ST211

HyMARC Seedling

Optimal Adsorbents for Low-Cost Storage of Natural Gas and Hydrogen:

Computational Identification, Experimental Demonstration, and System-Level Projection

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2020 DOE Hydrogen and Fuel Cells Program Annual Merit Review

Overview

Timeline and Budget

Project Start Date: Jan. 1st, 2020

Project End Date: Dec. 31st, 2022

Total Project Budget: $1,250,000

Federal Share:

UM: $900,000

SRNL: $100,000

Total: $1,000,000

$300,000 (Y1)
$350,000 (Y2)
$350,000 (Y3)

Cost Share: $250,000 (UM)

Total Funds Spent:* ~$80,000

*Estimated as of 4/1/20

Barriers

Barriers addressed

- Volumetric Density
- Gravimetric Density

Partners

Interactions/collaborations:

Ford Motor Company, Hydrogen Storage Engineering Center of Excellence (HSECoE)

Project lead:

Don Siegel, University of Michigan

Relevance (1)

- The Natural Gas Vehicle Research Roadmap[1] has identified vehicle driving range "and the associated challenges with on-board storage of fuel" as a "significant barrier for natural gas vehicles across all vehicle classes."
  - This challenge is attributed to the "storage capacity, size, weight, shape, and cost of compressed natural gas cylinders."
  - Storage via adsorption in MOFs is promising due to their fast kinetics, reversibility, and tunable properties
- A viable adsorbent must exhibit a high intrinsic (i.e., materials level) natural gas capacity, and pack in a dense fashion at the system level

Project goal: Demonstrate adsorbents that when incorporated into an adsorbed NG system have the potential to surpass the capacity of CNG systems, allowing for systems that are smaller and lighter, yet operate at lower pressures.

Relevance (2)

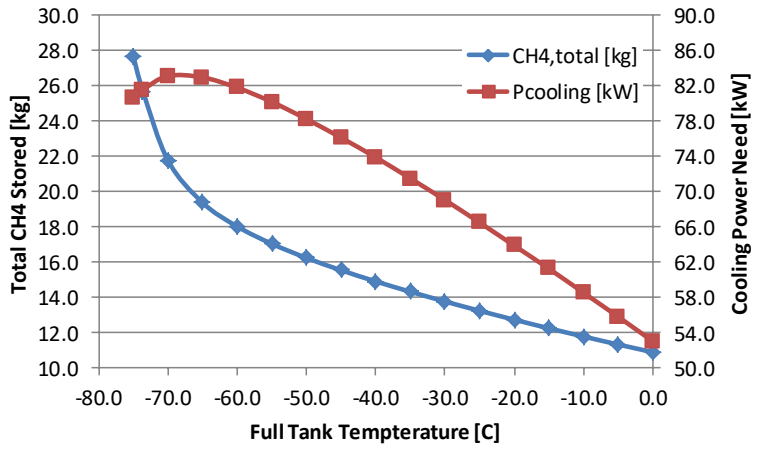
- The number of known MOFs greatly exceeds the number experimentally investigated for methane/H_2 storage.
- Virtual high throughput screening requires both quality structural information and robust prediction strategies.
  - Many interactions with coordinatively unsaturated metal sites are not well described by simple theory
- The design principles for new high capacity NG sorbents are not well understood
  - The simple relationship between high surface area and high gravimetric hydrogen storage does not have an analog in NG
  - Additional selectivity issues arise due to the complex composition of NG
- Once target MOFs are identified they must be produced in activated form with intact structure.

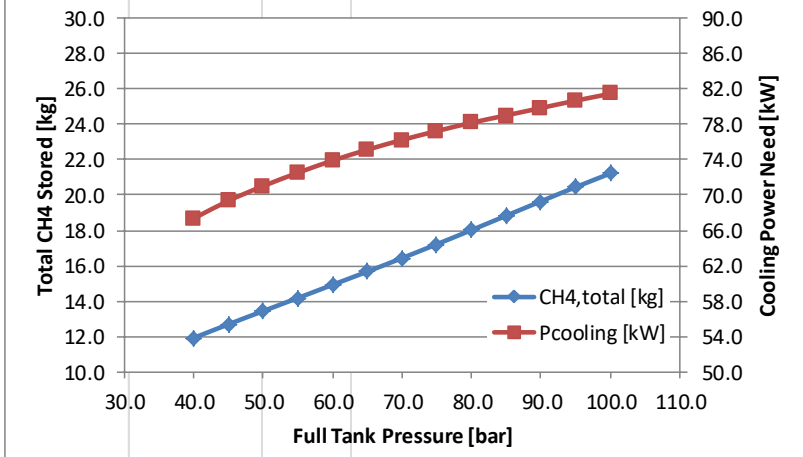
Approach

- High-throughput computational screening coupled to machine learning will be used to identify MOFs that simultaneously achieve high usable gravimetric and volumetric capacities for natural gas (NG).
- The most promising materials pinpointed by computation will be synthesized and characterized experimentally.
- The performance of the best materials will be projected to the system level using a modeling framework initially developed by the Hydrogen Storage Engineering Center of Excellence (HSECoE).
  - As part of this project the developer of these models, Savanah River National Laboratory, will extend the HSECoE models to NG.
- A distinguishing feature of this project is the application of computational models to optimize and project the performance of the full-scale MOF-based storage system.

ANG Systems Overview

	System	T_{empty} [°C]	P_{empty} [bar]	T_{full} [°C]	P_{full} [bar]	$CH4_{stored}$ [kg]	Vol_{sys} [L]	$Mass_{sys}$ [kg]	$Cost_{sys}$ [$]	Volumetric Capacity [MJ/L_{sys}]	Gravimetric Capacity [g/g_{sys}]	V-to-V (0 °C, 1 bar)	System Notes
CNG System	#0	25.00	5.00	79.16	312.50	22.421	176.03	104.83	$2,276.80	6.368	0.2139	243.71	-- No cooling during refueling -- Equilibrium with ambient prior to refueling -- Allowed 25% overpressure (temp. corr.)
Adsorbent only	#1	25.00	5.00	64.81	60.00	7.448	176.03	84.83	**$1,177.48**	2.115	0.0878	68.07	-- No cooling during refueling -- Equilibrium with ambient prior to refueling
Adsorbent with Cold gas only	#2	(20.00)	5.00	17.64	60.00	8.079	176.03	96.09	**$1,301.80**	2.295	0.0841	85.53	-- Cold-gas cooling only -- No onboard cooling -- On-board heating available -- No guard bed
Adsorbent, cold gas, and off-board coolant	#3	65.00	5.00	(40.00)	60.00	14.918	176.03	105.12	**$1,447.57**	4.237	0.1419	159.82	-- On-board heating available -- Cold-gas supply available (-40 C) -- Off-board cooling system -- No guard bed
Adsorbent, cold gas, and off-board coolant	#3 T_{full} Variation	65.00	5.00	(73.62)	60.00	25.703	176.03	105.12	**$1,447.57**	**7.301**	**0.2445**	**275.36**	-- On-board heating available -- Cold-gas supply available (-73.62 C) -- Off-board cooling system -- No guard bed
Adsorbent, cold gas, and off-board coolant	#3 P_{full} Variation	65.00	5.00	(40.00)	100.00	21.217	176.03	130.99	**$1,561.92**	6.026	0.1620	227.30	-- On-board heating available -- Cold-gas supply available (-40 C) -- Off-board cooling system -- No guard bed





Project objectives (1)

- Systematically predict the *usable* methane capacities of ~500,000 real and hypothetical MOFs contained in the PI's MOF database using a combination of crystal structure analysis, Grand Canonical Monte Carlo (GCMC), and machine learning (ML).
- Generate a database of 3 million metal-substituted CUS MOFs; apply the PI's customized interatomic potential to predict CH_4 uptake in these MOFs via screening and ML.
- Disseminate the computational data generated by these screening studies to the public via the HyMARC Data Hub.
- Based on the computational predictions, synthesize, activate, and characterize the CH_4 capacities of the most promising MOFs.

Project objectives (2)

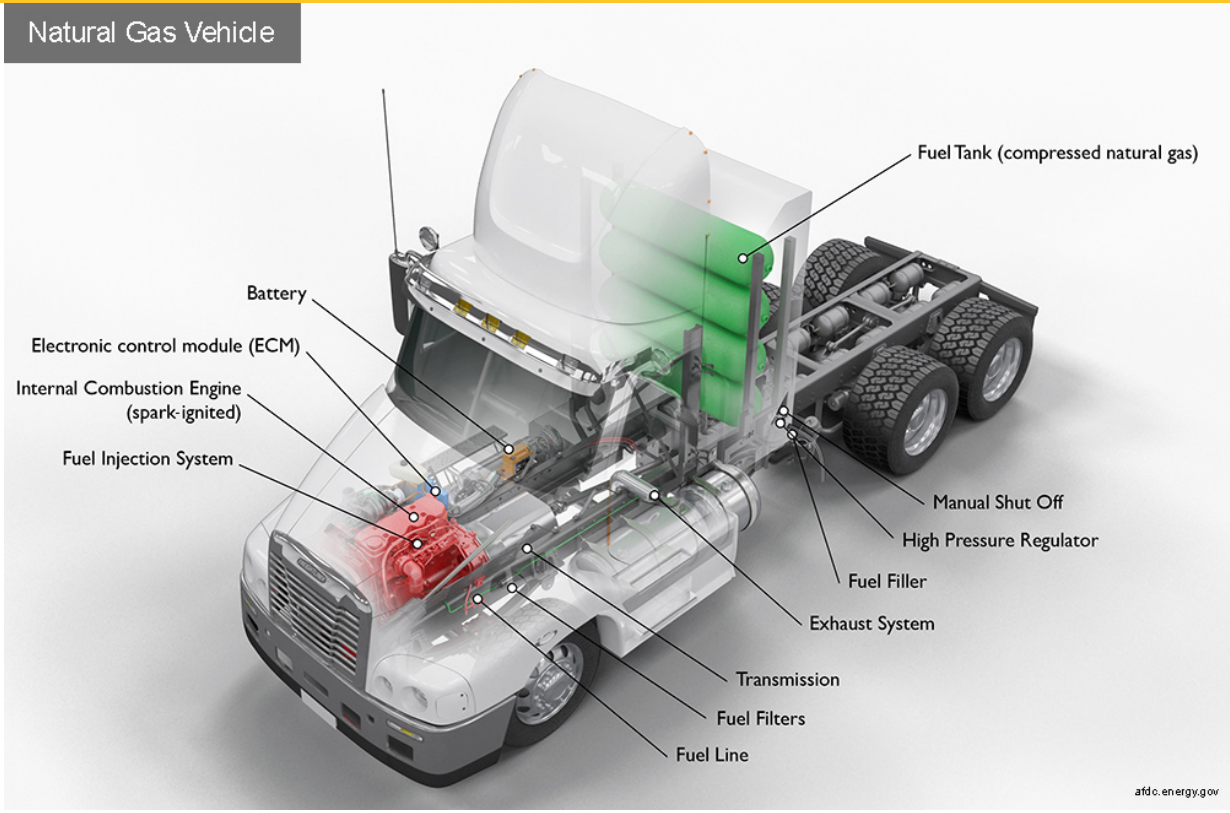
- For the highest-capacity MOFs, quantify robustness with respect to minority species (beyond CH_4) present in realistic NG streams.
- Adapt system-level storage models initially developed by the HSECoE for H_2 storage to NG; perform parametric analyses with these models to determine the optimum system parameters (e.g. tank type, dimensions, heat exchanger, MOF compaction level, etc.) and operating conditions (e.g. maximum pressure, minimum/maximum temperature, etc.).
- For the highest-capacity MOFs and optimal system designs, project performance to the system level.
- In total, establish a new high-water mark for adsorptive NG storage by demonstrating MOFs that surpass the capacity of state-of-the-art NG adsorbents (such as HKUST-1) by at least 15% and that exhibit resilience to common NG impurities.

