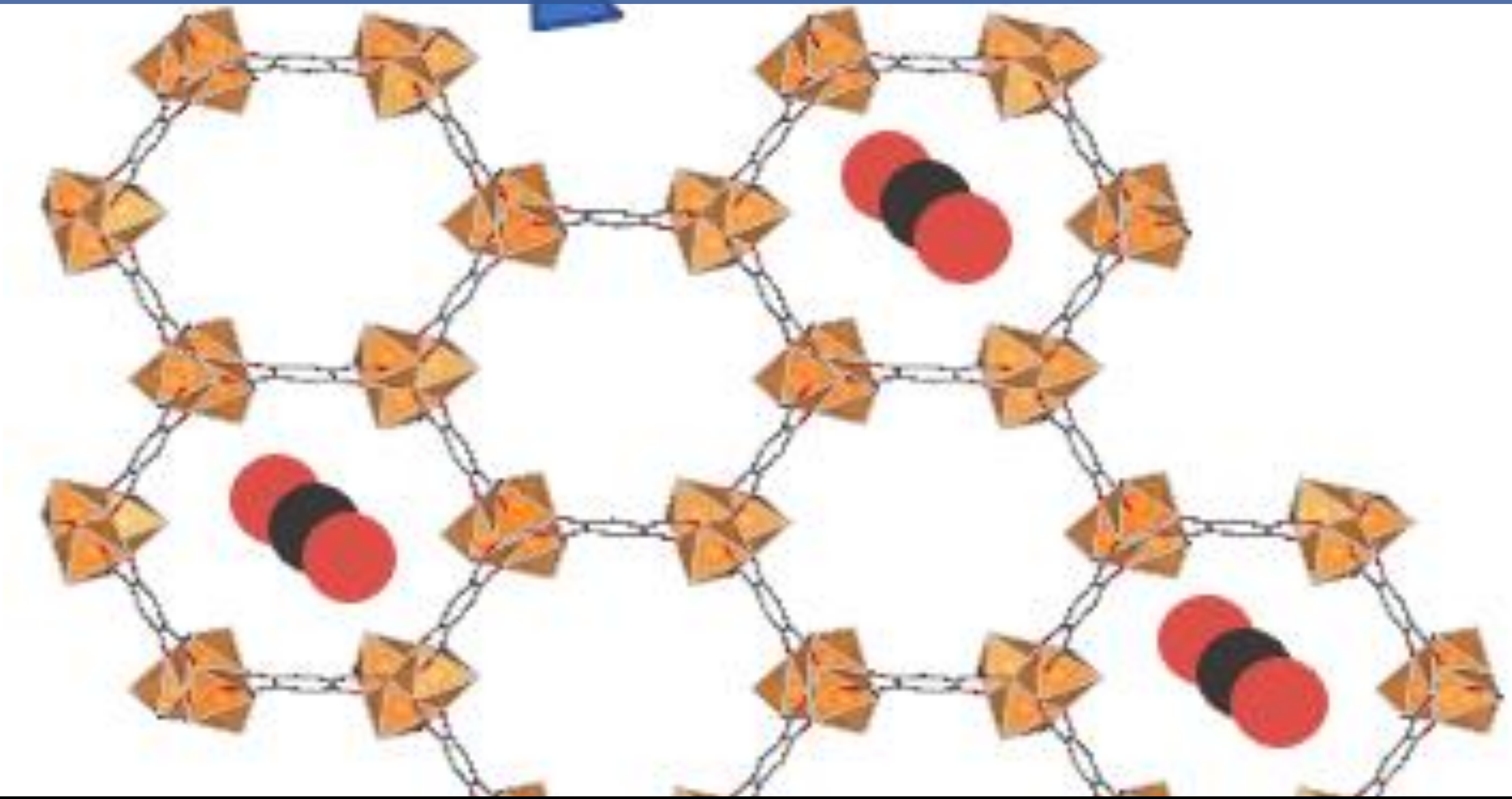
Development and Optimization of Metal Organic Framework (MOF) Sorbents for Direct Air Capture (DAC) of CO_2

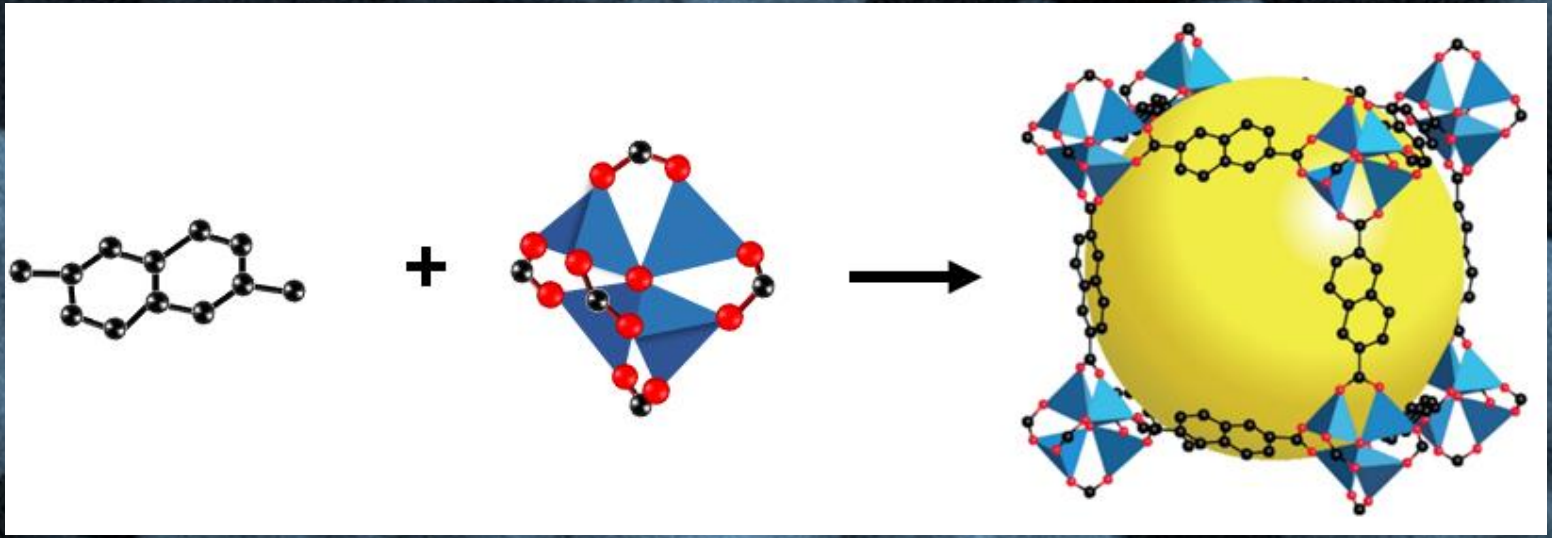


Amanda Morris and Stephen Martin
Virginia Tech

UCFER Annual Review
October 5, 2021

What are MOFs?

- Coordination polymers formed by inorganic nodes connected by multidentate ligands.
- Permanent porosity demonstrated by Yaghi in 1998.
- Extremely high in surface area - can reach 7000 m^2/g

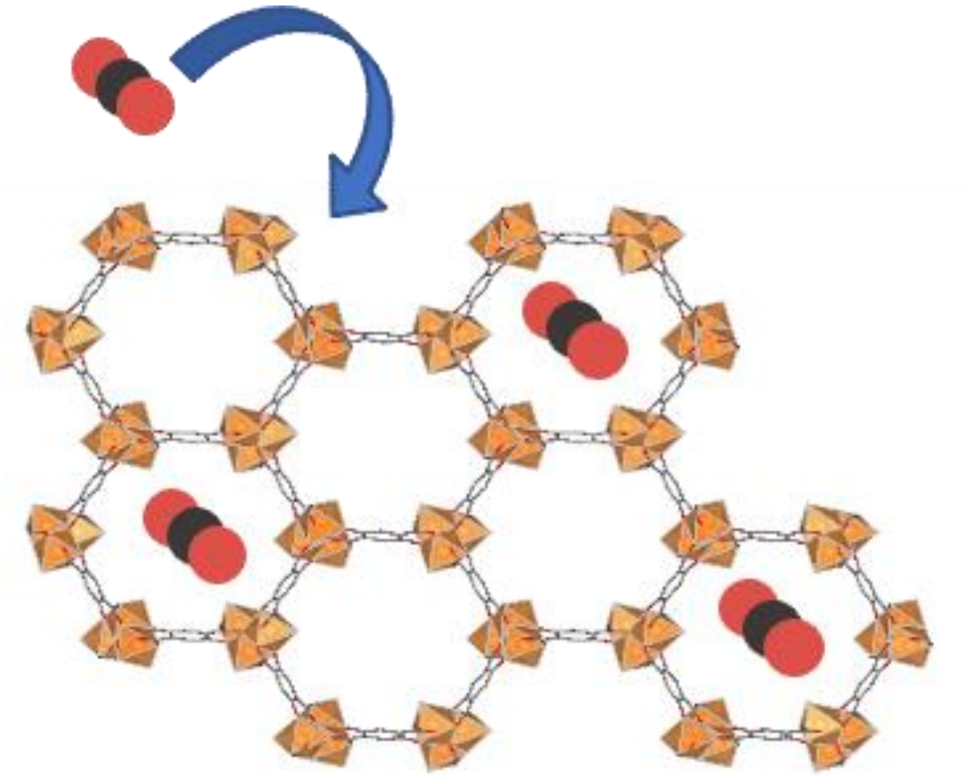


- Three dimensional structure, including pore size and pore type, is tunable based on ligand and metal node choice
- Commercial applications in gas storage (NuMat Technologies)

Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. The Chemistry and Applications of Metal-Organic Frameworks. *Science (80).* **2013**, *341* (6149).

Metal Organic Frameworks in Direct Air Capture

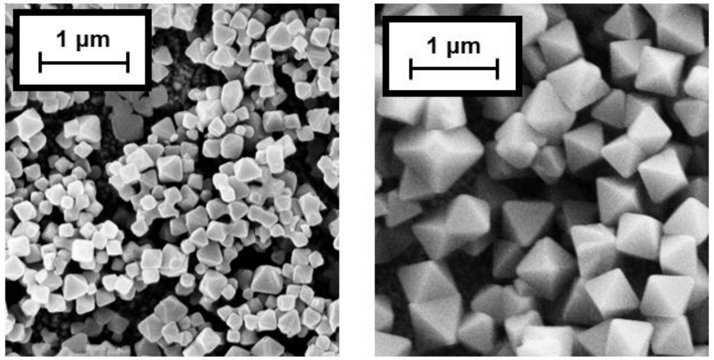
- CO_2 mainly captured by physisorption (low regeneration energy, low absorption capacity)
  - Competition with H_2O
  - Stability in humidity
- Little DAC performance data (mostly single-component CO_2 capacity)
  - SIFSIX-3-Cu,Ni (Eddaoudi, Zaworotko)
  - Mg-MOF-74 (Long, Zaworotko)
  - HKUST-1 (Zaworotko)
- Synthesis at lab scale



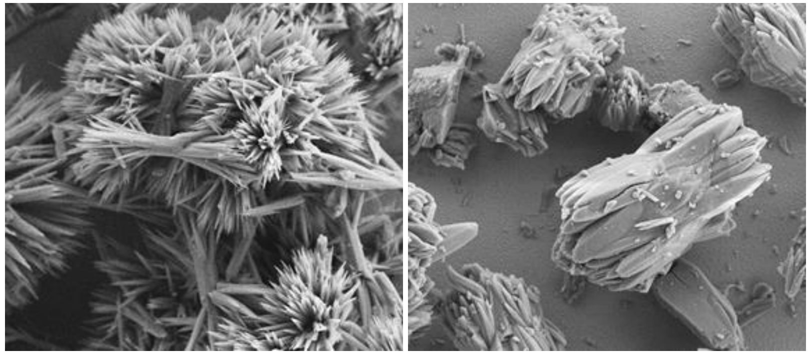
(1) Belmabkhout, Y.; Guillerm, V.; Eddaoudi, M. Low Concentration CO2 Capture Using Physical Adsorbents: Are Metal–Organic Frameworks Becoming the New Benchmark Materials? Chemical Engineering Journal 2016, 296, 386–397. (2) Custelcean, R. Direct Air Capture of CO_2 via Crystal Engineering. Chemical Science 2021. (3) Hu, Z.; Wang, Y.; Shah, B. B.; Zhao, D. CO_2 Capture in Metal–Organic Framework Adsorbents: An Engineering Perspective. Advanced Sustainable Systems 2019, 3 (1), 1800080.

