Heteroatom-Modified and Compacted Zeolite-Templated Carbons for Gas Storage

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May 30, 2020

Project ID: ST214

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Overview

Timeline

- Project Start Date: 10/01/19
- Phase I End Date: 12/31/20
- Phase II End Date: 12/31/22[a]

[a] Project continuation to Phase II based on achieving the Go/No-Go criterion

Budget

- Total Project Budget: $1,093,477
  - Total Recipient Share: $218,696
  - Total Federal Share: $874,781
  - Total DOE Funds Spent: $13,905[b]

[b] As of 3/31/2020

Barriers

Barriers identified in the 2015 MYRDD:

- O. Lack of Understanding of (Methane) Physisorption
- A. System Weight and Volume
- B. System Cost

Partners

- Project Lead: Montana State University (materials synthesis and primary characterization)
- Subcontract: Caltech (adsorption measurements, electron microscopy)
- Partner: HyMARC (PNNL for NMR, LLNL for XAS)
- Partner: Tohoku University (materials densification)

Relevance

Objectives

- **Volumetric Energy Density Improvement** via:
  - **Surface Homogeneity of the Adsorbent** – synthesis of zeolite-templated carbon (ZTC) as a *chemically* and *structurally* homogeneous surface for methane adsorption, toward constant/increasing binding energy upon loading up to high pressures
  - **Compaction of the Adsorbent** – densification of ZTC into mechanically robust pellets with high bulk density, toward 1 gram of ZTC per milliliter
  - **Chemical Tuning of the Adsorbent** – substitution of carbon by boron and/or nitrogen to tailor the binding energy toward methane, toward increase of 1-2 kJ mol^{-1}
- **Cost Reduction of the Storage System** via:
  - **Reduction of the Working Pressure** – tailoring of material properties to achieve energy storage targets at < 100 bar, toward cost-effective aluminum pressure vessels
  - **Cost-Effective Synthesis of ZTC** – development of single-step procedure to obtain large quantities of high-fidelity ZTC, toward cost reduction by 50%

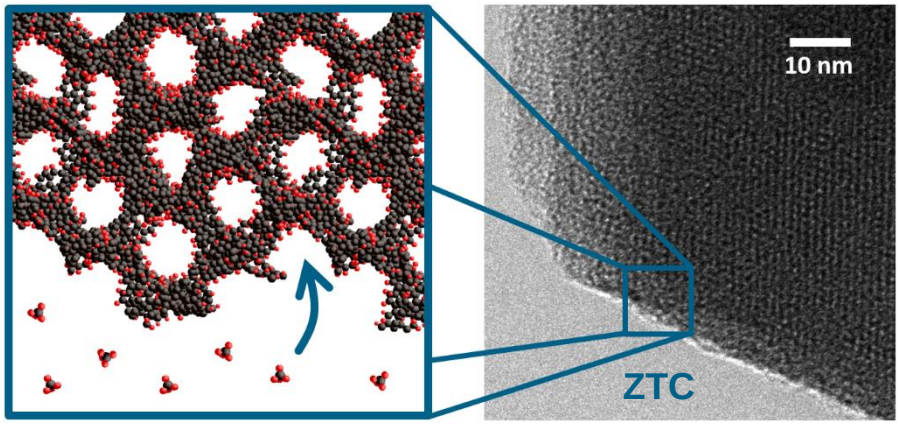
Impact in 2020

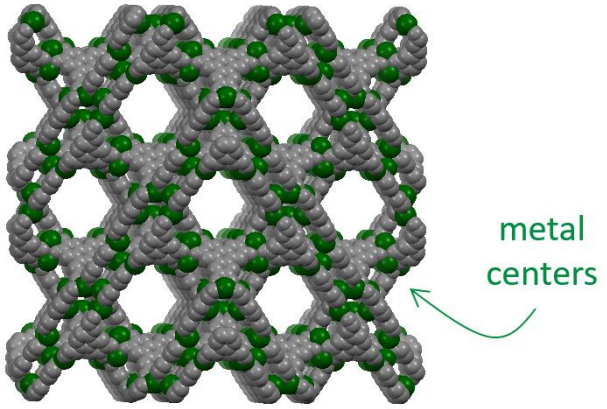
- Synthesis of native ZTC powder – high surface area and pore regularity
- Confirmation of constant/increasing binding energy of methane upon loading (13-14 kJ mol^{-1} up to 37% loading at 273 K) – methane delivery of 0.31 g g^{-1} (100 bar)

