Project ID: ST122

Hydrogen Adsorbents with High Volumetric Density:

New Materials and System Projections

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[3]Ford Motor Company

DOE Annual Merit Review, June 15, 2018, Washington, DC

Overview

Timeline and Budget

Project Start Date: August 1st, 2015
Project End Date: July 31st, 2018

Total Project Budget: $1,040,000

Federal Share:

UM: $800,000
Ford: $192,000
Total: $992,000

Cost Share: $48,000 (Ford)

Total Funds Spent:* ~$925,000

*Estimated as of 3/31/18

Barriers

Barriers addressed

- Volumetric Density
- Gravimetric Density

Partners

Interactions/collaborations:

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

Project lead:

D. Siegel, University of Michigan

Background

- A high-capacity, low-cost method for storing hydrogen remains one of the primary barriers to the widespread commercialization of fuel cell vehicles
- Storage via adsorption is a promising approach due to its fast kinetics, reversibility, and high gravimetric densities
- An unfortunate characteristic of adsorptive storage is that high gravimetric densities typically come at the expense of volumetric density (total basis)
- HSECoE developed a 100 bar MOF-5-based storage system that approached competitiveness with 700 bar compressed. Our work in the HSECoE identified additional MOFs that may out-perform MOF-5, potentially resulting in a low-pressure system that could *surpass* 700 bar

Project goal: Demonstrate best-in-class MOFs that achieve high volumetric and gravimetric H_2 densities *simultaneously*, while maintaining reversibility and fast kinetics

Relevance

Objective 1: Demonstrate MOFs with high volumetric *and* gravimetric hydrogen densities, exceeding those of MOF-5

- Prior studies typically focus on maximizing gravimetric density alone
- Synthetic efforts guided by high-throughput screening
- If successful, these compounds will **set a new high-water mark** for H_2 density in adsorbents at cryogenic conditions

✓ **Computationally screened H_2 capacity of ~500,000 MOFs**

✓ **Identified and demonstrated several compounds that exceed the performance of MOF-5 benchmark**

Objective 2: System-level projections

- Project performance of most promising compounds to the system level by parameterizing models developed by the HSECoE
- Clarify how materials properties impact system performance

✓ **Completed projections for several MOFs**

✓ **Quantified how materials improvements translate to the system**

Approach

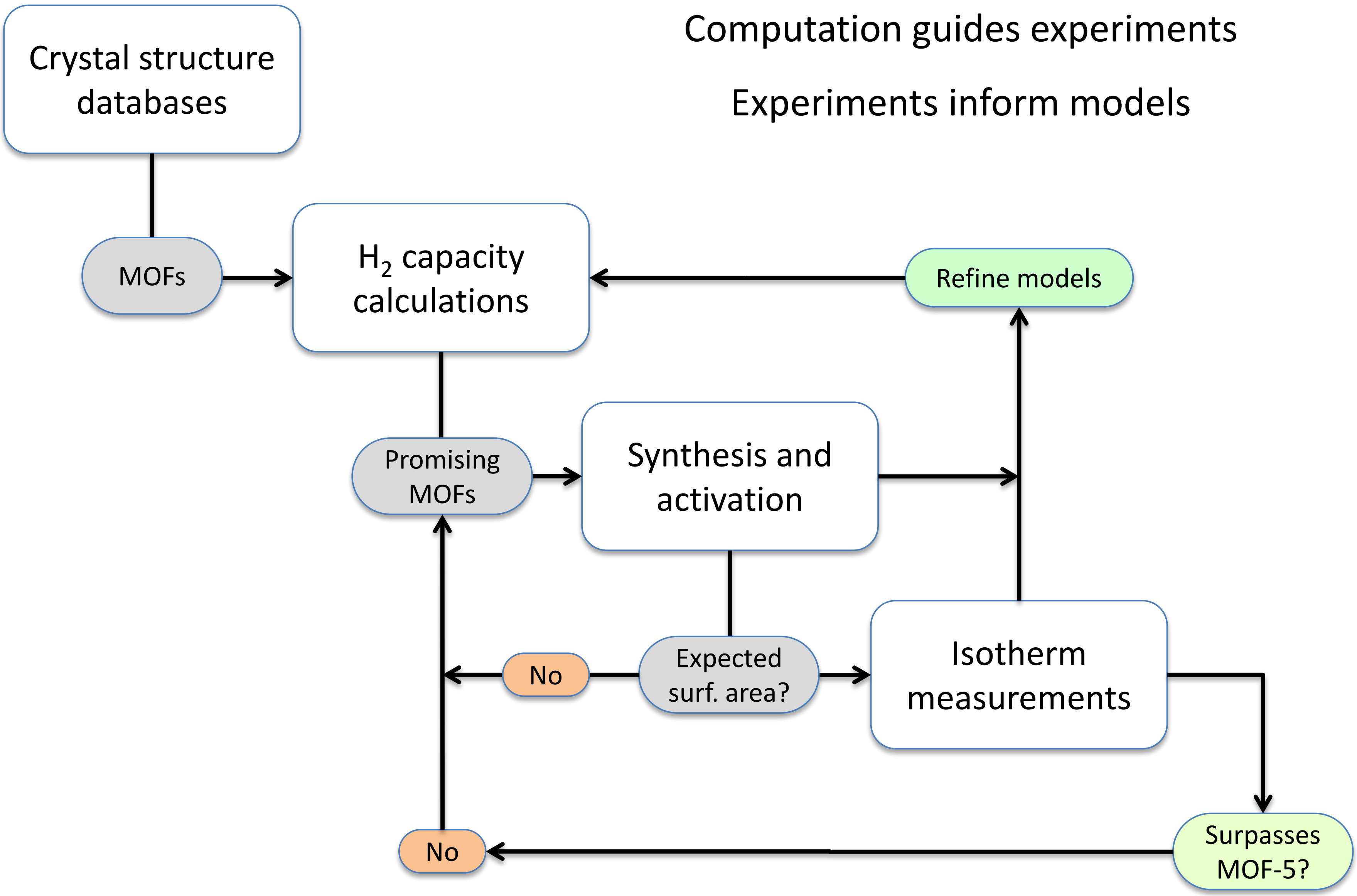
Notes:

- Unless otherwise stated, all volumetric hydrogen densities reported assume single-crystal MOF densities.
- Unless otherwise stated, all measurements and calculations are performed at T = 77 K.

Concept

Computation guides experiments

Experiments inform models



Year 3 Milestones

Our approach links atomic scale computation, experimental synthesis & characterization, and system-level modeling

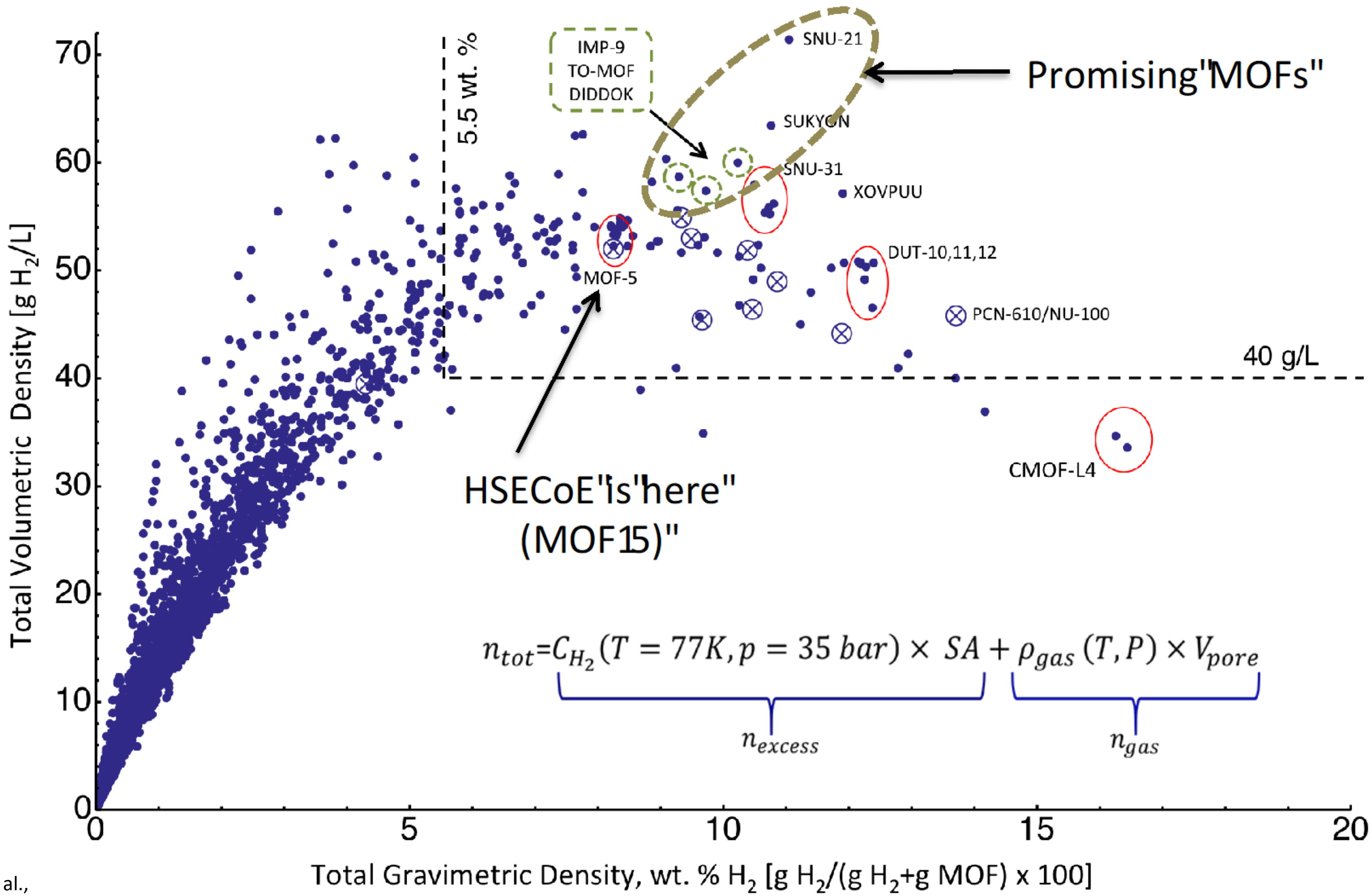
Year	Milestone or Go/No-Go	Due	Description	Status
3	Milestone	7/31/18	• Extend computational screening to temperature+pressure-swing conditions. • Synthesize most promising compounds and measure hydrogen uptake experimentally.	**On Track**. Majority of MOF database has been screened. Experimental testing of promising materials is continuing.
3	Milestone	7/31/18	• Extend system modeling projections to SNU-70, UMCM-9, and NU-100. • Project pathway to meet DOE targets. • Quantify how materials improvements translate to system-level improvements	**Complete**.

1	**Go/No-Go**	7/31/16	Demonstrate at least 1 MOF with >90% projected SA, >3,000 m^2/g, and H_2 capacity matching MOF-5 baseline	**IRMOF-20 demonstrated**

2	**Go/No-Go**	7/31/17	Demonstrate at least 1 MOF with hydrogen capacities exceeding baseline MOF-5 by 15%	**SNU-70 and NU-100 demonstrated**

High-throughput Screening

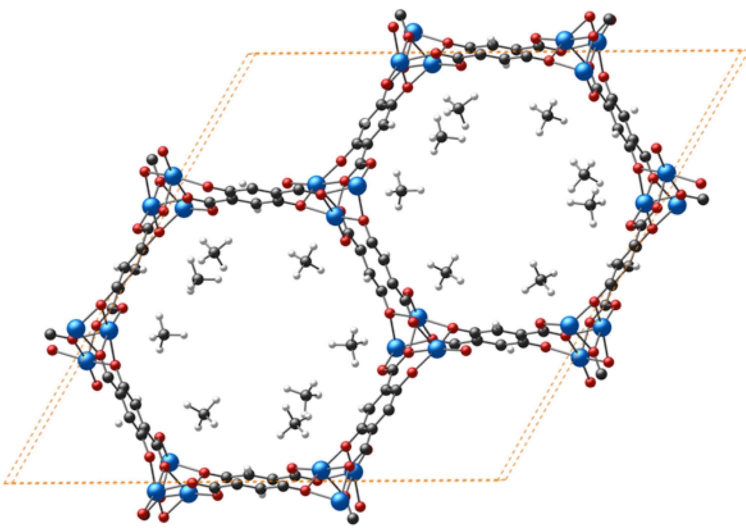
Prior work: developed a database of MOFs by mining the CSD. Chahine rule and crystal structure were used to predict H_2 capacity in thousands of compounds



J. Goldsmith, et al.,
Chem. Mater., **25**, 3373 (2013).

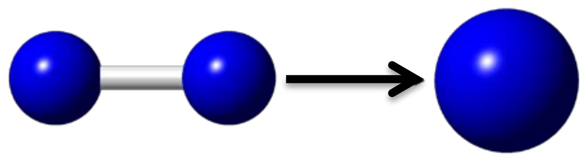
Grand Canonical Monte Carlo

- GCMC = atomistic method that calculates the total amount of H_2 (adsorbed + gas phase) contained within the pore space of a MOF at given T, P
- Does not rely on empirical correlations such as the Chahine-rule



Example GCMC simulation of CH_4 adsorption in Ni-DOBDC at 298 K and 35 bar

- Calculations employ the MGS* and the **Pseudo-FH**** unified atom models for H_2-MOF interactions
- MOF atoms are fixed



$$U_{ij}(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

Force Field	Sigma (Å)	Epsilon/k_B (K)
MGS	2.958	36.7
Pseudo-FH	3.064	30.1

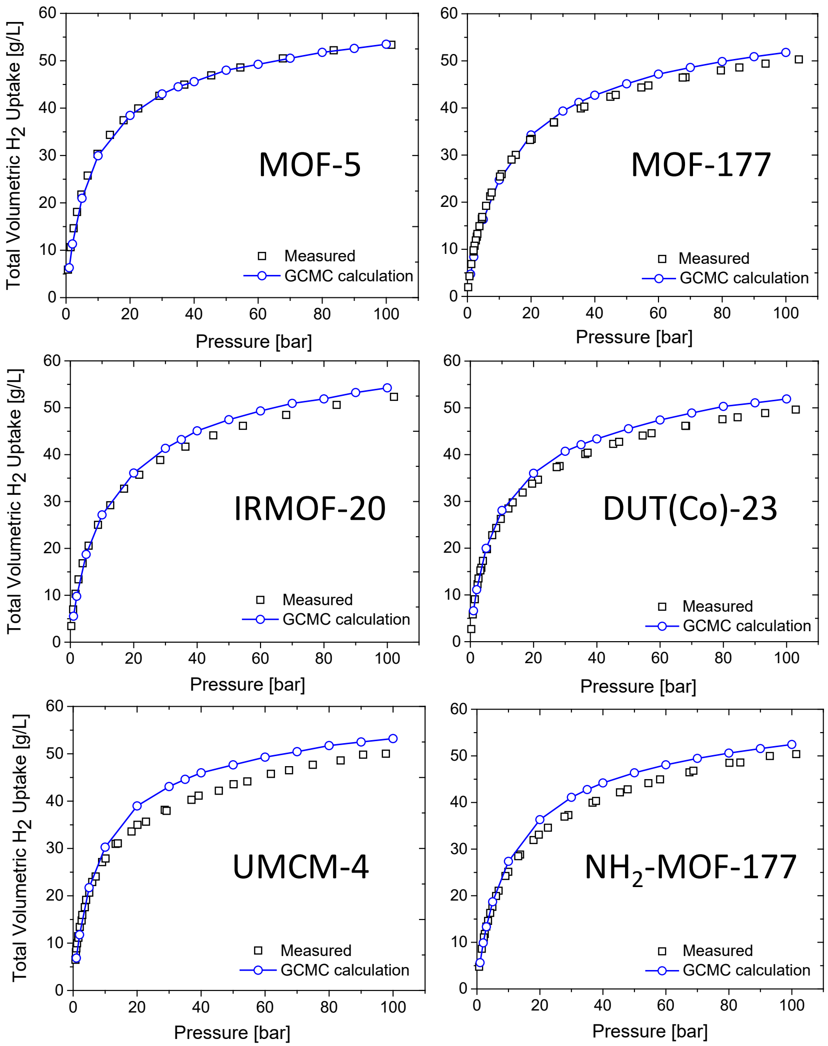
*Michels, de Graaff and Seldam, *Physica*, **1960**, 26, 393; Ryan, Broadbelt, and Snurr, *Chem. Comm.* 2008, 4134

Fischer, Hoffmann, Fröba, *ChemPhysChem*, **2009,10, 2647.

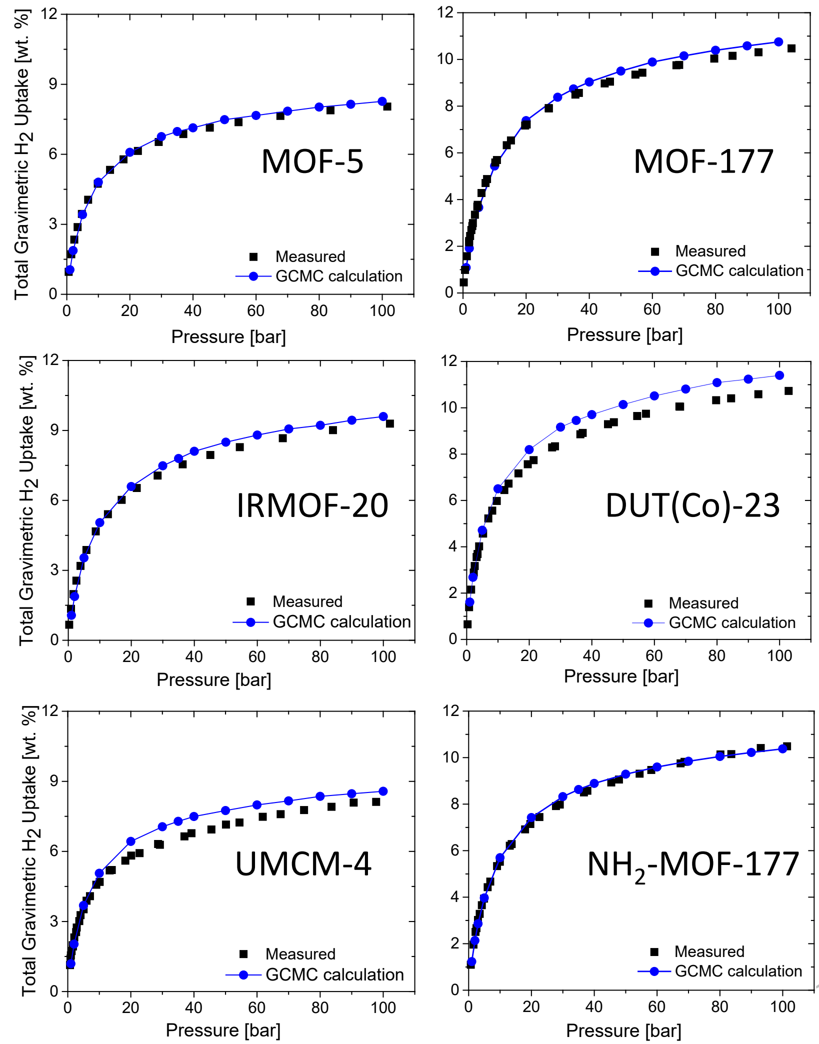
Examples of Simulated Isotherms

GCMC isotherms calculated with the pseudo-Feynman-Hibbs interatomic potential are in very good agreement with our measured isotherms

Total Volumetric H_2 Uptake

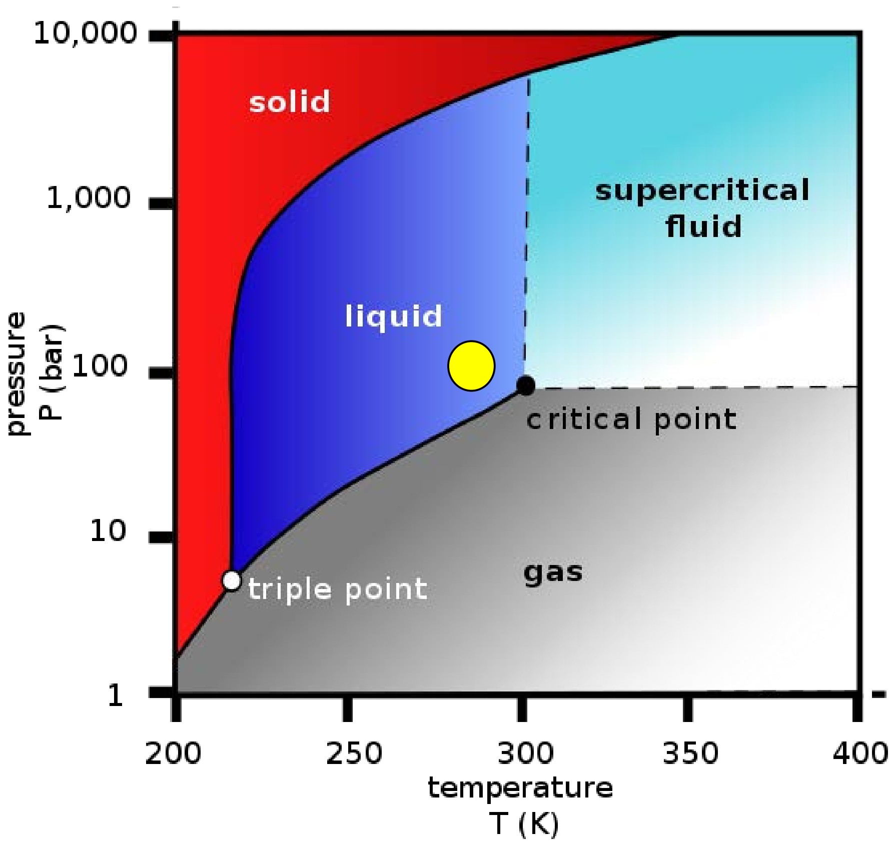


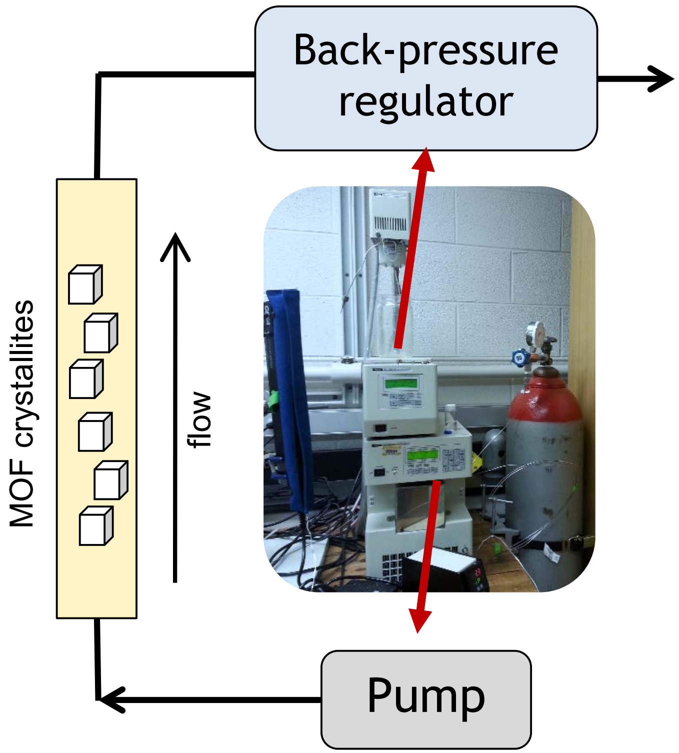
Total Gravimetric H_2 Uptake



Flowing Supercritical CO_2 Activation

Flowing supercritical CO_2 activation is milder than vacuum activation
→ minimizes pore collapse and maximizes surface area





Batch activation: Nelson, A. P.; Farha, O. K.; Mulfort, K; Hupp, J. T. *J. Am. Chem. Soc.* **2009**, *131*, 458.
Flow activation: Liu, B.; Wong-Foy, A. G.; Matzger, A. J. *Chem. Commun.* **2013, *49*,** 1419.