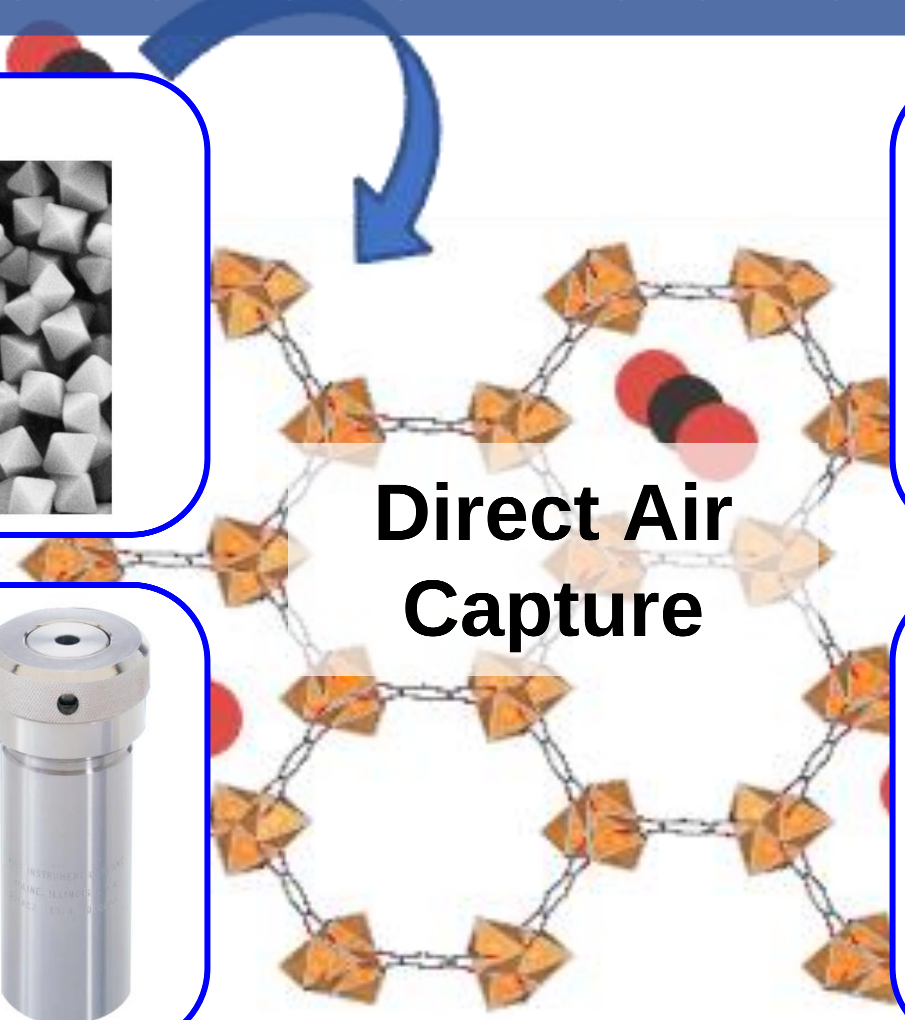
Toward Commercialization - Parameters for Optimization

Particle size



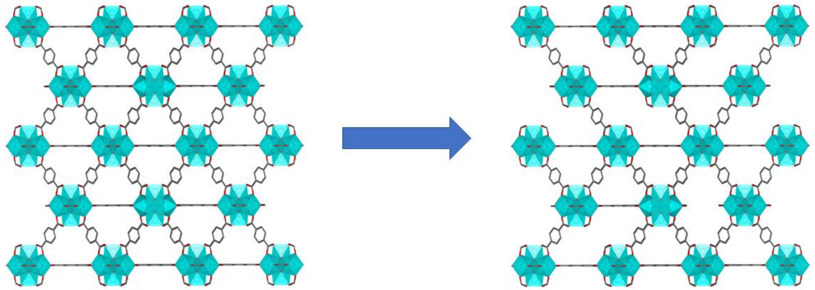
Morphology





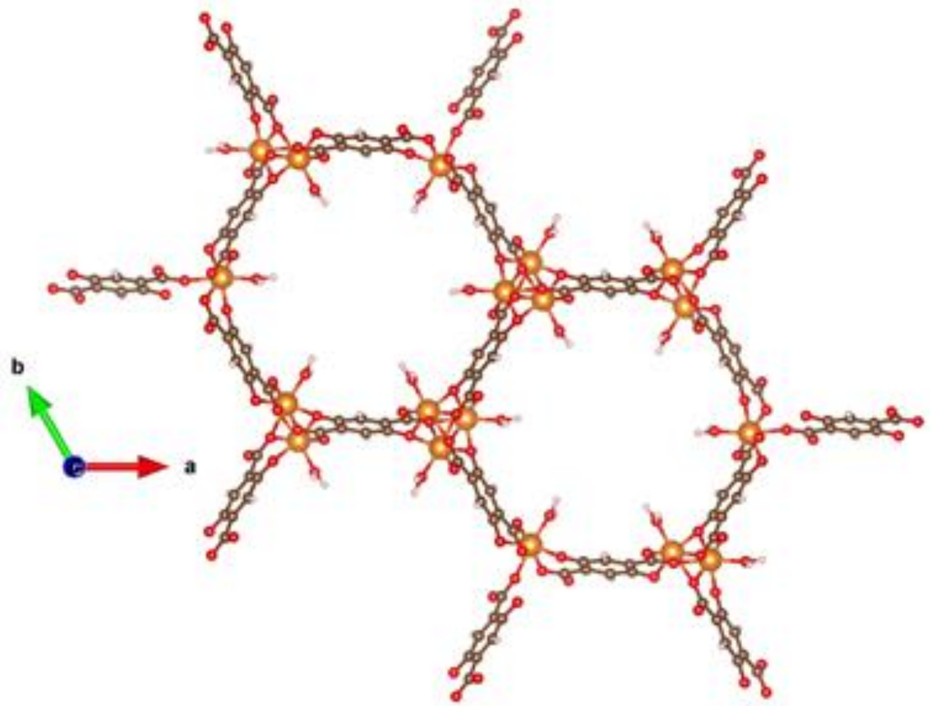
Scale

Defect level



Metal Organic Frameworks Selected for Study

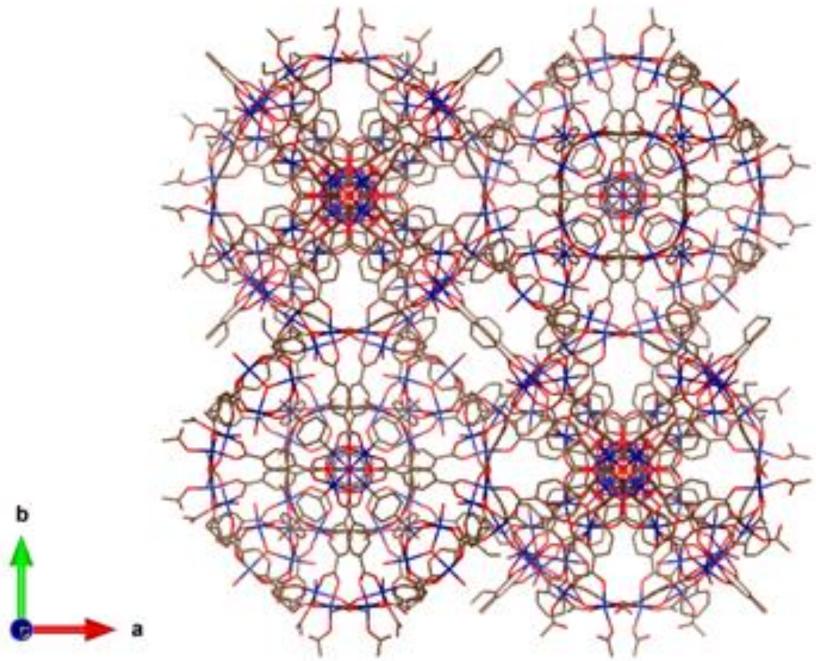
Mg-MOF-74



Q_{st} = 47 kJ/mol
Capacity = 2.39-7.30 mmol/g

Optimal Q_{st} =
35 to 50 kJ/mol

MIL-101-Cr



Q_{st} = 25 kJ/mol
Capacity = 0.495 mmol/g

(1) Liu, J.; Wei, Y.; Zhao, Y., Trace Carbon Dioxide Capture by Metal–Organic Frameworks. *ACS Sustainable Chemistry & Engineering* **2018,** *7* (1), 82-93. (2) Caskey, S. R.; Wong-Foy, A. G.; Matzger, A. J. Dramatic Tuning of Carbon Dioxide Uptake via Metal Substitution in a Coordination Polymer with Cylindrical Pores. *J. Am. Chem. Soc.* **2008**, *130*, 10870–10871.

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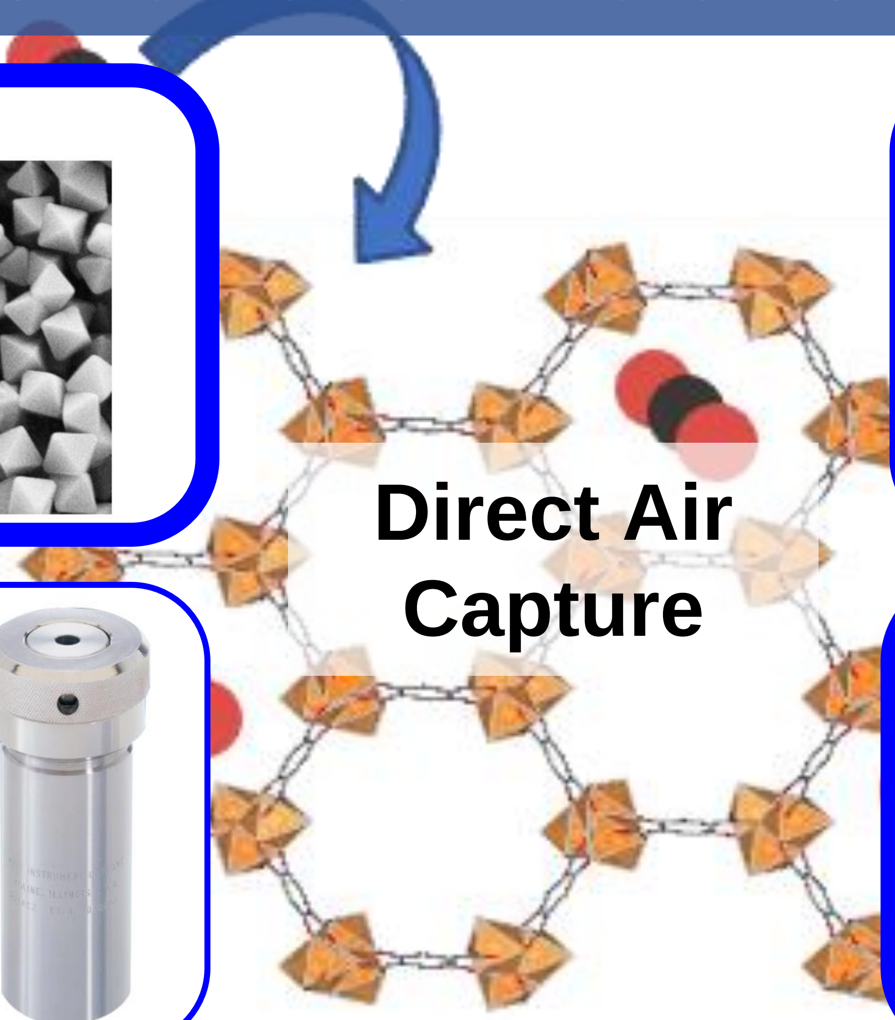
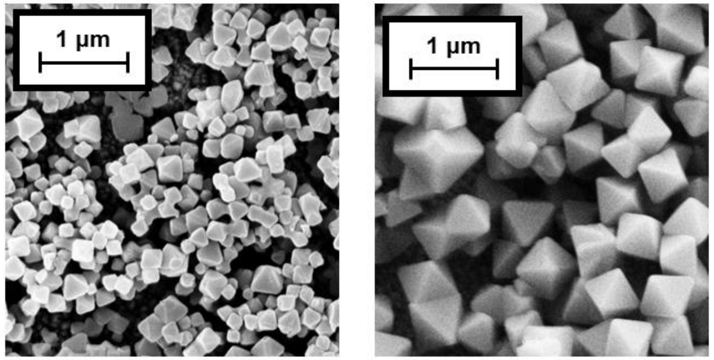
Toward Commercialization - Parameters for Optimization