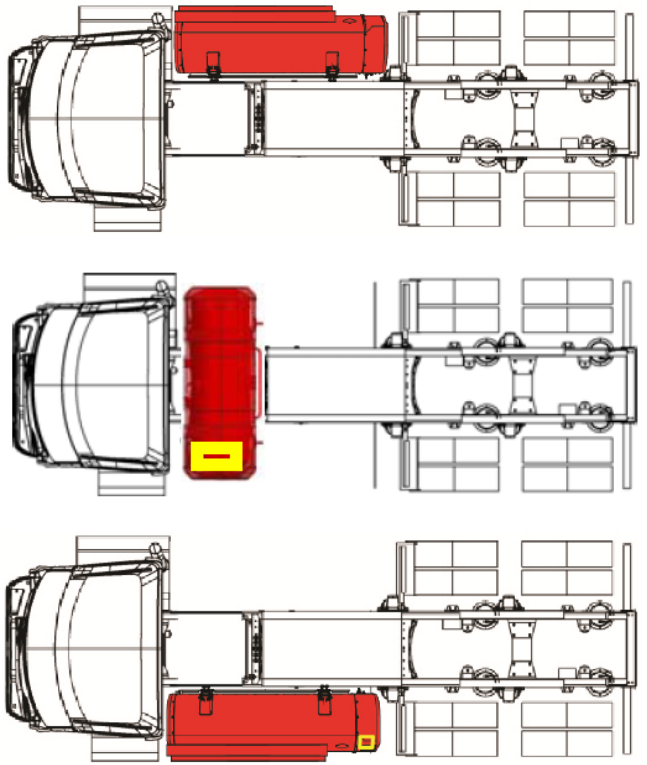
Year 1 Milestones

Milestone Summary Table				
Recipient Name:		University of Michigan (PI: Siegel)		
Project Title:		Optimal Adsorbents for Low-Cost Storage of Natural Gas and Hydrogen: Computational Identification, Experimental Demonstration, and System-Level Projection		
Task Number	**Task or Subtask Title**	**Milestone Type**	**Milestone Description**	**Quarter (from Start)**
1.1	Computational Screening – Force-field validation	Milestone	Predict isotherms for several benchmark MOFs, including HKUST-1 and UTSA-76, as a function of interatomic potential	1
2.1	Experiments – Benchmark Adsorbents	Milestone	Synthesize & characterize methane uptake on several benchmark MOFs, including HKUST-1 and UTSA-76. Based on comparison with computed isotherms, identify accurate interatomic potential	2
1.2	Computational Screening – Initial CUS screening	Milestone	Complete pre-screening of structural properties on database of ~180,000 CUS MOFs; Run GCMC on subset; use this subset as initial target MOFs for experiments, and as a training set for ML.	3
3.1	System Modeling – Establish baseline CNG system performance	Milestone	Complete baseline CNG system model for heavy duty vehicles; apply model to predict gravimetric capacity, volumetric capacity, and to estimate costs	4
1.3	Computational Screening + Experiments	Go/No-Go	Demonstrate one of the following: **For Methane**: Based on computational screening of up to 180,000 CUS MOFs: (a) experimentally demonstrate at least one MOF that exceeds the usable methane capacity of HKUST-1 (nominally 190-200 v/v for P_{max} = 80 or 65 bar, P_{min} = 5 bar) or (b) computationally identify at least 100 MOFs that are predicted to exceed the methane capacity of HKUST-1 on a usable basis, or **For Hydrogen**: (c) Using an interatomic potential optimized for H_2/CUS interactions, complete screening on at least 7,000 CUS MOFs for their H_2 capacities, and upload this data to the HyMARC Data Hub	4

Accomplishments and Progress

Natural Gas Storage System (1)

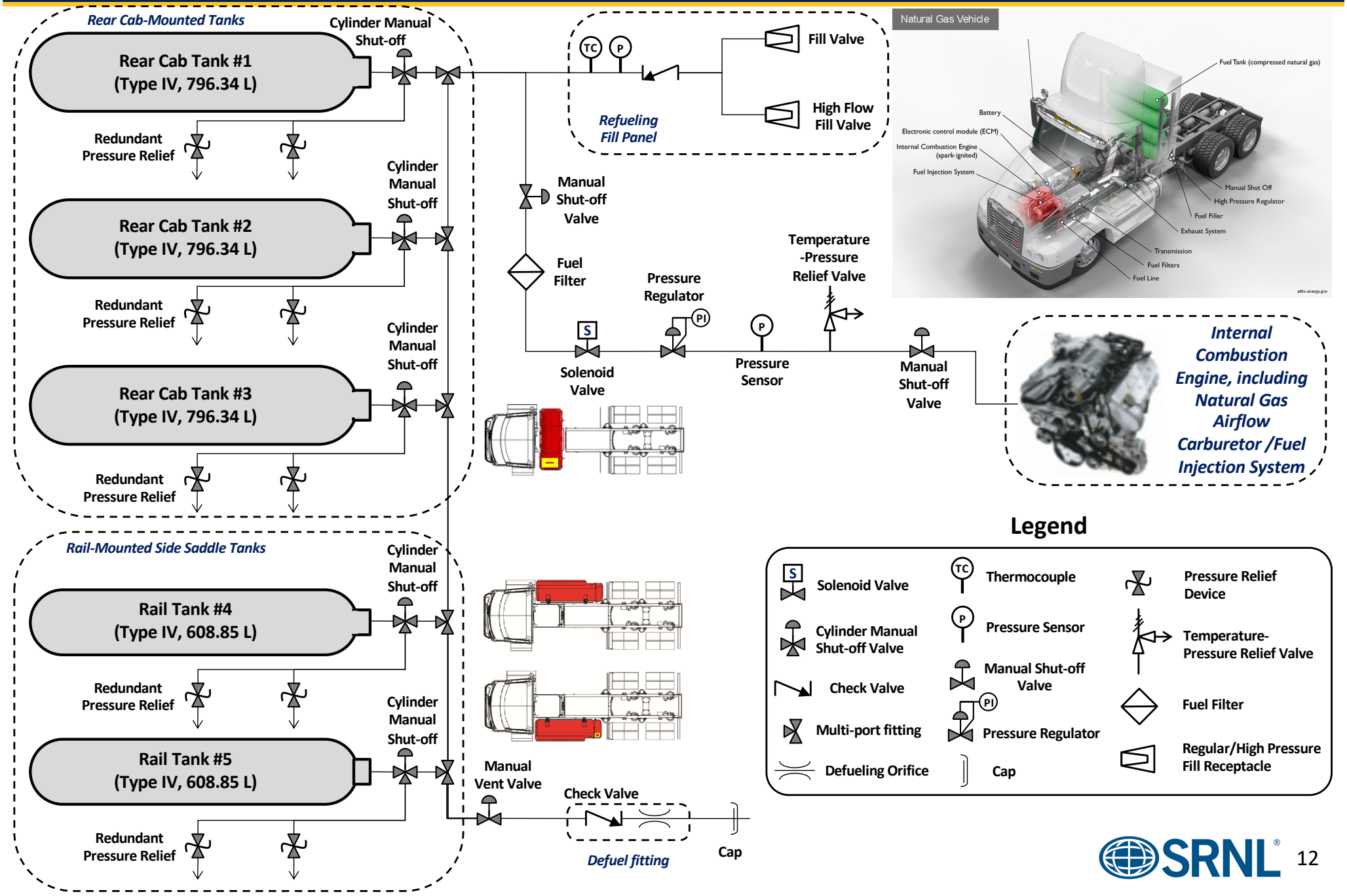




- CNG Storage System Design is based on the Side/Rail-mounted and Rear Cab-mounted storage systems from Quantum Fuel Systems (www.qtww.com)
- Rear Cab-mounted CNG storage:
  - Total gas storage (3x pressure vessels) – 450.4 kg of NG
  - Total usable storage (20 to 250 bar at 20 °C) – 391.4 kg of NG
- Side/Rail-mounted CNG storage:
  - Total gas storage (2x pressure vessels) – 231.3 kg of NG
  - Total usable storage (20 to 250 bar at 20 °C) – 200.5 kg of NG
- Expected range – 1392 miles at 6 mpge

SRNL

Natural Gas Storage System (2)



Storage Targets

ARPA-E MOVE Target

Volumetric energy density	Gravimetric energy density
> 315 cm^3 (STP) /cm^3 (sorbent)	> 0.5 g_{CH4} /$g_{sorbent}$

Temperature range: -40 ℃ (233 K) to 85℃ (358 K)
Adsorption pressure: < 3600 psi, or 250 bar
Desorption pressure: > 70 psig, or 4.83 bar
Engine inlet pressure must be greater than 70 psig.

"A specific natural gas storage and compression pressure is not prescribed, except that the system should not exceed 250 bar (3,600 psi). Instead, this program establishes an overall system energy density requirement that should meet or exceed CNG (250 bar)."
Source: https://arpa-e.energy.gov/sites/default/files/documents/files/MOVE_ProgramOverview.pdf

The initial target for this project is to exceed the performance of state-of-the-art materials HKUST-1 and UTSA-76

Pressure Swing: 65/5 bar at 298 K

MOF	Usable gravimetric capacity (g/g)	Usable volumetric capacity cm^3/cm^3
HKUST-1	0.154	190
UTSA-76	0.201	197

Pressure Swing: 80/5 bar at 298 K

MOF	Usable gravimetric capacity (g/g)	Usable volumetric capacity cm^3/cm^3
HKUST-1	0.162	200
UTSA-76	No data	No data

Michigan Open Metal Site (MOMS) Potential

MOMS = (OMS - CH_4 Interactions) + (Non-metal Site - CH_4 Interactions)

Non-metal Site - CH_4 Interactions:

Lennard-Jones Potential, LJ (12, 6): $U(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$

$\varepsilon \rightarrow$ Depth of the potential well in binding energy curve

$\boldsymbol{\sigma} \rightarrow$ Distance at which the interatomic potential is zero

OMS - CH_4 Interactions:

Morse Potential: $U(r) = D_0\left[\left(1 - e^{-\alpha(r-R_0)}\right)^2 - 1\right]$

$\boldsymbol{\alpha} \rightarrow$ Regulates overall shape of the curve

D_0 (analogous to ε in LJ potential) $\rightarrow$ Depth of the potential well

R_0 (analogous to $\boldsymbol{\sigma}$ in LJ potential) $\rightarrow$ Distance at which the interatomic potential is zero

1. H. S. Koh, M. K. Rana, A. G. Wong-Foy, D. J. Siegel, J. Phys. Chem. C **119**, 24, 13451-13458 (2015).

Interatomic Potentials from the Literature

Molecular Representation for Interatomic Potential Development

All atom CH_4 molecule United atom (UA)/pseudo CH_4 model

Interatomic Potential Parameters for CH_4 Molecule

Interatomic Potential	Developer	Molecule	ε (K)	σ (Å)	Interaction type
TraPPE-UA	Siepmann & co-workers [1]	Pesudo-CH_4	148	3.73	Lennard-Jones (12,6)
OPLS-UA	Jorgensen & co-workers [2]	Pesudo-CH_4	147.9	3.73	Lennard-Jones (12,6)
VSH-UA	Hasse & coworkers [3]	Pesudo-CH_4	148.55	3.7281	Lennard-Jones (12,6)
YZLZ-UA	Zhao & coworkers [4]	Pesudo-CH_4	147.947	3.751	Lennard-Jones (12,6)
GWMW-UA	Quirke & coworkers [5]	Pesudo-CH_4	147.95	3.73	Lennard-Jones (12,6)

Interatomic Potential Parameters for MOF Atoms were adapted from the Universal Force Field [6]

1. **TraPPE-UA:** M. G. Martin and J. I. Siepmann, J. Phys. Chem. B **102**, 2569-2577 (1998).
2. **OPLS-UA:** W. L. Jorgensen, D. S. Maxwell and J. Tirado-Rives, J. Am. Chem. Soc. **118**, 11225−11236 (1996).
3. **VSH-UA:** J. Vrabec, J. Stoll and H. Hasse, J. Phys. Chem. B **105**, 12126-12133 (2001).
4. **YZLZ-UA:** Q. Yuan, X. Zhu, K. Lina and Y.-P. Zhao, Phys. Chem. Chem. Phys. **17**, 31887-31893 (2015).
5. **GWMW-UA:** S. J. Goodbody, K. Watanabe, D. MacGowan, J. P. R. B. Walton and N. Quirke, J. Chem. Soc., Faraday Trans. **87**, 1951-1958 (1991).
6. **UFF:** A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard III and W. M. Skiff, J. Am. Chem. Soc. **114**, 10024-10035 (1992).