Vacuum *vs.* Flow Activation

MOFs activated with flowing sc-CO_2 generally exhibit superior properties

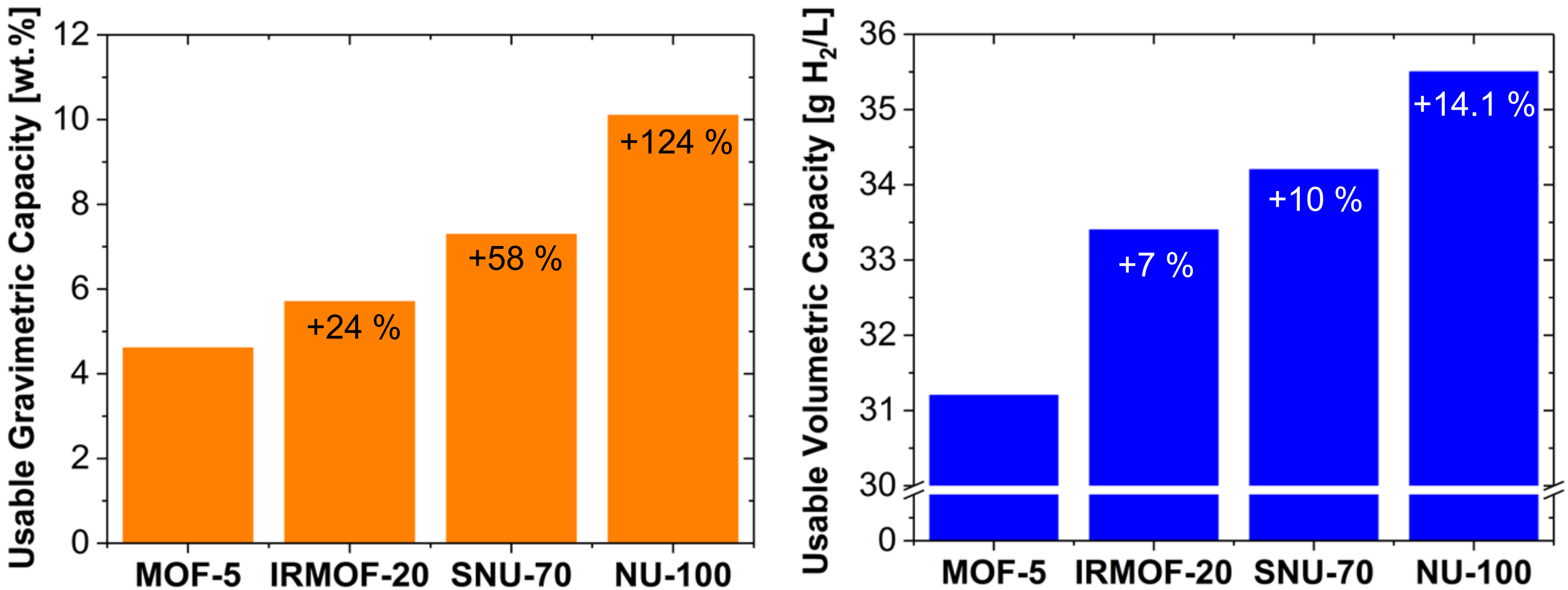
Material	Surface area (flow Sc-CO_2 activation)	Surface area (vacuum/batch Sc-CO_2 activation)
UMCM-9	5357 m^2/g	1330 m^2/g (vac)
FJI	4813 m^2/g	4043 m^2/g (batch)
MOF-74 (Zn/DOBDC)	1108 m^2/g	750-950 m^2/g (vac)
UMCM-10	4001 m^2/g	Structure collapses under vacuum activation
UMCM-12	4849 m^2/g	Structure collapses under vacuum activation
IRMOF-8 (non-interpenetrated)	4461 m^2/g	Structure collapses under vacuum activation
A series of functionalized IRMOF-8 (non-interpenetrated)	~4000 m^2/g	-
HKUST-1	1710-1770 m^2/g (heating required)	682-1944 m^2/g (vac)

Liu, B.; Wong-Foy, A. G.; Matzger, A. J. *Chem. Commun.* **2013,** *49,* 1419.
Dutta, A.; Wong-Foy, A. G.; Matzger, A. J. *Chem. Sci.* **2014,** *5,* 3729.
Feldblyum, J. I.; Wong-Foy, A. G.; Matzger, A. J. *Chem. Commun.* **2012,** *48,* 9838.
Tran, L. D.; Feldblyum, J. I.; Wong-Foy, A. G.; Matzger, A. J. *Langmuir* **2015,** *31,* 2211.

Accomplishments and Progress

2nd Go/No-Go Milestone

Computationally identified, and experimentally demonstrated 3+ MOFs (IRMOF-20 SNU-70, and NU-100) that out-perform MOF-5 baseline



Compound	Single Crystal Density [g/cm³]	Pore Volume [cm³/g]	Gravimetric Surface Area [m²/g]	Volumetric Surface Area [m²/cm³]	Void Fraction	Pore Diameter/ Aperture [Å]	Gravimetric H_2 Capacity: Total/usable [wt.%]	Volumetric H2 Capacity: Total/usable [g H_2/L]
MOF-5	0.60	1.36	3,563	2,172	0.81	15.1/7.9	8.0 / 4.5	53 / 31.1
IRMOF-20	0.51	1.65	3,913	2,000	0.84	17.3/9.3	9.3 / 5.7	52 / 33.4
SNU-70	0.40	2.14	4,756	1,905	0.86	16.8/10	10.7 / 7.3	49 / 34.2
NU-100	0.29	3.17	5,777	1,613	0.92	28.7/11.5	14.1 / 10.1	47.9 / 35.5

MOF Databases

Compiled a MOF database of ~500,000 compounds

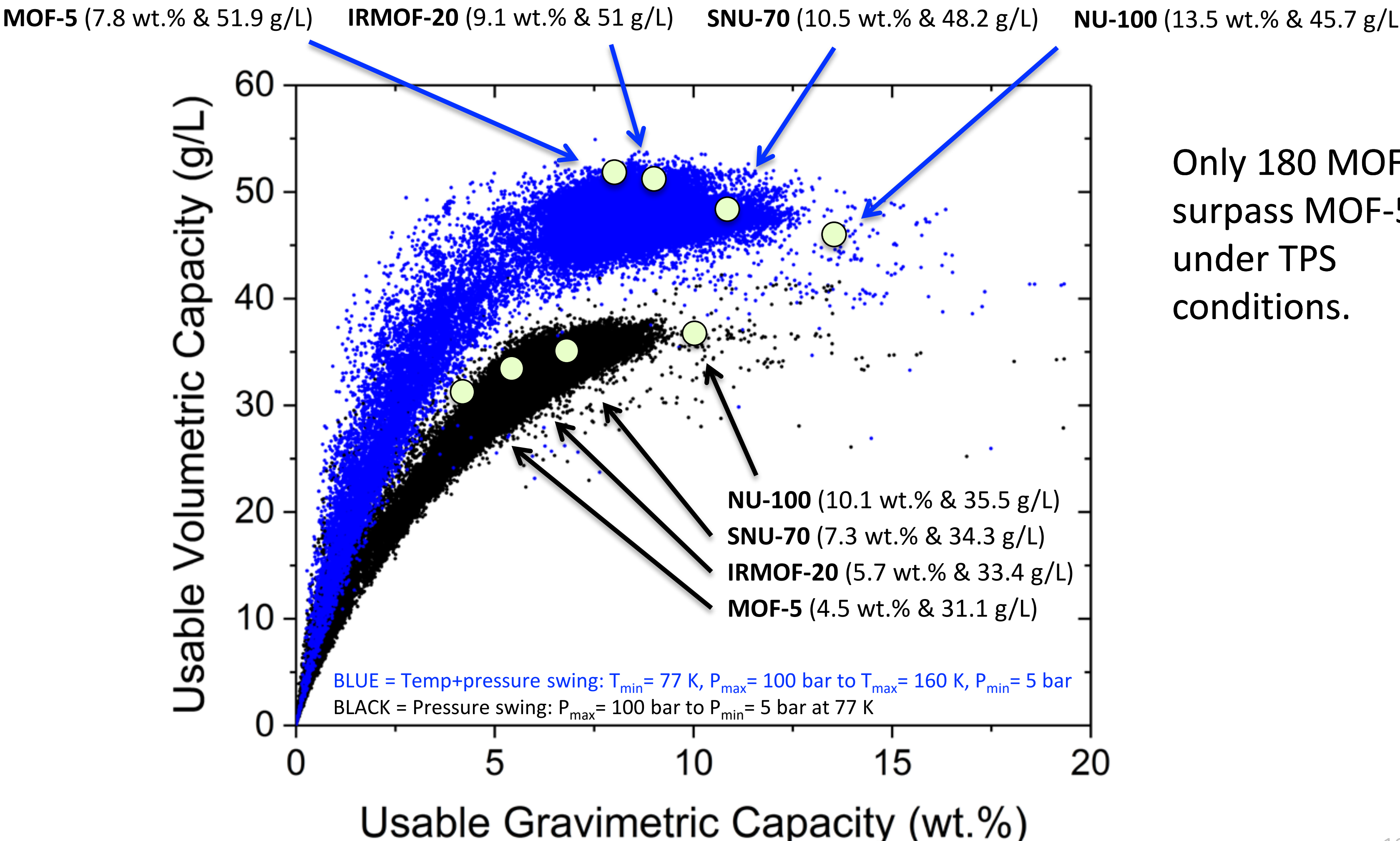
- 43,000+ MOFs assessed by GCMC for temperature + pressure swing storage
- ~100,000 MOFs assessed by GCMC for pressure swing storage
- ~500,000 MOFS assessed by GCMC + machine learning for pressure swing storage

Source	Available in database	Zero surface area	H_2 capacity evaluated empirically	H_2 capacity evaluated with GCMC
UM+CoRE+CSD17 (RM)	15,235	2,950	12,285	12,799
Mail-Order MOFs (MO)	112	4	108	112
In Silico MOFs (IS)	2,816	154	2,662	466
In Silico Surface MOFs (ISS)	8, 885	283	8,602	1,058
MOF-74 Analogs (M74)	61	0	61	61
ToBaCCo (TB)	13,512	214	13,298	290
Zr-MOFs (ZR)	204	0	204	204
NW Hypothetical MOFs (NW)	137,000	30,160	106,840	12,374
UO Hypothetical MOFs (UO)	324,500	32,993	291,507	16,372
In-house MOF designs	18	0	18	5
Total	**493,458**	**66,758**	**435,585**	**43,741**

RM: (a) **UM:** J.Goldsmith, A. G. Wong-Foy, M. J. Cafarella, and D. J. Siegel, *Chem. Mater.,* 25 , 3373–3382 (2013); (b) **CoRE:** Y. G. Chung, *et al.*, *Chem. Mater*., 26, 6185–6192 (2014); (c) **CSD17**: P. Z. Moghadam et al., *Chem. Mater.,* 29, 2618–2625 (2017).
MO: R. L. Martin, L.-C. Lin, K. Jariwala, B. Smit, M. Haranczyk, *J. Phys. Chem. C* 117, 12159-12167 (2013);
IS: Y. Bao, R. L. Martin, M. Haranczyk, M. W. Deem, *J. Phys. Chem. C* 119, 186-195 (2015).
ISS: Y. Bao, R. L. Martin, C. M. Simon, M. Haranczyk, B. Smit, M. W. Deem, *Phys. Chem. Chem. Phys.,* 17, 11962-11973 (2015).
M74: M. Witman, S. Ling, S. Anderson, L. Tong, K.C. Stylianou, B. Slater, B. Smit, M. Haranczyk, *Chem. Sci*., 7, 6263-6272 (2016).
TB: Y. J. Colón, D. A. Gómez-Gualdrón, and R. Q. Snurr, *Cryst. Growth Des.,* 17, 5801–5810 (2017).
ZR: D. A. Gómez-Gualdrón, O.V. Gutov, V. Krungleviciute, B. Borah, J. E. Mondloch, J. T. Hupp, T. Yildirim, O.K. Farha, R.Q. Snurr, *Chem. Mater.* 26, 5632-5639 (2014).
NW: C. E. Wilmer, M. Leaf, C. Y. Lee, O. K. Farha, B. G. Hauser, J. T. Hupp, R. Q. Snurr, *Nat. Chem.* 4, 83–89 (2012).
UO: M. Z. Aghaji, M. Fernandez, P. G. Boyd, T. D. Daff, and T. K. Woo, *Eur. J. Inorg. Chem.,* 2016, 4505–4511 (2016).

High-Throughput Screening

Predicted usable H_2 capacities for PS and TPS conditions



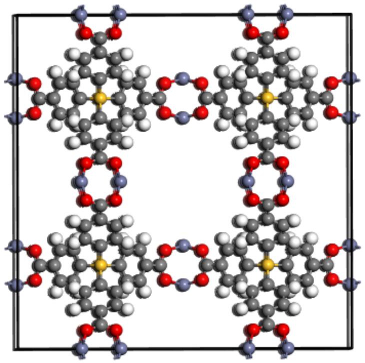
Only 180 MOFs surpass MOF-5 under TPS conditions.

Top 20 MOFs at TPS Conditions

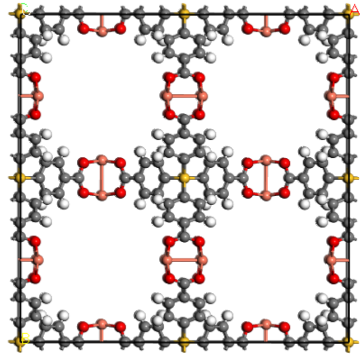
Name	Source	Density (g/cm³)	Gravimetric Surface Area (m²/g)	Volumetric Surface Area (m²/cm³)	Void Fraction	Pore Volume (cm³/g)	Largest Cavity Diameter (Å)	Pore Limiting Diameter (Å)	UG at PS (wt.%)	UV at PS (g/L)	UG at TPS (wt.%)	UV at TPS (g/L)
hypotheticalMOF_5056615_i_1_j_29_k_2_m_2_cat_1	NW	0.56	4388	2474	0.79	1.41	7.9	9.6	4.4	28.6	8.6	53.7
ODIXEG	RM	0.55	4090	2259	0.84	1.42	10.4	7.5	4.9	31.2	8.8	53.7
hypotheticalMOF_5057692_i_1_j_29_k_19_m_2	NW	0.55	4546	2489	0.80	1.47	7.2	9.4	4.7	29.9	8.8	53.6
ENITAX	RM	0.57	4021	2304	0.83	1.36	10.1	7.2	4.7	31.0	8.5	53.5
TEQPEM	RM	0.57	3456	1980	0.86	1.45	17.2	9.2	5.2	34.0	8.5	53.5
RAYMIP	RM	0.50	4101	2062	0.90	1.61	13.5	9.8	5.0	29.4	9.6	53.3
hypotheticalMOF_5057684_i_1_j_29_k_19_m_2	NW	0.52	4776	2468	0.81	1.56	7.1	9.9	5.2	31.3	9.2	53.1
hypotheticalMOF_5058504_i_1_j_29_k_28_m_2_cat_1	NW	0.57	4164	2372	0.80	1.40	9.8	10.7	4.3	28.3	8.5	53.1
hypotheticalMOF_5031348_i_0_j_29_k_10_m_2	NW	0.58	3766	2169	0.82	1.42	7.3	10.8	4.8	31.8	8.4	53.0
hypotheticalMOF_5032270_i_0_j_29_k_20_m_2_cat_2	NW	0.52	4282	2234	0.81	1.55	10.8	12.8	4.9	29.6	9.1	53.0
hypotheticalMOF_5082354_i_2_j_29_k_19_m_5	NW	0.55	4088	2263	0.77	1.40	7.1	10.2	3.5	22.9	8.7	52.9
hypotheticalMOF_5033226_i_0_j_29_k_28_m_0_cat_2	NW	0.49	5106	2483	0.80	1.66	9.4	11.3	5.2	29.5	9.7	52.9
hypotheticalMOF_5033222_i_0_j_29_k_28_m_0_cat_2	NW	0.49	4876	2371	0.80	1.65	9.8	11.4	5.2	29.6	9.7	52.9
hypotheticalMOF_5056349_i_1_j_28_k_28_m_2_cat_1	NW	0.55	3949	2156	0.80	1.46	9.7	11.1	4.6	28.9	8.8	52.8
hypotheticalMOF_5055308_i_1_j_28_k_19_m_2_cat_1	NW	0.54	4173	2240	0.80	1.49	8.3	9.8	4.7	28.9	8.9	52.8
hypotheticalMOF_5058508_i_1_j_29_k_28_m_2_cat_1	NW	0.51	4269	2165	0.81	1.60	8.6	11.1	5.2	30.8	9.4	52.8
hypotheticalMOF_5081896_i_2_j_29_k_12_m_0_cat_2	NW	0.48	4953	2380	0.79	1.64	7.5	10.9	5.0	28.3	9.8	52.8
hypotheticalMOF_5083172_i_2_j_29_k_28_m_2_cat_1	NW	0.57	3905	2219	0.80	1.40	8.4	9.8	4.2	27.6	8.4	52.8
hypotheticalMOF_5027031_i_0_j_28_k_4_m_2	NW	0.61	4186	2560	0.80	1.31	7.2	9.4	4.4	30.3	7.9	52.8
hypotheticalMOF_5058646_i_1_j_29_k_29_m_1_cat_2	NW	0.56	4009	2239	0.78	1.40	7.3	10.9	4.2	27.1	8.6	52.7
MOF-5											**7.8**	**51.9**
MOF-5 + 5%											**8.2**	**54.5**

Examples of High Capacity MOFs

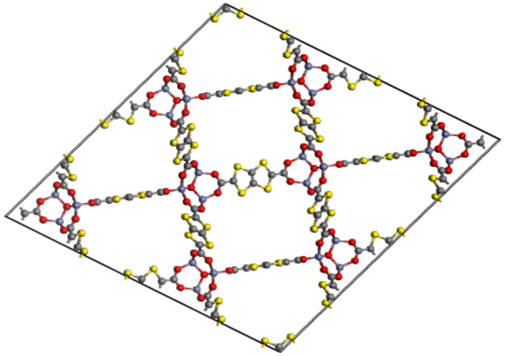
Examples drawn from screening of MOF databases with TPS conditions



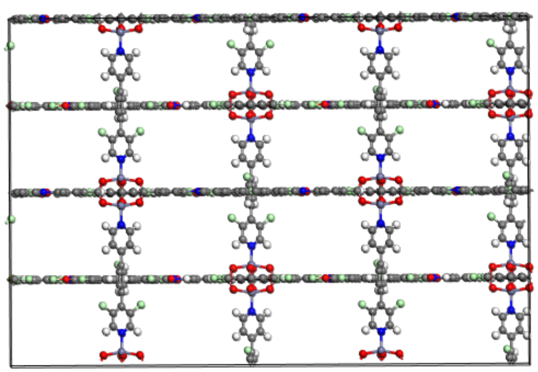
RM: ODIXEG
UG: 8.8 wt.%; UV: 53.7 g/L
GSA: 4090 m^2/g; D: 0.55 g/cm^3
PV: 1.4 cm^3/g; VF: 0.84



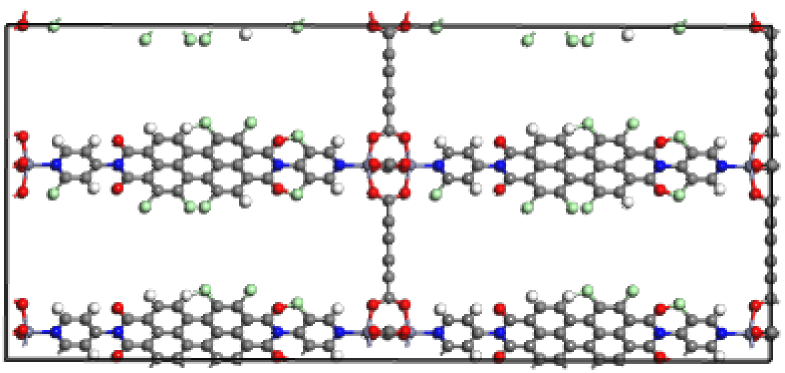
RM: ENITAX
UG: 8.5 wt.%; UV: 53.5 g/L
GSA: 4021 m^2/g; D: 0.57 g/cm^3
PV: 1.36 cm^3/g; VF: 0.83



RM: TEQPEM
UG: 8.5 wt.%; UV: 53.5 g/L
GSA: 3456 m^2/g; D: 0.57 g/cm^3
PV: 1.45 cm^3/g; VF: 0.86



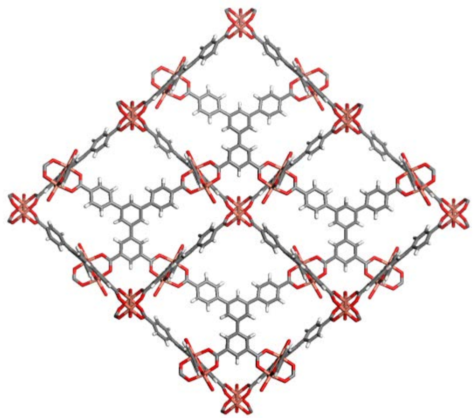
NW: hypotheticalMOF_5056615_i_1_j_29_k_2_m_2_cat_1
UG: 8.6 wt.%; UV: 53.7 g/L
GSA: 4388 m^2/g; D: 0.56 g/cm^3
PV: 1.41 cm^3/g; VF: 0.79