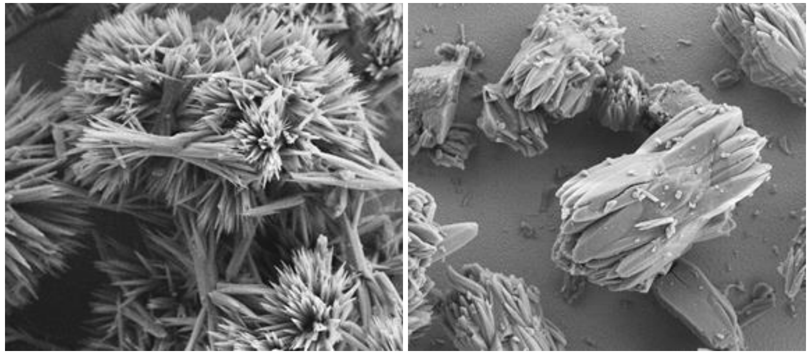


Direct Air Capture

Particle size

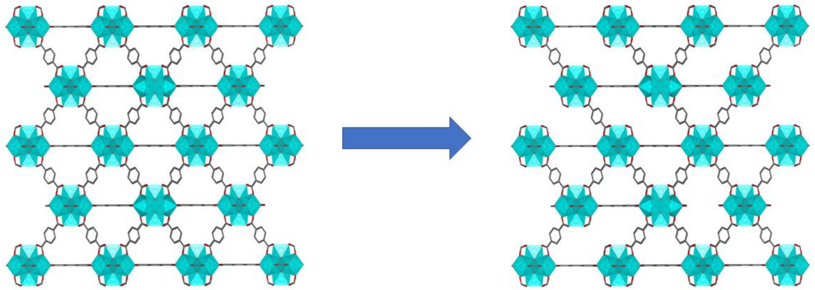


Morphology

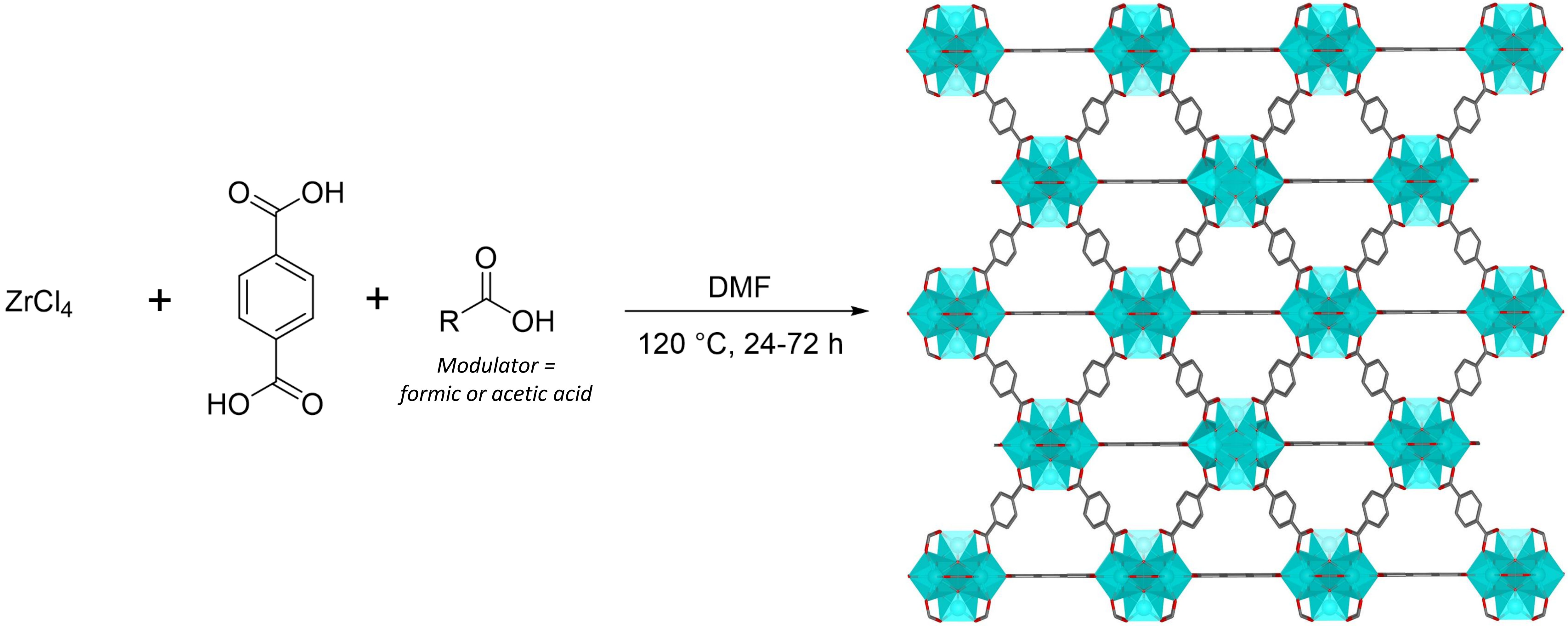


Scale

Defect level



Model Metal Organic Framework - Preparation



(1) Katz, M. J.; Mondloch, J. E.; Totten, R. K.; Park, J. K.; Nguyen, S. T.; Farha, O. K.; Hupp, J. T., Angew. Chemie - Int. Ed. 2014, 53 (2), 497–501. (2) Mondloch, J. E.; Katz, M. J.; Isley III, W. C.; Ghosh, P.; Liao, P.; Bury, W.; Wagner, G. W.; Hall, M. G.; DeCoste, J. B.; Peterson, G. W.; Snurr, R. Q.; Cramer, C. J.; Hupp, J. T.; Farha, O. K., Nat. Mater. 2015, 14, 512. (3) Kirlikovali, K. O.; Chen, Z.; Islamoglu, T.; Hupp, J. T.; Farha, O. K., ACS Appl. Mater. Interfaces 2020, 12 (13), 14702–14720. (4) Shearer, G. C.; Chavan, S.; Bordiga, S.; Svelle, S.; Olsbye, U.; Lillerud, K. P. *Chem. Mater.* **2016**, *28* (11), 3749–3761.

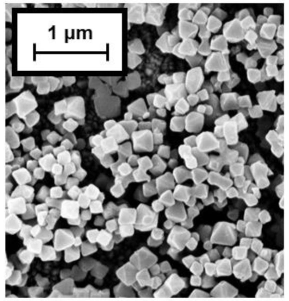
Systematic Tuning of Defect Level and Particle Size

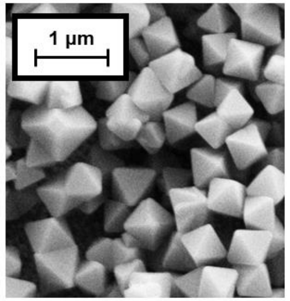
Defect series

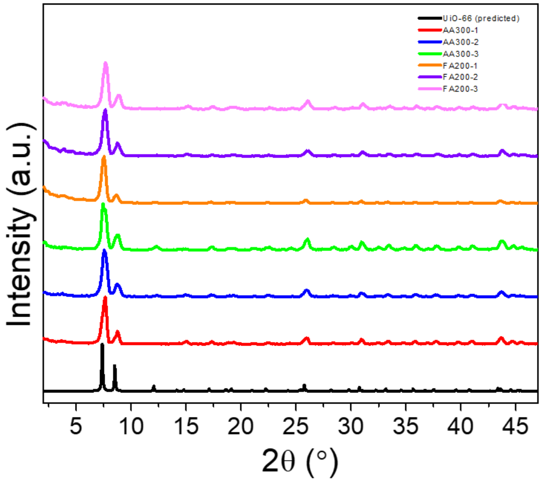
Sample	*Defect level (%)*	*Size (nm)*
Pristine	3 ± 2	440 ± 100
AA 300	14 ± 1	600 ± 100
FA 200	22 ± 3	580 ± 80

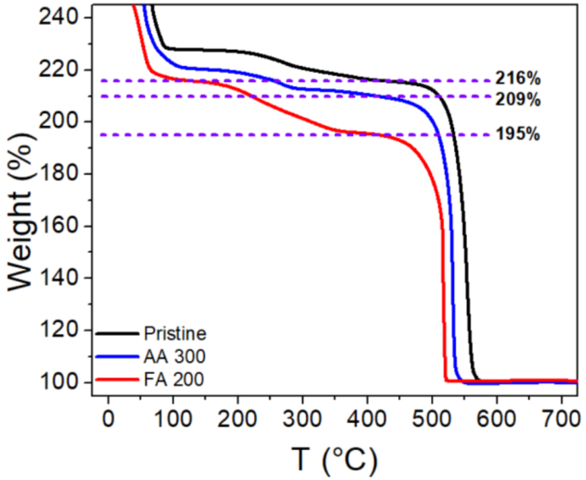
Size series

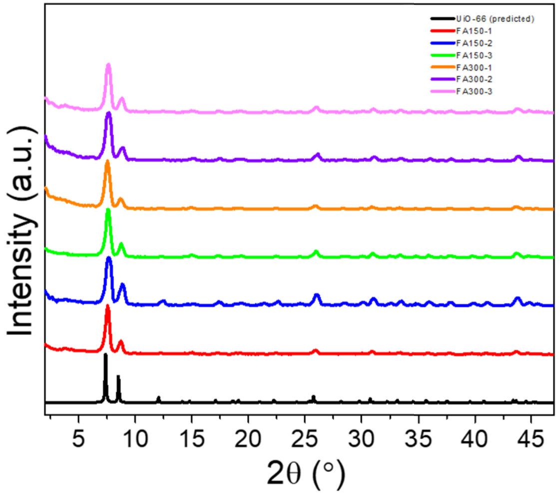
Sample	*Defect level (%)*	*Size (nm)*
FA 100	22 ± 2	140 ± 40
FA 150	19.1 ± 0.5	250 ± 60
FA 300	20 ± 3	600 ± 100

