# High-Capacity and Low-Cost Hydrogen-Storage Sorbents for Automotive Applications

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Project ID # ST 121

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# Overview

## Timeline

- Project Start: Aug, 01, 2015
- Project Length: 3 years
- Percent complete: 16%

## Barriers

- Inadequate hydrogen uptake
- Inadequate understanding of MOF activation processes
- Inadequate understanding of hydrogen adsorption processes

## Budget

- Total Project Budget: $ 885,115
  - Total Recipient Share: $0
  - Total Federal Share: $ 885,115
- Total DOE Funds Spent: $ 227,768

## Partners

- EERE: Sponsor and Funding
- Argonne National Lab
- Texas A&M University

# Relevance

- Design robust materials that will allow for systems to meet DOE gravimetric and volumetric targets
  - DOE System Target of 0.055 kg $H_2$/kg$_{_system}$ and 0.040 kg $H_2$ / L$_{_system}$
- Keep costs down by reducing synthetic steps for precursors
- Determine strategies which allow for materials to exceed the Chahine's rule limit of 1 wt% excess uptake for each 500m$^2$/g

# Approach

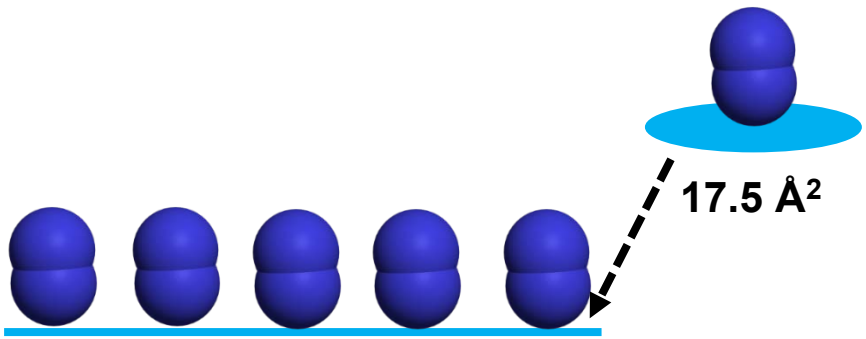
## Judicious design of high-valent metal MOFs

- Increase hydrogen affinity relative to surface area
  - Inclusion of open metal sites and proper activation
  - Pore volume control is also important to ensure a lack of "dead space"
- Understand activation process at the metal center
  - Use X-ray techniques to study oxidation state and solvation changes

| Milestone | Quarter | Description | Status |
|---|---|---|---|
| D1 | 2 | Show PCN-250 has uptake of 6.75 wt% @ 40 bar (Best current measurement 4.8 wt% excess @ 27 bar 77 K by NREL) | Missed |
| M2 | 3 | Perform X-ray absorption experiments to determine oxidation state and coordination changes during activation | Initial study completed |
| D2 | 4 | Demonstrate one Material with >1.5x Chahine's Rule uptake with surface area >2000 $m^2$ / g and volumetric uptake >60 g / L @ 77 K <100 bar | In Progress |
| M6 | 7 | Identify the most promising strategies and develop over 5 MOF sorbents with surface area over 2500 $m^2$ / g and gravimetric capacity of 50% over Chahine Rule (>9 wt% excess) at 77 K and less than 100 bar. | |

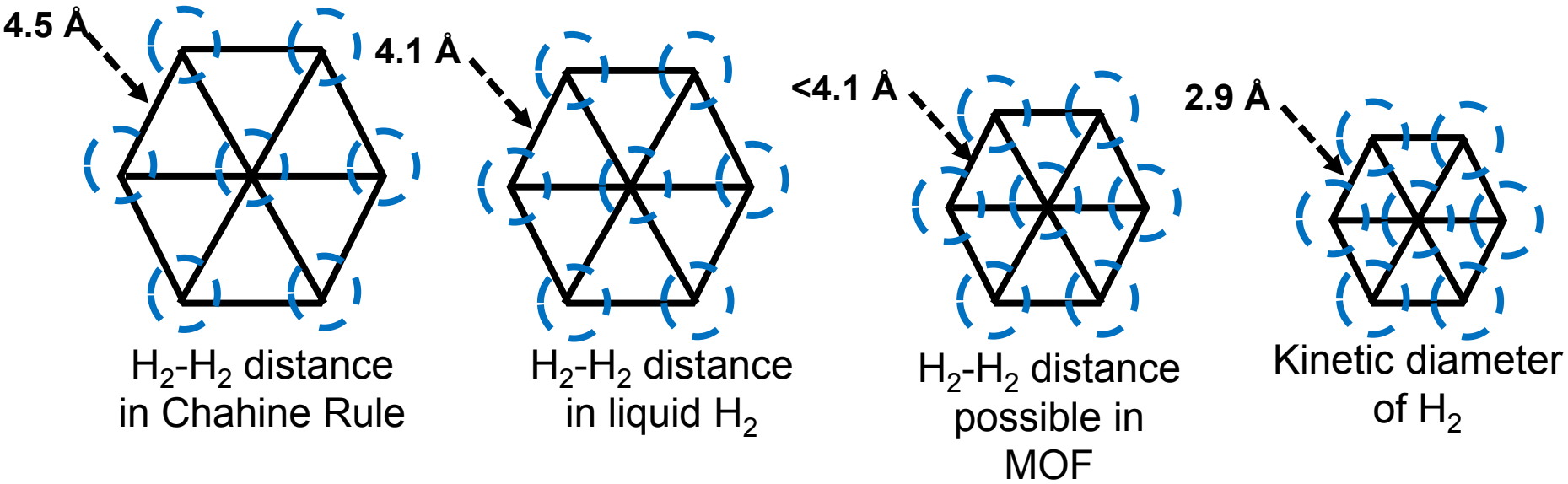
# Accomplishments and Progress: Understanding of Chahine's Rule

- What is Chahine's Rule?