Grand Canonical Monte Carlo (GCMC)

CH_4 storage capacities in MOFs are predicted using Grand Canonical Monte Carlo (GCMC)

- Equilibration cycles: 2,000
- Data collection cycles: 3,000
- Cycle = Random (Insertion + Deletion +Translation) moves. All moves have equal probability.
- Monte Carlo Steps ≈ Number of cycles × Number of molecules in the simulation cell at the beginning of the simulation
- Interactions between non-metallic UFF [1] MOF atoms and TraPPE [2] pseudo-CH_4 molecules were calculated using Lorentz-Berthelot [3,4] mixing rules:

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2}$$

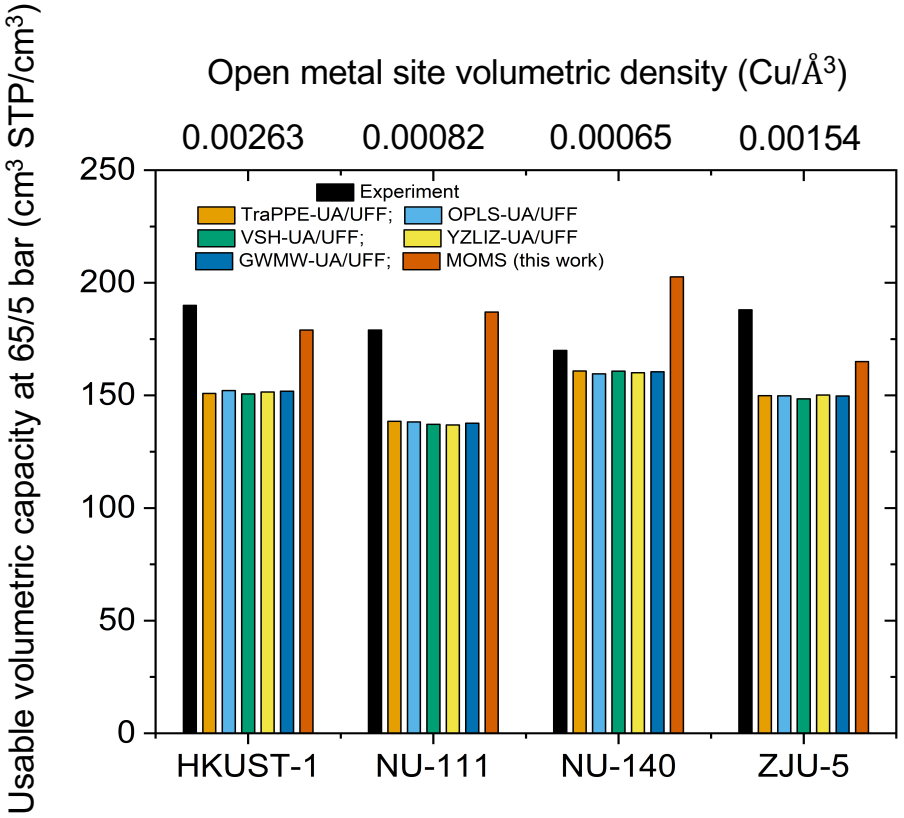
$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}$$

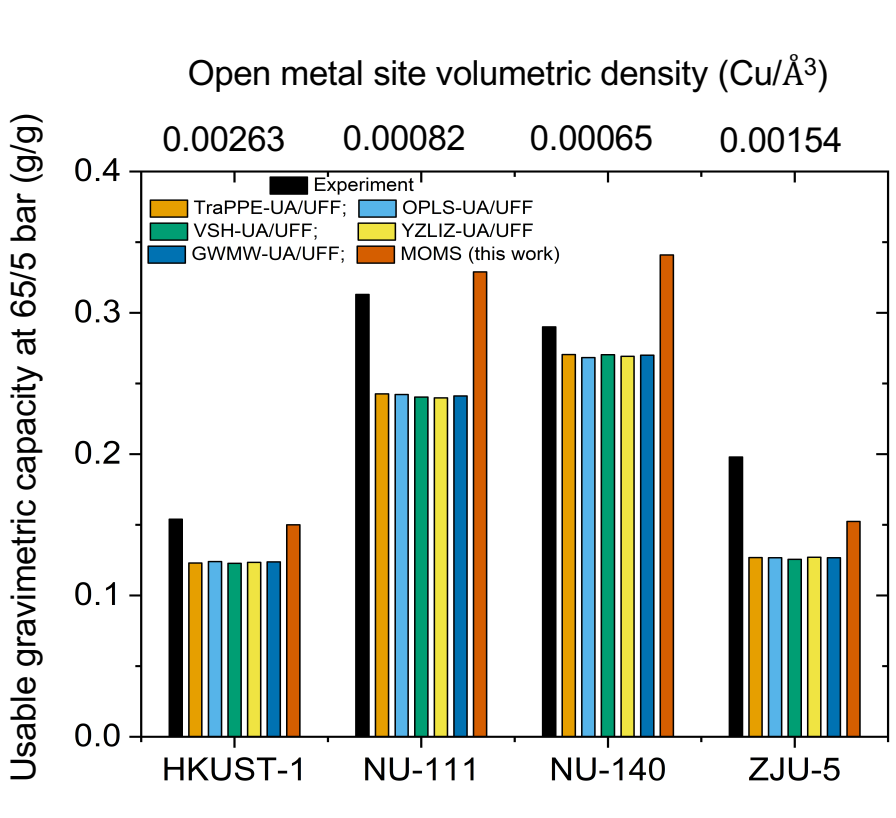
- All simulations were carried out using the RASPA [5] code.
- Crystallographic properties were calculated using the Zeo++ [6] code.

1. A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard III and W. M. Skiff, J. Am. Chem. Soc. **114**, 10024-10035 (1992).
2. M. G. Martin and J. I. Siepmann, J. Phys. Chem. B **102**, 2569-2577 (1998).
3. H. A. Lorentz, Annalen der Physik. **248**, 127–136 (1881).
4. D. Berthelot, Comptes rendus hebdomadaires des séances de l'Académie des Sciences, **126**, 1703-1855 (1898).
5. D. Dubbeldam, S. Calero, D. E. Ellis and R. Q. Snurr, Mol. Sim. **42**, 81-101 (2016).
6. T.F. Willems, C.H. Rycroft, M. Kazi, J.C. Meza, and M. Haranczyk, Microporous Mesoporous Mater. **149**, 134-141 (2012)

Comparison of Interatomic potentials for OMS MOFs

Compared to other potentials, the MOMS interatomic potential more accurately predicts experimental CH_4 uptake in Cu-paddlewheel MOFs.





Experiment: Y. He, F. Chen, B. Li, G. Qian, W. Zhou, B. Chen, Coord. Chem. Rev. **373**, 167-198 (2018)
MOMS: H. S. Koh, M. K. Rana, A. G. Wong-Foy, D. J. Siegel, J. Phys. Chem. C **119**, 13451-13458 (2015).
TraPPE-UA: M. G. Martin and J. I. Siepmann, J. Phys. Chem. B **102**, 2569-2577 (1998).
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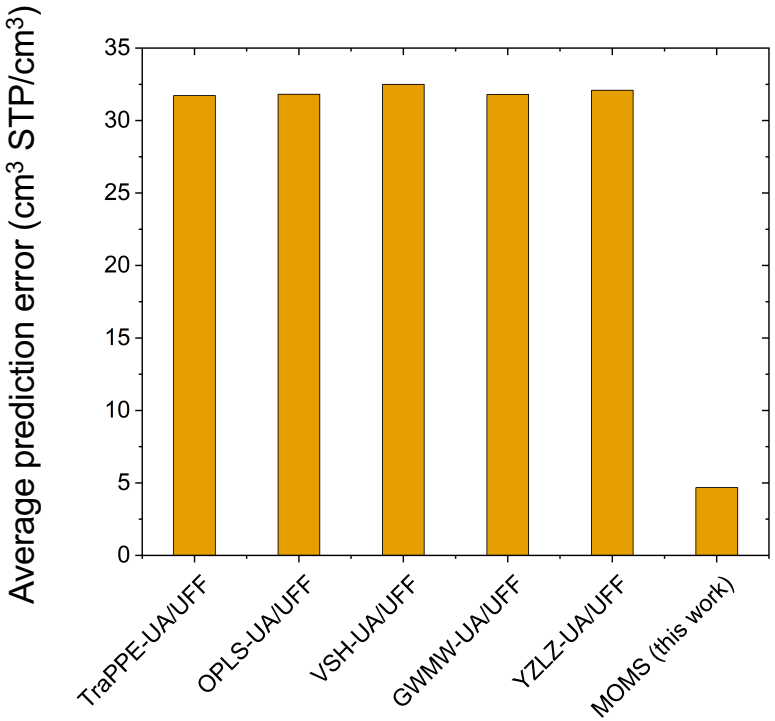
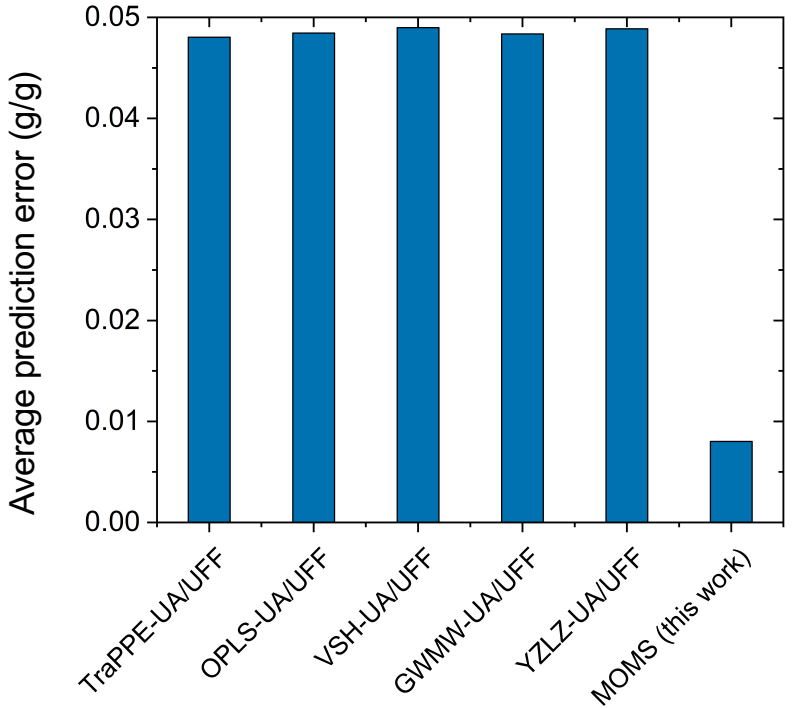
Comparison of Interatomic potentials for OMS MOFs

MOMS potential yields good accuracy in the prediction of CH_4 adsorption in Cu-paddlewheel MOFs.