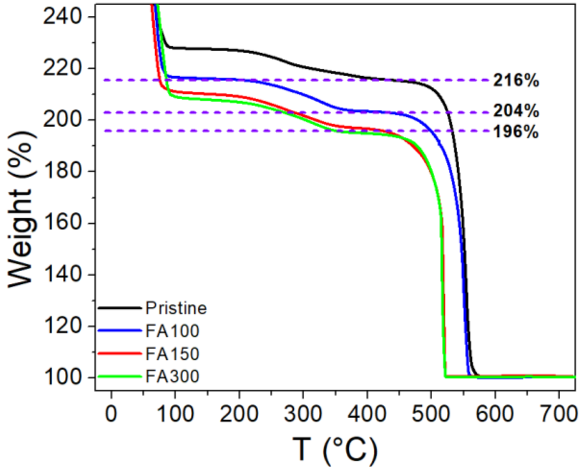








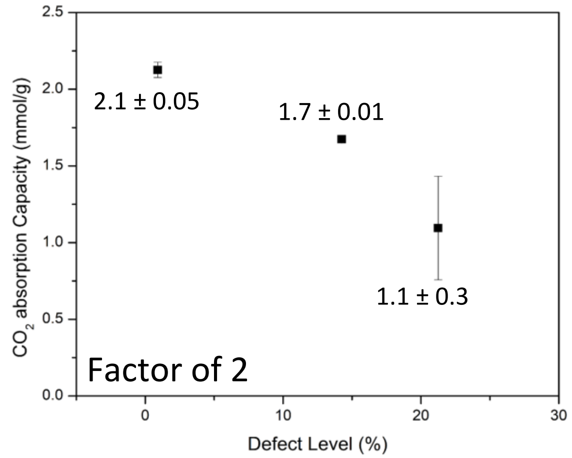




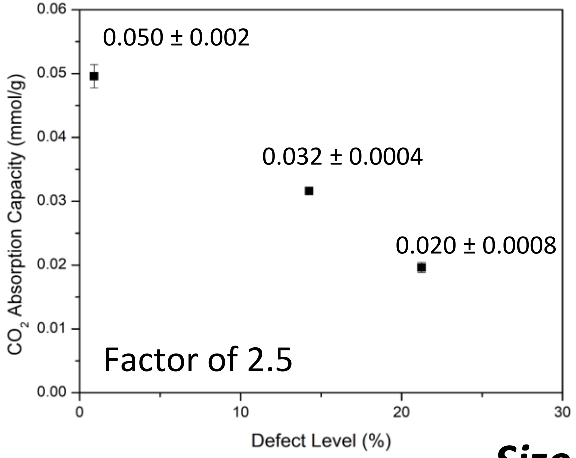
Sorption Capacity and Breakthrough

Defect Series

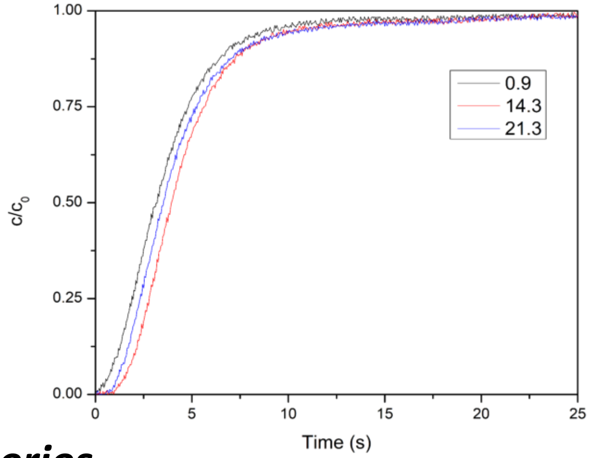
Pure CO_2 Capacity – 1 atm



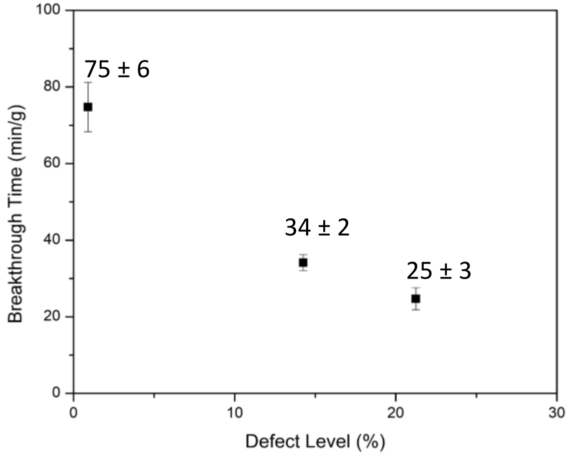
DAC CO_2 Capacity – 0.0004 atm



CO_2 Breakthrough

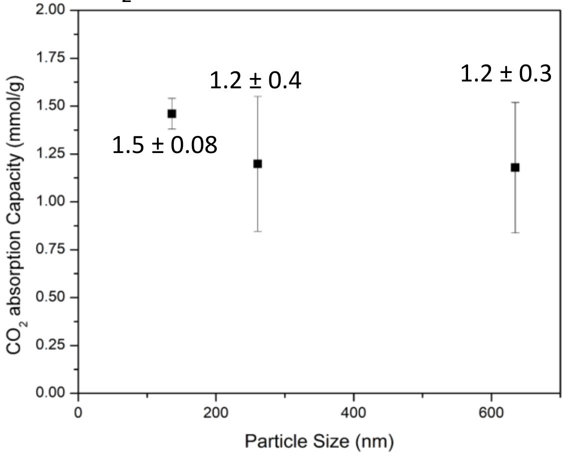


CO_2 Breakthrough Time

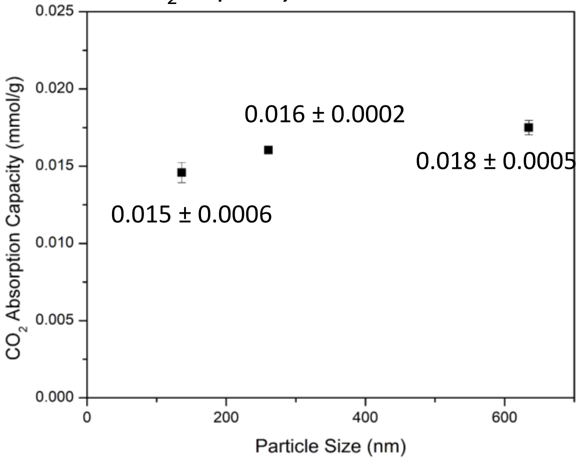


Size Series

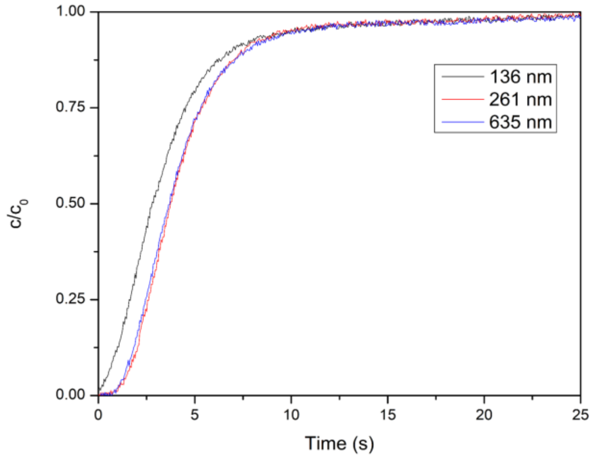
Pure CO_2 Capacity



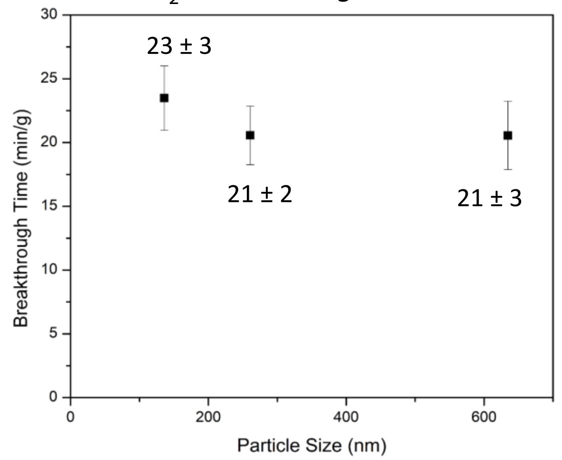
DAC CO_2 Capacity



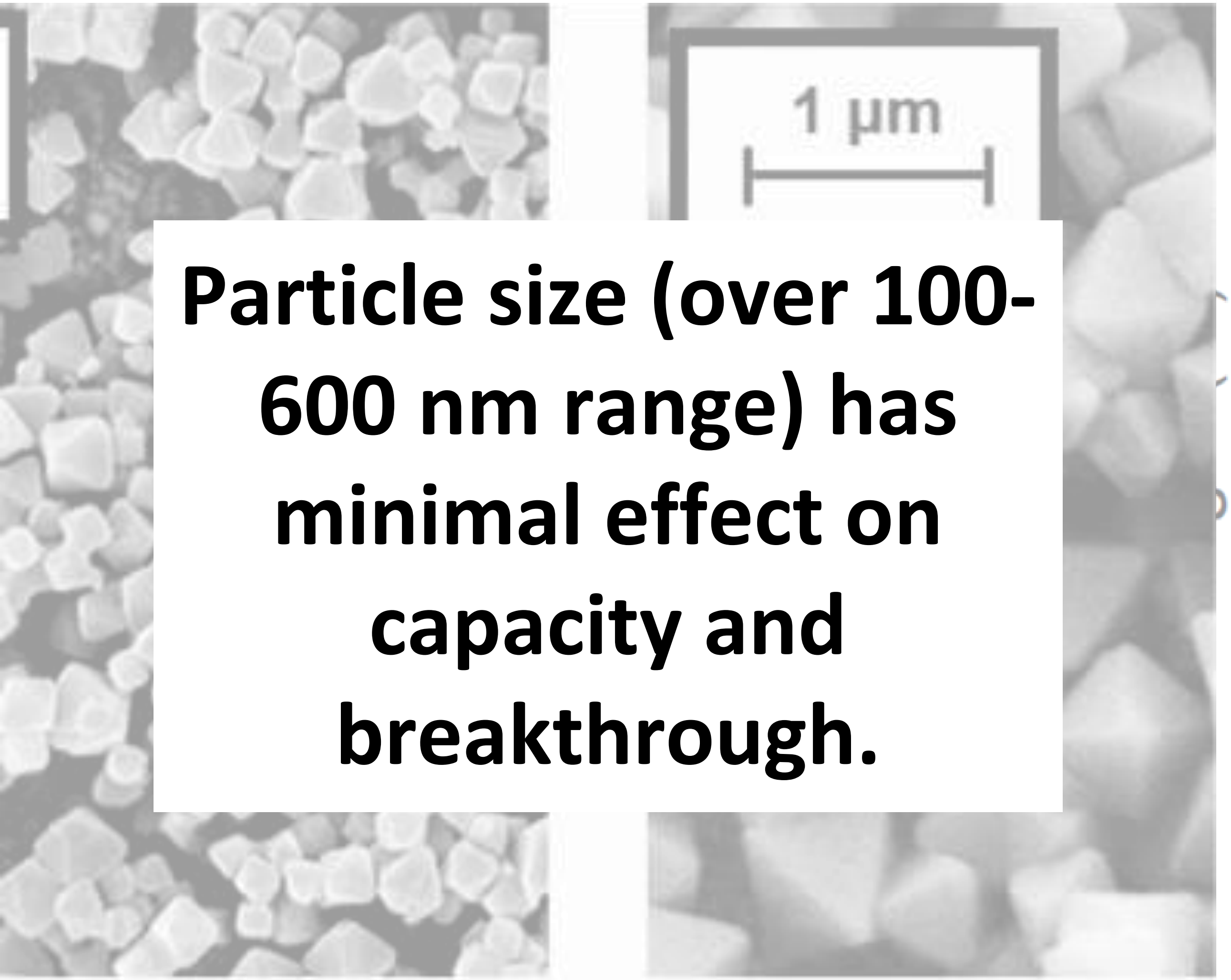
CO_2 Breakthrough



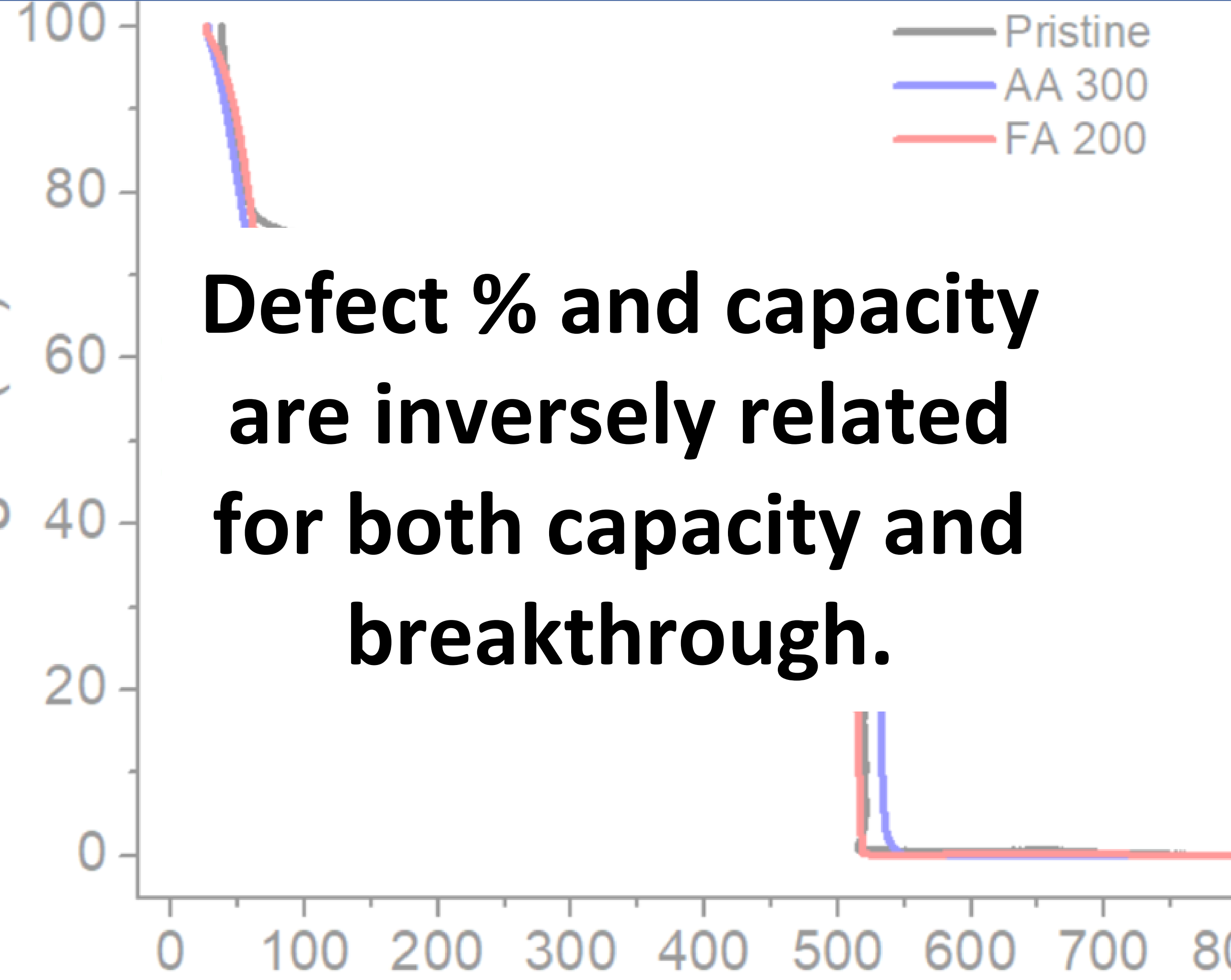
CO_2 Breakthrough Time



Design Rules



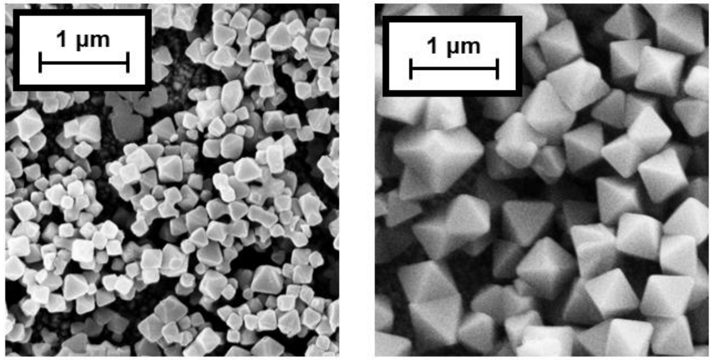
Particle size (over 100-600 nm range) has minimal effect on capacity and breakthrough.

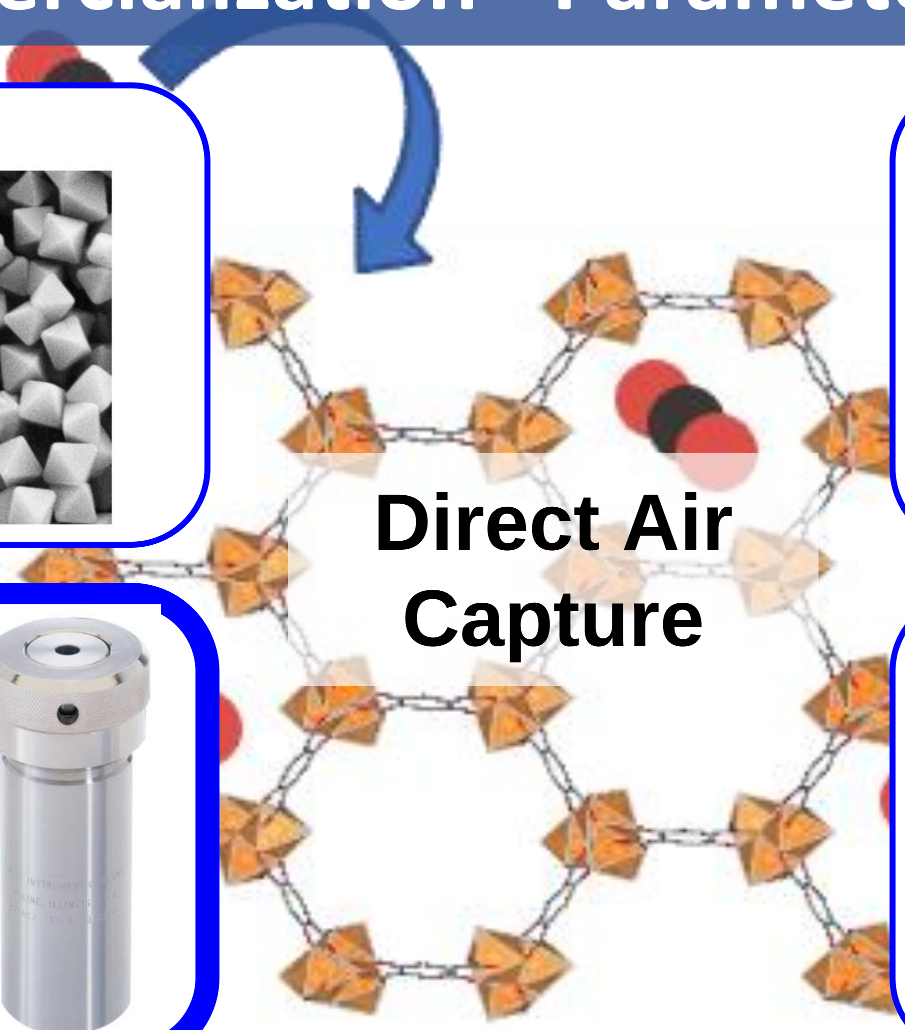


Defect % and capacity are inversely related for both capacity and breakthrough.