1 wt% $H_2$ per every 500 $m^2$ / g

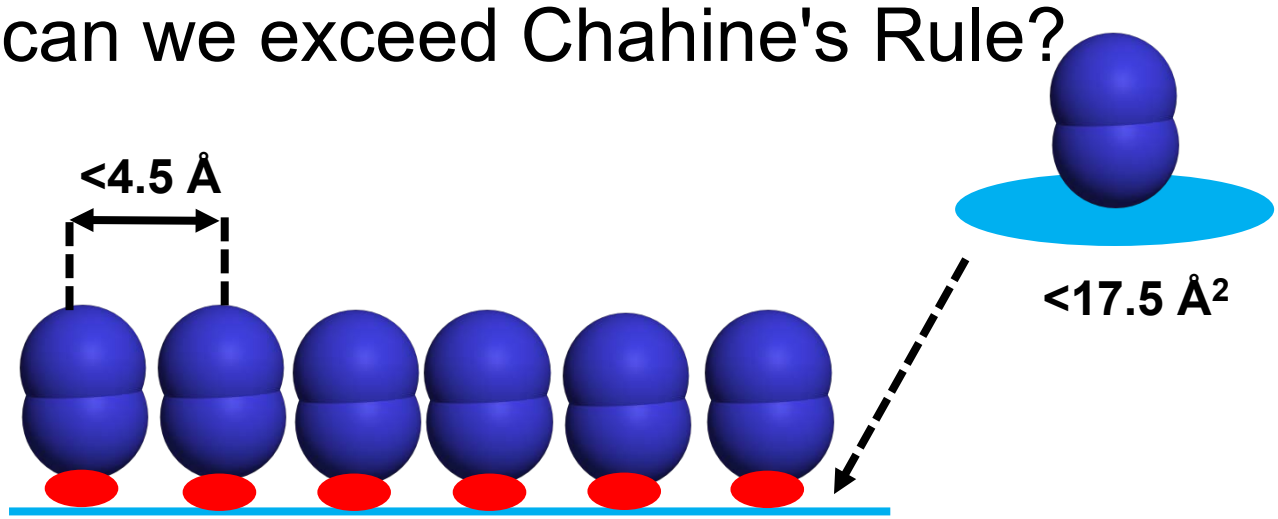
- How can we exceed Chahine's Rule?




Roth, S., *et al. Carbon*, **2005**, *43*, 2209;
Long, J., *et al. Chem. Soc. Rev.*, **2009**, *38*, 1294.

# Accomplishments and Progress: Understanding of Chahine Rule

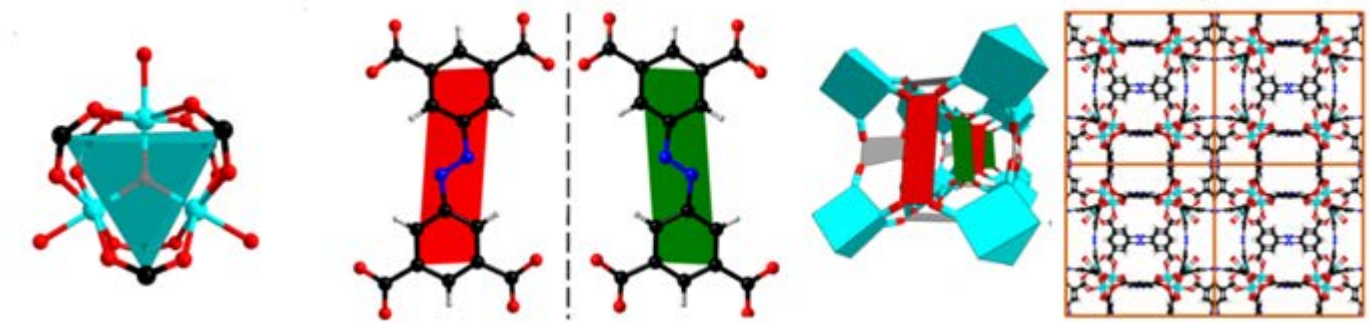
- How can we exceed Chahine's Rule?