Experiment: Y. He, F. Chen, B. Li, G. Qian, W. Zhou, B. Chen, Coord. Chem. Rev. **373**, 167-198 (2018)
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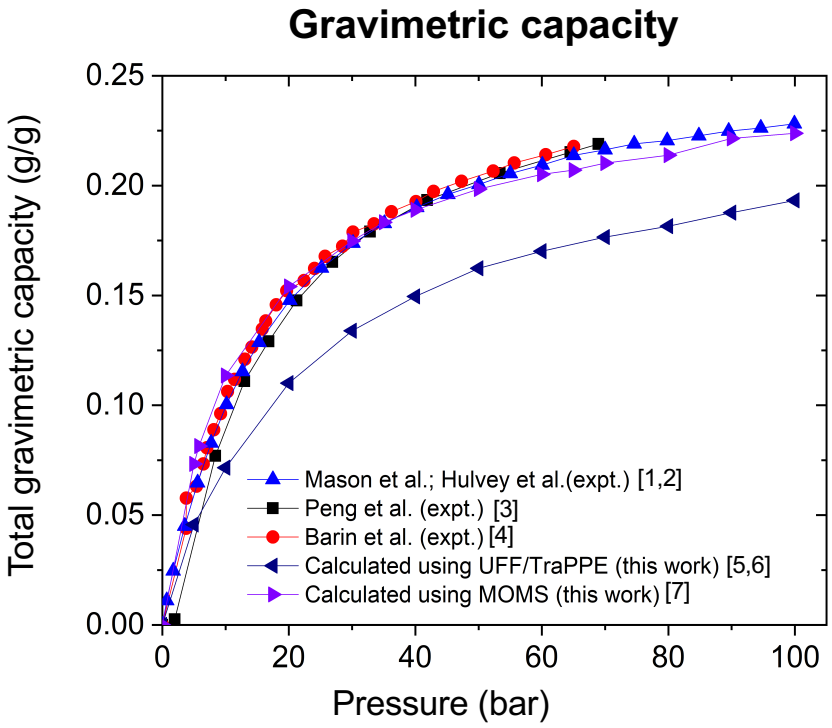
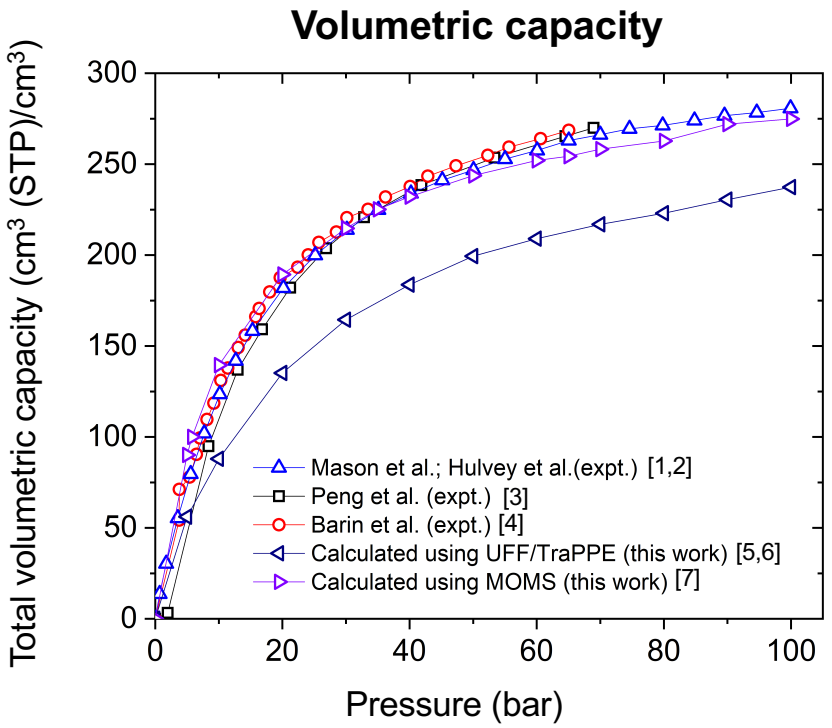
Benchmarking Interatomic Potentials for HKUST-1 (1)

- Recent experiments [1-4] report reproducible measurement of CH_4 uptake in HKUST-1.
- General (UFF/TraPPE) [6,7] interatomic potential under-predicts CH_4 uptake in HKUST-1.
- MOMS potential shows improved accuracy.





1. J. A. Mason, M. Veenstra and J. R. Long, Chem. Sci. **5**, 32-51 (2014).
2. Z. Hulvey, B. Vlaisavljevich, J. A. Mason, E. Tsivion, T. P. Dougherty, E. D. Bloch, M. Head-Gordon, B. Smit, J. R. Long, C. M. Brown, J. Am. Chem. Soc. **137**, 10816−10825 (2015).
3. Y. Peng, V. Krungleviciute, I. Eryazici, J. T. Hupp, O. K. Farha, T. Yildirim, J. Am. Chem. Soc. **135**, 11887-11894 (2013).
4. G. Barin, V. Krungleviciute, I. Eryazici, J. T. Hupp, O. K. Farha, T. Yildirim, Inorg. Chem. **53**, 6914-6919 (2014).
5. A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard III and W. M. Skiff, J. Am. Chem. Soc. **114**, 10024-10035 (1992). [UFF interatomic potential]
6. M. G. Martin and J. I. Siepmann, J. Phys. Chem. B **102**, 2569-2577 (1998). [TraPPE interatomic potential]
7. H. S. Koh, M. K. Rana, A. G. Wong-Foy, D. J. Siegel, J. Phys. Chem. C **119**, 13451-13458 (2015). [MOMS interatomic potential]

Benchmarking Interatomic Potentials for HKUST-1 (2)

Michigan Open Metal Site (MOMS) has been successful in calculating measured CH_4 uptakes in HKUST-1.

Gravimetric capacity

Source	Total at 5bar (g/g)	Total at 65 bar (g/g)	Usable 65/5 bar (g/g)
Mason et al. (expt.) [1,2]	0.064	0.213	0.152
Peng et al. (expt.) [3]	0.062	0.216	0.154
Brain et al. (expt.) [4]	0.063	0.218	0.155
Koh et al. (MOMS calculated) [5]	0.070	0.220	0.150

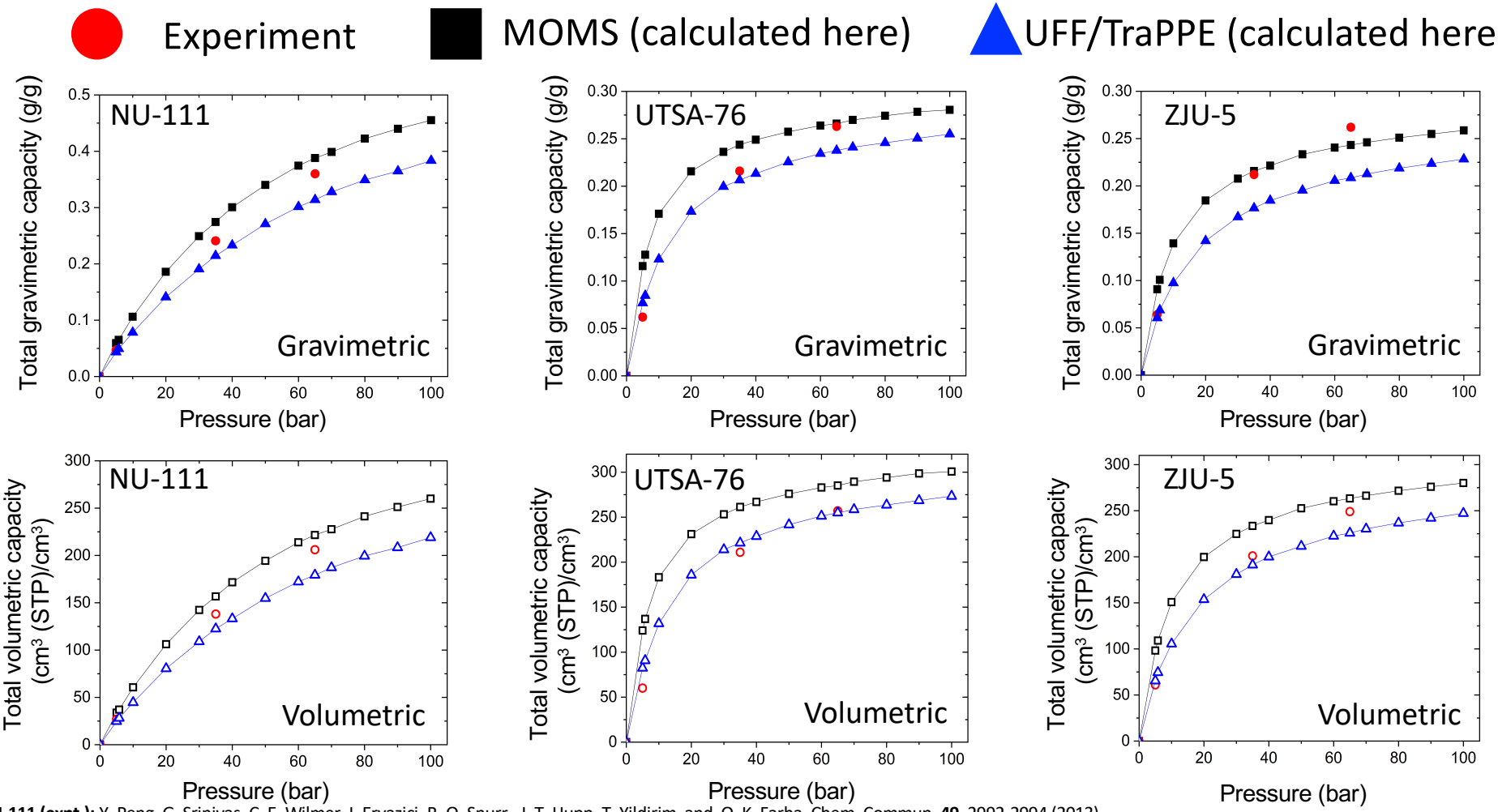
Volumetric capacity

Source	Total at 5bar (cm^3 (STP)/cm^3)	Total at 65 bar (cm^3 (STP)/cm^3)	Usable 65/5 bar (cm^3 (STP)/cm^3)
Mason et al. (expt.) [1,2]	76	263	187
Peng et al. (expt.) [3]	77	267	190
Brain et al. (expt.) [4]	77	267	190
Koh et al. (MOMS calculated) [5]	83	262	179

1. J. A. Mason, M. Veenstra and J. R. Long, Chem. Sci. **5**, 32-51 (2014)
2. Z. Hulvey, B. Vlaisavljevich, J. A. Mason, E. Tsivion, T. P. Dougherty, E. D. Bloch, M. Head-Gordon, B. Smit, J. R. Long, C. M. Brown, J. Am. Chem. Soc. **137**, 10816−10825 (2015)
3. Y. Peng, V. Krungleviciute, I. Eryazici, J. T. Hupp, O. K. Farha, T. Yildirim, J. Am. Chem. Soc. **135**, 11887-11894 (2013).
4. G. Barin, V. Krungleviciute, I. Eryazici, J. T. Hupp, O. K. Farha, T. Yildirim, Inorg. Chem. **53**, 6914-6919 (2014)
5. H. S. Koh, M. K. Rana, A. G. Wong-Foy, D. J. Siegel, J. Phys. Chem. C **119**, 13451-13458 (2015).