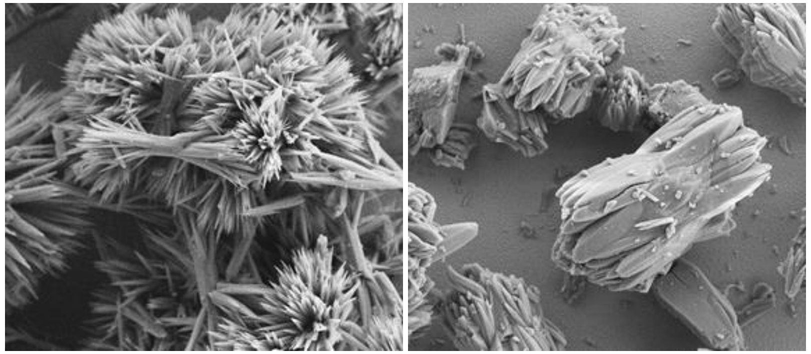
Toward Commercialization - Parameters for Optimization

Particle size



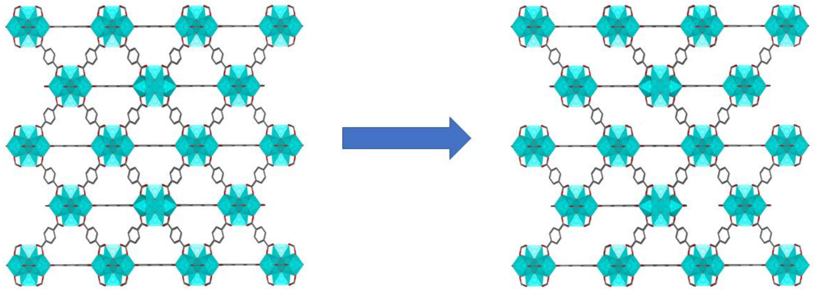


Morphology

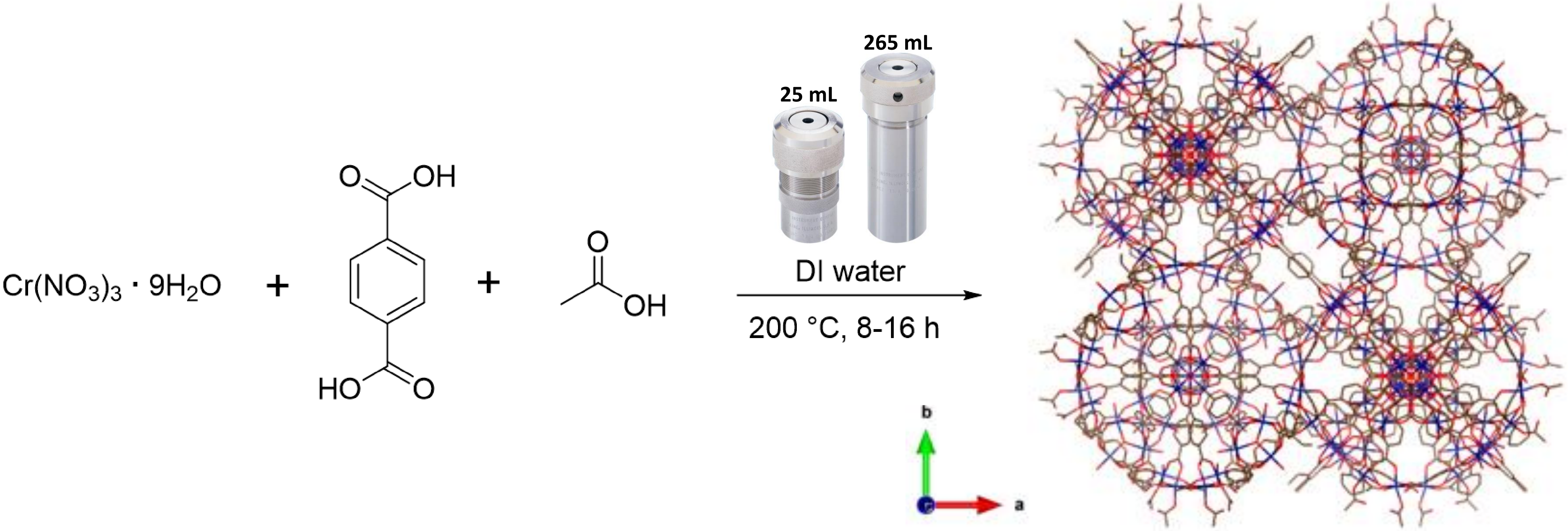


Scale

Defect level



Synthesis MIL-101-Cr



(1) Huang, C. Y.; Song, M.; Gu, Z. Y.; Wang, H. F.; Yan, X. P. Probing the Adsorption Characteristic of Metal-Organic Framework MIL-101 for Volatile Organic Compounds by Quartz Crystal Microbalance. *Environ. Sci. Technol.* **2011**, *45*, 4490–4496. (2) Feng, L.; Wang, K. Y.;Powell, J.; Zhou, H. C. Controllable Synthesis of Metal-Organic Frameworks and Their Hierarchical Assemblies. *Matter* **2019**, *1*, 801–824. (3) Zhong, R.; Yu, X.; Meng, W.; Liu, J.; Zhi, C.; Zou, R. Amine-Grafted MIL-101(Cr) via Double-Solvent Incorporation for Synergistic Enhancement of CO_2 Uptake and Selectivity. *ACS Sustain. Chem. Eng.* **2018**, *6*, 16493–16502. (4) Zhao, T.; Li, S. H.; Shen, L.; Wang, Y.; Yang, X.