NW: hypotheticalMOF_5057692_i_1_j_29_k_19_m_2
UG: 8.8 wt.%; UV: 53.6 g/L
GSA: 4546 m^2/g; D: 0.55 g/cm^3
PV: 1.47 cm^3/g; VF: 0.80

MOFs Synthesized

Projected high capacity MOF under TPS conditions (currently being tested)



ANUGIA (UMCM-152)

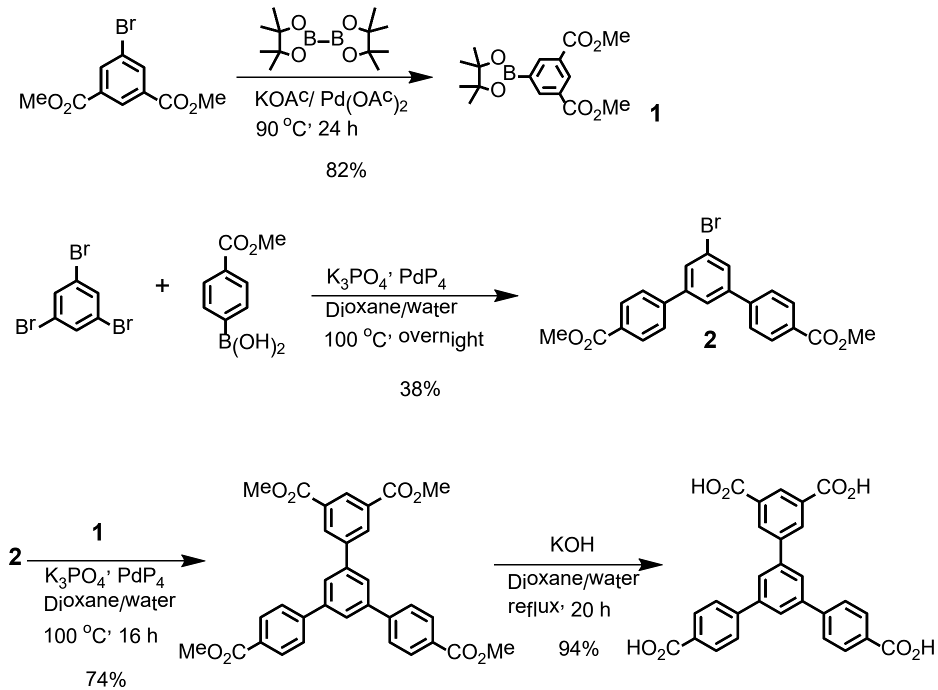
Surface Area

Measured BET	= 3195-3225 m^2/g
Calculated	= 3762 m^2/g
Literature	= 3480 m^2/g

Usable capacities:
P-swing between 5 bar 160 K and 100 bar at 77 K

GCMC calculated grav.	= 8.3 wt.%
GCMC calculated vol.	= 52.3 g/L

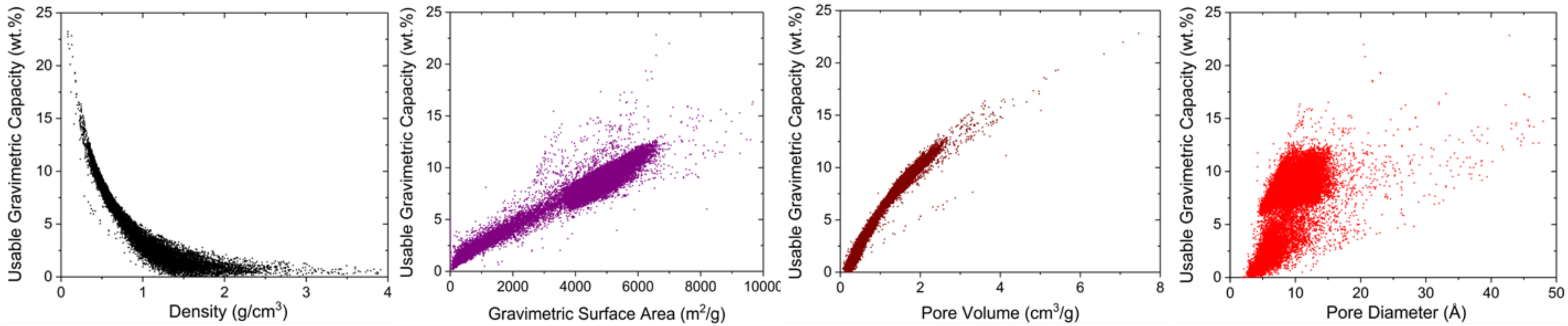
Linker synthesis



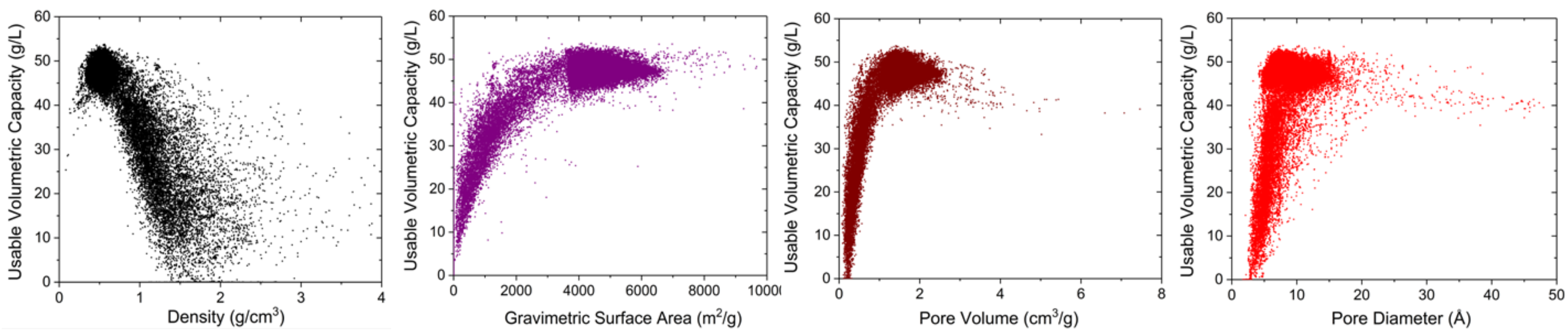
Matzger et. al., *J. Am. Chem. Soc.* **2010**, *132*, 13941.

Structure-Capacity Relationships

Assuming TPS conditions



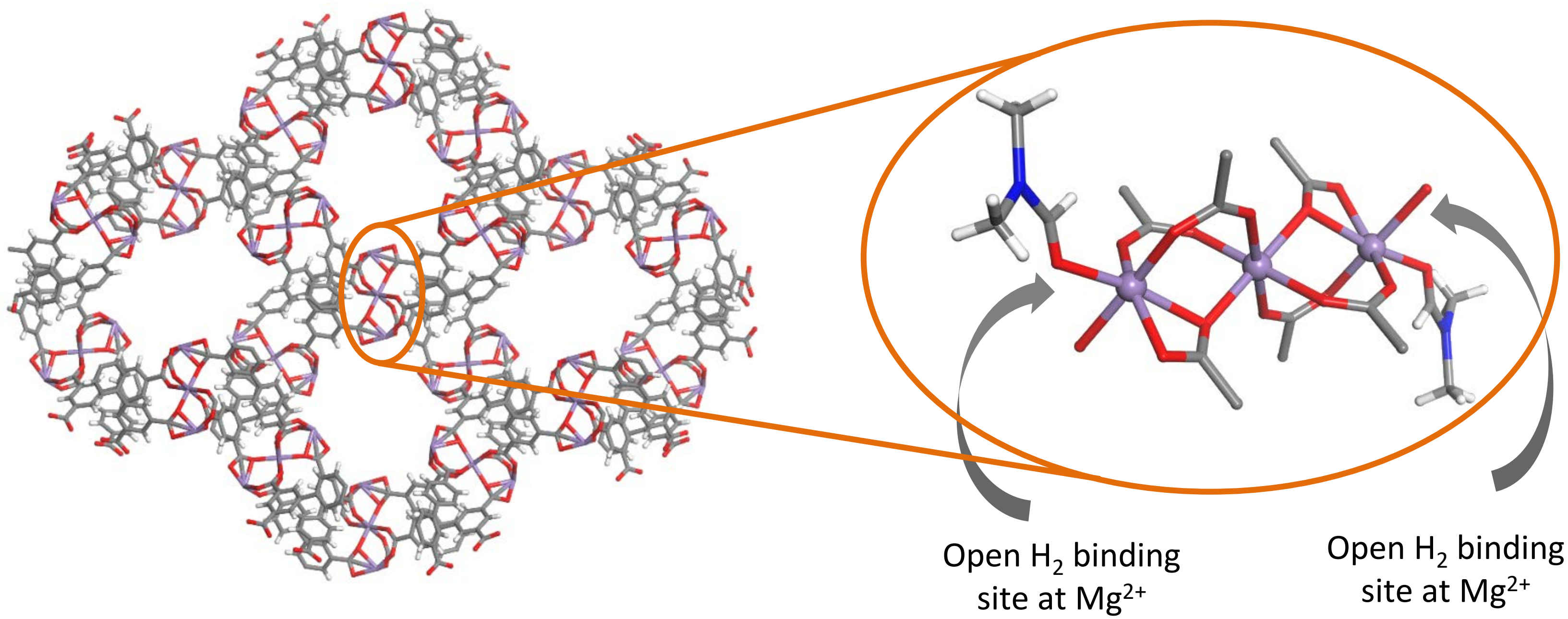
Usable Volumetric Capacity at Temperature+Pressure Swing from (T_{min}= 77 K, P_{max}= 100 bar) to (T_{max}= 160 K, P_{min}= 5 bar).



Density | **Gravimetric Surface Area** | **Pore Volume** | **Pore Diameter**

Mg-MOF with Open Metal Sites

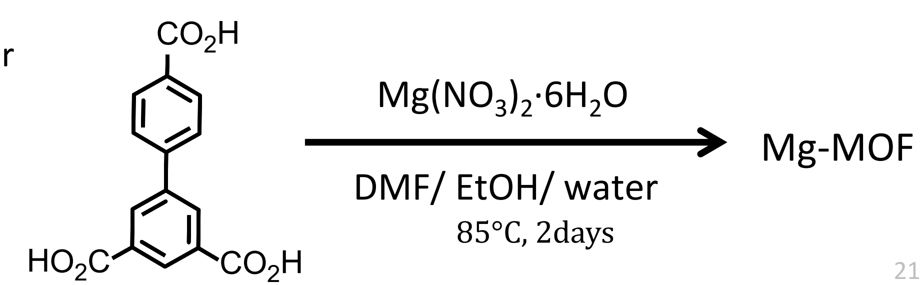
Explored an open metal site MOF with potential to bind multiple H_2



$[Mg_3(BHTC)_2(H_2O)_2(DMF)_2]$

- Crystal Density: 0.639 g/cc
- Four available coordination sites per metal cluster
- BET SA: 1290 m^2g^{-1}
- Calculated SA: 2333 m^2g^{-1}

MOF Synthesis



Activation of Mg-MOF

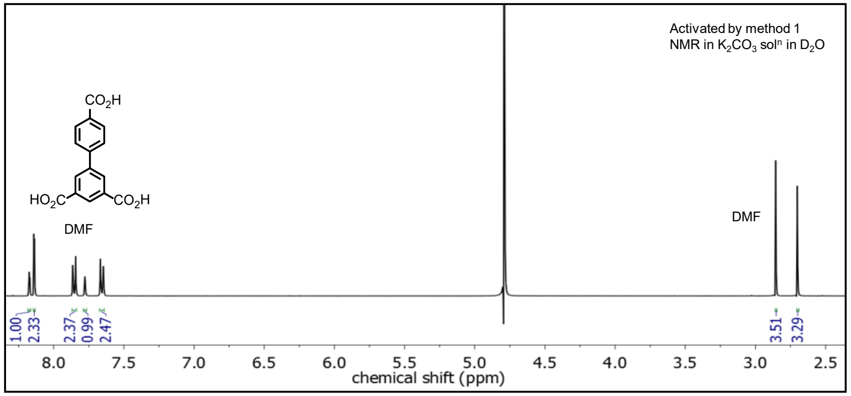
Unable to activate this MOF in a form having high surface area

Activation method 1

Solvent exchange: DMF-DCM

activated at 110 °C for 48h

BET SA: 1280-1350 m^2g^{-1}

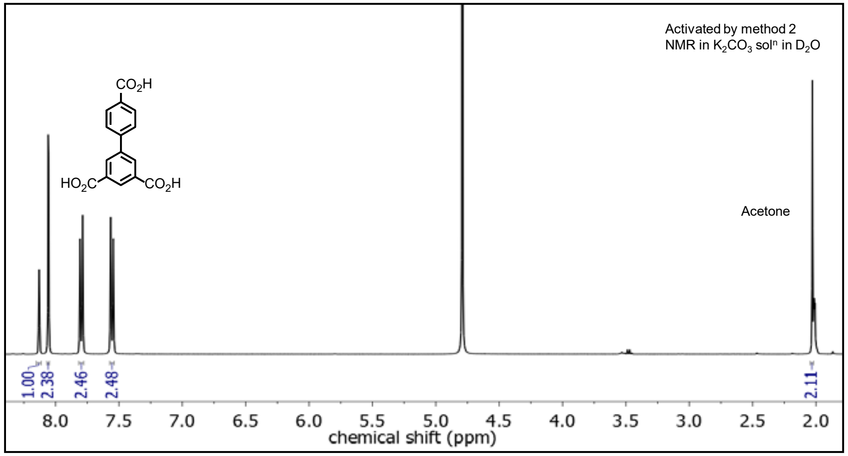


Activation method 2

Solvent exchange: DMF-acetone-hexane

activated at 110 °C for 20h

BET SA: 1290-1320 m^2g^{-1}



Activation method 3

Solvent exchange: DMF-acetone

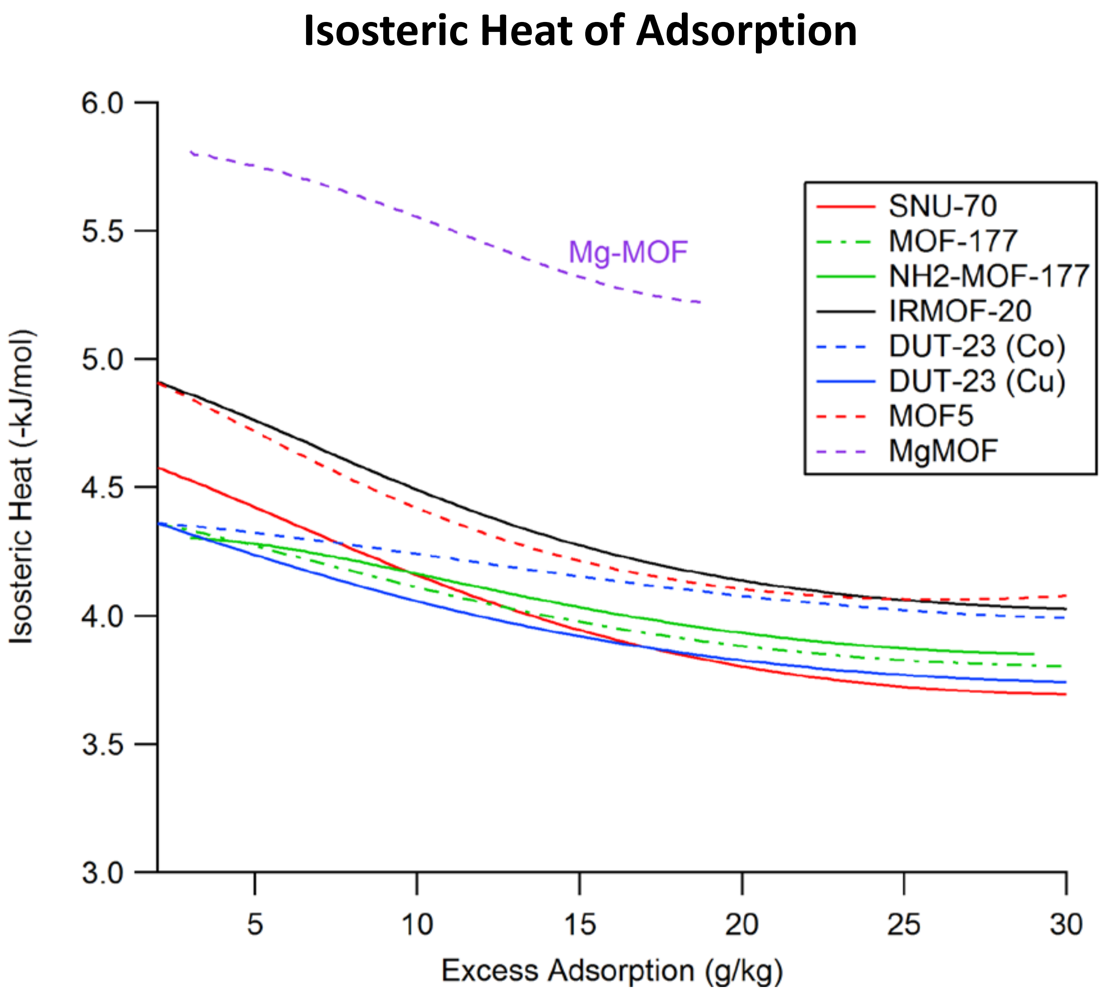
SC CO_2 activation

material collapses

Complete removal of metal-coordinated solvent leads to material collapse; critical amount of solvent must be present in order to retain the framework integrity.

Mg-MOF Characterization

Mg-MOF heat of adsorption is ~1 kJ/mol higher than other MOFs examined



System Model

Type-1 Al tank with MOF and honeycomb HX

Single, Aluminum (6061-T6)
Type 1 Tank
Length:Diameter ratio = 4:1

Balance of plant (BOP)

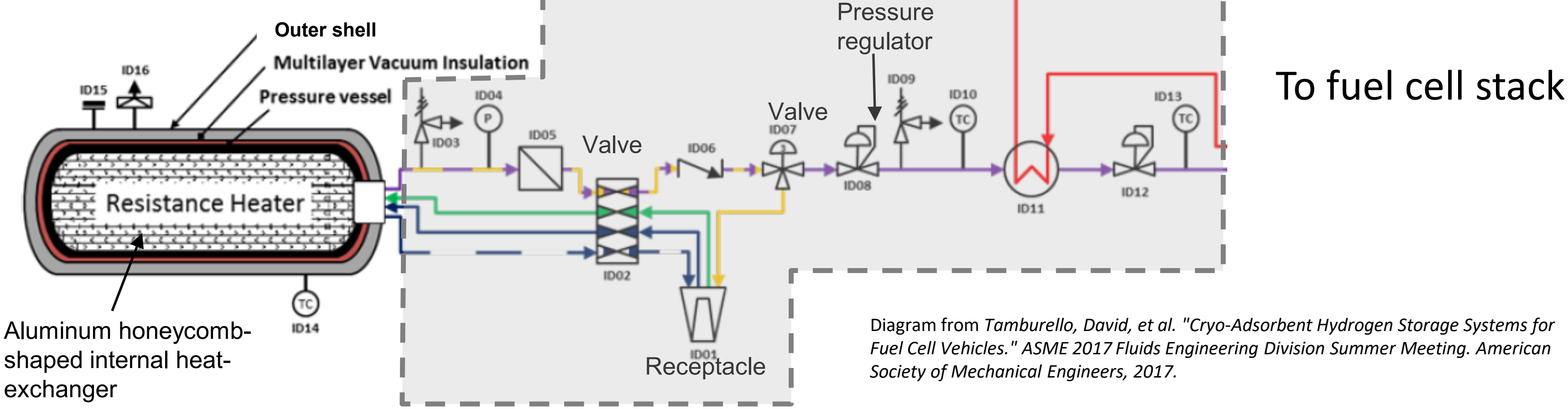
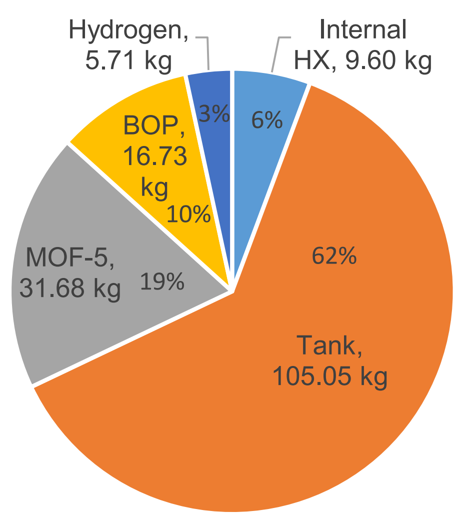


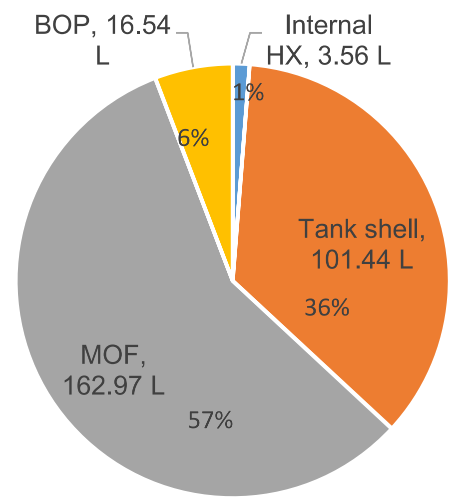
Diagram from *Tamburello, David, et al. "Cryo-Adsorbent Hydrogen Storage Systems for Fuel Cell Vehicles." ASME 2017 Fluids Engineering Division Summer Meeting. American Society of Mechanical Engineers, 2017.*

System Properties

Initial/Full Pressure:	100 bar
Initial/Full Temp:	80 K
Final/Empty Pressure:	5.5 bar
Final/Empty Temp:	160 K
Useable Hydrogen:	5.6 kg
Heat Exchanger:	HexCell
MOF Density: ~0.2 g/cc	
Pressure Vessel:	Type 1 Al
Insulation Thickness:	23 mm
LN2 Chiller Channel:	3/8 inch