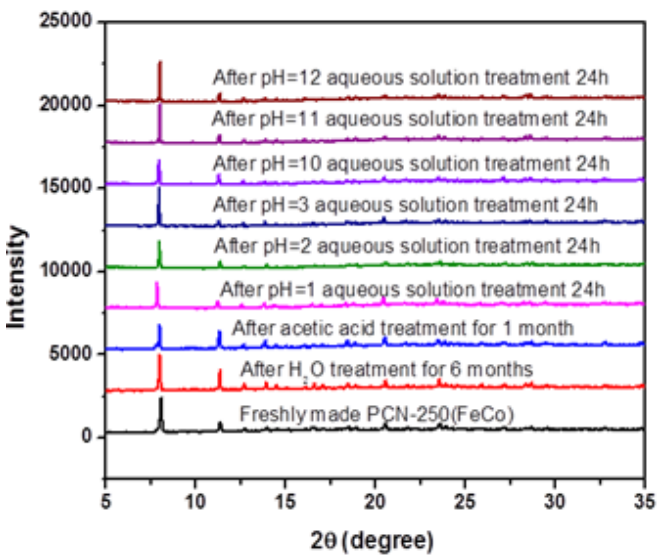


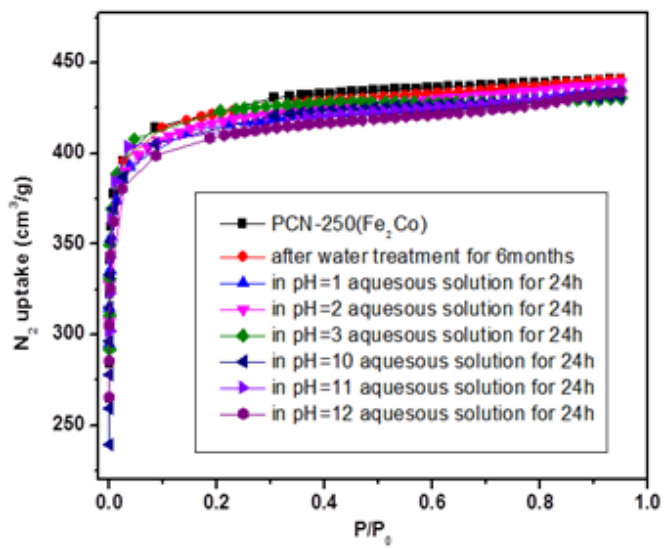

- To exceed Chahine's Rule, a high density of strong interaction sites is necessary to reduce the distance between adsorbed $H_2$:
  1. Improve hydrogen – sorbent interaction through optimizing the size of cage/channel
  2. Improve hydrogen – sorbent interaction through open metal site

# Accomplishments and Progress: Advantages of PCN-250

- PCN-250 is a promising MOF for $H_2$ storage:
  - Costs could be <$ 50 / kg to manufacture
  - Extremely robust



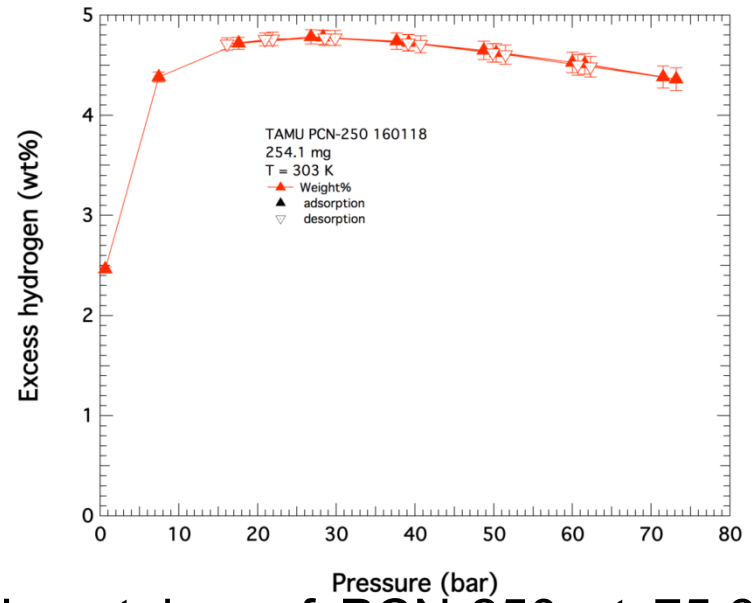


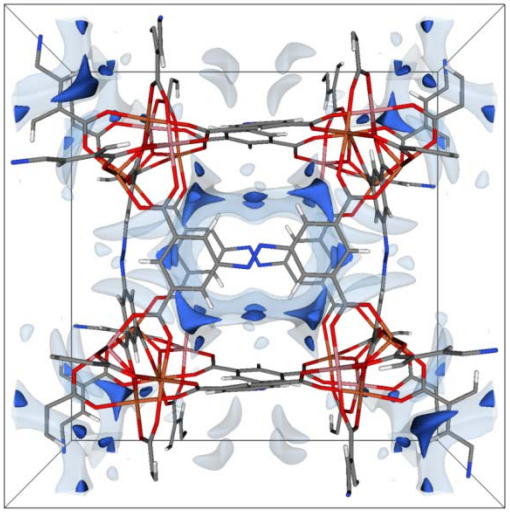

Zhou, H.C., *et al. Nat. Commun.*, **2015**, *5*, 5723.

# Accomplishments and Progress: Advantages of PCN-250

- PCN-250 is a promising MOF for $H_2$ storage:
  - Suitable cage size with high density of open metal sites