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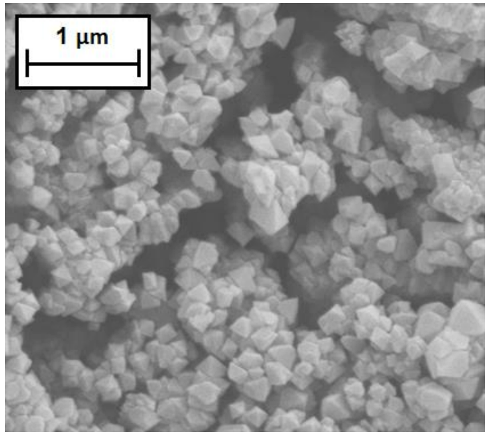
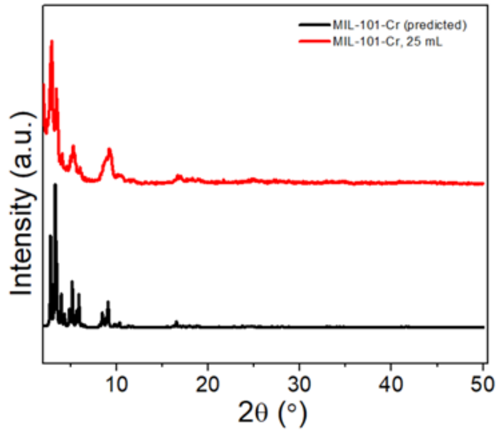
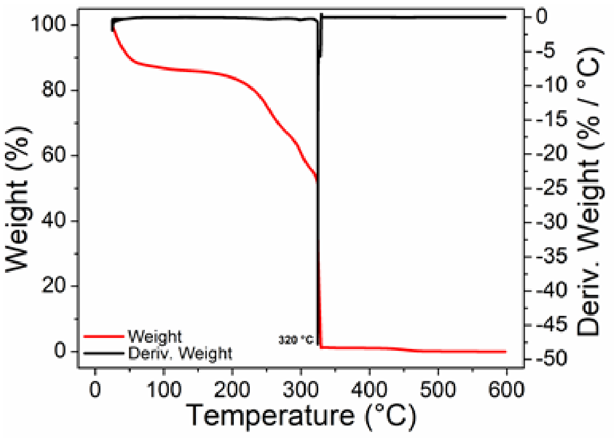
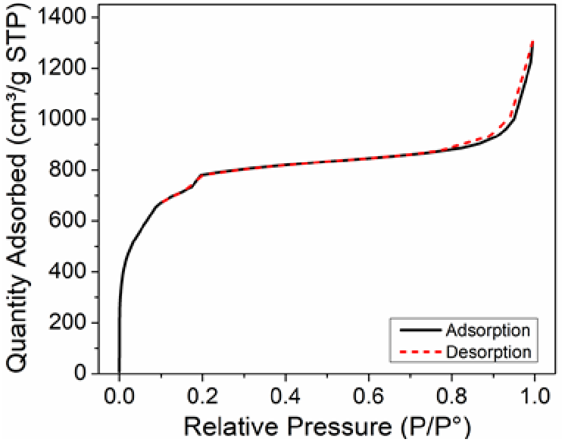
Characterization

25 mL, 300 mg scale

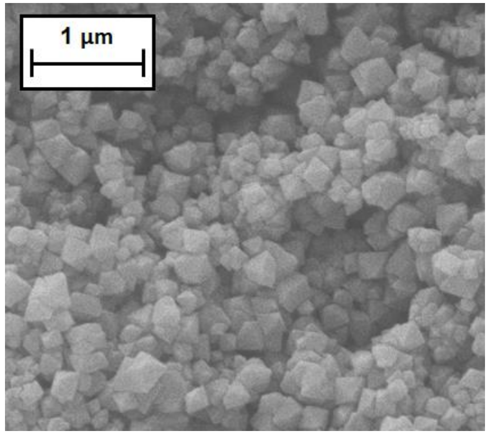


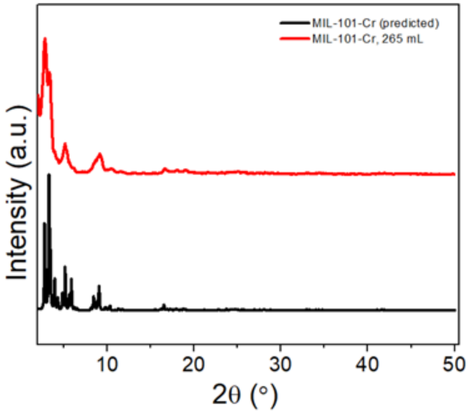


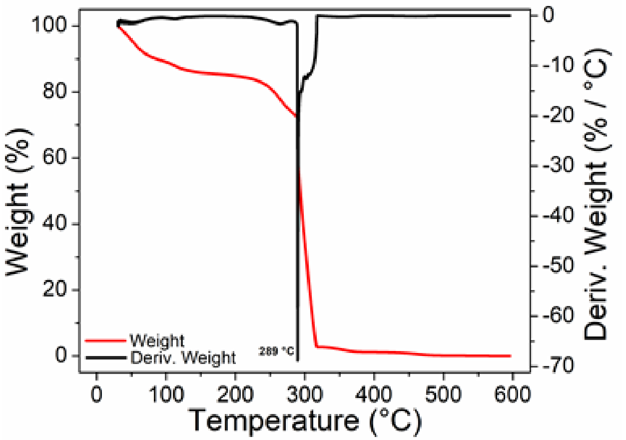


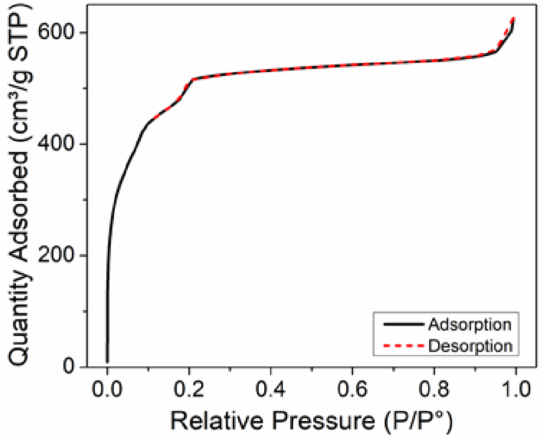


265 mL, 4 g scale









(1) Bhattacharjee, S.; Chen, C.; Ahn, W. S. Chromium Terephthalate Metal-Organic Framework MIL-101: Synthesis, Functionalization, and Applications for Adsorption and Catalysis. *RSC Adv.* **2014**, *4*, 52500–52525. (2) Joshi, J. N.; Zhu, G.; Lee, J. J.; Carter, E. A.; Jones, C. W.; Lively, R. P.; Walton, K. S. Probing Metal-Organic Framework Design for Adsorptive Natural Gas Purification. *Langmuir* **2018**, *34*, 8443–8450. (3) Liu, Q.; Ning, L.; Zheng, S.; Tao, M.; Shi, Y.; He, Y. Adsorption of Carbon Dioxide by MIL-101(Cr): Regeneration Conditions and Influence of Flue Gas Contaminants. *Sci. Rep.* **2013**, *3*, 1–6.

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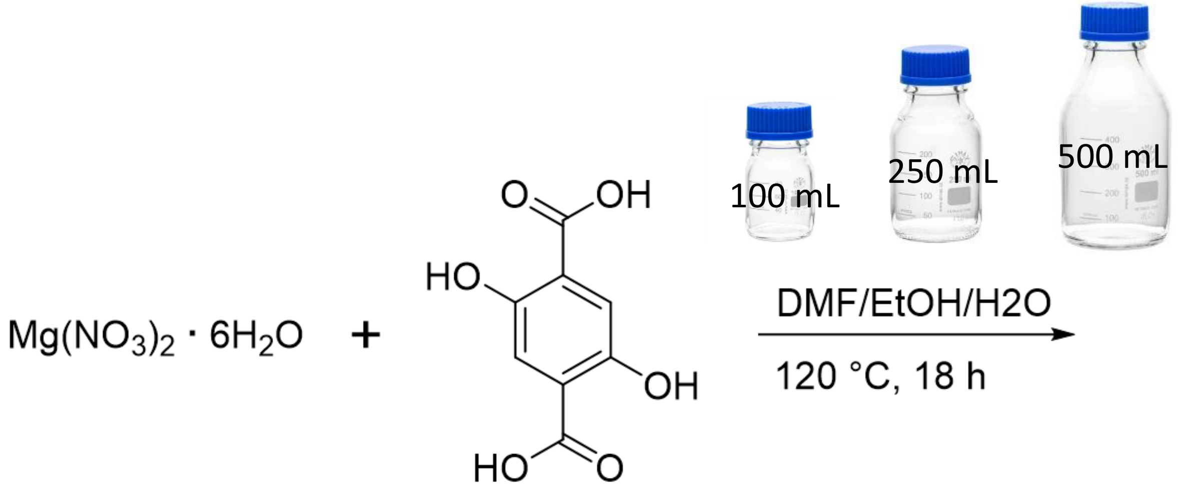
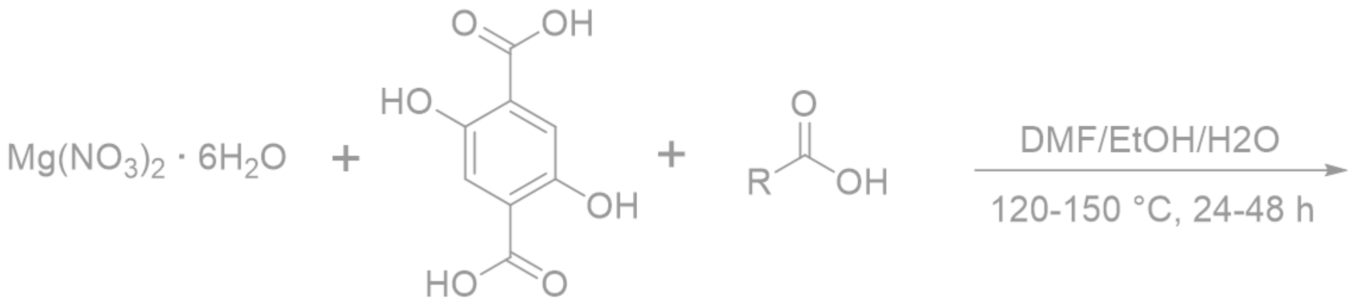
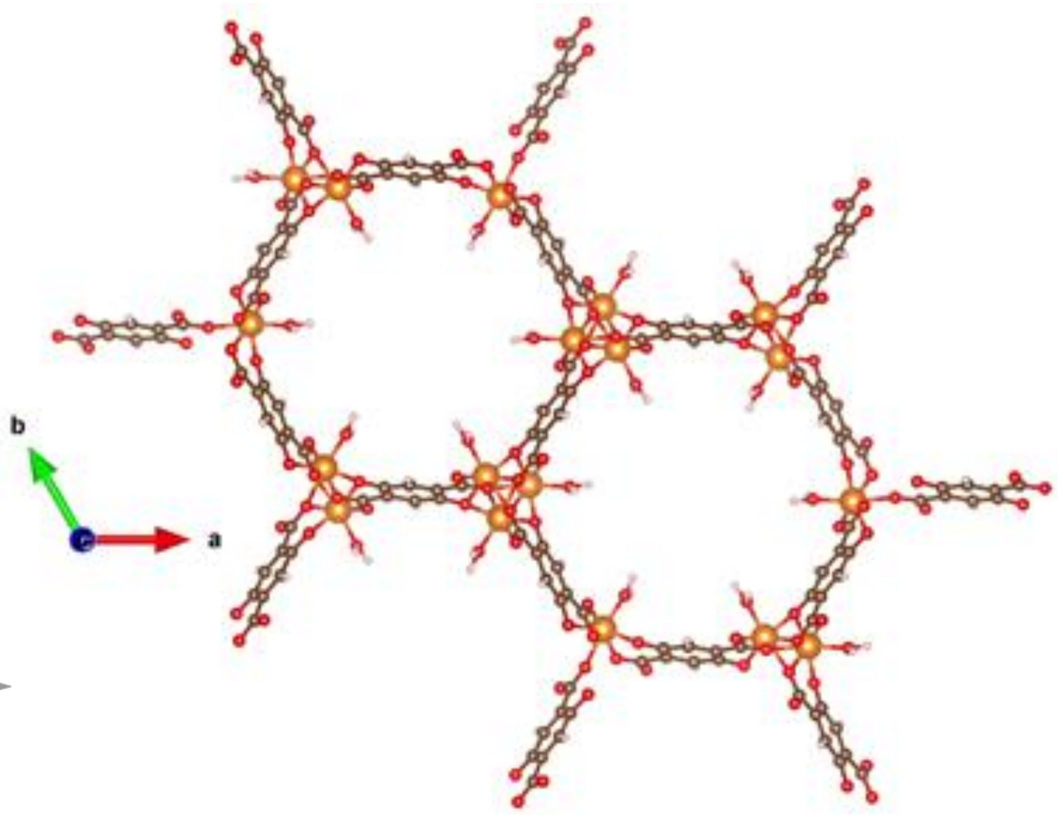
Synthesis Mg-MOF-74