Benchmarking on Additional MOFs

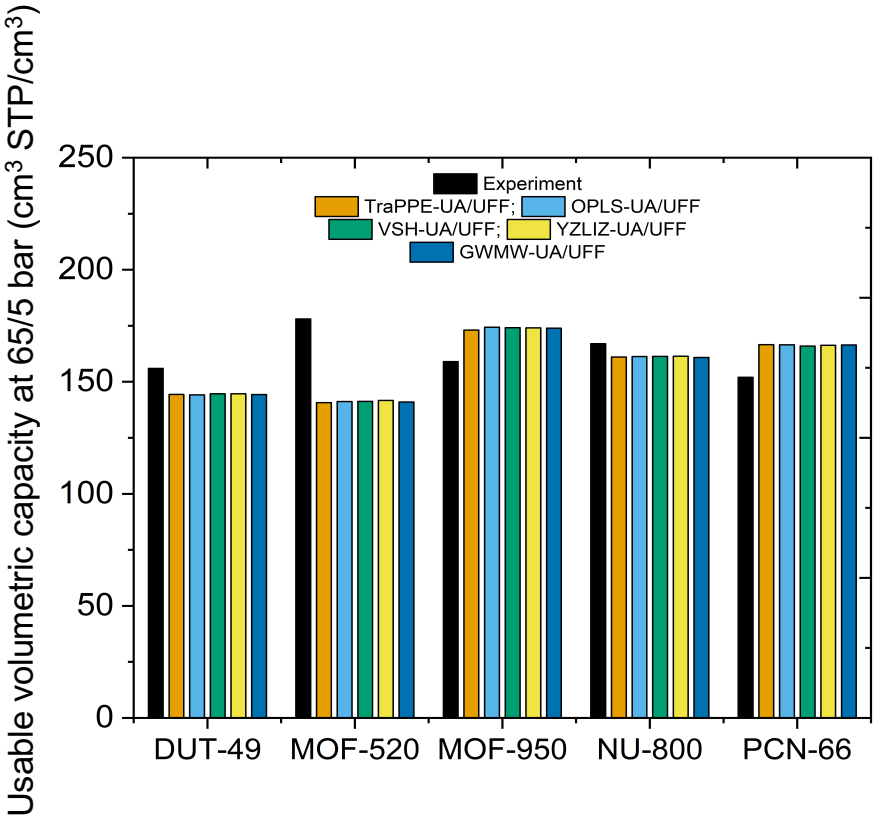
MOMS potential shows reasonable agreement with experimental measurements of CH_4 uptake in Cu-paddlewheel open metal site MOFs

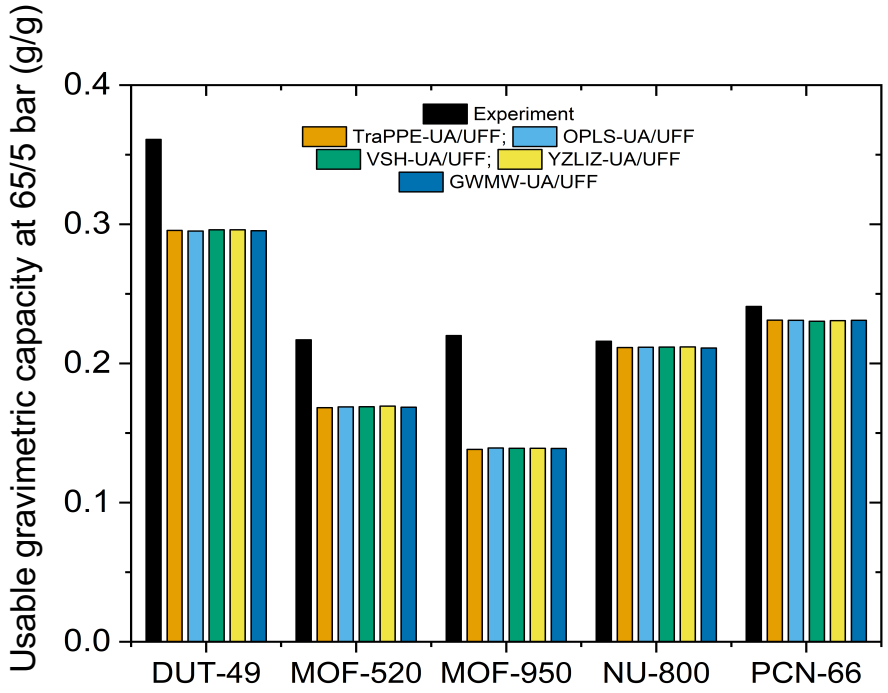


NU-111 (expt.): Y. Peng, G. Srinivas, C. E. Wilmer, I. Eryazici, R. Q. Snurr, J. T. Hupp, T. Yildirim and O. K. Farha, Chem. Commun. **49**, 2992-2994 (2013).
UTSA-76 (expt.): B. Li, H.-M. Wen, H. Wang, H. Wu, M. Tyagi, T. Yildirim, W. Zhou and B. Chen, J. Am. Chem. Soc. **136**, 6207-6210 (2014).
ZJU-5 (expt.): X. Rao, J. Cai, J. Yu, Y. He, C. Wu, W. Zhou, T. Yildirim, B. Chen and G. Qian, Chem. Commun. **49**, 6719-6721 (2013).
MOMS: H. S. Koh, M. K. Rana, A. G. Wong-Foy, D. J. Siegel, J. Phys. Chem. C **119**, 13451-13458 (2015).
TraPPE-UA: M. G. Martin and J. I. Siepmann, J. Phys. Chem. B **102**, 2569-2577 (1998).
UFF: A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard III and W. M. Skiff, J. Am. Chem. Soc. **114**, 10024-10035 (1992).

Benchmarking Interatomic Potentials on MOFs Without Open Metal Sites (1)

A combination of the UFF and TraPPE interatomic potentials appear to be the best choice for calculating CH_4 uptake in MOFs.

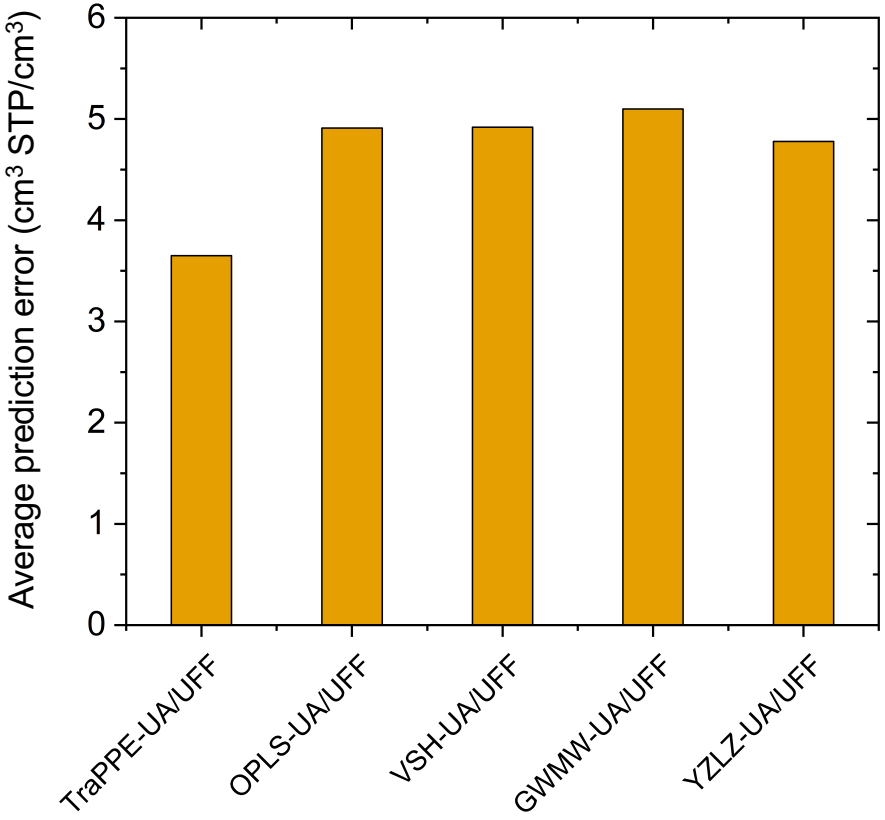


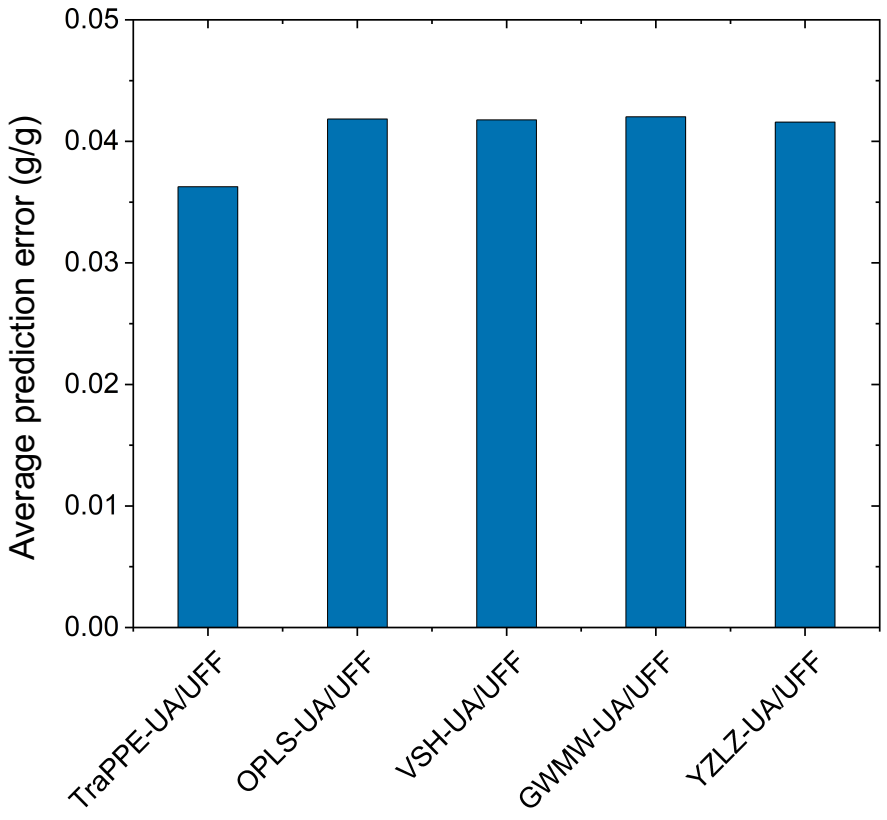


Experiment: Y. He, F. Chen, B. Li, G. Qian, W. Zhou, B. Chen, Coord. Chem. Rev. **373**, 167-198 (2018)
TraPPE-UA: M. G. Martin and J. I. Siepmann, J. Phys. Chem. B **102**, 2569-2577 (1998).
OPLS-UA: W. L. Jorgensen, D. S. Maxwell and J. Tirado-Rives, J. Am. Chem. Soc. **118**, 11225−11236 (1996).
VSH-UA: J. Vrabec, J. Stoll and H. Hasse, J. Phys. Chem. B **105**, 12126-12133 (2001).
YZLZ-UA: Q. Yuan, X. Zhu, K. Lina and Y.-P. Zhao, Phys. Chem. Chem. Phys. **17**, 31887-31893 (2015).
GWMW-UA: S. J. Goodbody, K. Watanabe, D. MacGowan, J. P. R. B. Walton and N. Quirke, J. Chem. Soc., Faraday Trans. **87**, 1951-1958 (1991).
UFF: A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard III and W. M. Skiff, J. Am. Chem. Soc. **114**, 10024-10035 (1992).