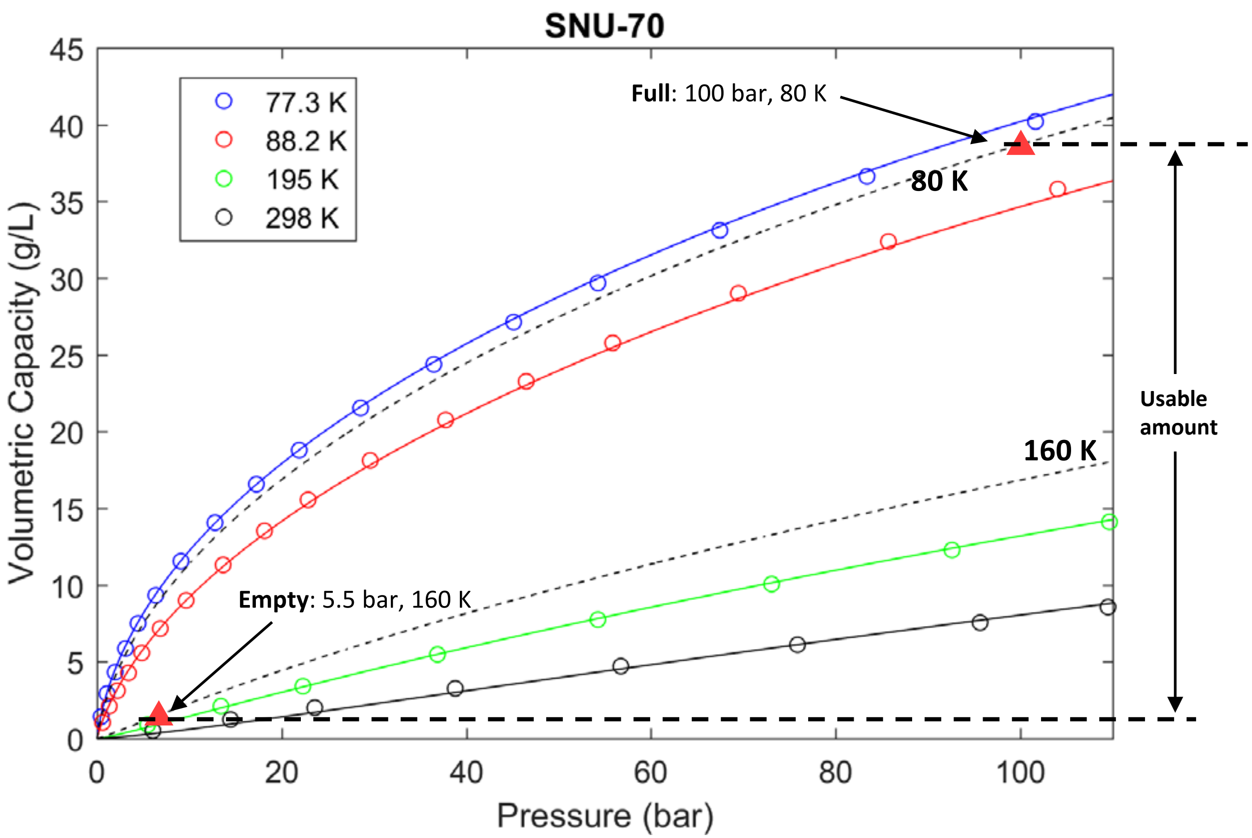
Component Mass



Component Volumes

Usable H_2 Storage Capacity

Materials-level H_2 storage capacities at 80 K and 160 K are estimated from the modified D-A isotherm model



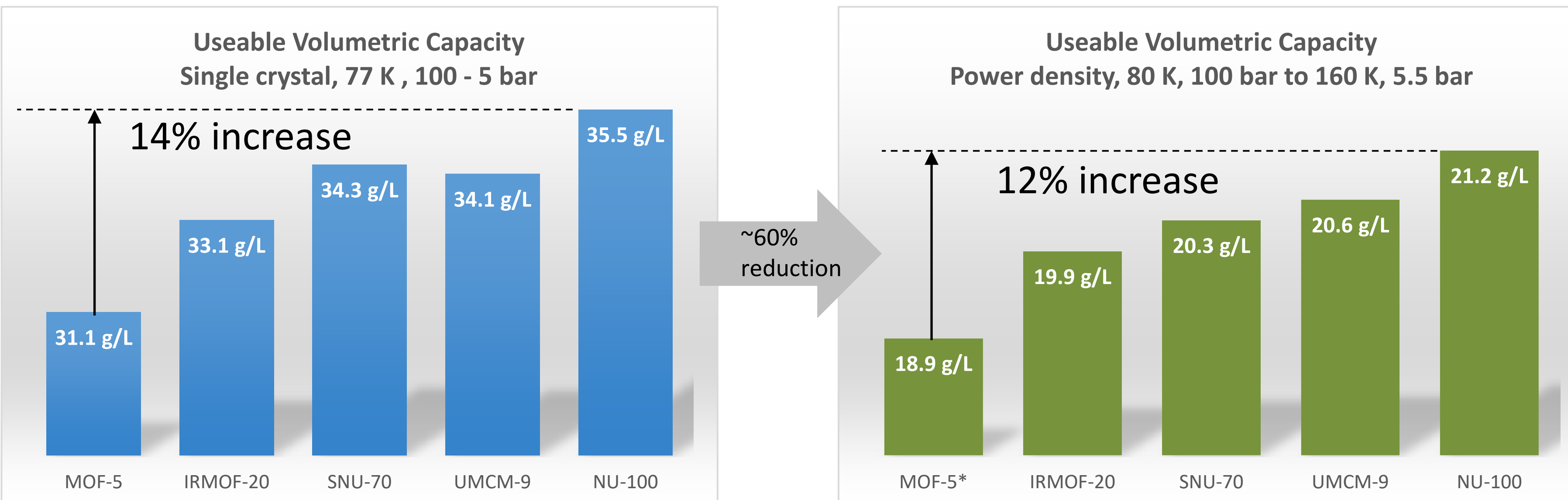
Assumes powder MOF density of 0.2 g/cm^3

System Volumetric Capacity

Conversion of materials-level usable capacity (single crystal density) to system-level capacity at a realistic powder packing density

Material-level capacity at intrinsic crystal density

System capacity at powder packing density



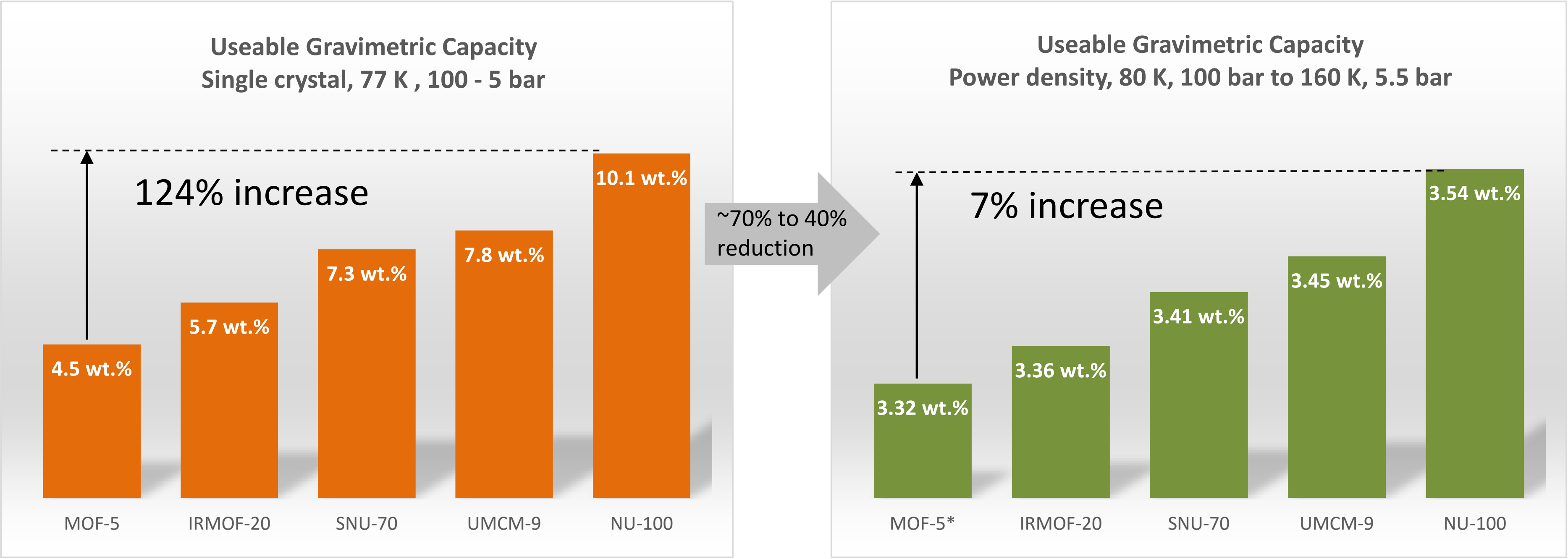
*HSECoE MOF-5 HexCell Projection, ST008 2016 (ρ = 0.13 g/cm^3)
Assumes powder packing density of 0.2 g/cm^3 for other MOFs

System Gravimetric Capacity

Improvements to materials-level gravimetric capacity has limited impact on system-level gravimetric capacity

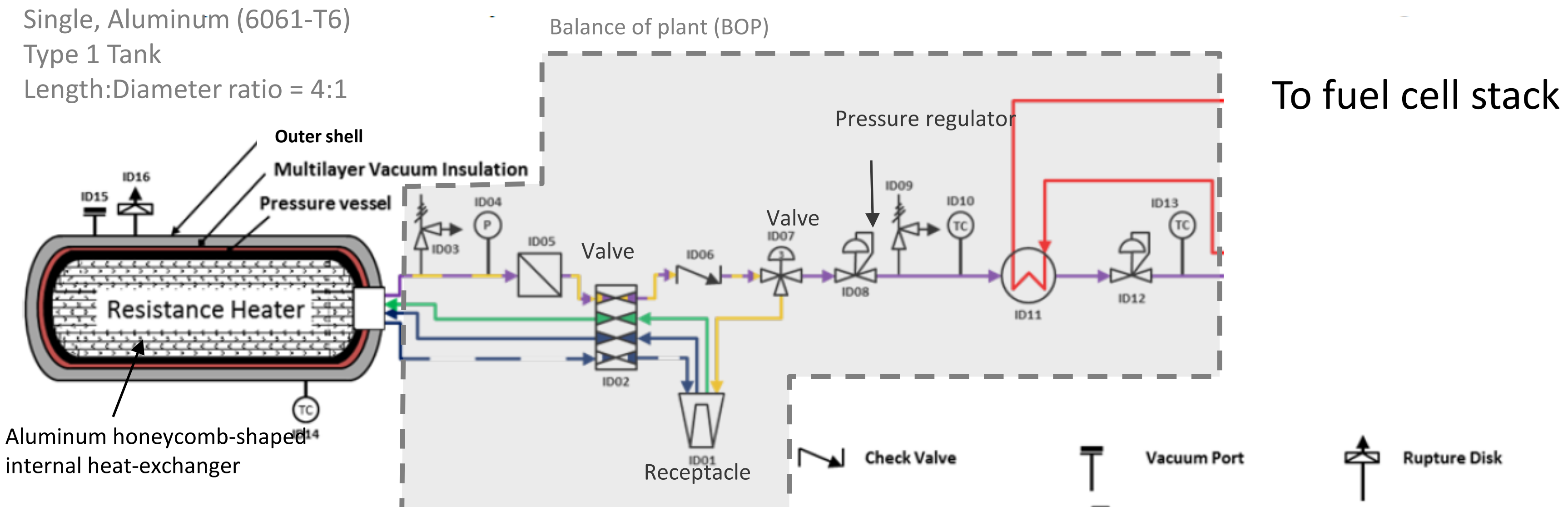
Material-level capacity at intrinsic crystal density

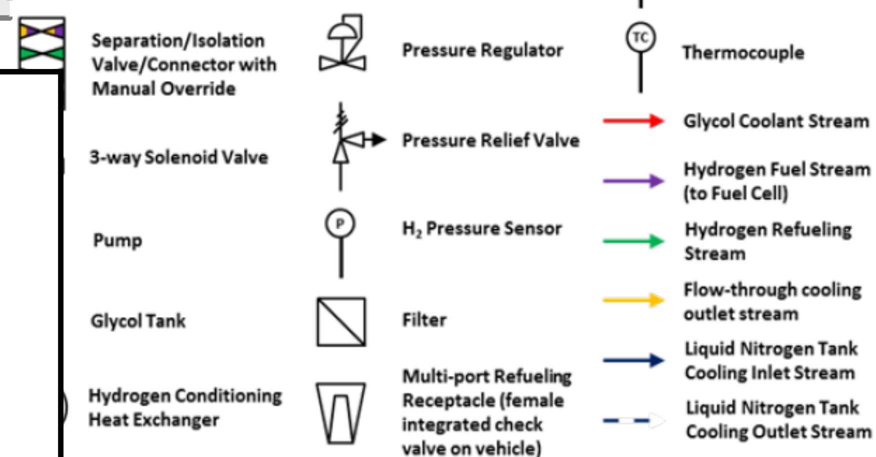
System capacity at powder packing density



*HSECoE MOF-5 HexCell Projection, ST008 2016 ($\rho = 0.13\ g/cm^3$)
Assumes powder packing density of 0.2 g/cm^3 for other MOFs

Engineering Improvements





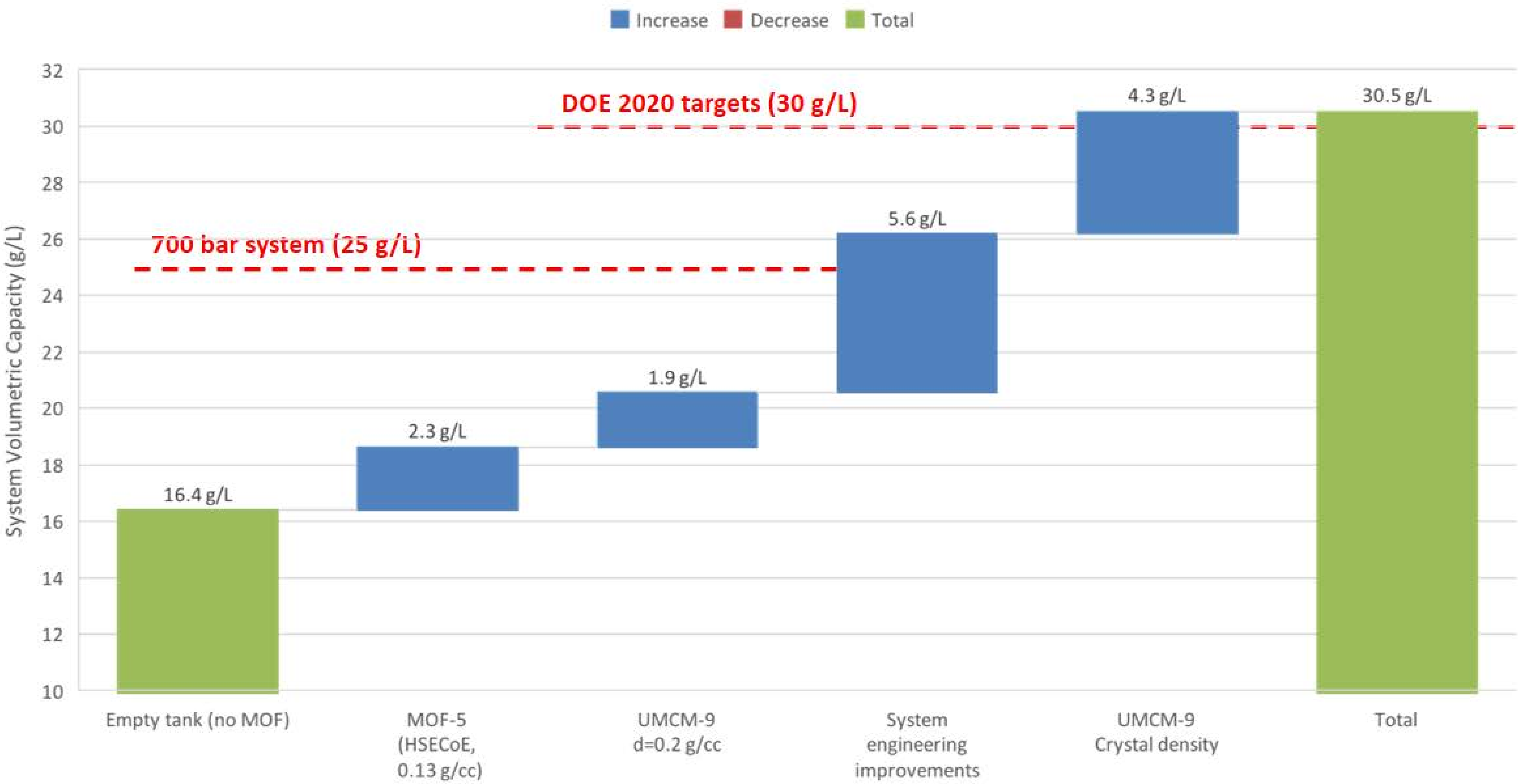
System Properties

Initial/Full Pressure:	100 bar
Initial/Full Temp:	80 K ← **77 K**
Final/Empty Pressure:	5.5 bar
Final/Empty Temp:	160 K
Useable Hydrogen:	5.6 kg
Heat Exchanger:	HexCell
MOF Density: ~0.2 g/cc	
Pressure Vessel:	Type 1 Al ← **(316 SS Type 1 Tank)**
Insulation Thickness:	23 mm ← **10 mm**
LN2 Chiller Channel:	3/8 inch ← **¼ inch**

Diagram from *Tamburello, David, et al. "Cryo-Adsorbent Hydrogen Storage Systems for Fuel Cell Vehicles." ASME 2017 Fluids Engineering Division Summer Meeting. American Society of Mechanical Engineers, 2017.*

Strategies for Increasing Capacity

System-level volumetric capacity as a function of engineering modifications



Storing 5.6 kg H2

Full: 80 K, 100 bar
Empty: 160 K, 5.5 bar

23 mm insulation
3/8 inch LN2 channels
Aluminum Type-1 tank

Storing 5.6 kg H2

MOF-5 compacted to 0.13 g/cc

Full: 80 K, 100 bar
Empty: 160 K, 5.5 bar

Storing 5.6 kg H2

UMCM-9 compacted to 0.2 g/cc

Full: 80 K, 100 bar
Empty: 160 K, 5.5 bar

10 mm insulation
¼ inch LN2 channels

Full: 77 K, 100 bar
Empty: 160 K, 5.5 bar

316 SS Type-1 tank

UMCM-9 compacted to crystal density (assuming no decrease in excess H_2 adsorption)

Collaborations

University of Michigan, Mechanical Engineering

- Atomistic simulation and project management

University of Michigan, Dept. of Chemistry

- Synthesis and characterization of targeted MOFs

Ford Motor Company (sub-contractor)

- PCT measurements
- Materials augmentation, characterization, scale-up, and system modeling

HSECoE/SRNL (unfunded collaborator)

- Assistance with system models (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

Potential Future Work

- Project is nearly complete: July 31, 2018 end date
- Continue experimental efforts aimed at demonstrating MOFs that out-perform MOF-5 under temperature + pressure swing conditions
- Archive computational data for easy access by others
- Revise and submit publications

Any proposed future work is subject to change based on funding levels

Summary

- **Goal**: demonstrate MOFs that achieve high volumetric *and* gravimetric H_2 densities simultaneously (at cryogenic conditions)
  - Establish new high-water mark for H_2 storage in adsorbents
- **Approach**: (*Atoms to systems*) High-throughput screening in combination with experimental synthesis, activation, characterization, and system-level projections
- **Accomplishments:**
  - Identified and experimentally demonstrated several MOFs whose usable capacities exceed that of MOF-5
  - Nearly 500,000 MOFs assessed computationally under PS and TPS conditions.
  - This large database (linking properties and performance) will be a resource for the community in establishing design rules
  - System level projections were provided for the highest-performing MOFs; these projections reveal how materials-level improvements translate to the system level

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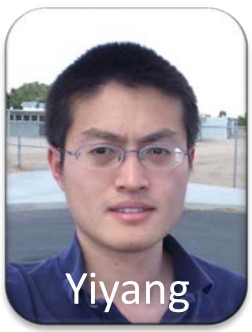
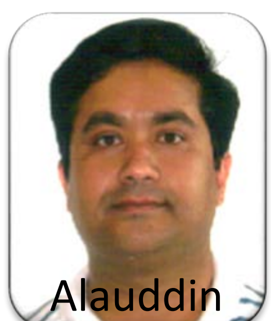
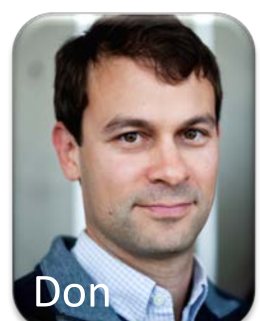
The Team



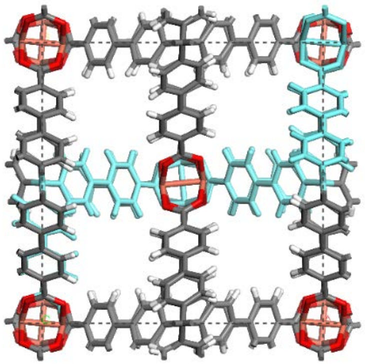




Technical Backup Slides

MOFs Synthesized (1)

Several promising MOFs could not be synthesized with high surface area

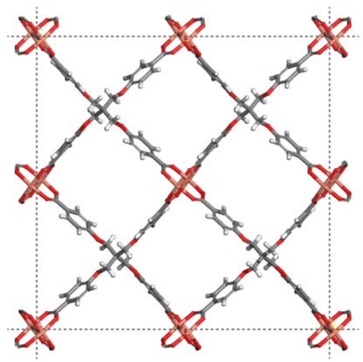


SUKYON

Ma, L. et al., *Angew. Chem. Int. Ed.* **2009**, *48*, 9905.

BET S.A. = 2152 m^2/g (fresh)
[= 2081 m^2/g (6 days under N_2)]
Calculated = 4965 m^2/g
Literature = 1020 m^2/g

Chahine rule capacities:
Total grav. = 11.2 wt. %
Total vol. = 61 g/L

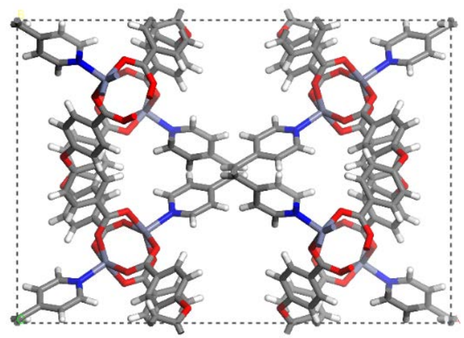


EPOTAF (SNU-21)

Kim, T. K. et al., *Chem. Commun.* **2011**, *47*, 4258.

BET S.A. = 27 m^2/g
Calculated = 5208 m^2/g
Literature = 905 m^2/g

Chahine rule capacities:
Total grav. = 11 wt. %
Total vol. = 71 g/L



DIDDOK

Kondo, M. et al., *J. Organomet. Chem.* **2007**, *692*, 136.