Approach

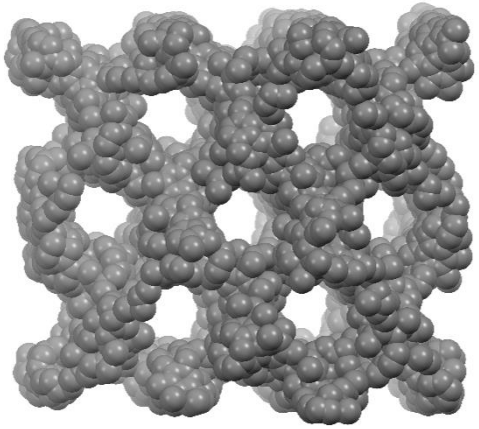
ZTCs as Homogeneous Carbon-Based Surfaces

- **Activated Carbons**
  - Limited control of pore size/chemistry ✘
  - Modest volumetric surface area ✘
- **Metal-Organic Frameworks**
  - Excellent control of pore size/chemistry ✓
  - High volumetric surface area ✓
  - Heterogeneous binding sites for methane ✘
- **Zeolite-Templated Carbons (ZTCs)**
  - Good control of pore size/chemistry ✓
  - High volumetric surface area ✓
  - Homogeneous binding sites for methane ✓





Metal-Organic Framework



Zeolite-Templated Carbon
(metal-free)

Approach

ZTCs as Homogeneous Carbon-Based Surfaces

- **Barrier "O" Addressed: What is the role of the metal-coordination clusters in the thermodynamics of CH_4 storage in designed, carbon-based porous frameworks?**
  - Metal-based sites serve as *strong binding* sites in MOFs
  - Carbon-based linkers serve as *moderate binding* sites in MOFs
  - Open-pore space serves as *low binding* sites in MOFs

  } heterogeneity

  - Metal-free porous carbon frameworks (ZTCs) exhibit *homogeneous* binding energy, leading to *higher CH_4 delivery*

Go/No-Go 1: produce pelletized ZTC with ≥ 180 v/v CH_4 delivered at 273 K, 5-100 bar

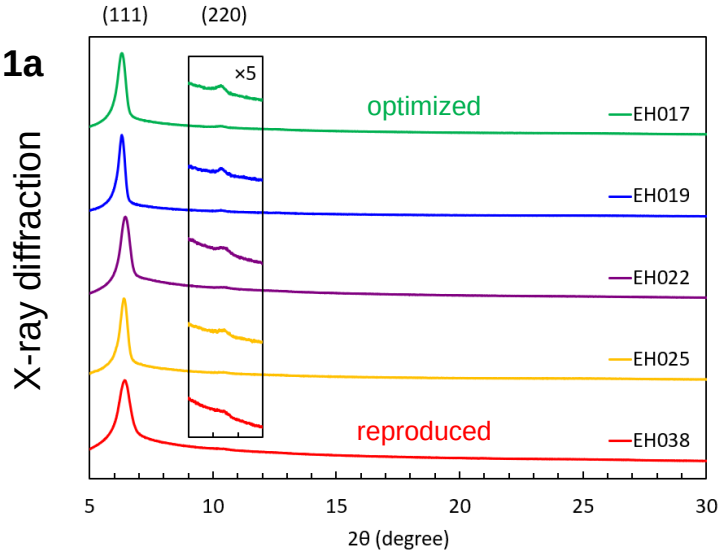
- **Barriers "O/A" Addressed: What is the role of boron or nitrogen inclusions in the thermodynamics of CH_4 storage in designed, carbon-based porous frameworks?**
  - Does boron increase or decrease binding energy?
  - Does nitrogen increase or decrease binding energy?