Benchmarking Interatomic Potentials on MOFs Without Open Metal Sites (2)

A combination of the UFF and TraPPE interatomic potentials appear to be the best choice for calculating CH_4 uptake in MOFs.



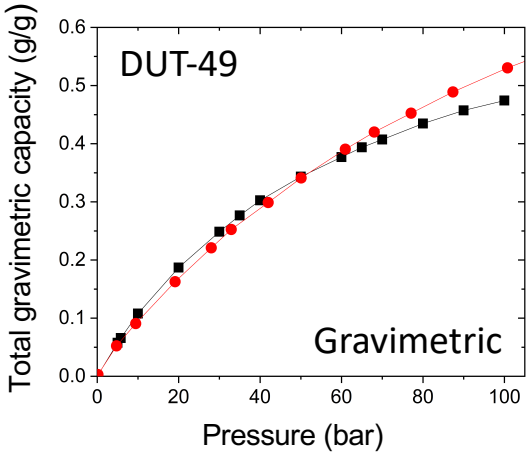


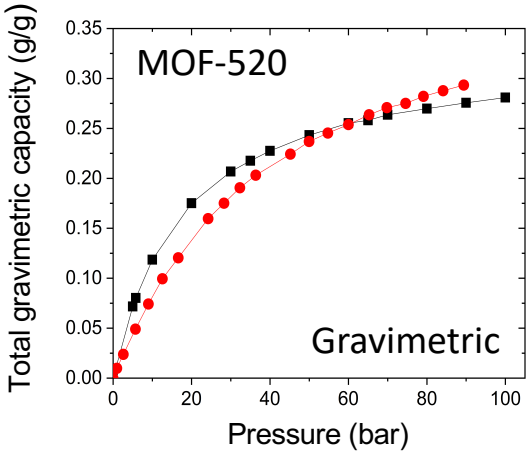
TraPPE-UA: M. G. Martin and J. I. Siepmann, J. Phys. Chem. B **102**, 2569-2577 (1998).
OPLS-UA: W. L. Jorgensen, D. S. Maxwell and J. Tirado-Rives, J. Am. Chem. Soc. **118**, 11225−11236 (1996).
VSH-UA: J. Vrabec, J. Stoll and H. Hasse, J. Phys. Chem. B **105**, 12126-12133 (2001).
YZLZ-UA: Q. Yuan, X. Zhu, K. Lina and Y.-P. Zhao, Phys. Chem. Chem. Phys. **17**, 31887-31893 (2015).
GWMW-UA: S. J. Goodbody, K. Watanabe, D. MacGowan, J. P. R. B. Walton and N. Quirke, J. Chem. Soc., Faraday Trans. **87**, 1951-1958 (1991).
UFF: A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard III and W. M. Skiff, J. Am. Chem. Soc. **114**, 10024-10035 (1992).

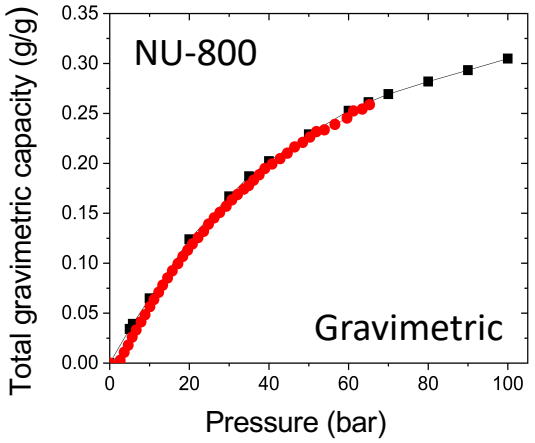
Benchmarking Interatomic Potentials on MOFs Without Open Metal Sites (3)

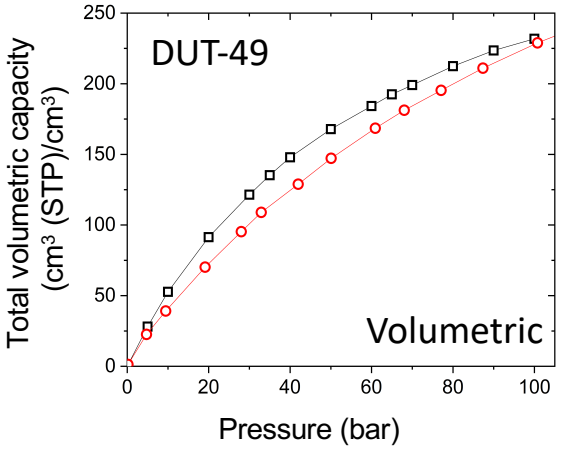
A combination of the UFF and TraPPE interatomic potentials appear to be the best choice for calculating CH_4 uptake in MOFs.

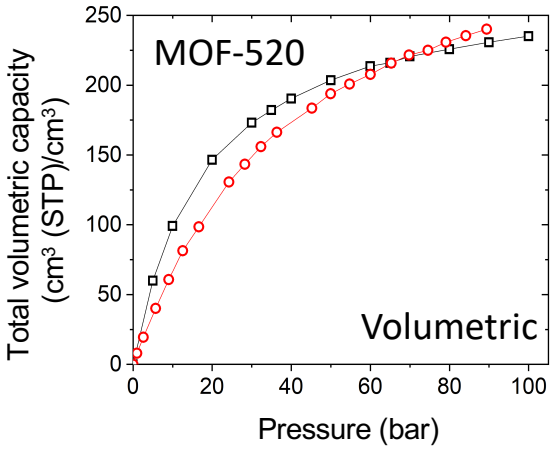
Experiment UFF/TraPPE (calculated here)

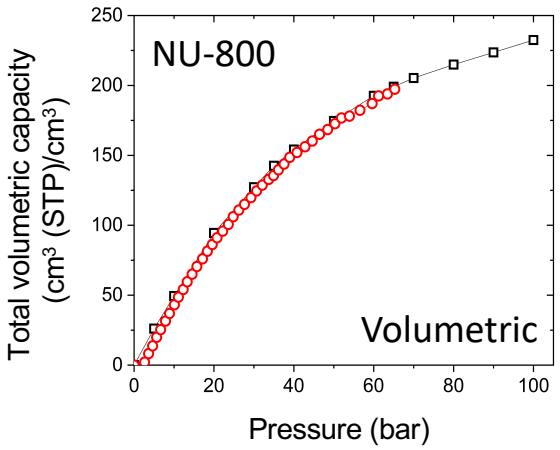












DUT-49 (expt.): U. Stoeck, S. Krause, V. Bon, I. Senkovska, and S. Kaskel, Chem. Commun. **48**, 10841-10843 (2012).
MOF-520 (expt.): F. Gándara, H. Furukawa, S. Lee, O. M. Yaghi, J. Am. Chem. Soc. **136,** 14, 5271-5274 (2014).
NU-800 (expt.): D. A. Gomez-Gualdron, O. V. Gutov, V. Krungleviciute, B. Borah, J. E. Mondloch, J. T. Hupp, T. Yildirim, Omar K. Farha, R. Q. Snurr, Chem. Mater. **26**, 19, 5632-5639 (2014).
TraPPE-UA: M. G. Martin and J. I. Siepmann, J. Phys. Chem. B **102**, 14, 2569-2577 (1998).
UFF: A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard III and W. M. Skiff, J. Am. Chem. Soc. **114**, 25, 10024-10035 (1992).

GCMC Screening of CoRE-2019 MOF Database (1)

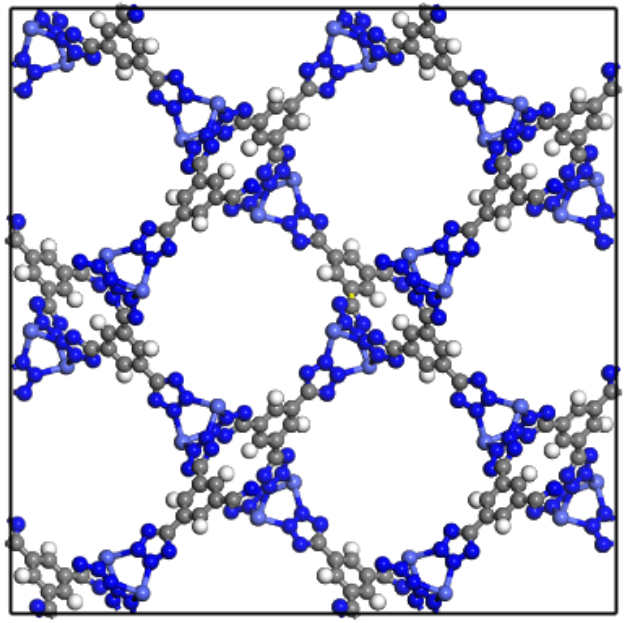
- Screened 7,817 open metal site MOFs [1] using the MOMS [2] interatomic potential.
- Identified 8 candidates predicted to surpass HKUST-1 at 298 K under 65/5 bar pressure swing.

MOF name (CSD refcode)	Usable gravimetric capacity (g/g)	Usable volumetric capacity (cm^3 STP/cm^3)	Single crystal density (g/cm^3)	Volumetric surface area (m^2/cm^3)	Gravimetric surface area (m^2/g)	Void fraction	Pore volume (cm^3/g)	Pore diameter (Å)	Open metal sites
ARPA-E	**0.5**	**315**							
HKUST-1 (expt.)	**0.154**	**190**							
HKUST-1 (calc.)	**0.160**	**179**							
UTSA-76	**0.201**	**197**							
ECOLEP_CoRE_2019	0.386	219	0.41	1819	4466	0.87	2.13	11.6	Co
BAZFUF01_CoRE_2019	0.446	213	0.34	1831	5354	0.86	2.52	20.1	Cu
BAZFUF_CoRE_2019	0.448	213	0.34	1825	5368	0.86	2.54	20.2	Cu
YIXBIQ_CoRE_2019	0.130	212	1.17	1743	1492	0.75	0.64	16.1	Cu
cg501560z_si_003_CoRE_2019	0.232	201	0.62	2302	3704	0.81	1.30	10.6	Mn
XOVPUU_CoRE_2019	0.346	195	0.40	2012	4969	0.84	2.09	11.5	Cu
AVAKAL_CoRE_2019	0.671	194	0.21	1259	6072	0.91	4.40	26.3	Cu
AVAKEP_CoRE_2019	0.564	193	0.24	1421	5800	0.89	3.63	25.2	Cu
AWUPOZ_CoRE_2019	0.382	189	0.35	1737	4916	0.85	2.41	18.4	Mn
AWUPAL_CoRE_2019	0.387	189	0.35	1743	5001	0.85	2.45	18.4	Fe
NATKIF_CoRE_2019	0.389	187	0.35	1901	5504	0.86	2.48	17.0	Cu
UKAZEM_CoRE_2019	0.170	187	0.79	2030	2572	0.78	0.98	10.8	Cu
LASREF_CoRE_2019	0.166	187	0.80	1998	2482	0.78	0.97	11.0	Cu
QIYDIN_CoRE_2019	0.676	187	0.20	1310	6629	0.92	4.65	30.0	Cu
LASRIJ_CoRE_2019	0.178	186	0.75	1958	2615	0.81	1.08	11.1	Cu
VOLRAQ01_CoRE_2019	0.237	185	0.56	1861	3315	0.84	1.50	16.9	Zn
LASRAB_CoRE_2019	0.157	184	0.84	2115	2517	0.78	0.93	10.2	Cu
LIKDOA_CoRE_2019	0.245	183	0.54	1958	3650	0.82	1.52	18.5	Cu
WIJXIY_CoRE_2019	0.276	183	0.48	1730	3642	0.82	1.73	14.2	Zn

1. CoRE-2019: Y. G. Chung, E. Haldoupis, B. J. Bucior, M. Haranczyk, S. Lee, H. Zhang, K. D. Vogiatzis, M. Milisavljevic, S. Ling, J. S. Camp, Ben Slater, J. I. Siepmann, D. S. Sholl, R. Q. Snurr, J. Chem. Eng. Data **64**, 5985-5998 (2019).
2. MOMS: H. S. Koh, M. K. Rana, A. G. Wong-Foy, D. J. Siegel, J. Phys. Chem. C **119**, 13451-13458 (2015).