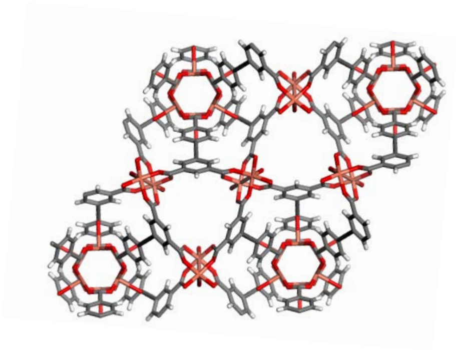
BET S.A. = 578 m^2/g
Calculated = 4652 m^2/g
Literature = not reported

Chahine rule capacities:
Total grav. = 10.2 wt. %
Total vol. = 60 g/L

MOFs Synthesized (2)

Several promising MOFs could not be synthesized with high surface area

OGEBAF (ZJU-32)



Cai, J. et al., *Chem. Commun.* **2014**, *50*, 1552.

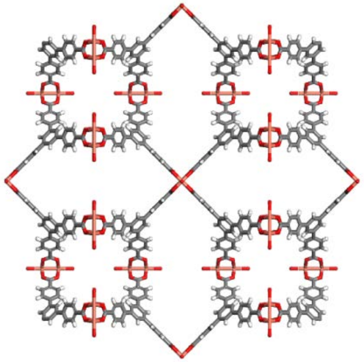
Surface Area

Measured BET = 3714 m^2/g
Calculated = 5163 m^2/g
Literature = 3831 m^2/g

Usable capacities:
P-swing between 5 and 100 bar at 77 K

GCMC calculated grav. = 6.9 wt.%
GCMC calculated vol. = 33.3 g/L

BAZFUF (MOF-143)



Furukawa, H. et al., *Inorg. Chem.* **2011,** *50*, 9147.

Surface Area

Measured BET = 4829 m^2/g
(Unstable after activation; collapses over time)
Calculated = 5470 m^2/g
Literature = not reported

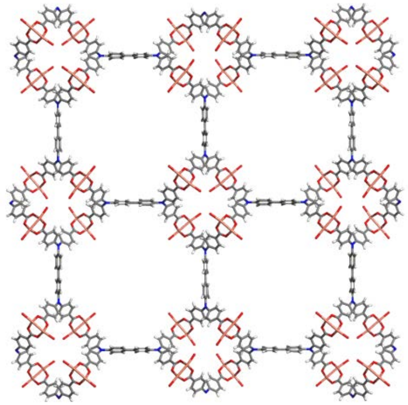
Usable capacities:
P-swing between 5 and 100 bar at 77K

GCMC calculated grav. = 9.1 wt.%
GCMC calculated vol. = 37.1 g/L

MOFs Synthesized (3)

Several promising MOFs could not be synthesized with high surface area

XAFFUH [DUT-12]



Grünker, R. et al., *Eur. J. Inorg. Chem.* **2010**, 3835.

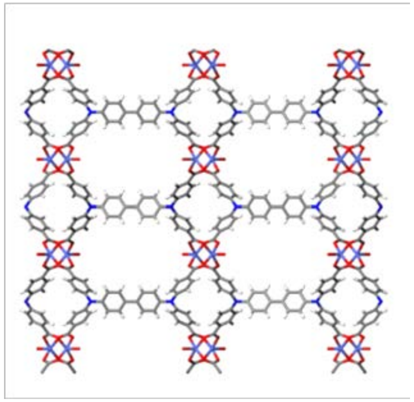
Surface Area

Measured BET	= 958 m^2/g
Calculated	= 5152 m^2/g
Literature	= 824 m^2/g

Usable capacities:

GCMC calculated grav.	= 8.8 wt.%
GCMC calculated vol.	= 34.8 g/L

XAFFIV [DUT-10(Co)]



Grünker, R. et al., *Eur. J. Inorg. Chem.* **2010**, 3835.

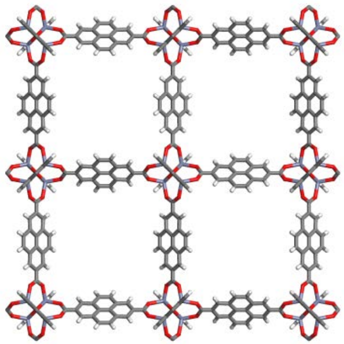
Surface Area

Measured BET	= 456 m^2/g
Calculated	= 5329 m^2/g
Literature	= not reported

Usable capacities:

GCMC calculated grav.	= 8.5 wt.%
GCMC calculated vol.	= 36.6 g/L

EDUVOO (IRMOF-14)



Eddaoudi, M. et al., *Science* **2002**, *295*, 469.

Surface Area

Measured BET	= not phase pure
Calculated	= 4857 m^2/g
Literature	= not reported

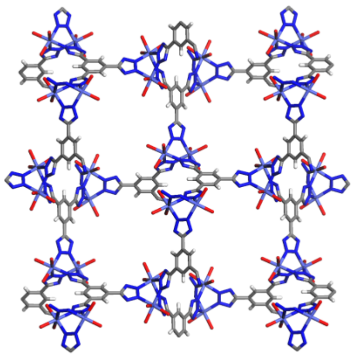
Usable capacities:

GCMC calculated grav.	= 8.0 wt.%
GCMC calculated vol.	= 35.5 g/L

MOFs Synthesized (4)

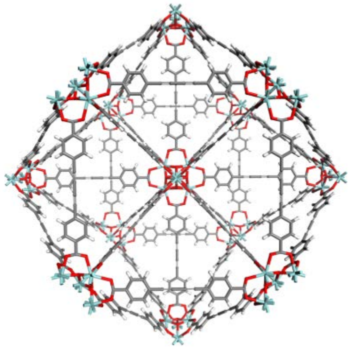
Several promising MOFs could not be synthesized with high surface area

ECOLEP



Li. et al., *Cryst. Growth Des.* **2011**, *11*, 2510.

UKIBIB



Zhou et al., *Dalton Trans.* **2017**, *46, 14270*.

Surface Area (ECOLEP)

Measured BET	= not phase pure
Calculated	= 4510 m^2/g
Literature	= 202 m^2/g

Usable capacities:

GCMC calculated grav.	= 8.2 wt.%
GCMC calculated vol.	= 39 g/L

Surface Area (UKIBIB)

Measured BET	= 2700 m^2/g, not phase pure
Calculated	= 4232 m^2/g
Literature	= 4825 m^2/g

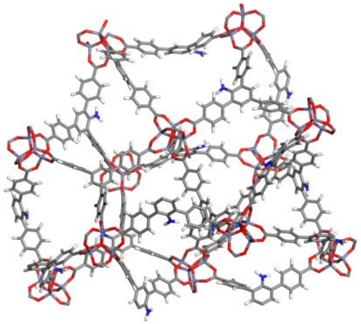
Usable capacities:

GCMC calculated grav.	= 7.2 wt.%
GCMC calculated vol.	= 35.6 g/L

MOFs Synthesized (5)

Examples of high surface area MOFs with unsatisfactory volumetric capacity

MOF-177-NH2



Dutta, A. et al., *Angew. Chem. Int. Ed.* **2015**, *54*, 3983.

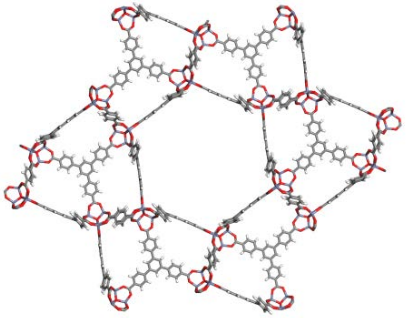
Surface Area

Measured BET = 4280 m^2/g (fresh)
Calculated = 4514 m^2/g
Literature = 4631 m^2/g

Usable capacities:
P-swing between 5 and 100 bar at 77 K

Measured grav. = 6.4 wt.%
GCMC calculated grav. = 6.4 wt.%
Measured vol. = 32.6 g/L
GCMC calculated vol. = 33.7 g/L

UMCM-1



Koh, K. et al., *Angew. Chem. Int. Ed.* **2008**, *47*, 677.

Surface Area

Measured BET = 4122 m^2/g
Calculated = 4391 m^2/g
Literature = 4160 m^2/g

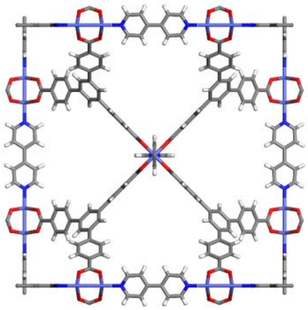
Usable capacities:
P-swing between 5 and 100 bar at 77K

Measured grav. = 6.8 wt.%
GCMC calculated grav. = 7.6 wt.%
Measured vol. = 32.6 g/L
GCMC calculated vol. = 34.9 g/L

MOFs Synthesized (6)

Examples of high surface area MOFs with unsatisfactory volumetric capacity

ICAQIO [DUT-23(Co)]



Klein, N. et al., Chem. *Eur. J. Chem.* **2011**, *17*, 13007.

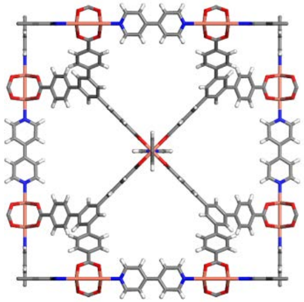
Surface Area

Measured BET = 4044 m^2/g (fresh)
Calculated = 4714 m^2/g
Literature = 4850 m^2/g

Usable capacities:
P-swing between 5 and 100 bar at 77 K

Measured grav. = 6.2 wt.%
GCMC calculated grav. = 6.7 wt.%
Measured vol. = 30.2 g/L
GCMC calculated vol. = 31.9 g/L

ICAQOU [DUT-23(Cu)]



Klein, N. et al., Chem. *Eur. J.. Chem.* **2011**, *17*, 13007.

Surface Area

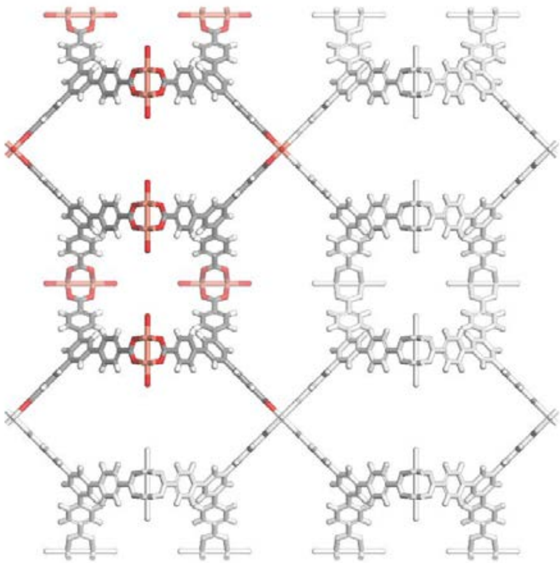
Measured BET = 4601 m^2/g (fresh)
Calculated = 4664 m^2/g
Literature = 4730 m^2/g

Usable capacities:
P-swing between 5 and 100 bar at 77 K

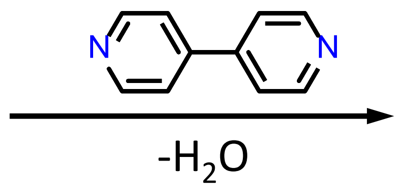
Measured grav. = 6.7 wt.%
GCMC calculated grav. = 6.6 wt.%
Measured vol. = 32.4 g/L
GCMC calculated vol. = 31.7 g/L

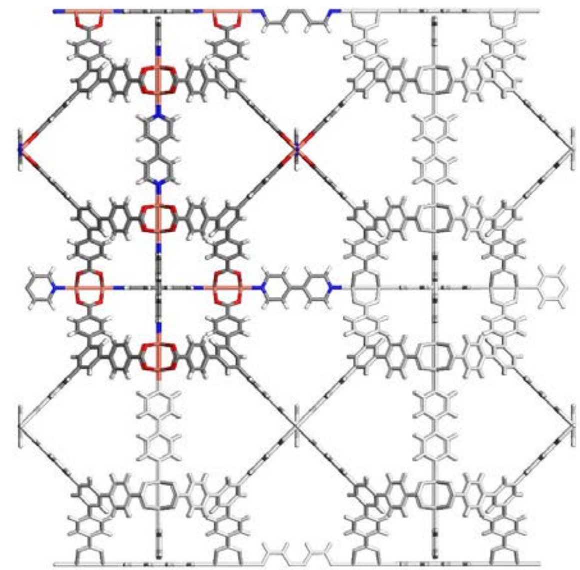
Stability of BAZFUF vs ICAQOU

Can potentially be achieved by use of bridging 4,4'-bipyridine between Cu centers



BAZFUF





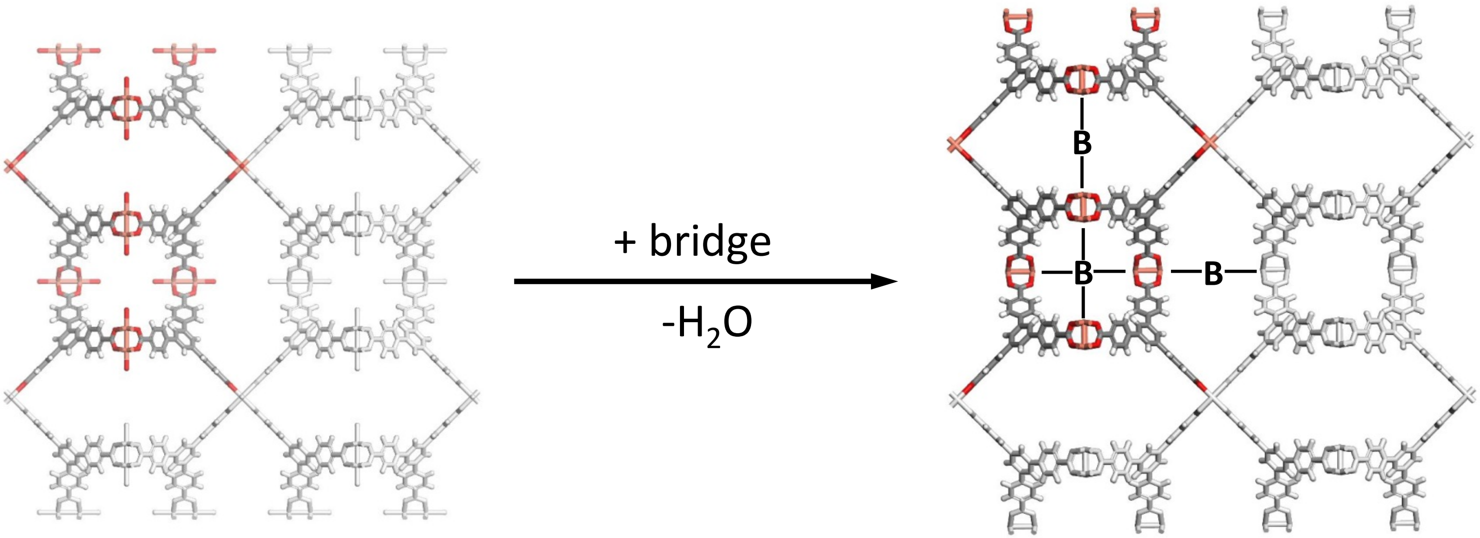
ICAQOU

$scCO_2$ activated material collapses over time: SA decreases even after storage under N_2 atmosphere

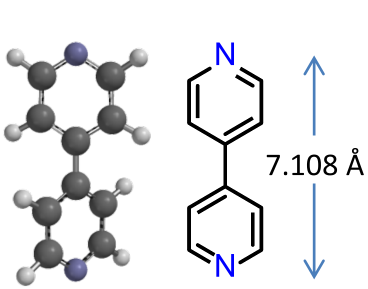
Stable after $scCO_2$ activation

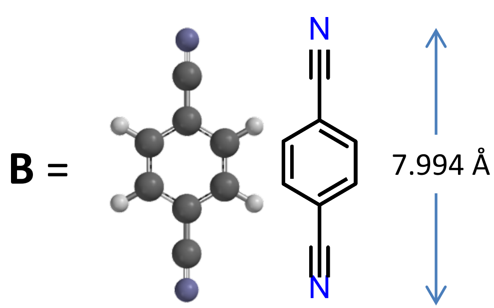
Strengthening the Structure of BAZFUF

Q: Can we increase the structural rigidity of the BAZFUF framework, while preserving its volumetric capacity?

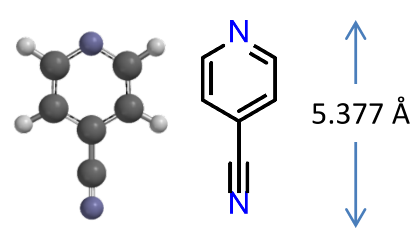


No incorporation of bridge!





1,4-dicyanobenzene

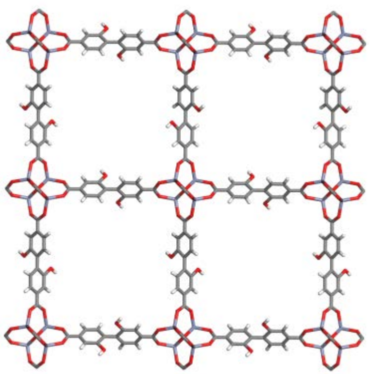


4-cyanopyridine

MOFs Synthesized (7)

Several promising MOFs could not be synthesized with high surface area

ZELROZ



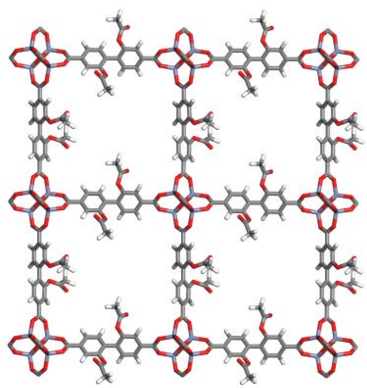
Surface Area

Measured BET	= 3500 m^2/g
Calculated	= 4998 m^2/g
Literature	= 2631 m^2/g

Usable capacities:
P-swing between 5-100 bar at 77 K

GCMC calculated grav.	= 8.7 wt.%
GCMC calculated vol.	= 36.8 g/L

ZELROZ (OAc Variant)



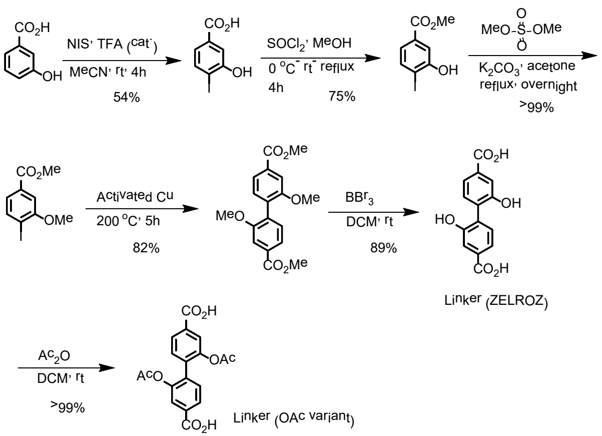
Surface Area

Measured BET	= 3600 m^2/g
Calculated	= 5122 m^2/g
Literature	≈ 3200 m^2/g

Usable capacities:
P-swing between 5-100 bar at 77 K

GCMC calculated grav.	= 6.3 wt.%
GCMC calculated vol.	= 32.3 g/L

Linker synthesis

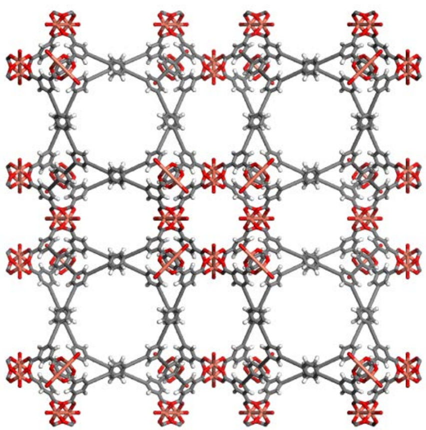


Rankine, D. et al., *Chem. Commun.* **2012**, *48*, 10328.

MOFs Synthesized (8)

Example of **real MOF** having high usable volumetric capacity

GAGZEV (NU-100)



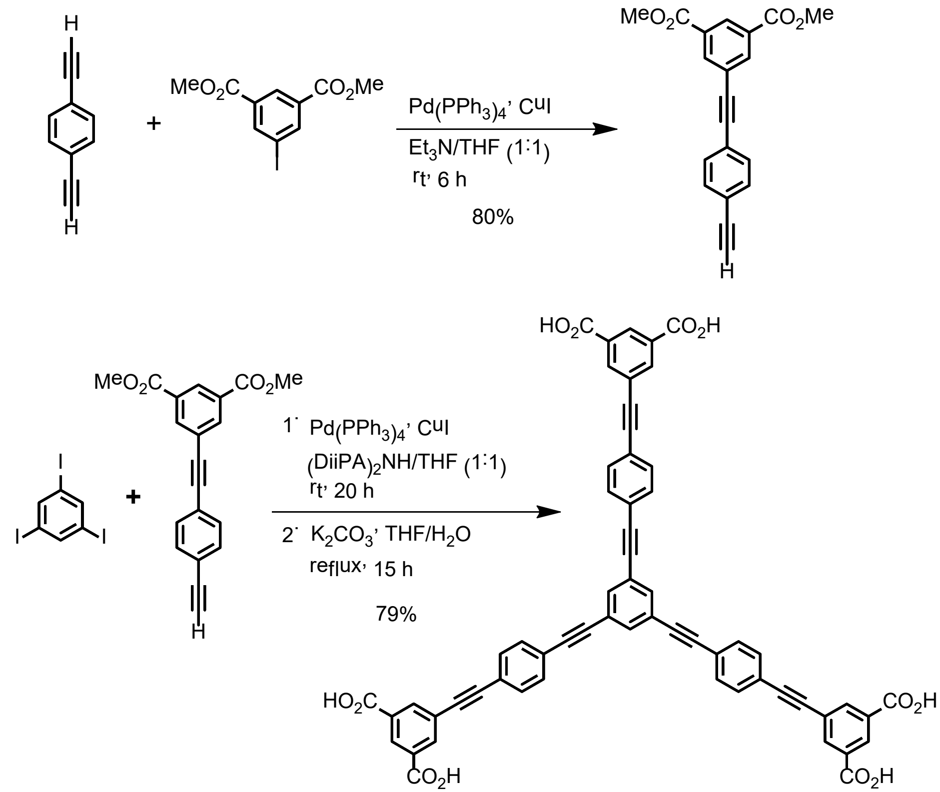
Surface Area

Measured BET	= 5800-6300 m^2/g
Calculated	= 5777 m^2/g
Literature	= 6143 m^2/g

Usable capacities:
P-swing between 5 and 100 bar at 77 K

Measured gravimetric = 10.1 wt.% (GCMC calc. = 10.8 wt.%)
Measured volumetric = 35.5 g/L (GCMC calc. = 37.0 g/L)

Linker synthesis

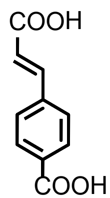
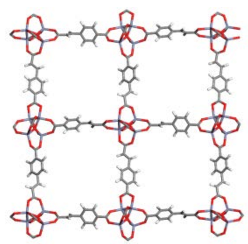
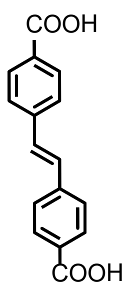
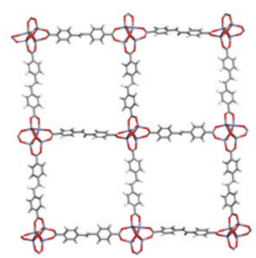


- 7 steps in the original synthesis
- can be made in 3 steps by modified method

Yuan, D. et al., *Angew. Chem. Int. Ed.* **2010**, *49*, 5357.
Farha, O. K. et. al., *Nat. Chem.* **2010**, *2*, 944.