Scale series



Morphology series





(1) Siegelman, R. L.; McDonald, T. M.; Gonzalez, M. I.; Martell, J. D.; Milner, P. J.; Mason, J. A.; Berger, A. H.; Bhown, A. S.; Long, J. R. Controlling Cooperative CO_2 Adsorption in Diamine-Appended Mg_2(dobpdc) Metal-Organic Frameworks. *J. Am. Chem. Soc.* **2017**, *139*, 10526–10538. (2) Wang, N.; Mundstock, A.; Liu, Y.; Huang, A.; Caro, J. Amine-Modified Mg-MOF-74/CPO-27-Mg Membrane with Enhanced H_2/CO_2 Separation. *Chem. Eng. Sci.* **2015**, *124*, 27–36.

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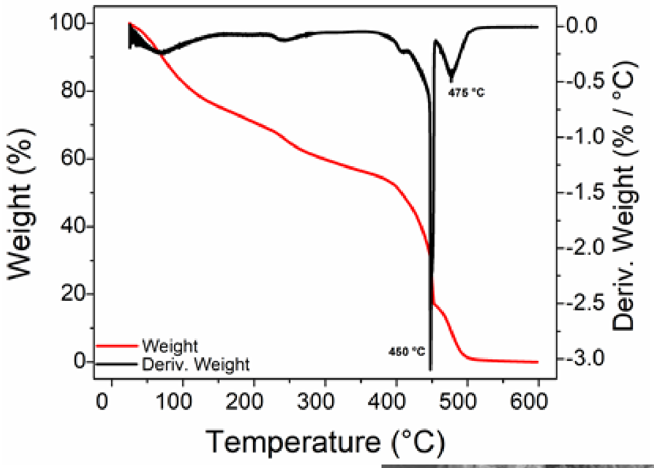
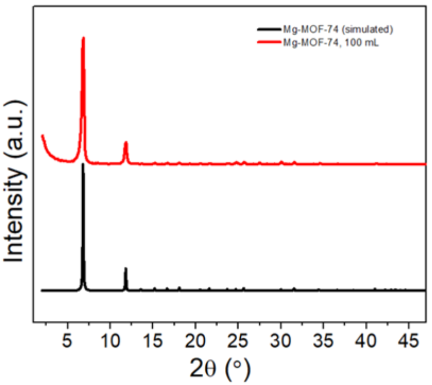
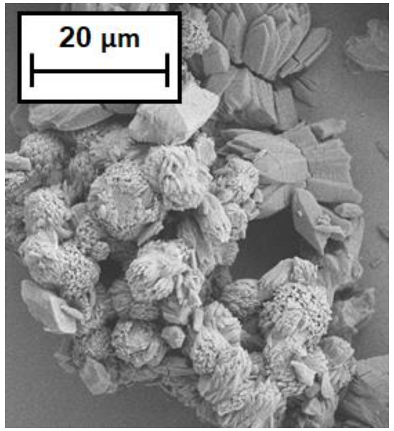
Characterization: Scale series

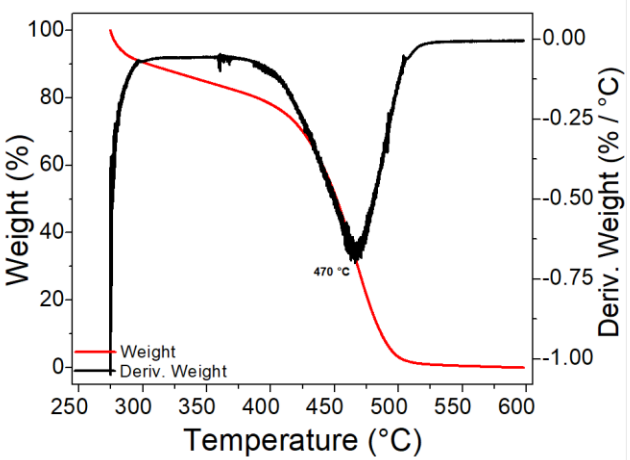
100 mL, 130 mg

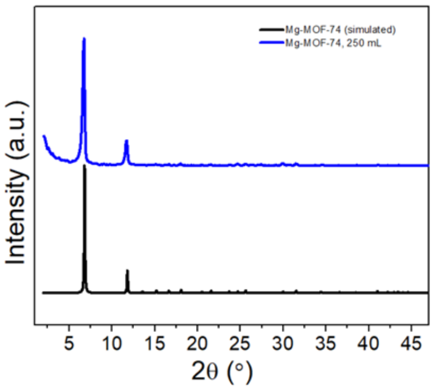


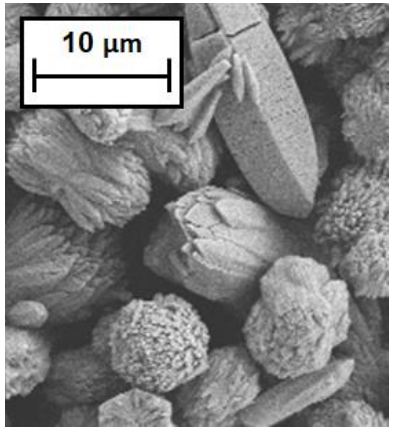




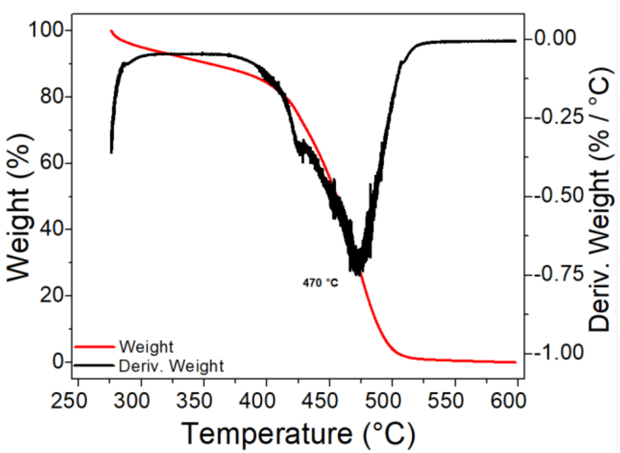
250 mL, 470 mg

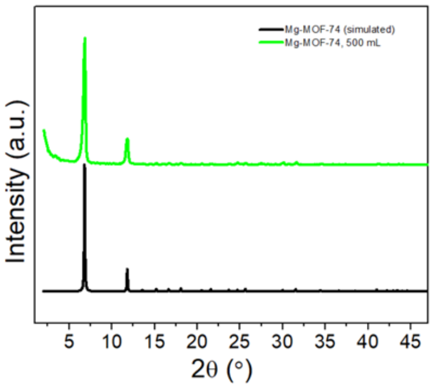


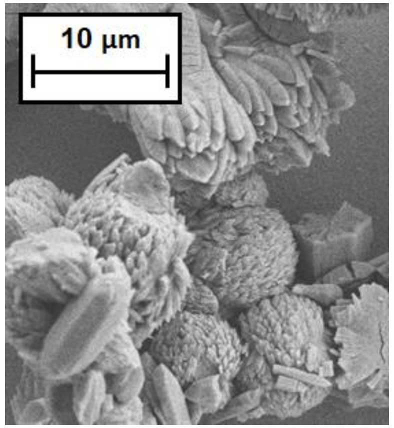




500 mL, 1 g



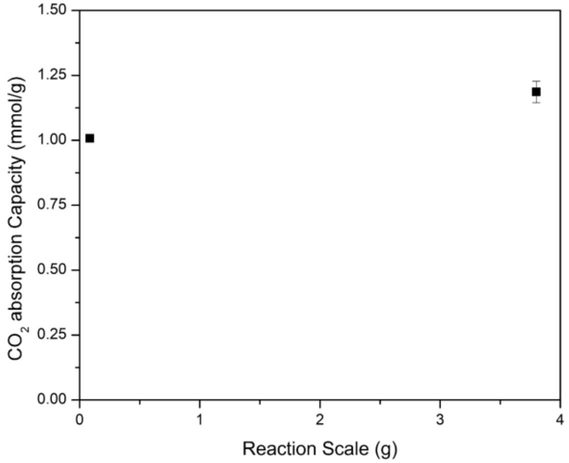




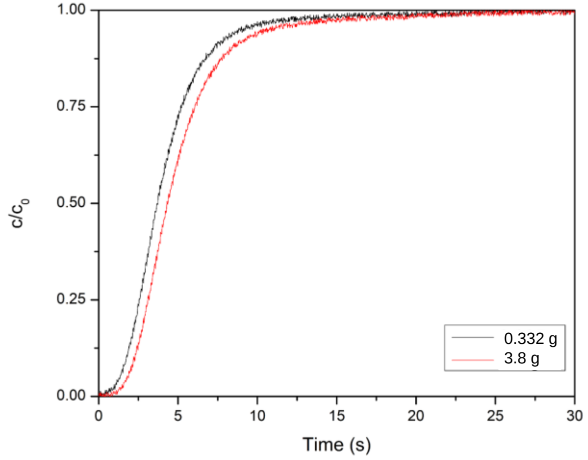
MIL-101-Cr Sorption Capacity and Breakthrough