GCMC Screening of CoRE-2019 MOF Database (2)

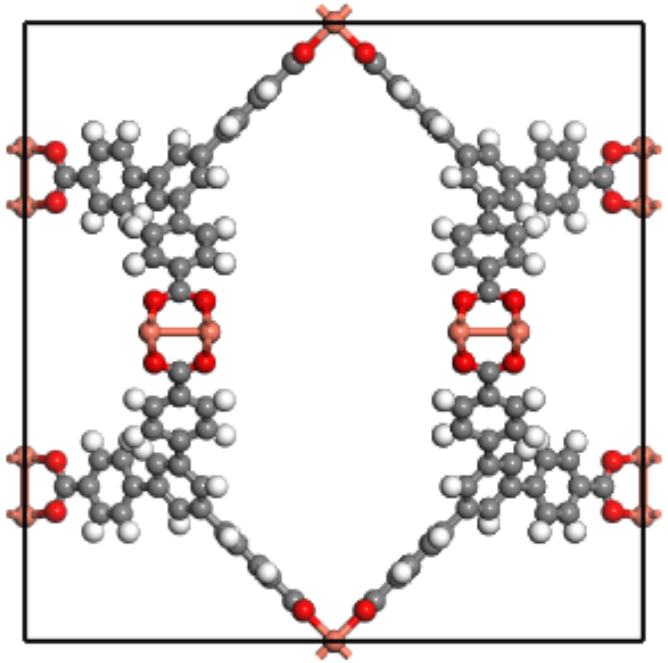
Crystal structures and predicted performance of top two promising MOFs identified from screening of the CoRE-2019 database



ECOLEP

Su & co-workers

Cryst. Growth Des. **11**, 2510-2514 (2011).



BAZFUF01

Kaskel & co-workers

Chem. -Eur. J. **17**, 13007 (2011)

CSD refcode	Usable gravimetric capacity (g/g)	Usable volumetric capacity (cm^3 STP/cm^3)	Single crystal density (g/cm^3)	Volumetric surface area (m^2/cm^3)	Gravimetric surface area (m^2/g)	Void fraction	Pore volume (cm^3/g)	Pore diameter (Å)	Open metal sites
ECOLEP_CoRE_2019	0.386	219	0.41	1819	4466	0.87	2.13	11.6	Co
BAZFUF01_CoRE_2019	0.446	213	0.34	1831	5354	0.86	2.52	20.1	Cu

1. CoRE-2019: Y. G. Chung, E. Haldoupis, B. J. Bucior, M. Haranczyk, S. Lee, H. Zhang, K. D. Vogiatzis, M. Milisavljevic, S. Ling, J. S. Camp, Ben Slater, J. I. Siepmann, D. S. Sholl, R. Q. Snurr, J. Chem. Eng. Data **64**, 5985-5998 (2019).

2. MOMS: H. S. Koh, M. K. Rana, A. G. Wong-Foy, D. J. Siegel, J. Phys. Chem. C **119**, 13451-13458 (2015).

GCMC Screening of *In Silico* MOF Database (1)

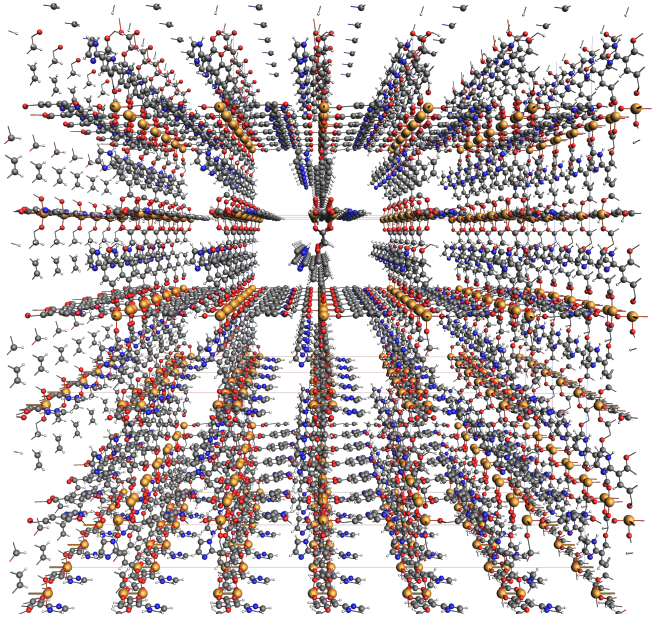
- Screened 1800 open metal site MOFs from the In Silico-1 database using MOMS [2] interatomic potential.
- 7 candidates indentified that are predicted to surpass HKUST-1 at 298K under 65/5 bar pressure swing conditions

MOF name	Usable gravimetric capacity (g/g)	Usable volumetric capacity (cm^3 STP/cm^3)	Single crystal density (g/cm^3)	Volumetric surface area (m^2/cm^3)	Gravimetric surface area (m^2/g)	Void fraction	Pore volume (cm^3/g)	Pore diameter (Å)	Open metal sites
ARPA-E	**0.5**	**315**							
HKUST-1 (expt.)	**0.154**	**190**							
HKUST-1 (calc.)	**0.160**	**179**							
UTSA-76 (expt.)	**0.201**	**197**							
cds_Syn038897	0.289	196	0.49	2501	5154	0.82	1.68	10.0	Cu
cds_Syn017990	0.272	195	0.51	2462	4816	0.80	1.57	10.4	Cu
cds_Syn019552	0.313	193	0.44	2126	4800	0.84	1.89	12.0	Cu
cds_Syn025928	0.329	193	0.42	2072	4934	0.84	2.00	12.1	Cu
cds_Syn027298	0.298	191	0.46	2519	5477	0.81	1.76	10.0	Cu
cds_Syn017381	0.226	191	0.60	2372	3930	0.76	1.26	9.3	Cu
cds_Syn012386	0.242	191	0.56	2516	4465	0.80	1.42	9.7	Cu
cds_Syn026319	0.114	190	1.19	2463	2074	0.73	0.61	7.2	Cu
cds_Syn021433	0.153	190	0.89	2523	2841	0.76	0.86	8.3	Cu
cds_Syn028362	0.342	189	0.40	2272	5733	0.83	2.10	11.7	Cu
nbo_Syn005497	0.256	189	0.53	1784	3376	0.80	1.51	16.0	Cu
cds_Syn001104	0.229	189	0.59	2552	4324	0.80	1.36	9.5	Cu
cds_Syn036586	0.273	189	0.49	2473	5002	0.81	1.64	10.2	Cu
cds_Syn029428	0.253	188	0.53	2484	4674	0.79	1.49	9.7	Cu
cds_Syn036887	0.186	187	0.72	2506	3480	0.77	1.07	9.2	Cu
cds_Syn000620	0.251	187	0.53	2611	4899	0.80	1.50	9.2	Cu

1. ***In silico*** **MOF Database-I:** Y. Bao, R. L. Martin, C. M. Simon, M. Haranczyk, B. Smit, M. W. Deem, J. Phys. Chem. C **119**, 186-195 (2015).
2. MOMS: H. S. Koh, M. K. Rana, A. G. Wong-Foy, D. J. Siegel, J. Phys. Chem. C **119**, 13451-13458 (2015).

GCMC Screening of *In Silico* MOF Database (2)

Crystal structure and predicted performance of the top candidate identified via screening of the *In Silico-1* MOF database using the MOMS interatomic potential.



cds_Syn038897 [1]

Open metal site MOF	Usable gravimetric capacity (g/g)	Usable volumetric capacity (cm^3 STP/cm^3)	Single crystal density (g/cm^3)	Volumetric surface area (m^2/cm^3)	Gravimetric surface area (m^2/g)	Void fraction	Pore volume (cm^3/g)	Pore diameter (Å)	Open metal sites
cds_Syn038897	0.289	196	0.49	2501	5154	0.82	1.68	10.0	Cu

1. *In silico* MOF Database-I: Y. Bao, R. L. Martin, C. M. Simon, M. Haranczyk, B. Smit, M. W. Deem, J. Phys. Chem. C **119**, 186-195 (2015).
2. MOMS: H. S. Koh, M. K. Rana, A. G. Wong-Foy, D. J. Siegel, J. Phys. Chem. C **119**, 13451-13458 (2015).

GCMC Screening of *In Silico* MOF Database (3)

- Screened 5,855 open metal site MOFs from the In Silico-2 database [1] using MOMS interatomic potential.
- Identified 281 MOFs that are predicted to surpass HKUST-1