*$H_2$ uptakes of PCN-250 at 75.6K. Collaboration with NREL

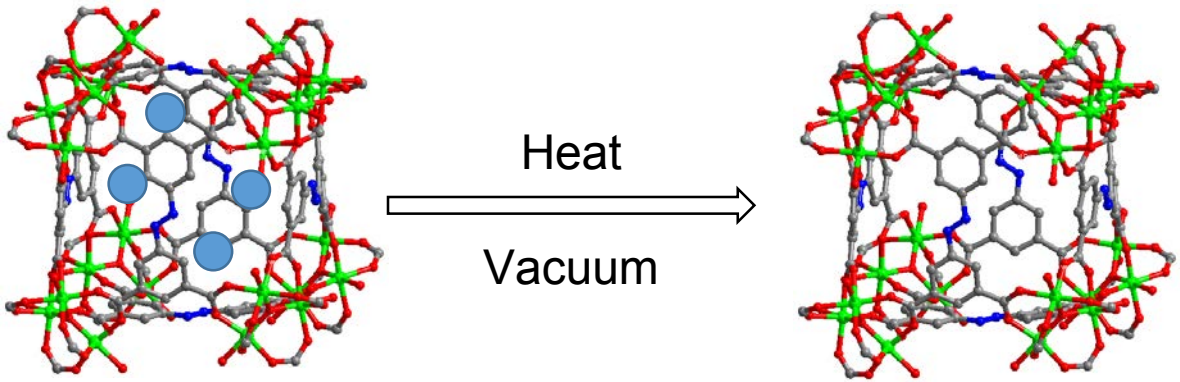


Potential energy contours of adsorbed $H_2$ in PCN-250

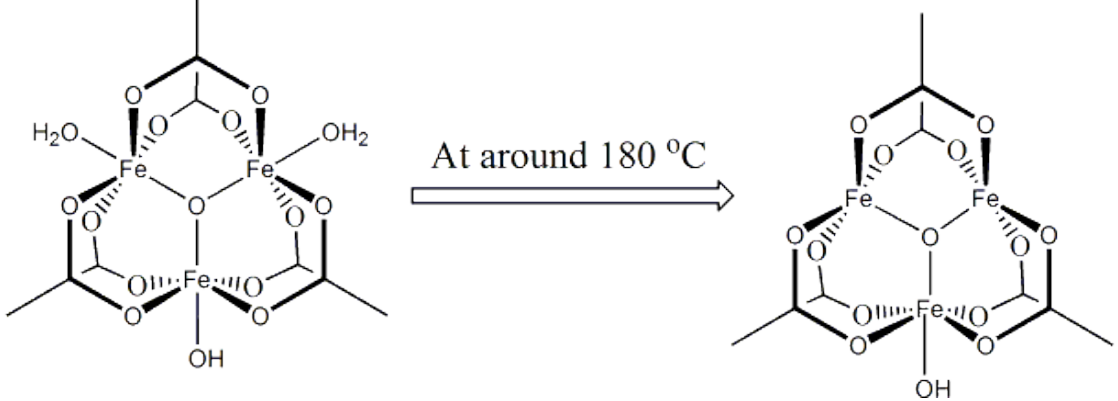
| | BET surface area ( $m^2$ / g ) | Excess $H_2$ uptake predicted by Chahine's Rule( wt%) | Experimental excess $H_2$ uptake ( wt% ) |
|---|---|---|---|
| PCN-250 | 1600 | 3.2 | 4.8 |

# Accomplishments and Progress: Understanding of MOF activation

- Activation of PCN-250-$Fe_3$
  - Stage 1: removal of the free solvent molecules inside the pore




  - Stage 2: removal of the free neutral species coordinated to the cluster

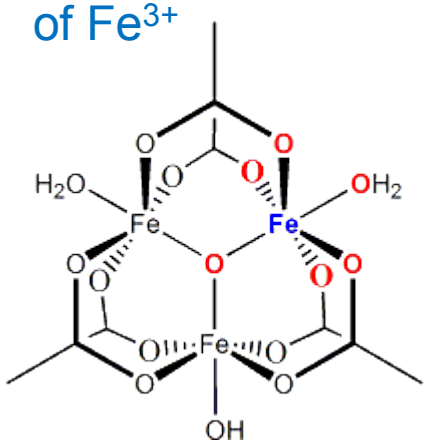


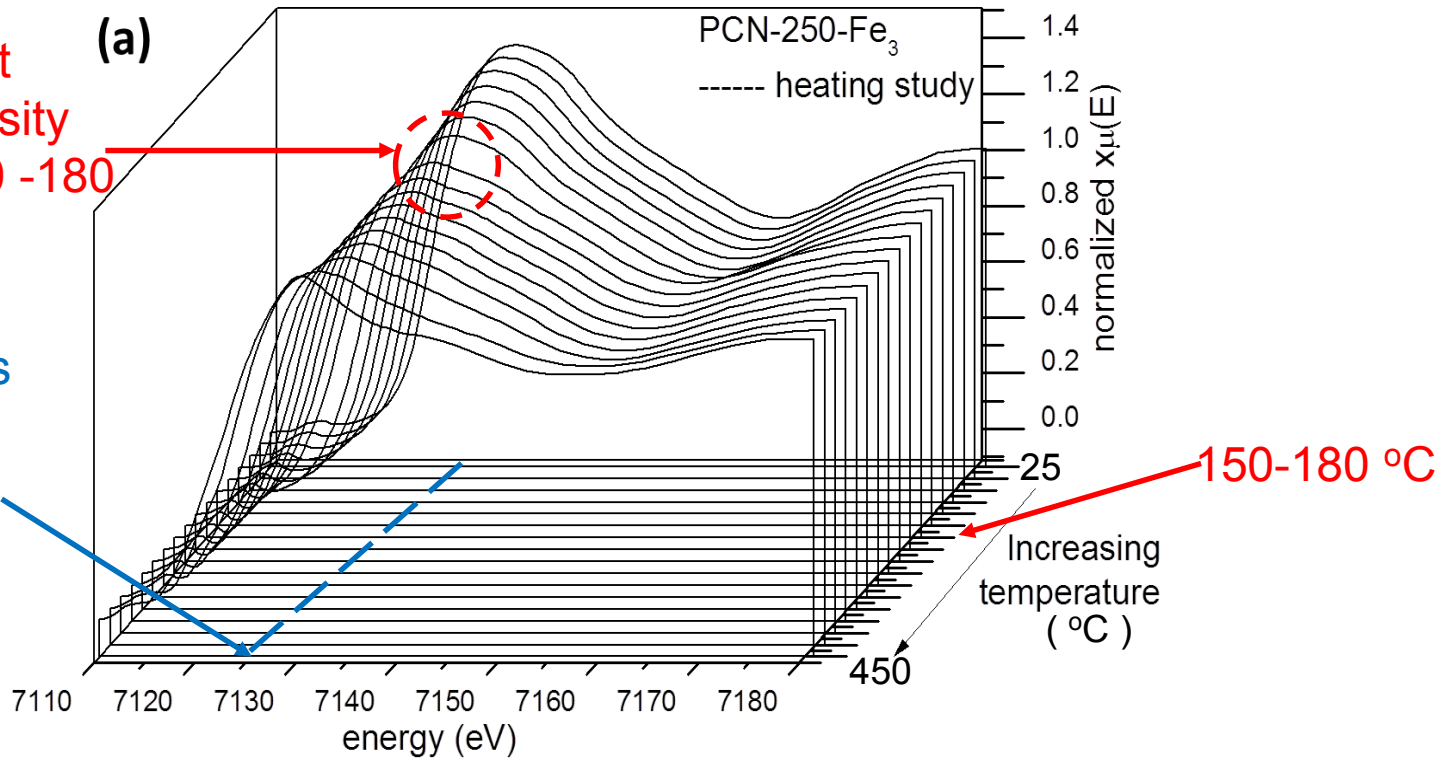
# Accomplishments and Progress: Understanding of MOF activation