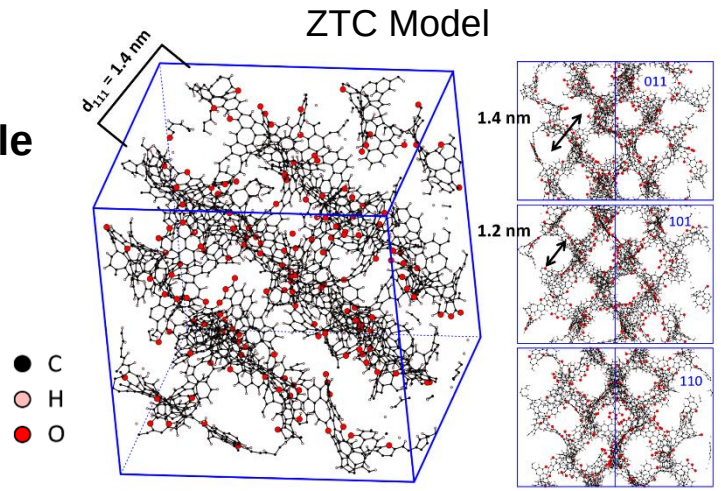
Go/No-Go 2: produce ZTC with *increased homogeneous* binding energy via B-/N- doping to achieve pelletized ZTC with ≥ 180 v/v CH_4 delivered at 273 K, 5-65 bar

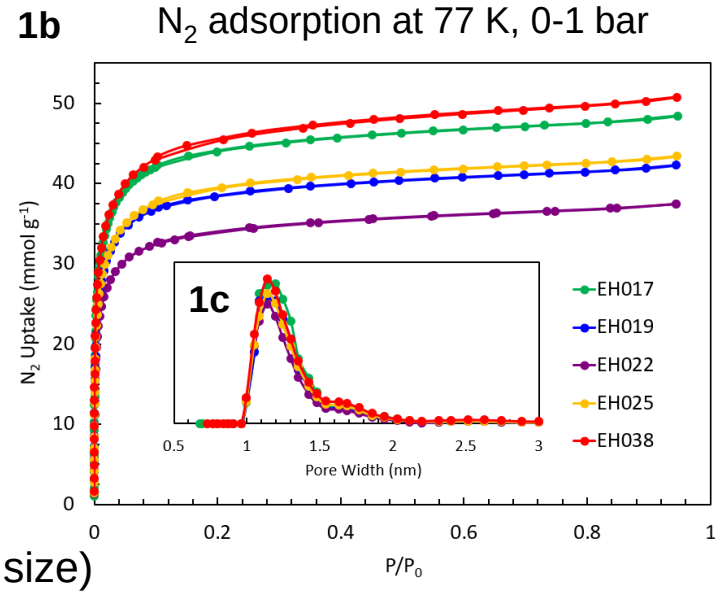
Accomplishments & Progress

Homogeneous Structure of ZTC

- **Native Powder ZTC Synthesized at the Gram Scale**
  - High template-fidelity in optimized samples (**1a**)
  - Surface area ≥ 3600 m^2 g^{-1} (**1b**)
  - Homogeneous pore size of ~1.2 nm (**1c**)







- **1a** X-ray diffraction patterns (establish pore-to-pore distance homogeneity)
- **1b-c** N_2 adsorption at 77 K (establishes high surface area and homogeneous pore size)

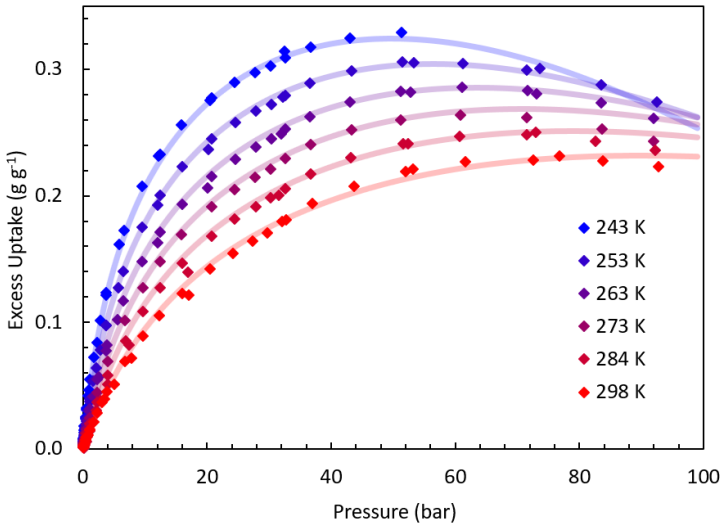
Accomplishments & Progress

Homogeneous Binding Energy of CH_4 on ZTC

- **Methane Adsorption Measurements at 243-298 K (2a)**
  - Excess methane uptake of 0.33 g g^{-1} at 243 K, 51 bar
  - Excess methane uptake of 0.26 g g^{-1} at 273 K, 61 bar
  - Deliverable "total" methane uptake of 0.314 g g^{-1} at 273 K, 5-100 bar