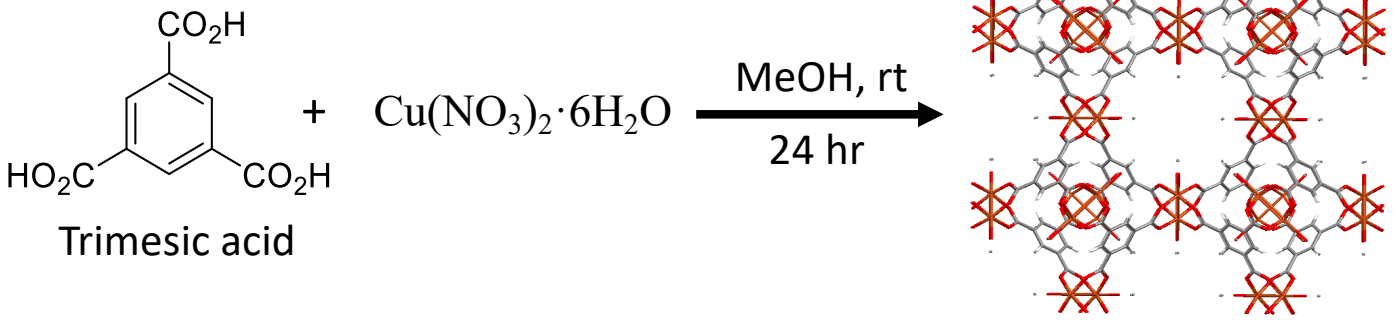
Name	UV_65bar (cm^3 STP/cm^3)	UG_65bar (g/g)	Density (g/cm^3)	Gravimetric Surface Area (m^2/g)	Volumetric Surface Area (m^2/cm^3)	Void Fraction	Pore Volume (cm^3/g)	Largest Cavity Diameter (Å)	Pore Limiting Diameter (Å)
ARPA-E	**0.5**	**315**							
HKUST-1 (expt.)	**0.154**	**190**							
HKUST-1 (calc.)	**0.160**	**179**							
UTSA-76 (expt.)	**0.201**	**197**							
cds_Syn025111	205.8	0.336	0.44	5320	2331	0.82	1.88	10.3	8.4
cds_A_Syn032059	205.7	0.367	0.40	6217	2498	0.83	2.06	11.1	8.7
cds_Syn033413	205.6	0.311	0.47	4997	2364	0.81	1.71	10.4	8.1
cds_Syn025391	205.5	0.325	0.45	5219	2366	0.81	1.79	10.6	8.1
cds_Syn039948	205.3	0.288	0.51	4882	2492	0.79	1.55	10.6	7.7
cds_A_Syn031980	204.9	0.351	0.42	5926	2477	0.82	1.96	10.6	7.6
cds_Syn036411	204.7	0.278	0.53	4410	2324	0.82	1.56	11.1	8.2
cds_A_Syn008583	204.3	0.334	0.44	5657	2477	0.81	1.86	10.5	8.2
cds_Syn036967	204.1	0.292	0.50	4666	2334	0.80	1.61	10.3	8.2
cds_A_Syn038352	203.1	0.309	0.47	5224	2458	0.80	1.70	10.0	7.4
cds_A_Syn009127	203.0	0.325	0.45	5439	2429	0.82	1.83	10.0	7.9
cds_A_Syn033573	202.8	0.302	0.48	5145	2478	0.80	1.66	10.2	7.5
cds_Syn037004	202.7	0.286	0.51	4694	2385	0.79	1.56	10.1	8.2
cds_A_Syn022389	202.6	0.347	0.42	5871	2452	0.82	1.96	10.3	8.4
cds_A_Syn010843	202.6	0.342	0.42	5861	2486	0.83	1.95	10.4	8.4
cds_Syn032491	202.5	0.239	0.61	3912	2372	0.80	1.32	10.5	7.8
cds_A_Syn018492	202.2	0.320	0.45	5557	2517	0.81	1.79	9.7	7.2
cds_A_Syn034869	202.1	0.323	0.45	5584	2503	0.82	1.82	11.3	7.7
cds_Syn022087	202.0	0.280	0.52	4642	2400	0.80	1.55	9.7	8.0
cds_Syn033804	201.5	0.315	0.46	4881	2238	0.82	1.79	11.7	9.4

1. ***In silico* MOF Database-II:** Y. Bao, R. L. Martin, M. Haranczyk, and M. W. Deem, Phys. Chem. Chem. Phys. **17,** 11962-11973 (2015).
2. **MOMS:** H. S. Koh, M. K. Rana, A. G. Wong-Foy, D. J. Siegel, J. Phys. Chem. C **119**, 13451-13458 (2015).

Synthesis of the Benchmark MOF HKUST-1

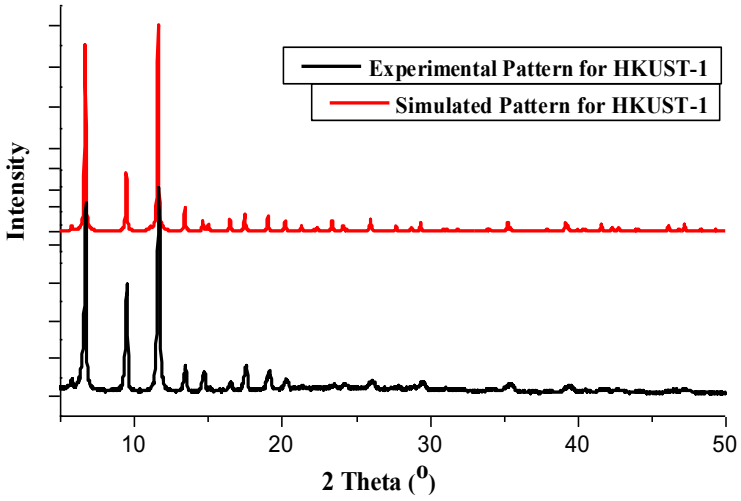
As surpassing the performance of HKUST-1 is one of our initial goals, we have begun the process of synthesizing and characterizing this MOF.

Procedure: Trimesic acid (10.00 mmol, 2.10 g) was dissolved in 25 ml of methanol. $Cu(NO_3)_2 \cdot 6H_2O$ (20.00 mmol, 4.66g) was dissolved separately in 25 ml of methanol. The solutions were combined and stirred for ~20 minutes and then allowed to stand for 24 hours. The blue colored precipitate was isolated and exchanged with methanol over three consecutive days, with two exchanges times each day. The sample was then activated under dynamic vacuum (0.03Torr) at 150 °C.



Trimesic acid

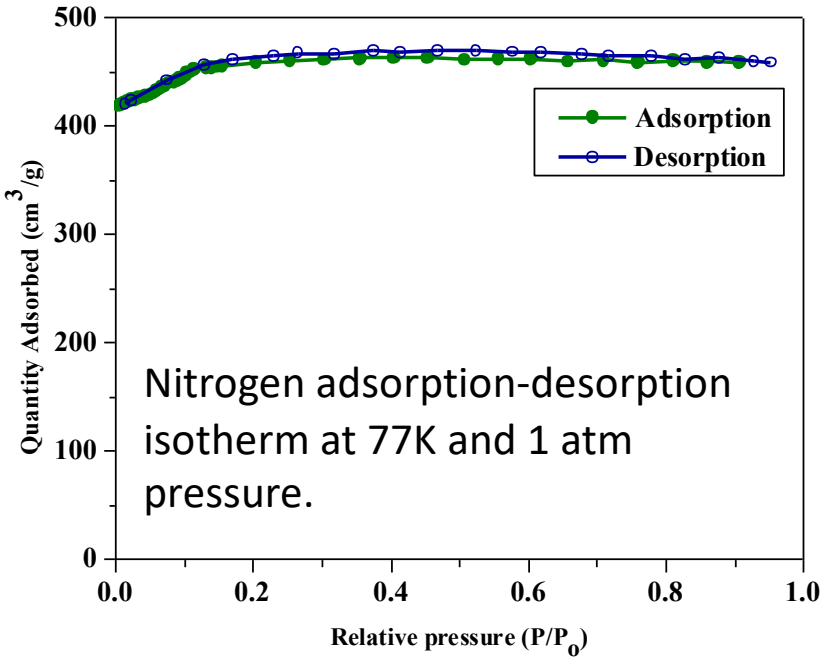
HKUST-1



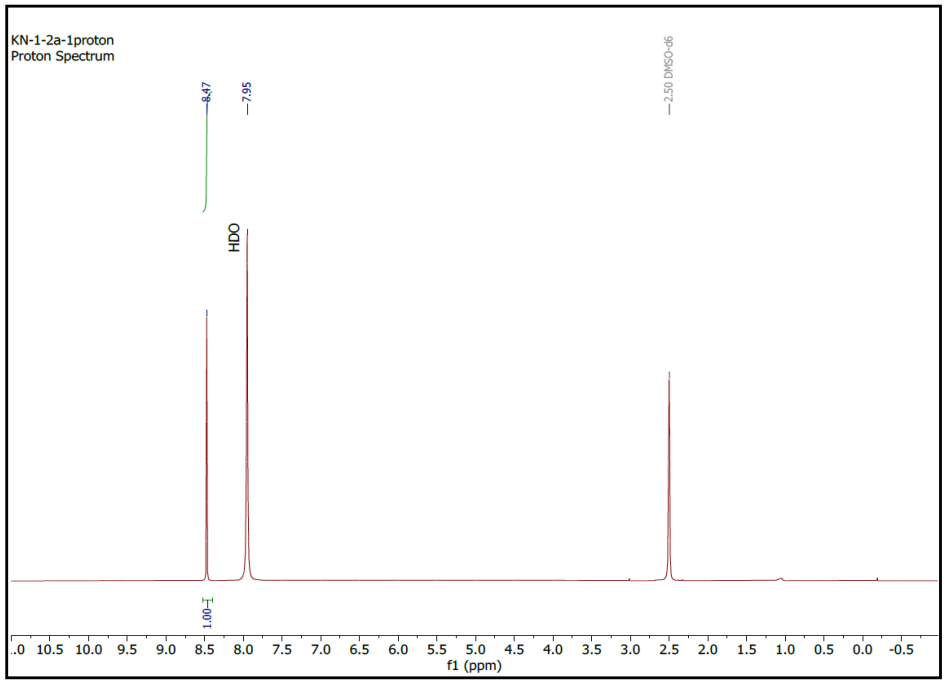
Comparison of simulated (red) and experimental (black) powder XRD patterns indicates the formation of single phase, pure material (HKUST-1).

Ref: adapted from *Chem. Eur. J.* **2017**, 23, 10758-10762

Characterization and Surface Area



Nitrogen adsorption-desorption isotherm at 77K and 1 atm pressure.



^{1}H NMR spectra of acid digested sample HKUST-1

BET Surface area (Literature)	BET Surface area (Calculated)	BET Surface area (Measured)
2014 m^2/g	1850 m^2/g	1797 m^2/g

- ✓ The blue colored precipitate was isolated and exchanged with methanol over three consecutive days, with two exchange times each day. The sample was then activated under dynamic vacuum (0.03Torr) at 150 ^{o}C for 24 hours.
- ✓ The NMR spectra of the acid digested sample of HKUST-1 reveals the complete loss of the solvent molecules in the activated framework.

Collaboration & Coordination

University of Michigan, Mechanical Engineering

- Atomistic simulation and project management

University of Michigan, Dept. of Chemistry

- Synthesis and characterization of targeted MOFs

Savannah River National Laboratory

- Development of system models (Carina Grady and David Tamburello)

Challenges and Barriers

- Many more compounds identified by computation than can be synthesized
  - Assessment by a human is needed before synthesis can proceed
  - This is a bottleneck
- Structure collapse or incomplete solvent removal during activation
  - “Can it be made?”
  - Failure to achieve expected surface area and porosity
  - Properties that control “synthesizability” are not well-understood
- Incorrect, incomplete, or disordered crystal structure data
  - Garbage in, garbage out
  - False positives in screening

Proposed Future Work

- Continue synthesis & characterization of methane uptake on several benchmark MOFs, including HKUST-1 and UTSA-76. Based on comparison with computed isotherms, finalize choice of interatomic potential for computational screening
- Complete pre-screening of structural properties on database of ~180,000 CUS MOFs; Run GCMC on subset; use this subset as initial target MOFs for experiments, and as a training set for ML.
- Complete baseline CNG system model for heavy duty vehicles; apply model to predict gravimetric capacity, volumetric capacity, and to estimate costs

Summary

Goal: Demonstrate adsorbents that when incorporated into an adsorbed NG system have the potential to surpass the capacity of CNG systems, allowing for systems that are smaller and lighter, yet operate at lower pressures

Approach:

- High-throughput screening and machine learning will identify MOFs that achieve high usable gravimetric and volumetric capacities for natural gas (NG)
- Promising materials will be synthesized and characterized experimentally
- The performance of the best materials will be projected to the system level

Accomplishments:

- New project: launched January 1, 2020
- Carefully benchmarked several interatomic potentials for their ability to predict CH_4 uptake in MOFs
- Using the most accurate potentials, screened 15,472 open-metal-site MOFs
  - Identified 296 MOFs with the potential to surpass the methane capacity of HKUST-1
- Initiated MOF synthesis and characterization activities

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