- The progression of XANES spectra of PCN-250

relatively fast drop of intensity between 150 -180 °C

Peak at 7125 eV is related to the first coordination shell of $Fe^{3+}$

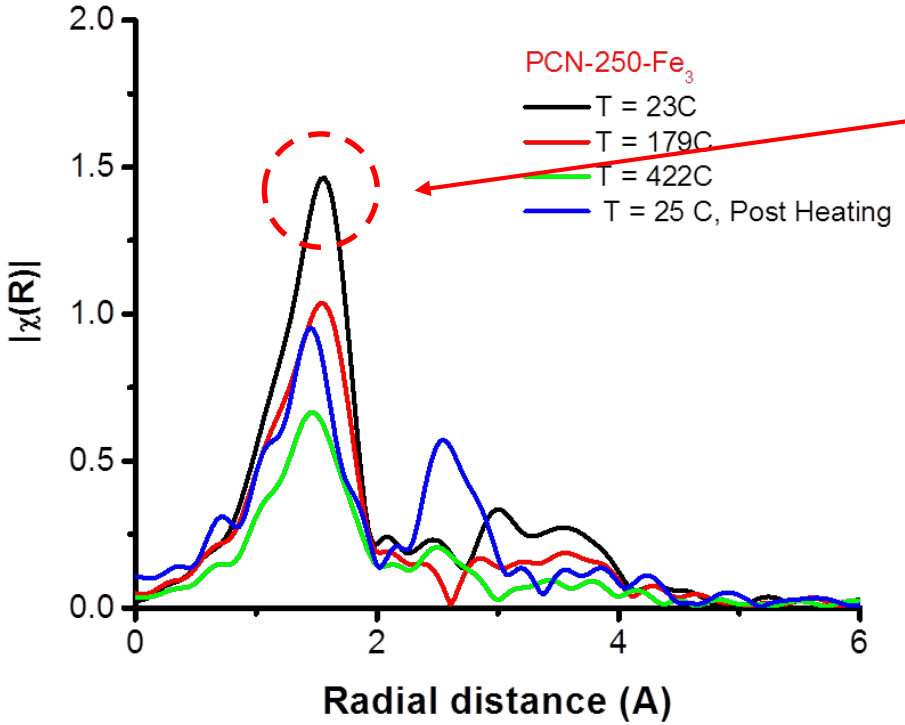


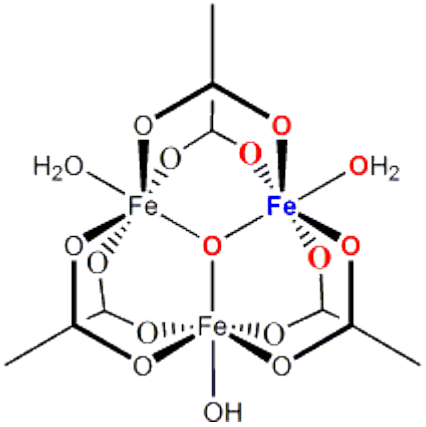

The progression of XANES spectra of (a) PCN-250-$Fe_3$ as the heating temperature increases.

# Accomplishments and Progress: Understanding of MOF activation

- Radial distribution functions of PCN-250



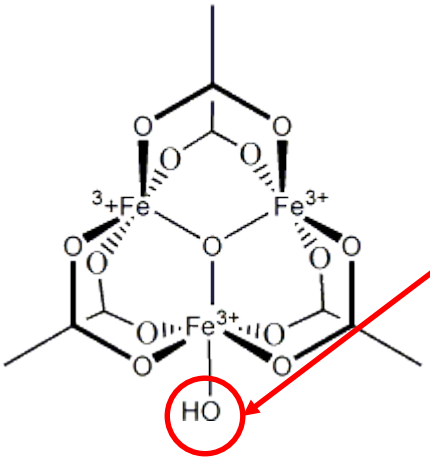

Related to the first coordination shells of $Fe^{3+}$




Radial distribution functions (RDF) of PCN-250-$Fe_3$ derived from Fourier transformation of EXAFS spectra taken at selected temperature. "Post Heating" refers to the EXAFS taken after the samples were cooled to the ambient temperature. RDF of iron foil was also included as the reference.