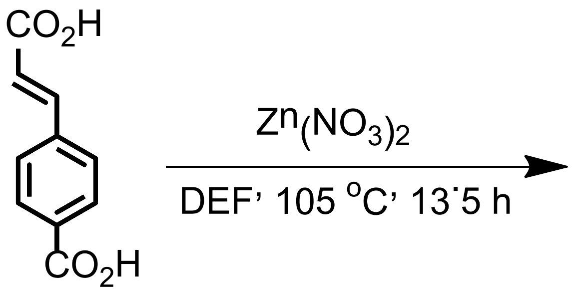
MOFs Synthesized (9)

Examples of **hypothetical MOFs** having high calculated volumetric capacities

Mail-Order MOF #	Organic Linker	Structure	Calc. Surface Area m^2/g	Calculated Usable Capacities (P-swing 5 to 100 bar)	
MOF-5_cooh_2_567 **aka SNU-70**			4756	8.0 wt. %	36.8 g/L
MOF-5_cooh_2_646 (doubly interpenetrated, Langmuir SA: 580 m^2g^{-1}) Ref: *JACS* **2007**, *129*, 7136.			5781	12.5 wt. %	36.7 g/L

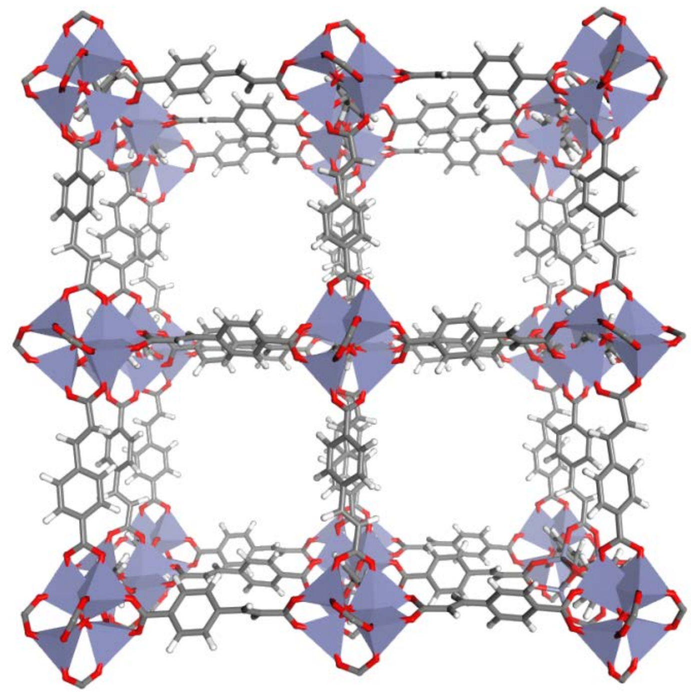
SNU-70: Better than IRMOF-20

Example of **hypothetical MOF** having high volumetric capacity



MOF-5_cooh_2_567

aka SNU-70



Surface Area

Measured BET	= 5560-5700 m^2/g
Calculated	= 4756 m^2/g
Literature	= 5290 m^2/g

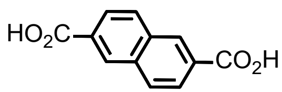
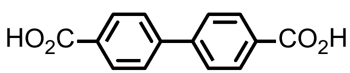
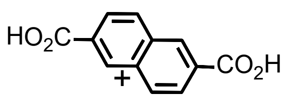
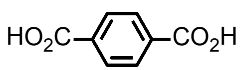
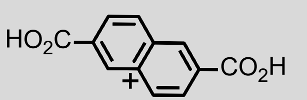
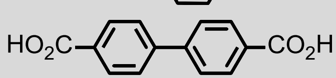
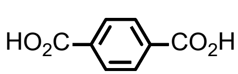
Usable capacities:
P-swing between 5 and 100 bar at 77 K

Measured gravimetric	= 7.3 wt.%
GCMC calculated grav.	= 8.0 wt.%
Measured volumetric	= 34.3 g/L
GCMC calculated vol.	= 36.8 g/L

Suh et. al. *Chem. Eur. J.* **2012**, *18*, 8673.

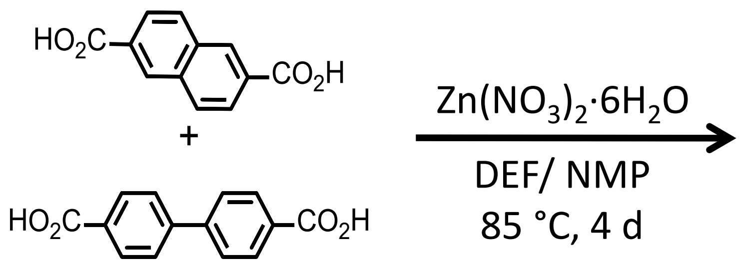
Highly porous MOFs Containing Zn_4O Cluster

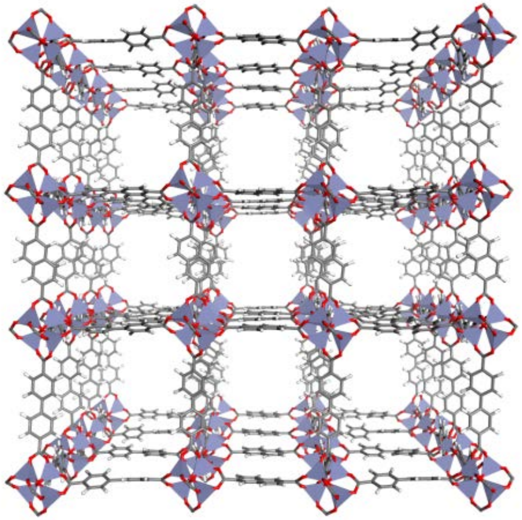
Designed MOFs based on crystallographic properties

Name	Linker	Usable Capacity at 77 K (between 5 and 100 bar)		Void Fraction	Gravimetric Surface Area (m^2/g)	Volumetric Surface Area (m^2/cm^3)	Density (g/cm^3)	Pore Volume (cm^3/g)
		UV [g/L]	UG [wt%]					
IRMOF-8-noninterpenetrated		35.3	6.8	0.83	4379	1964	0.45	1.86
IRMOF-10-noninterpenetrated		37.6	9.6	0.87	4999	1641	0.33	2.65
UMCM-8	 	33.4	5.7	0.82	4098	2096	0.51	1.61
UMCM-9	 	36.2	8.3	0.86	4847	1805	0.37	2.31
MOF-5		31.1	4.5	0.78	3563	2172	0.60	1.36

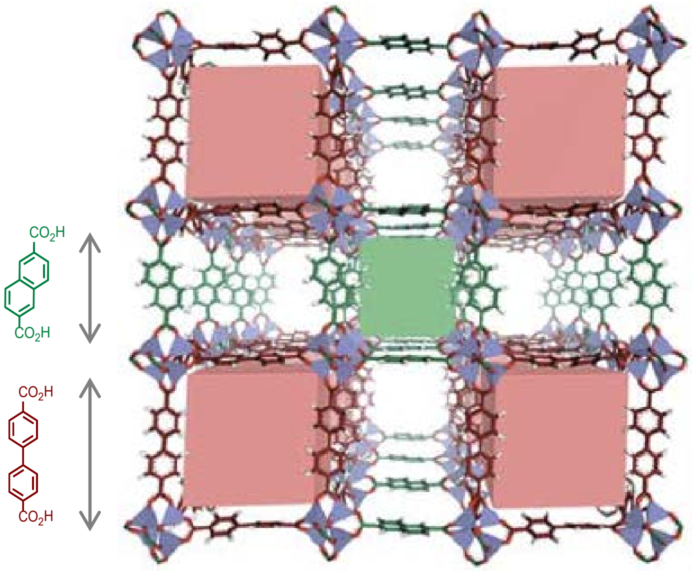
MOFs Synthesized (10)

UMCM-9: better than IRMOF-20 and similar as SNU-70





UMCM-9



Matzger et. al., *Chem. Sci.* **2012**, *3,* 2429.

Surface Area

Measured BET	= 5000-5250 m^2/g
Calculated	= 4847 m^2/g
Literature	= 4930-5030 m^2/g

Usable capacities:
P-swing between 5 and 100 bar at 77 K

Measured gravimetric = 7.8 wt.% (GCMC calc. = 8.3 wt.%)
Measured volumetric = 34.1 g/L (GCMC calc. = 36.2 g/L)

Capacity Definitions

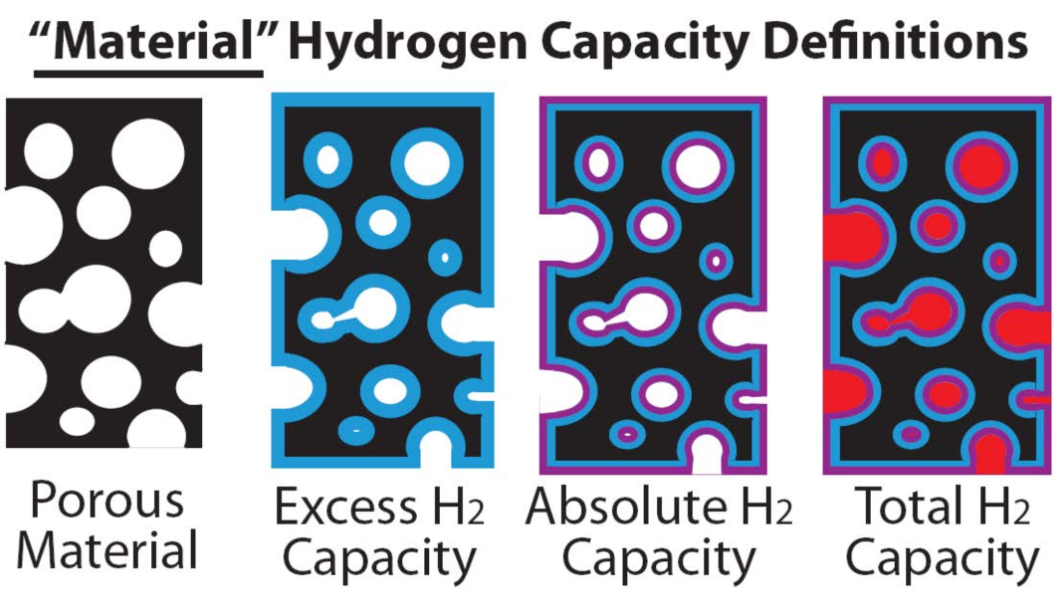
$$C_{tot} = C_{exc} + \frac{100 \times d_g V_{pore}}{1 + d_g V_{pore}}$$

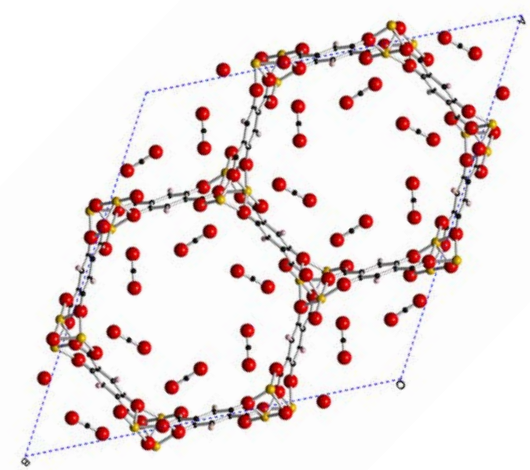
$$V_{pore} = \frac{d_{sk} - d_{bulk}}{d_{sk} d_{bulk}}$$

Recommended Best Practices for the Characterization of Storage Properties of Hydrogen Storage Materials, V3.34, p.223

C_{tot} = total adsorption capacity in wt.%
C_{exc} = excess adsorption in wt.%
V_{pore} = specific pore volume

d_g = density of H_2 gas at T,P
d_{sk} = skeletal density
d_{bulk} = bulk density



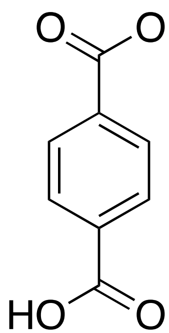


Synthesis of MOF-5

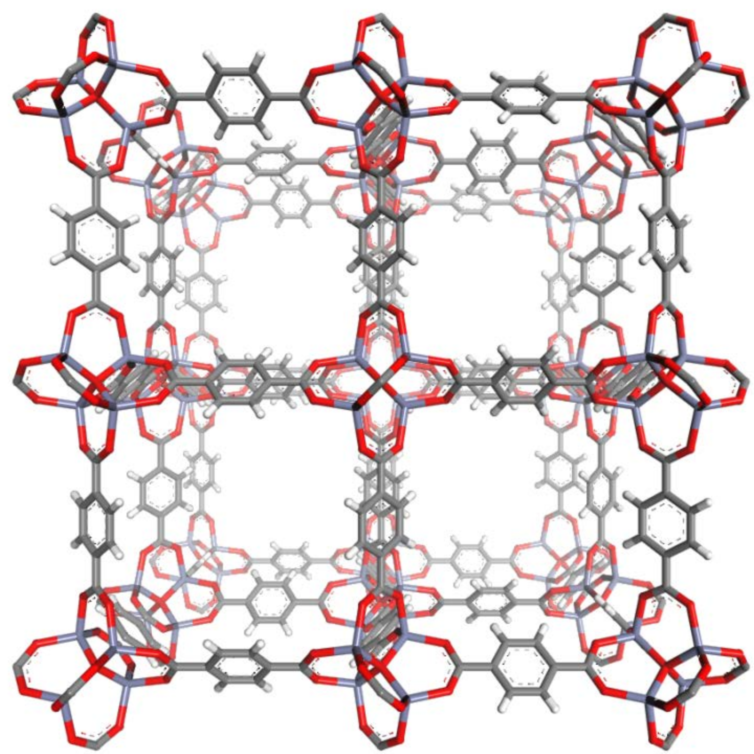
Performed air-free synthesis[1] of the benchmark compound MOF-5

$$H_2BDC + Zn(NO_3)_2 \bullet 6H_2O \xrightarrow[80\ ^{\circ}C]{N,N\text{-diethylformamide}} Zn_4O(BDC)_3$$

H_2BDC =



Benzenedicarboxylic acid



Activated by:

1) Multiple solvent exchanges
2) RT vacuum drying

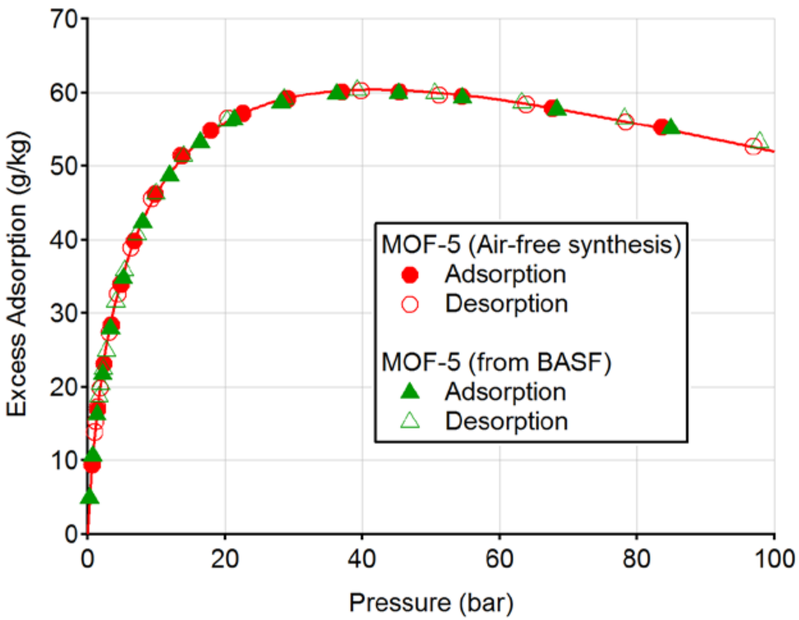
BET S.A. =	3512 m^2/g
Calculated =	3563 m^2/g
Literature =	3800 m^2/g [1]

[1]Kaye, Dailly, Yaghi, and Long, 2007. JACS, 129,14176: 8.4 wt.%, 54 g/L at 35 bar/77K

MOF-5 Hydrogen Uptake

- Measured performance of in-house MOF-5
  - H_2 uptake & BET surface area essentially identical to BASF-supplied MOF-5 (HSECoE)
- Usable capacity (pressure swing to 5 bar) adopted as benchmark

T = 77 K



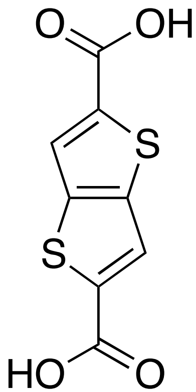
	Total		Usable (P-swing)	
p (bar)	Volumetric (g/L)	Gravimetric (wt.%)	Volumetric (g/L)	Gravimetric (wt.%)
5	22.2	3.5		
35	44.4	6.8	**22.2**	**3.3**
50	47.8	7.3	**25.6**	**3.8**
100	53.3	8.0	**31.1**	**4.5**

A Success Story: IRMOF-20

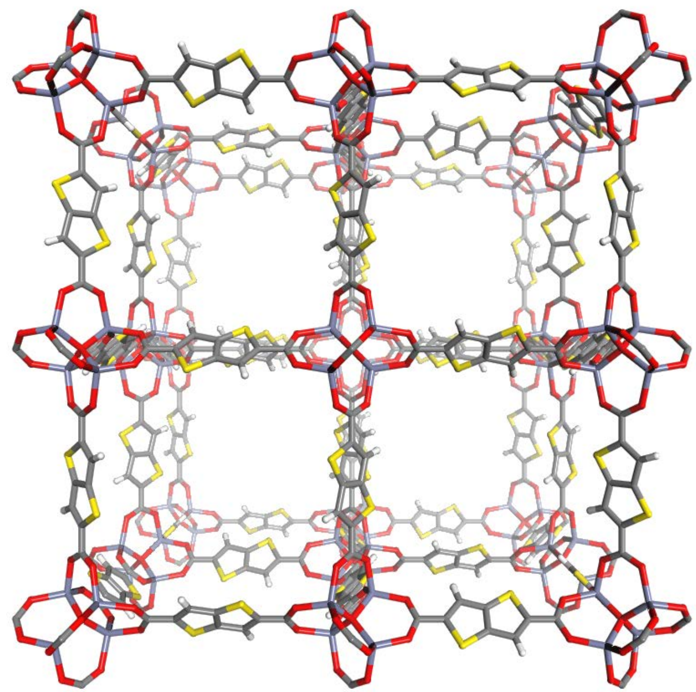
Synthesis of IRMOF-20 was attempted after computation identified it as a promising compound

$$H_2TTDC + Zn(NO_3)_2\bullet 4H_2O \xrightarrow[100\ ^{\circ}C]{\text{N,N-diethylformamide}} Zn_4O(TTDC)_3$$

H_2TTDC =



Thieno[3,2-*b*]thiophene-2,5-dicarboxylic acid



Rowsell, J. L. C.; Yaghi, O.M. *J. Am. Chem. Soc.* **2006**, *128*, 1304.

Activated by:

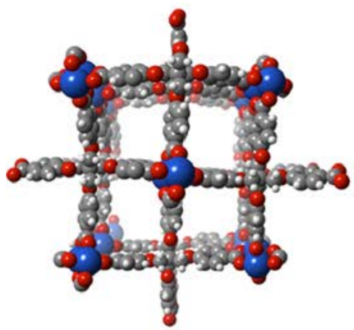
1) Multiple solvent exchanges
2) RT vacuum drying

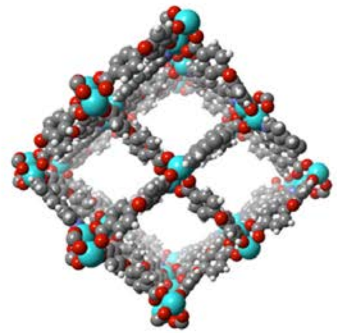
BET S.A. =	4073 m^2/g (94% of calc'd)
Calculated =	4324 m^2/g
Literature =	3409 m^2/g

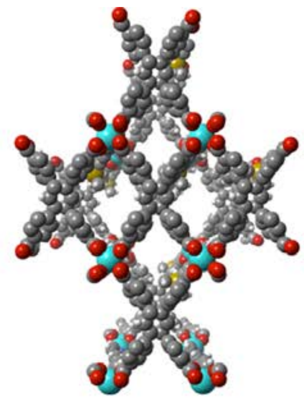
MOFs Identified by Prior Screening

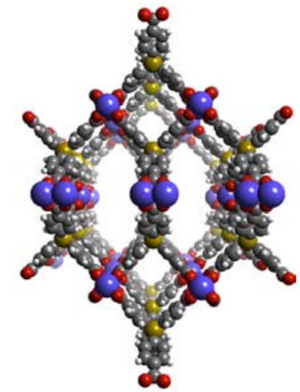
Several MOF “Targets of Opportunity” were identified

- Combine high gravimetric and volumetric densities
- Overlooked: no/limited experimental evaluation
- Can these be synthesized in a robust form?