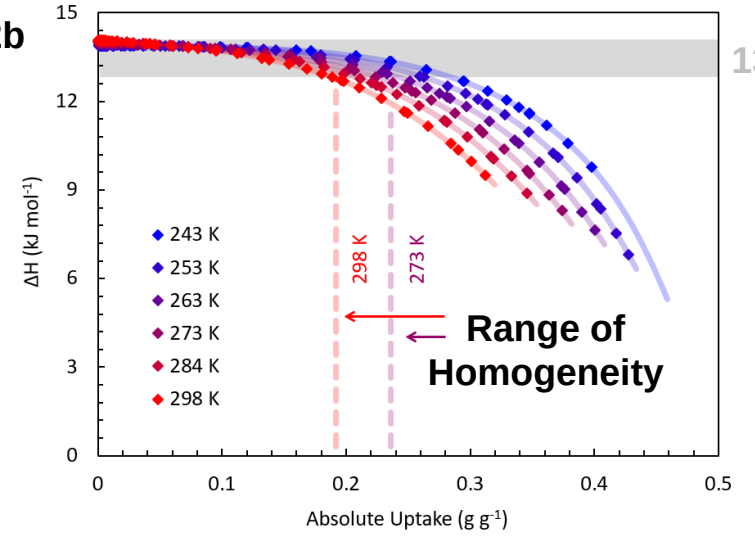
- **Constant Enthalpy of Adsorption of CH_4 on ZTC (2b)**
  - Enthalpy of adsorption (ΔH) is a proxy for binding energy
  - ΔH = 13-14 kJ mol^{-1} at 273 K, across 0-37% CH_4 uptake

2a



CH_4 adsorption measurements

2b



CH_4 binding energy calculations

Response to Past Comments

(this project was not reviewed last year)

Collaborations

Montana State University (lead)

- ZTC native powder synthesis
- Heteroatom-doping of ZTC
- Primary materials characterization
- Adsorption measurements (Sieverts III)

California Institute of Technology (sub)

- Adsorption measurements (Sieverts I and II)
- Transmission electron microscopy

Tohoku University (Prof. A. Gabe)

- Densification of ZTC

HyMARC* – PNNL (Dr. S. T. Autrey)

- High-pressure ^{11}B solid-state NMR

HyMARC* – LLNL (Dr. A. A. Baker)

- X-ray absorption spectroscopy (B K-edge)

*within the DOE Hydrogen and Fuel Cells program

Remaining Challenges

Densification of ZTC, Maintaining Homogeneity

- **Native Powder ZTC Exhibits a Low Tap Density of 0.18 g mL^{-1}**
  - Volumetric methane capacity in powder ZTC is low (< 80 v/v at 273 K, 100 bar)

- **Densification via Hot-Pressing is Possible, up to ~1 g mL^{-1}, but:**
  - How does densification affect adsorption capacity?
  - How does densification affect *binding energy homogeneity*?
  - Challenge: produce ZTC with high density, maintaining capacity and homogeneity

Heteroatom-Doping of ZTC, Maintaining Homogeneity

- **Boron/Nitrogen Incorporation within ZTC is Possible, but:**
  - How does boron-doping affect adsorption capacity?
  - How does nitrogen-doping affect adsorption capacity?
  - How does heteroatom modification affect *binding energy homogeneity*?
  - Challenge: produce ZTC with high B/N content, maintaining homogeneity

Future Work

Densification of ZTC, Maintaining Homogeneity

- **Prepare ZTC Pellets at Varying Densities up to ~1 g mL^{-1}**
  - Optimize conditions to achieve mechanically robust pellets
  - Measure methane adsorption between 243-298 K, 0-100 bar
  - Characterize binding energy as a function of pellet density and pellet structure:
    - volumetric surface area
    - pore density, pore-size distribution

Heteroatom-Doping of ZTC, Maintaining Homogeneity

- **Prepare ZTC Powders at Varying Compositions up to BC_3/NC_3**
  - Complete commissioning of heteroatom-doping reactor
  - Prepare preliminary samples containing at least 5 mol% boron/nitrogen
  - Measure methane adsorption between 243-298 K, 0-100 bar
  - Characterize binding energy as a function of boron/nitrogen content

Combine Densification/Doping to Meet Go/No-Go 1

- 180 v/v deliverable CH_4 storage at 273 K, 5-100 bar

Note: any proposed future work is subject to change based on funding levels.