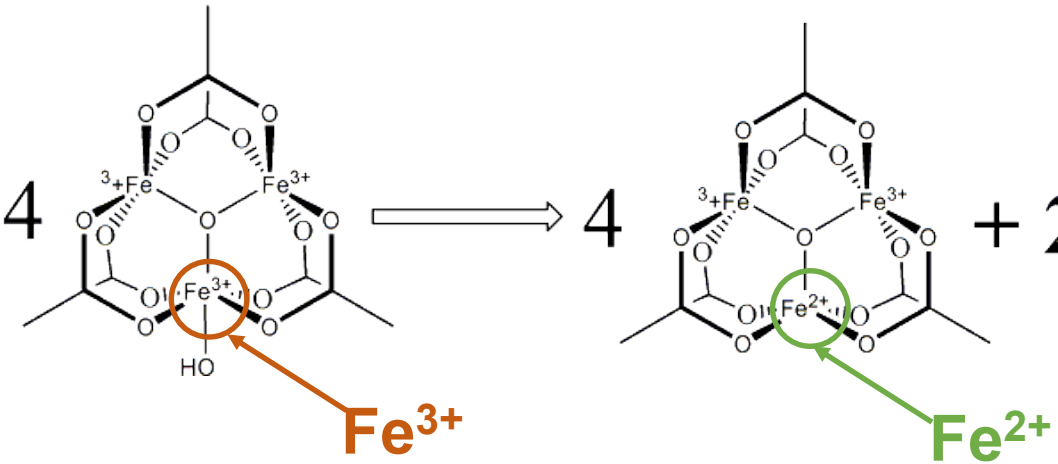
# Accomplishments and Progress: Understanding of MOF activation

- Activation of PCN-250-$Fe_3$
  - Stage 3: removal of the hydroxide group from cluster (very difficult)




Hydroxyl group is required to balance the charge of cluster

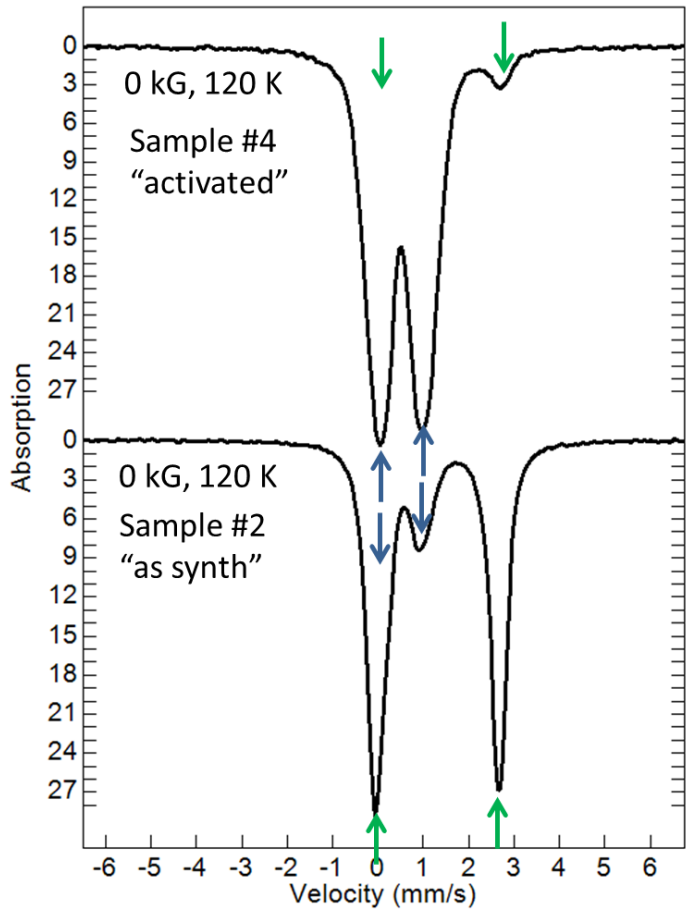
Unless the oxidation state of $Fe^{3+}$ could change




$$+ 2H_2O + O_2$$

# Accomplishments and Progress: Understanding of MOF activation

- Mössbauer spectrum of As-synthesized and activated MOF-74-Fe

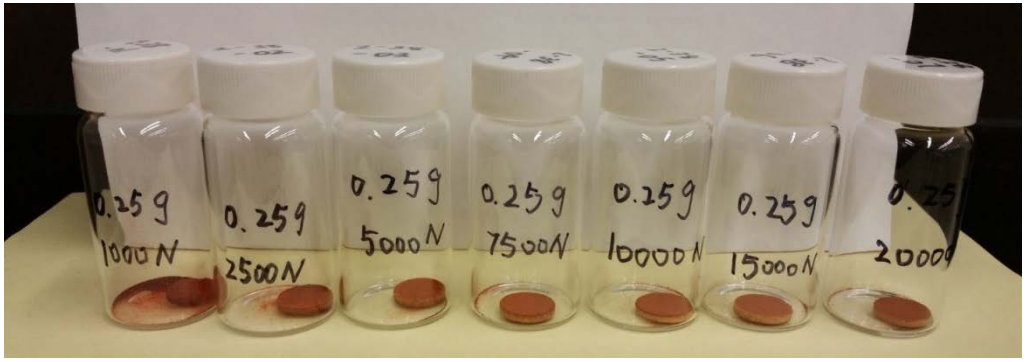



| Sample | $\Delta E_q$ | δ | Γ | % | species |
|---|---|---|---|---|---|
| Activated MOF-74-Fe | 2.69 | 1.28 | 0.35 | ~5 | HS Fe(II) |
| | 0.9 | 0.58 | 0.35 | ~90 | HS Fe(III) |
| As synthesized MOF-74-Fe | 2.69 | 1.28 | 0.35 | ~78 | HS Fe(II) |
| | 0.7 | 0.58 | 0.35 | ~20 | HS Fe(III) |

