taner Yildirim)
  - Testing and validation of results from NU
  - Novel sorbent synthesis by post-metalation of some sorbents provided from NU

Remaining Challenges and Barriers

Milestone Q1.2: Computational screening of MOF databases for catecholate/bipyridine sites

- Screen databases of real and hypothetical MOFs to find structures with highest density of potential catecholate/bipyridine sites. Down-select from these candidates to 10 most promising materials based on synthetic feasibility. Use atomistic simulations to study hydrogen adsorption in 10 promising materials identified in screening modified with Mg catecholate/bipyridine sites.

Milestone Q1.3: Computational screening of MOF databases for down-selecting topology

- Expand database of predicted MOFs to include 100,000 MOFs with various topologies as well as new building blocks from commercially available sources. Screen this database for hydrogen uptake at cryogenic temperatures and pressures of interest using machine learning algorithm and GCMC to find top 10 candidates in terms of both volumetric and gravimetric deliverable capacities.

Year 1 Q1.4: Demonstrate a material with H_2 working capacity exceeding **8 wt% and 52 g/L** under lower temperature swing operation (5-100 bar and 77-160 K); OR **2.8 wt% and 18 g/L** under higher temperature swing operation (5-100 bar and 233-296 K). Here all goals are at material level, not system level and wt% = (mass of H_2) / (mass of MOF + mass of H_2) × 100%).

Proposed Future Work

- Performance evaluation of the extended isoreticular frameworks discussed
- Identification of synthetically viable MOFs with catecholates and pyridines and optimization of metal loadings (trade-off between pore volume available and density of open metal sites)
- Designing alternative structures that are synthetically viable to the ones that are predicted from computational studies to have high performance but synthetically challenging
- Testing and validation of hydrogen uptakes of these materials
- Pre or post modification of the structures that reached one of the metrics (i.e. gravimetric or volumetric) to address the other metrics

Summary

- A highly porous aluminum MOF, NU-1500-Al, was synthesized and characterized
- The high pressure H_2 sorption of NU-1500-Al was measured at NIST which reached our gravimetric deliverable capacity target for Year 1
- From the simulation studies, total of 20 more MOFs were identified to meet both gravimetric and volumetric Year 1 targets (2.8 wt% and 18 g/L) simultaneously