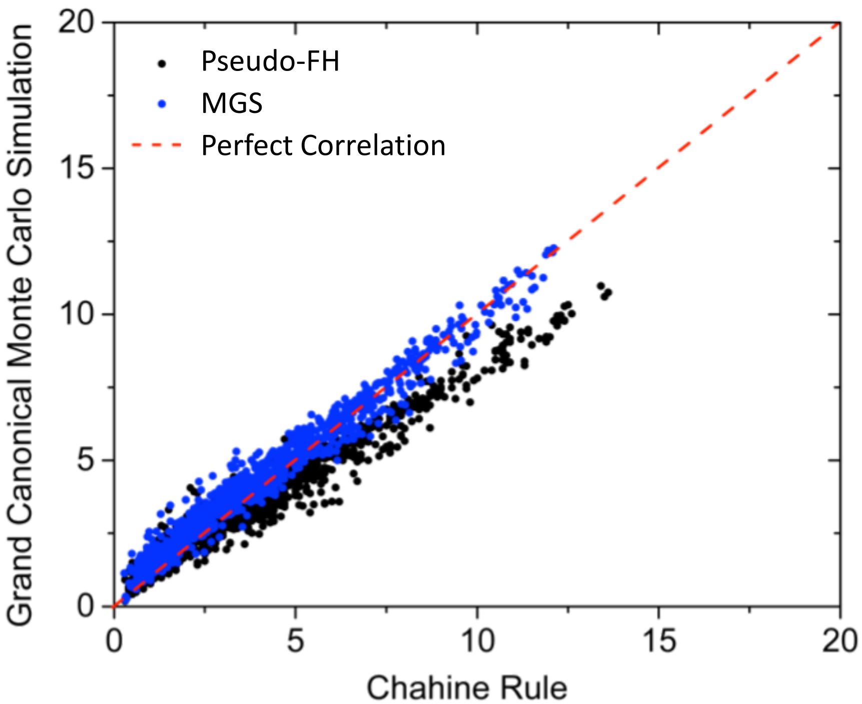


	EPOTAF (SNU-21)	DIDDOK	LURGEL (TO-MOF)	ENITAX (IMP-9)
Total Grav. (wt. %)	11	10.2	9.7	9.3
Total Volumetric (g/L)	71	60	57	59
Crystal Density (g/cm^3)	0.58	0.53	0.53	0.57
Calc’d/Meas. SA (m^2/g)	5208/700-900	4651	4386/680	4162
Notes	Best combination of grav. & vol. density. H_2 uptake measured previously: 5 wt %	No measurements	CO_2 uptake measured.	No measurements

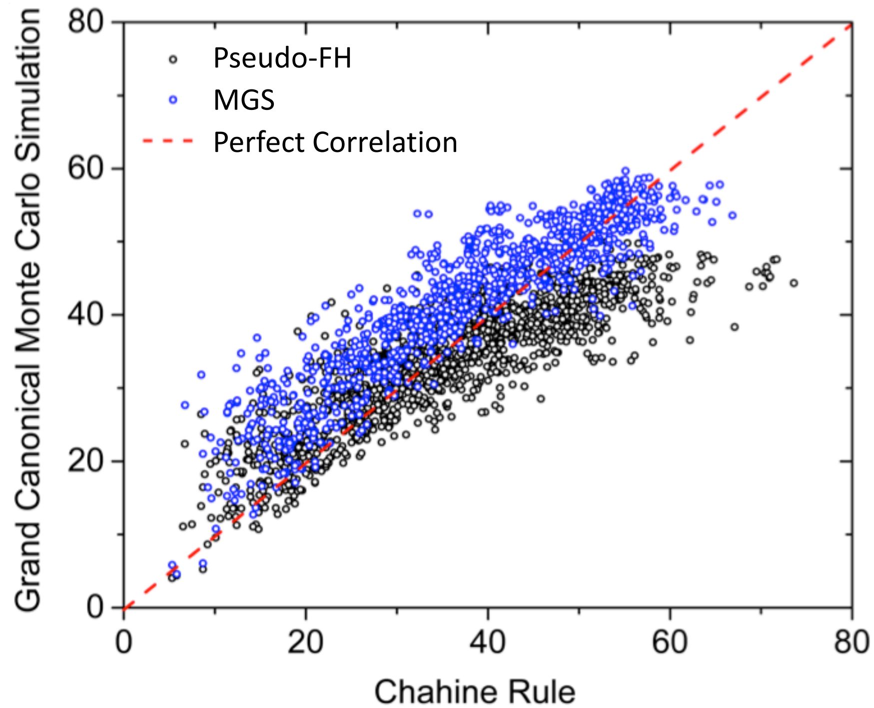
Accuracy of Simulated Isotherms

"Quick and dirty" Chahine-rule predictions of H_2 uptake in MOFs correlate strongly with GCMC calculations

Total gravimetric H_2 (wt.%)



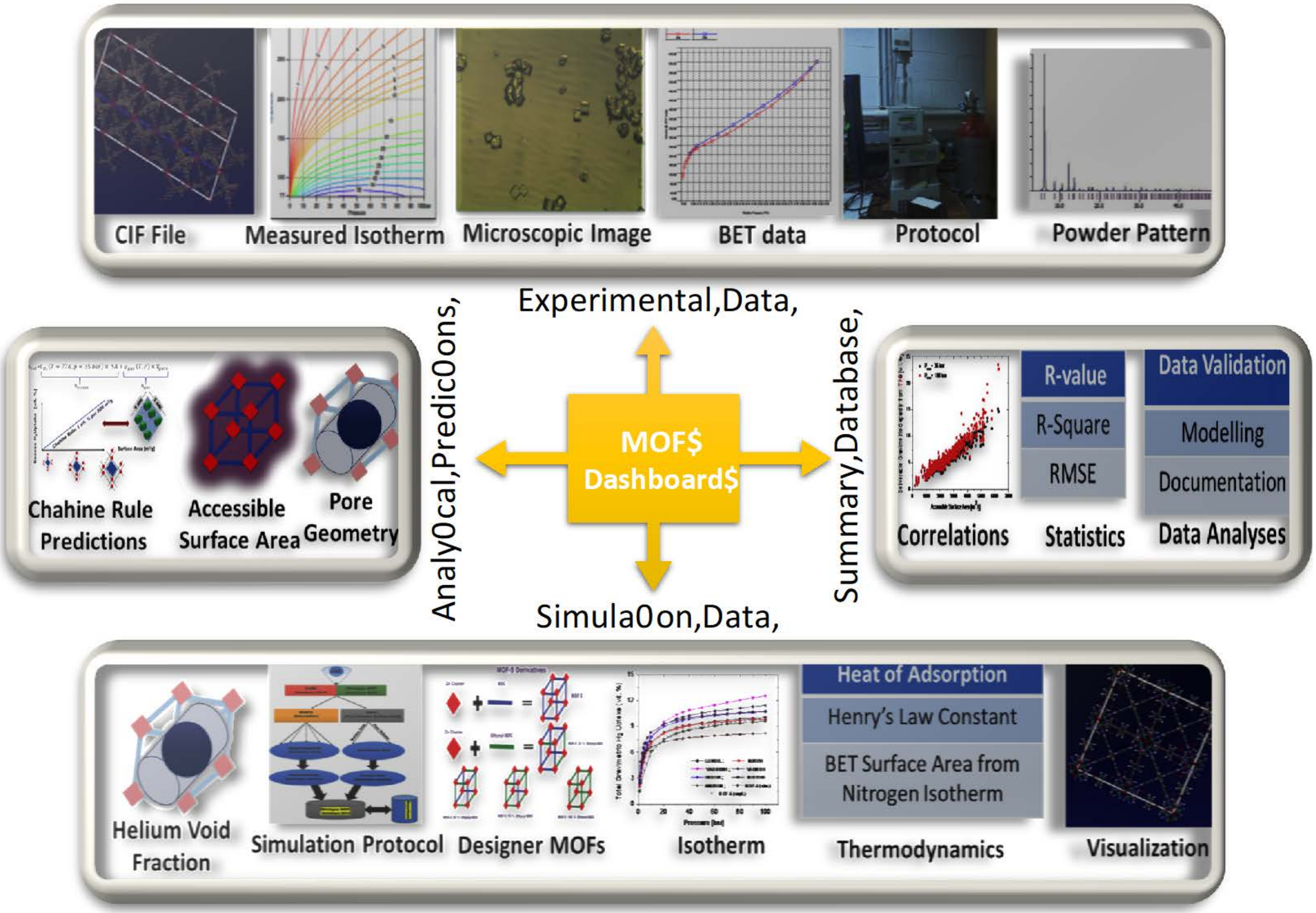
Total volumetric H_2 (g H_2/L MOF)



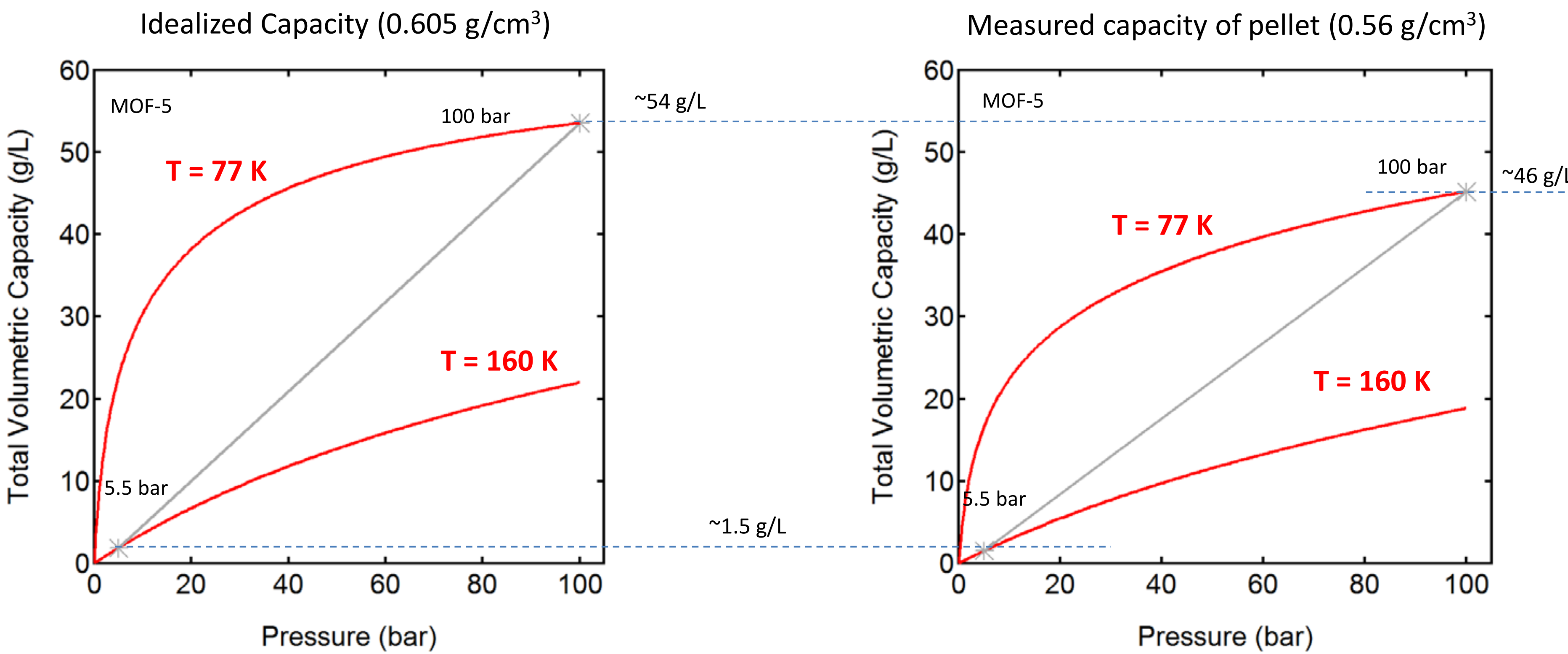
Although GCMC is more expensive, it provides access to full isotherm and allows estimation of usable capacities

MOF Dashboard

We have developed a database to track promising compounds and share data

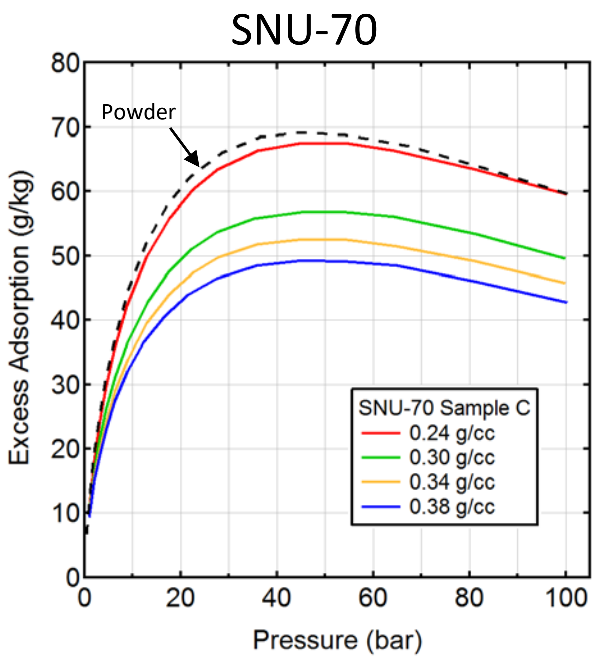


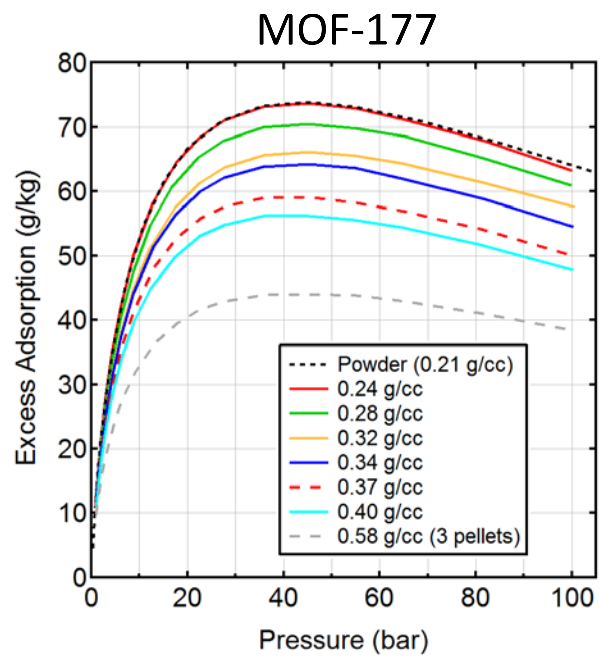
Usable capacity (ideal vs measured)

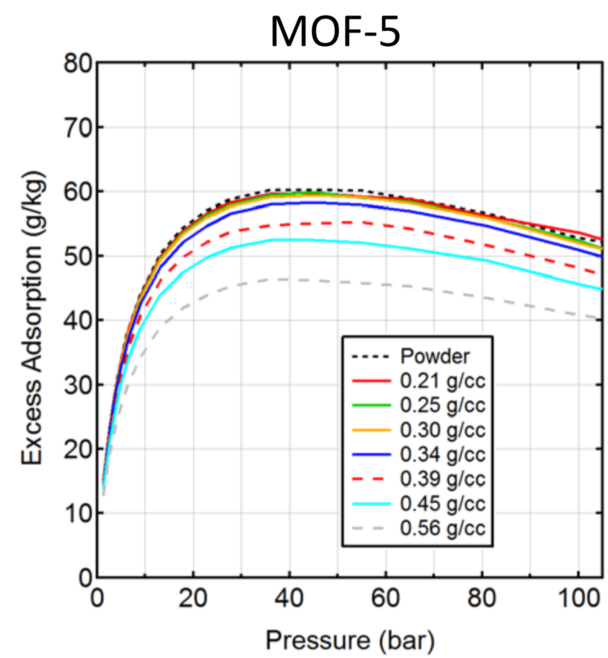


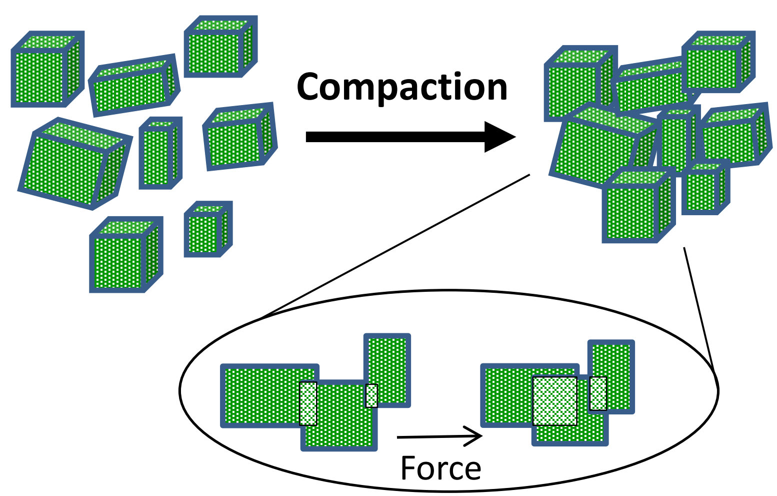
Idealized capacity (at the crystal density) does not translate 100% to an actual capacity for a MOF when compacted to high density.

Compaction Properties of MOFs

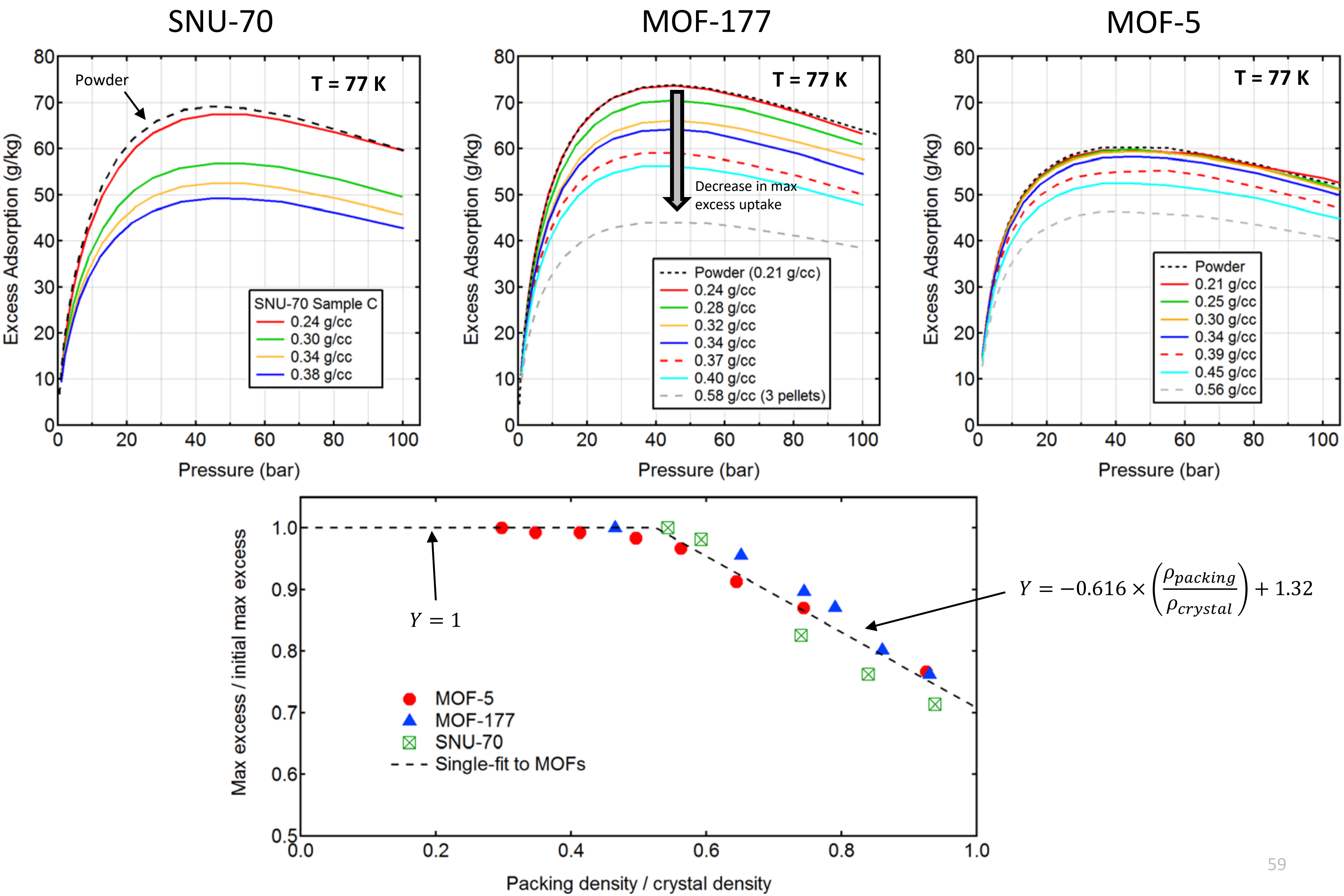






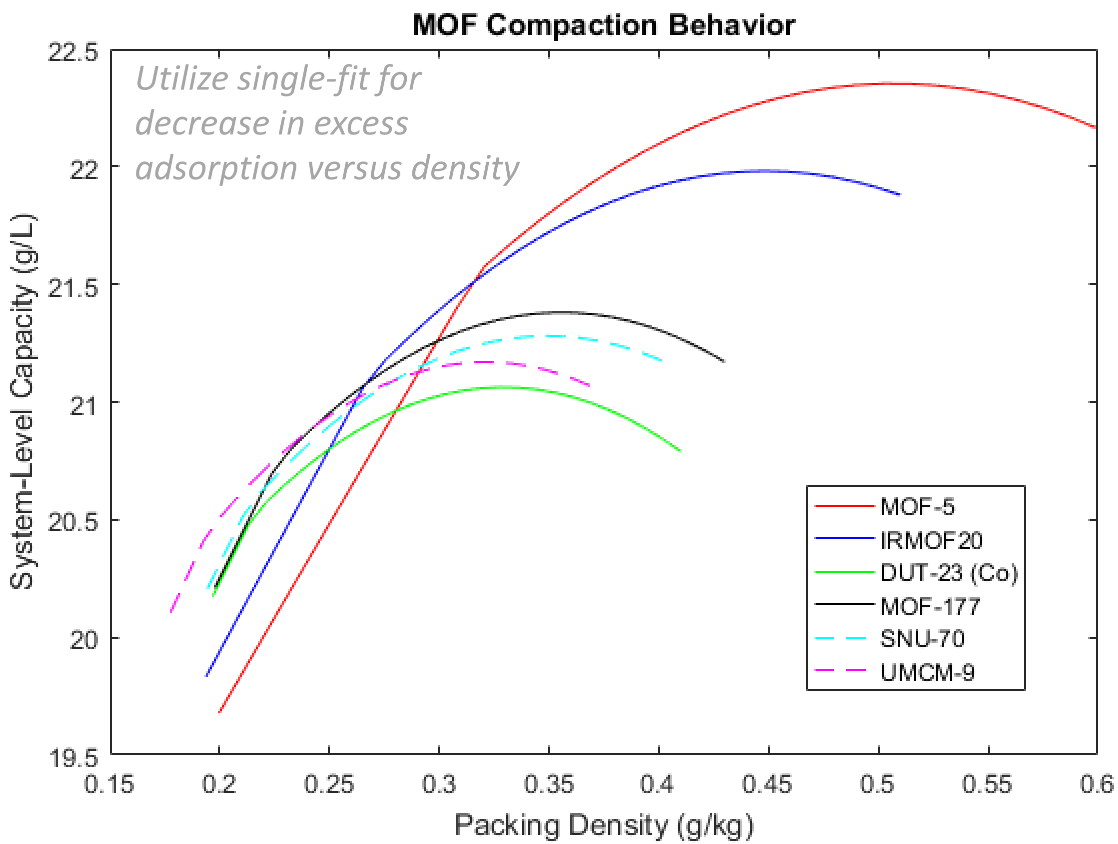


Compaction Properties of MOFs



$$Y = -0.616 \times \left(\frac{\rho_{packing}}{\rho_{crystal}}\right) + 1.32$$

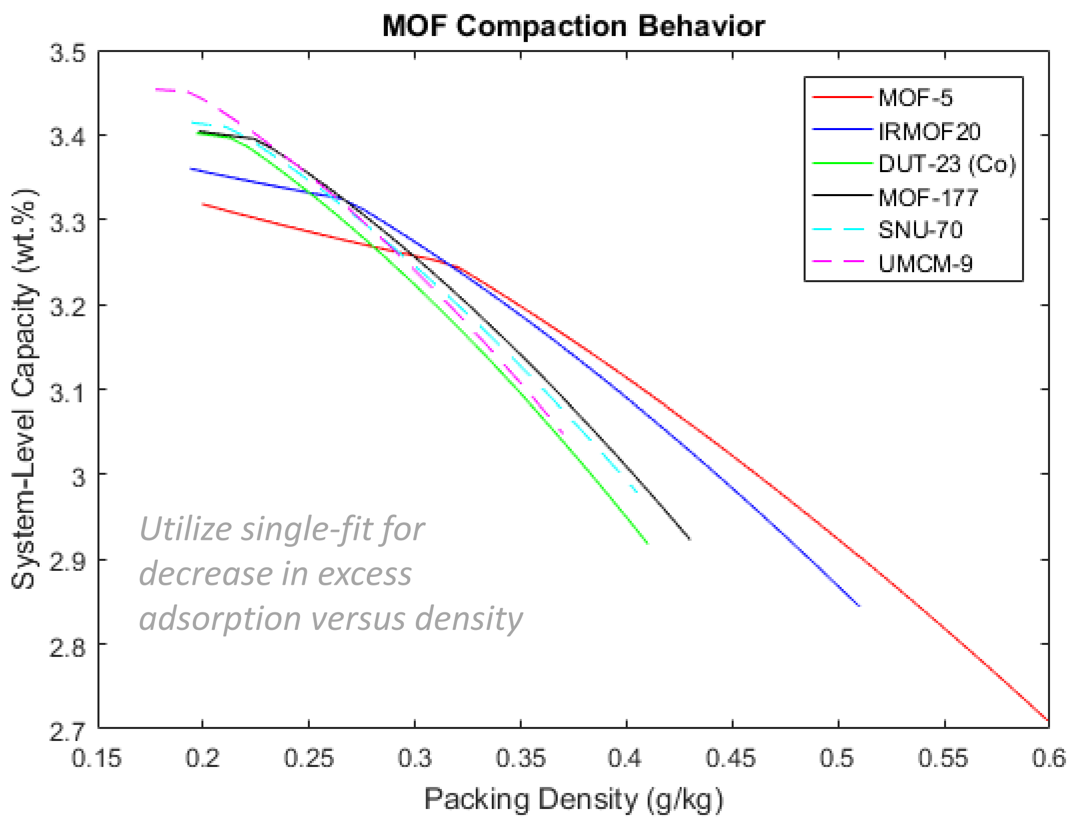
Volumetric System Capacity



System Assumptions:

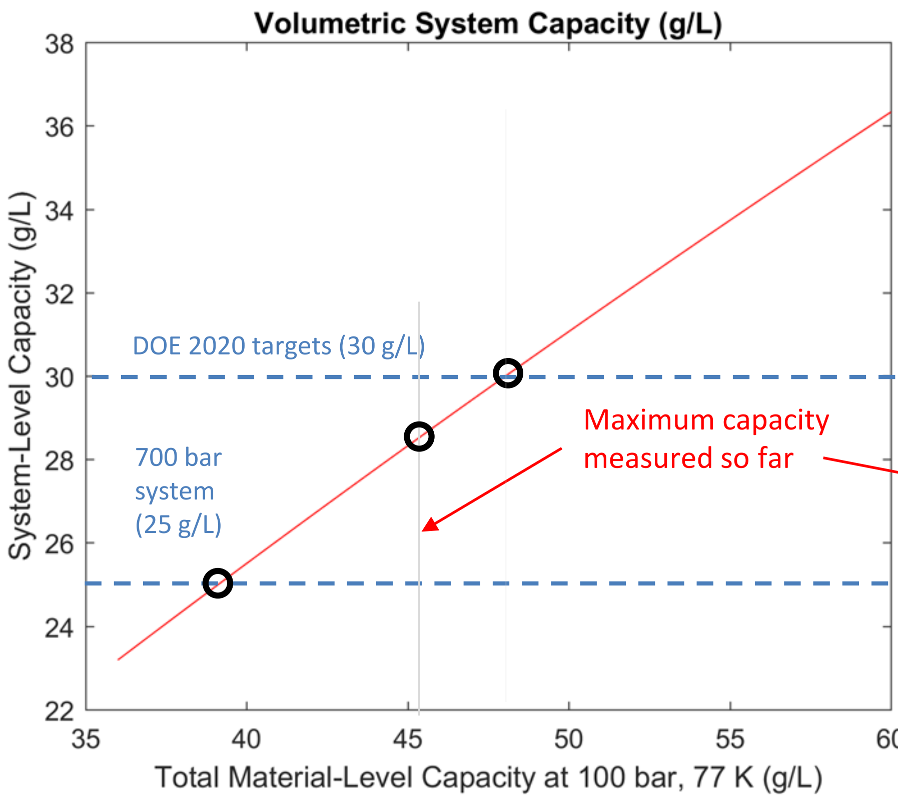
23 mm MLVI insulation
3/8 inch LN_2 channels
80 K fill temperature

Gravimetric System Capacity



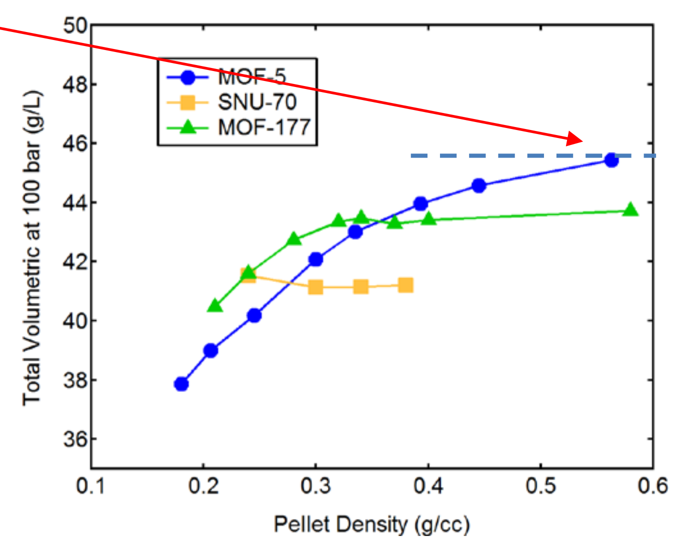
23 mm MLVI insulation
3/8 inch LN2 channels
80 K initial temperature

System Capacity vs Material Capacity



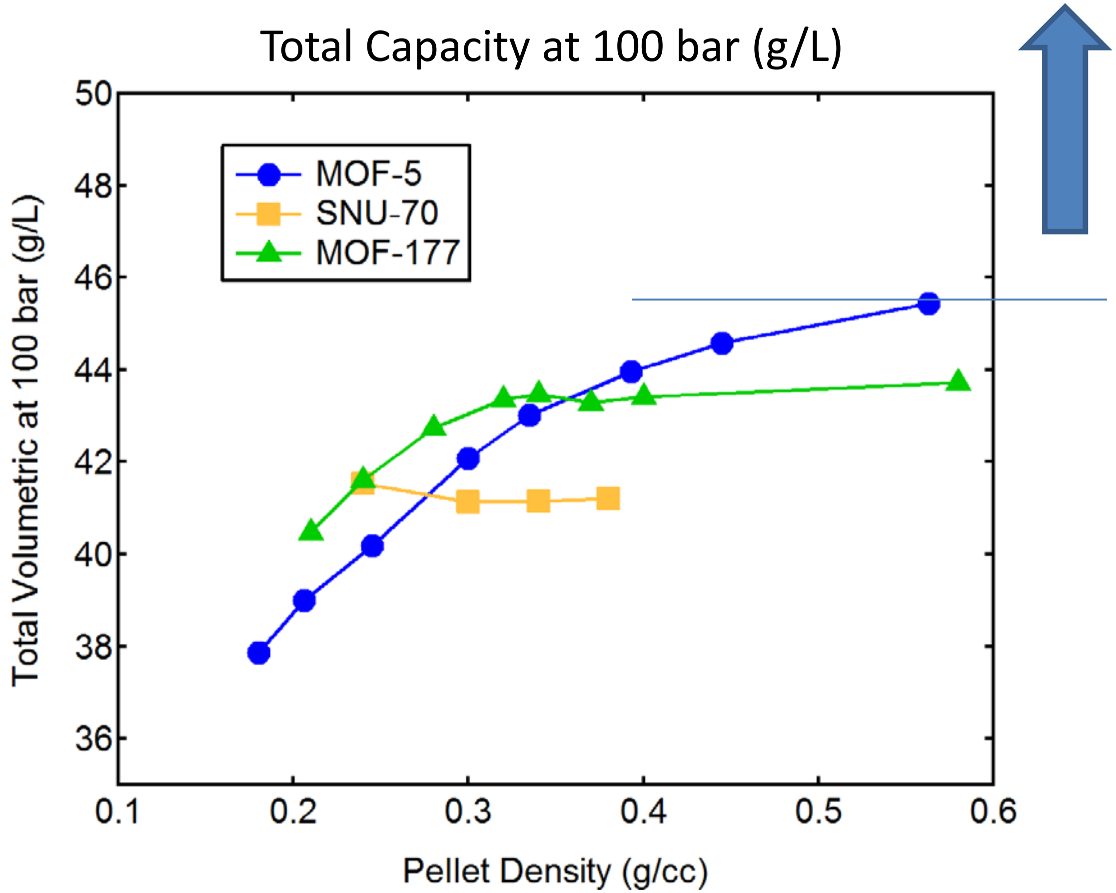
System Properties	
Initial/Full Pressure:	100 bar
Initial/Full Temp:	77 K
Final/Empty Pressure:	5.5 bar
Final/Empty Temp:	160 K
Useable Hydrogen:	5.6 kg
Heat Exchanger:	HexCell
MOF Density:	0.4 g/cc*
Pressure Vessel:	Type 1 SS
Insulation Thickness:	10 mm
LN2 Chiller Channel:	1/4 inch

* For this estimate, the system volumetric capacity depends on the material-level capacity and is independent of the MOF density



Translation of *material-level* volumetric capacity to system-level volumetric capacity.
(The material volumetric capacity at 160 K, 5.5 bar is assumed to be constant at 1.5 g/L).

Material-Level Volumetric Capacity of Densified MOFs



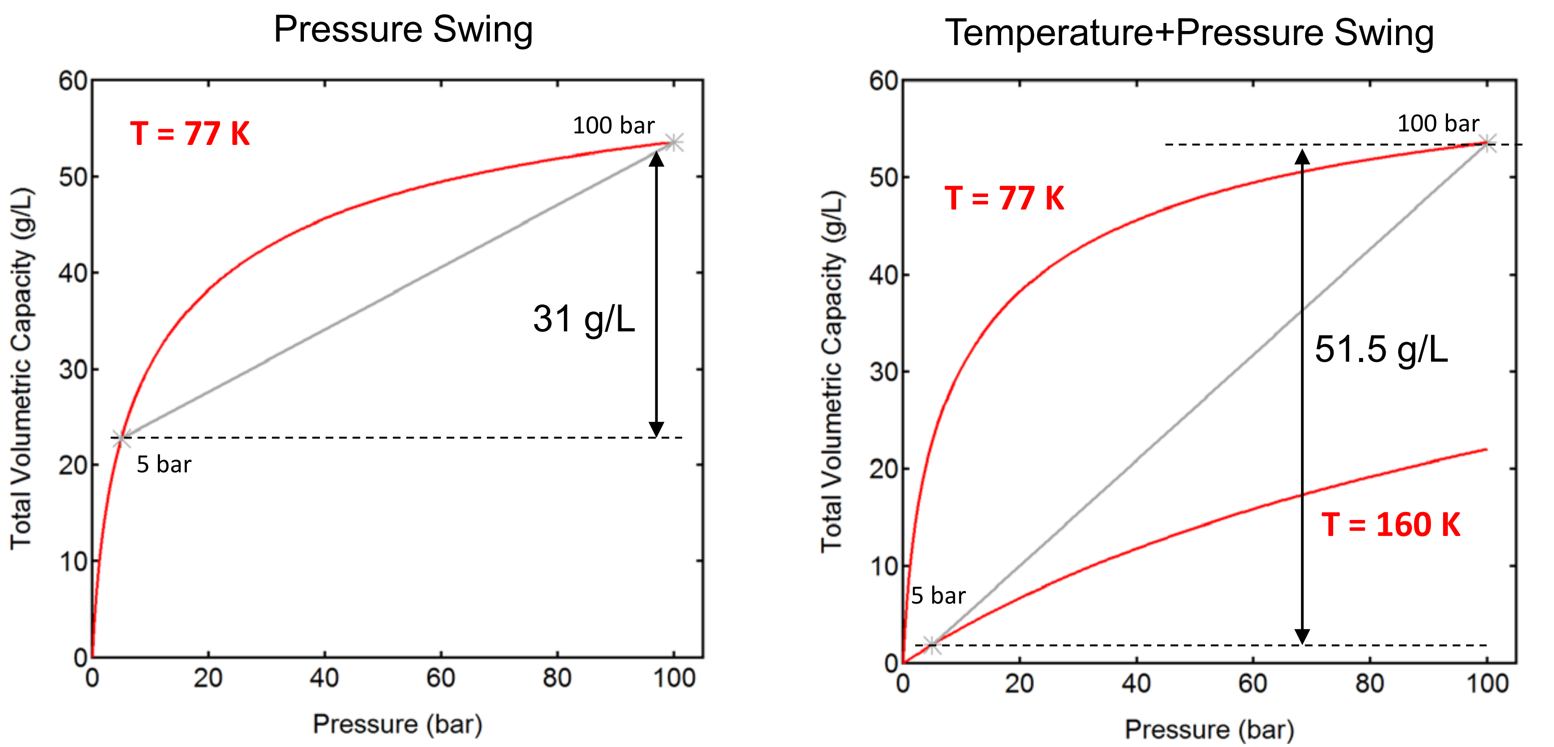
Ideal MOF-5 crystal density (54 g/cc), ~15% higher

Highest value measured so far ~ 46 g/cc

Usable = 46 g/L – 1.5 g/L

Defining Usable H_2 Storage Capacity

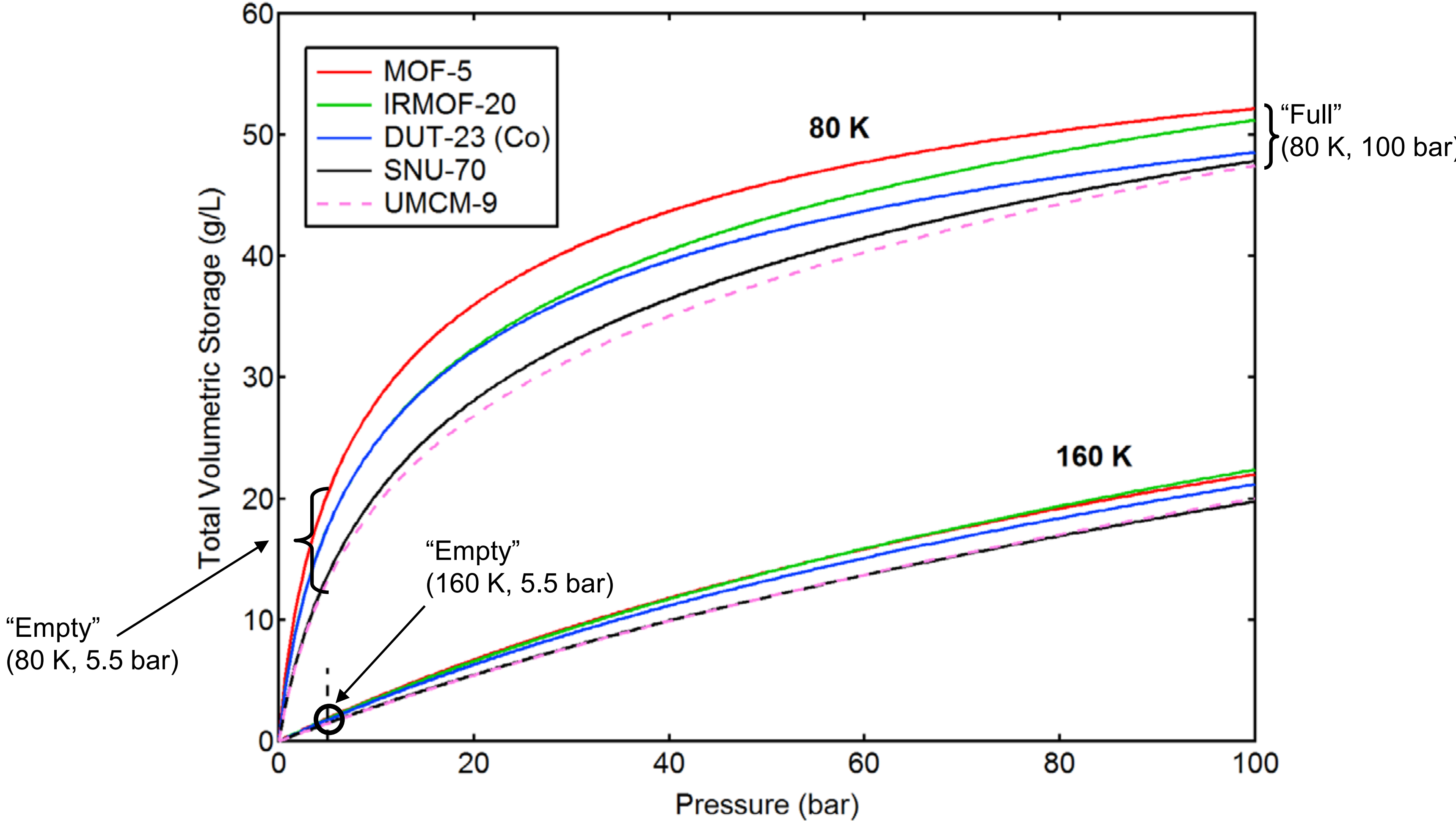
Hydorgen storage capacity of MOF-5 at crystal density ($\rho = 0.605$ g/cm^3)



Temperature+Pressure Swing (TPS) usable capacity is an alternative figure of merit. The sorbent can be heated up to release more H_2.

Usable H_2 Storage Capacity (MOFs at crystal density)

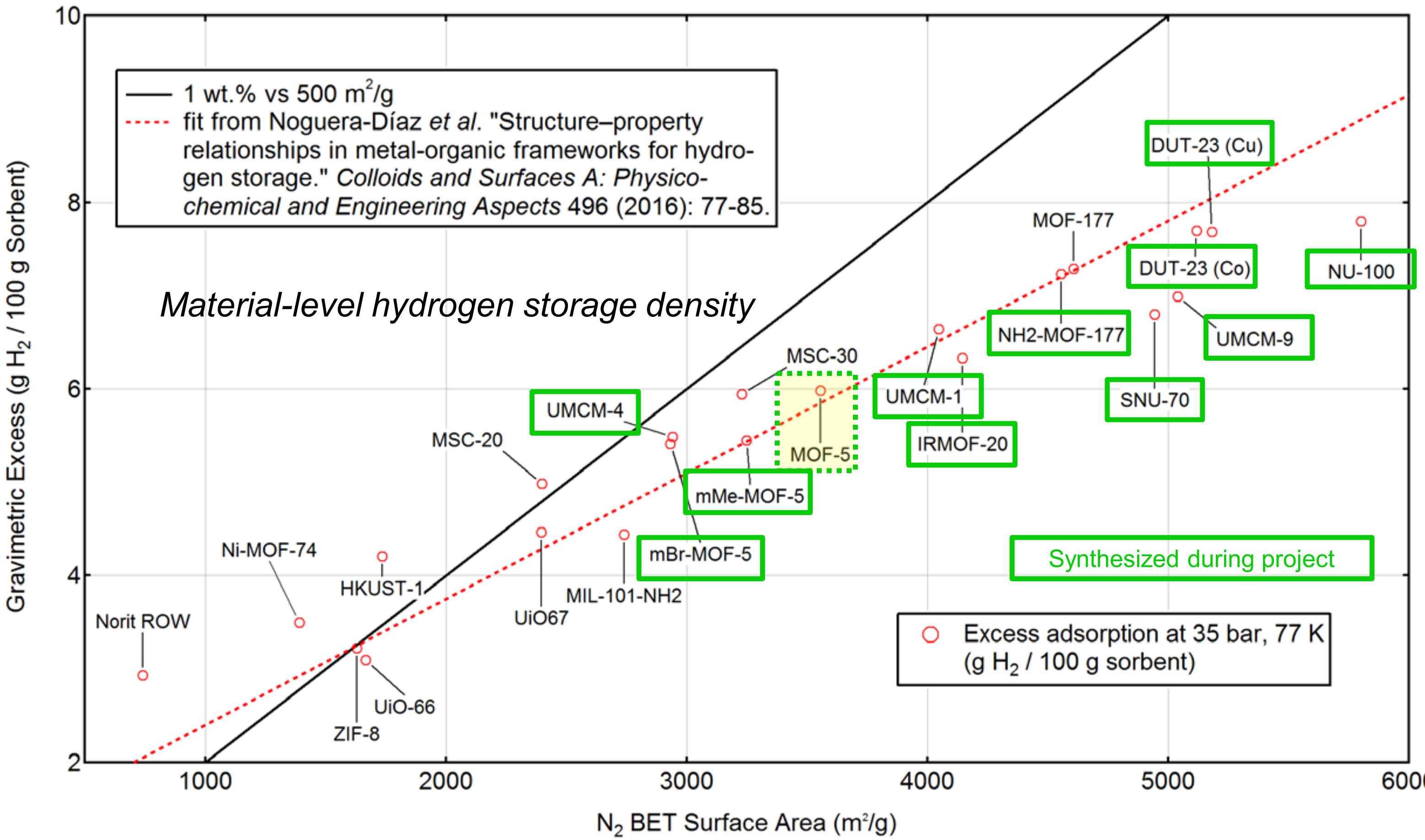
Volumetric H_2 storage capacity of MOFs at their single crystal density



The TPS capacity depends primarily on the capacity at 80 K / 100 bar.

Experimental Screening of MOFs

Summary of H_2 storage materials evaluated during project



Correlation between BET surface area (m^2/g) and gravimetric H_2 adsorption at 35 bar, 77 K