* The measurement of Mössbauer spectrum were conducted by the group of Professor Catalina Achim, Carnegie Mellon University

# Accomplishments and Progress: Improving Packing Density of PCN-250-$Fe_3$

- From powders to pellets



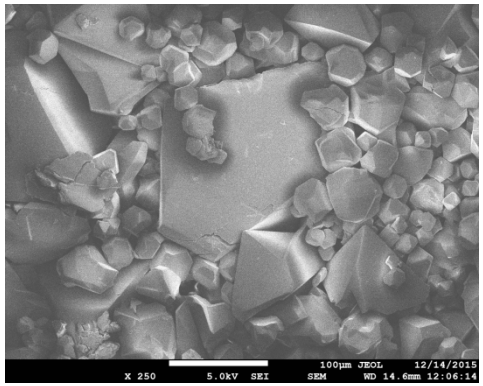
Load : 1000, 2500, 5000, 7500, 10000, 15000, and 20000 N.

Diameter of pellet: 12.8 mm

- SEM

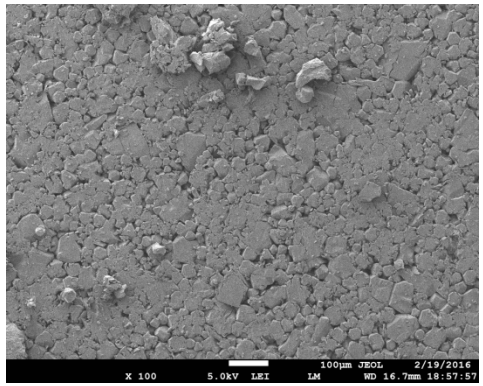
Under 1000 N

(A)




Under 15000 N

(B)



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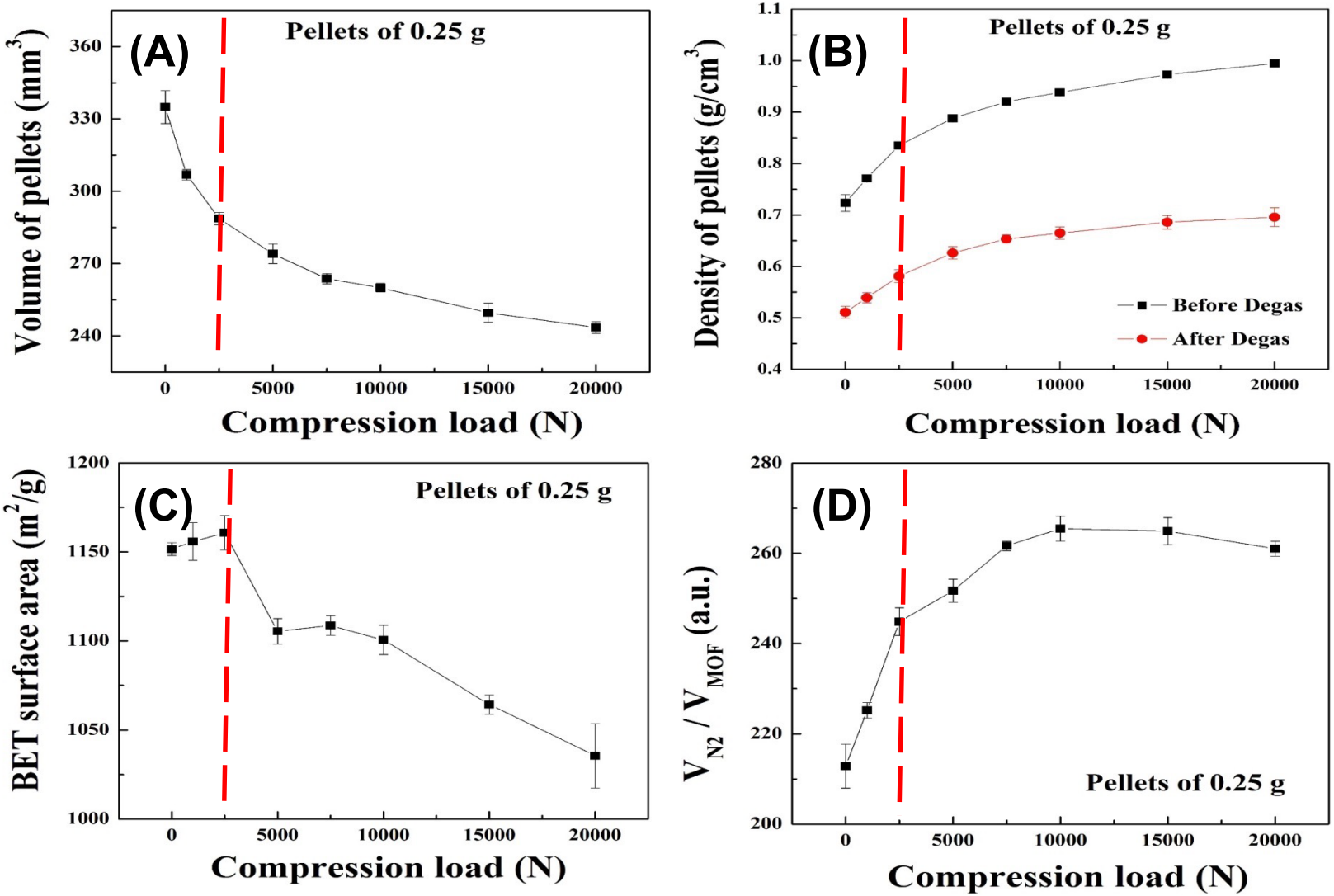