Technology Transfer

(none to date)

Summary

Objectives:

- Improvement of volumetric energy density of adsorbed natural gas storage, via:
  - Densification of zeolite-templated carbon (ZTC)
  - Heteroatom-doping of ZTC

Relevance:

- The role of metal/metal-oxo clusters in metal-containing porous materials on the thermodynamics of methane storage is severely under-investigated
- ZTC represents a metal-free carbon framework for direct investigation of effects of *surface homogeneity* on deliverable methane storage

Approach:

- Densification of ZTC via hot-pressing
- Tuning of ZTC composition by heteroatom-doping

Accomplishments:

- Successful synthesis of high-fidelity ZTC
- Homogeneous binding energy of CH_4 on ZTC demonstrated

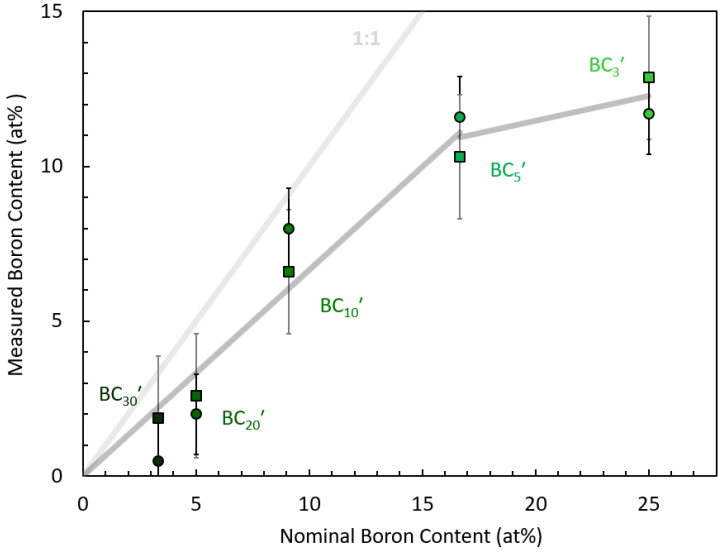
Collaborations:

- Caltech, Tohoku University, and HyMARC (PNNL and LLNL)

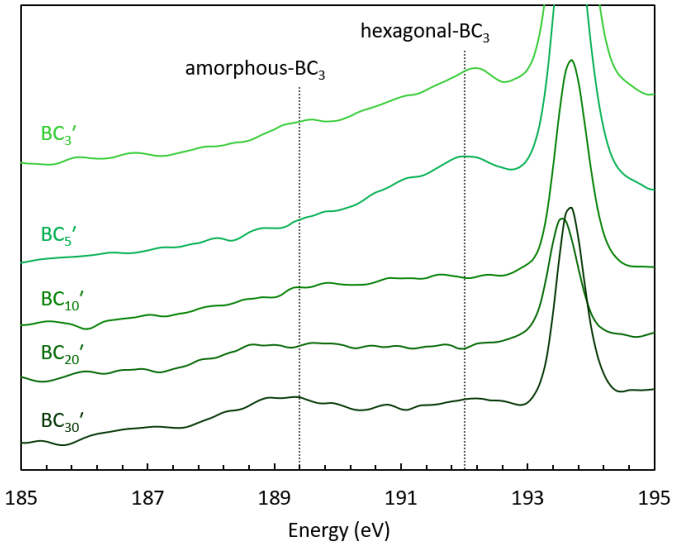
Accomplishments & Progress

Heteroatom Doping: Boron-Doped Graphitic Carbon

- **Direct Synthesis of Bulk Turbostratic BC_3**
  - Closed, one-step reaction of benzene (C_6H_6) and boron tribromide (BBr_3)
  - Structural characterization: X-ray diffraction (XRD), Raman spectroscopy
  - Composition: energy-dispersive X-ray spectroscopy (EDX) – maximum of 13 at% B
  - **Integrated collaboration**: X-ray absorption spectroscopy (XAS) with HyMARC (measurements performed at LBNL with partners from LLNL)



BC_x composition (EDX)



BC_x chemical environment (XAS)