# Accomplishments and Progress: Improving Packing Density of PCN-250-$Fe_3$

- Without optimization of packing:

| Max Gravimetric Excess ( wt% ) | Calculated crystal density ( g / L ) | Calculated Excess Volumetric ( g $H_2$ / L ) | Experimental Max Excess Volumetric ( g$H_2$ / L ) | Experimental packing efficiency (%) |
|---|---|---|---|---|
| 4.8 | 970 | 46.6 | 12 | ***25.8*** |

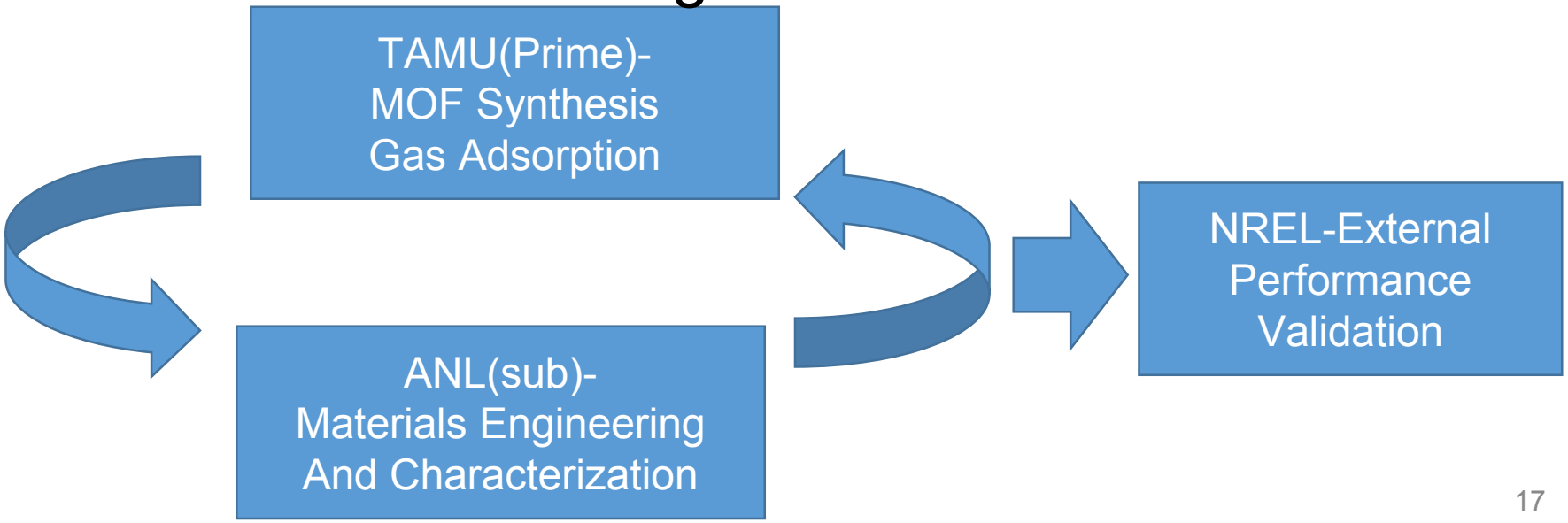
* The experimental volumetric $H_2$ uptake of PCN-250 at 75.6 K was measured by NREL.

- With optimization of packing:

| Calculated crystal density ( g / L) | Experimental pellet density ( g / L ) | Calculated packing efficiency (%) |
|---|---|---|
| 970 | 600 | ***61.8*** |

# Collaboration

- TAMU will design, synthesize, and characterize new MOF materials
- ANL will perform X-ray characterization studies, develop ZDC based binding agents and perform ALD Studies
- All deliverables will be sent to NREL  or another lab of EERE's choosing for Validation



# Remaining Challenges and Barriers

- Challenges:
  - The performance of different batches of MOF samples varies

- Planned resolutions:
  - To explore the optimized activation condition to trigger the oxidation state of iron ions in PCN-250 to remove the hydroxyl groups from clusters and increase porosity and sorbate-affinity of MOF
  - To cooperate with other research groups and institutes to confirm the repeatability and recyclability of PCN-250 in hydrogen storage

# Proposed Future Work

| Milestone Number | Milestone Description | Anticipated Quarter |
|---|---|---|
| 2 | ➢ Complete the first advanced X-ray absorption and Mössbauer spectroscopic (XAS) study of PCN-250 to explore the oxidation state change of $Fe^{3+}$ during activation<br>➢ Provide quantitative interpretation of exchanged oxidation state changes in relationship with adsorption enthalpy improvement for 4 MOFs | 3 |
| 3 | ➢ Develop over 4 MOF sorbents with surface area over 1500 $m^2$ / g and gravimetric capacity of 50% over Chahine Rule | 4 |

# Summary of Accomplishments and Progress

- Developed a fundamental pathway to exceed typical Chahine Rule Adsorption for MOFs
- Identified advantages of PCN-250 as a hydrogen storage material and measured $H_2$ uptake with good agreement with NREL data
- Detailed characterization of the activation procedure of PCN-250
  - ✓ Explored the required activation temperature to remove the coordinated solvent molecules
  - ✓ Observed the oxidation state change of $Fe^{3+}$ in MOF during activation, which could help to remove the hydroxyl group coordinated on cluster of PCN-250
- Improvement of Packing Density of PCN-250
  - ✓ By compressing MOF powder into pellets under optimized pressure, the packing density of PCN-250 is increased 2.4 times