Reaction Scale	*25 mL, 332 mg*	*265 mL, 3.8 g*	*Change (%)*
Pure CO_2 Capacity (mmol/g)	1.01 ± 0.01	1.19 ± 0.04	+17.8
DAC CO_2 Capacity (mmol/g)	0.021 ± 0.001	0.017 ± 0.001	- 19.1
Breakthrough time (min/g)	25.2 ± 0.6	16.8 ± 0.6	- 33.3

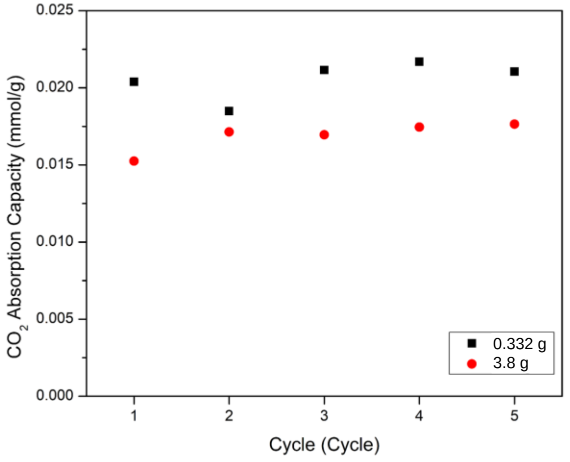
Pure CO_2 Capacity



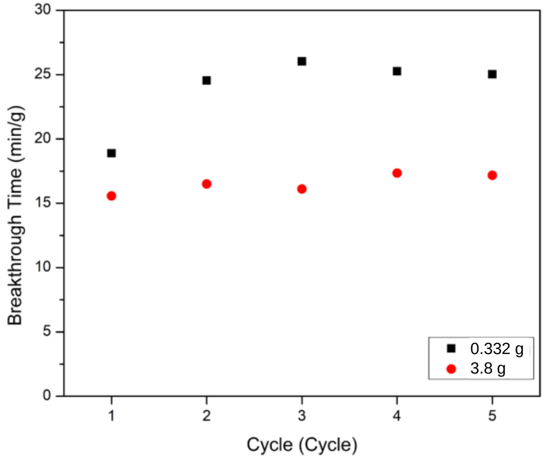
CO_2 Breakthrough



DAC CO_2 Capacity



CO_2 Breakthrough Time



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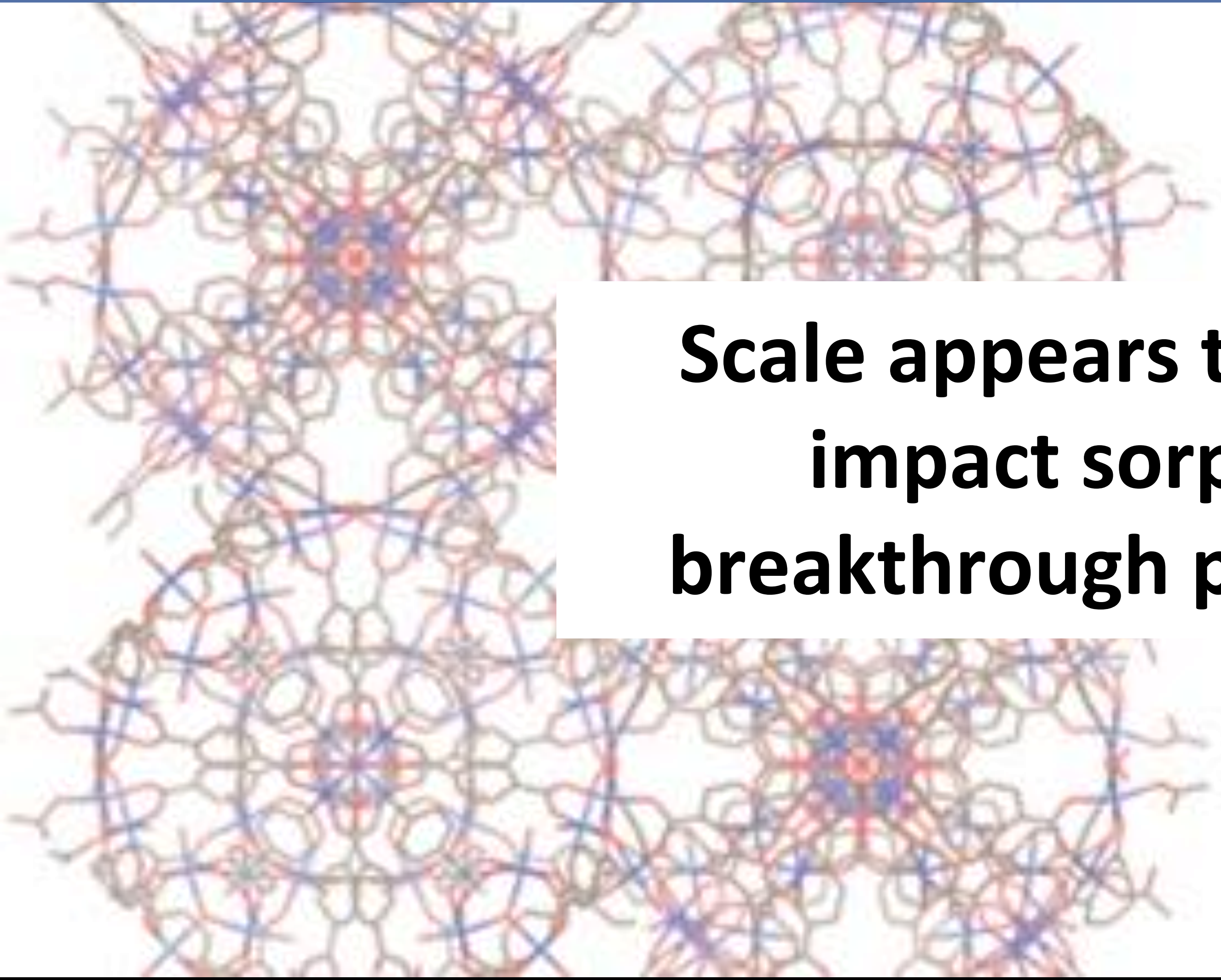
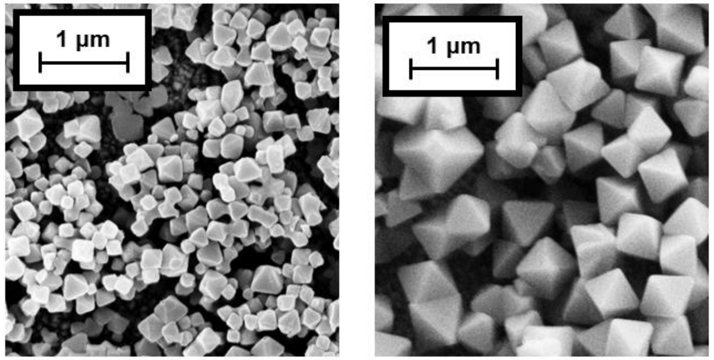
Design Rules



Scale appears to negatively impact sorption and breakthrough performance.

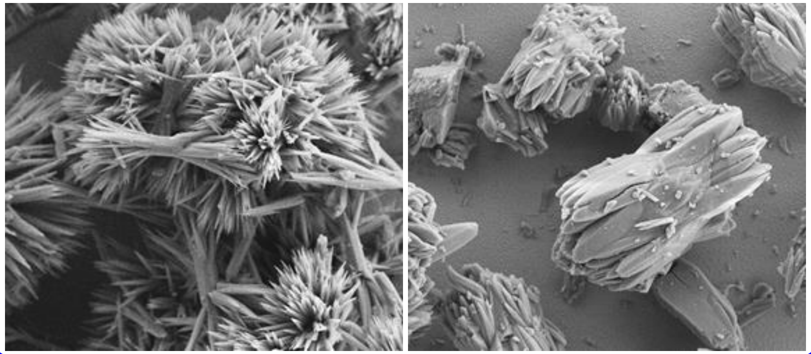
Toward Commercialization - Parameters for Optimization

Particle size

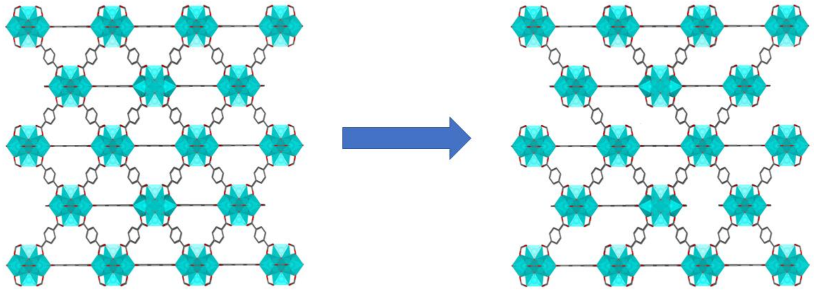


Scale

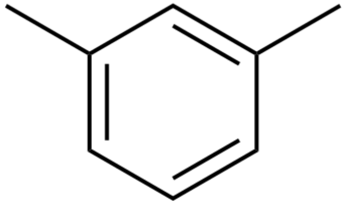
Morphology



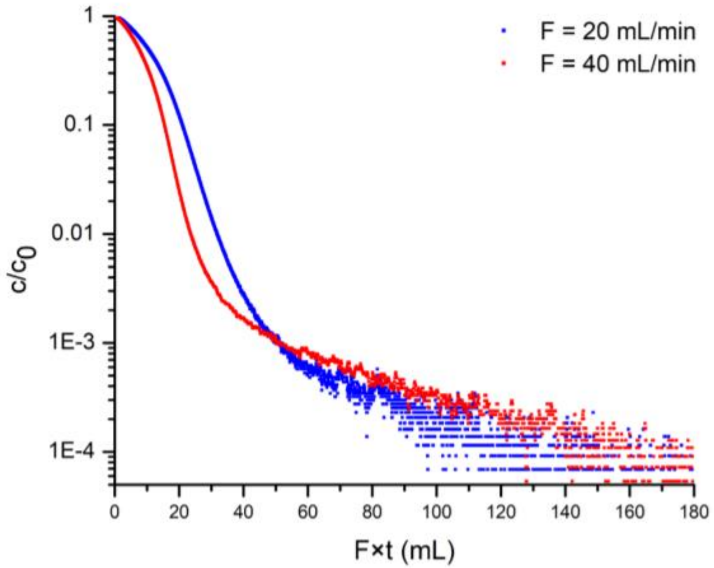
Defect level



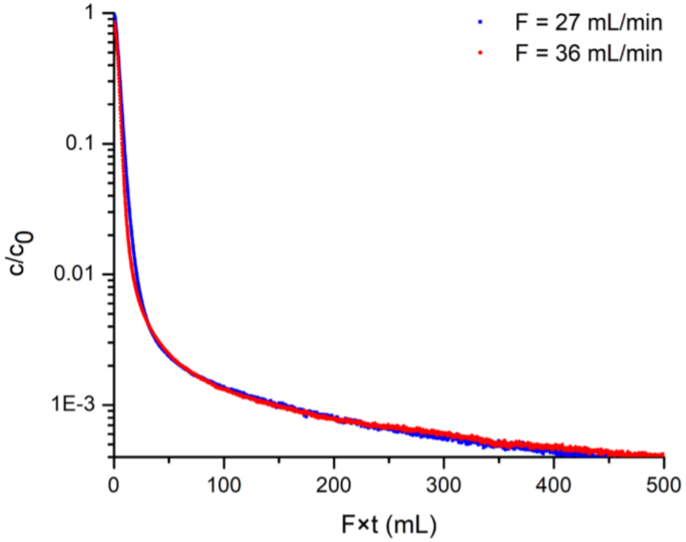
Recent Precedence for Impact of Morphology



m-xylene



Long crystallites



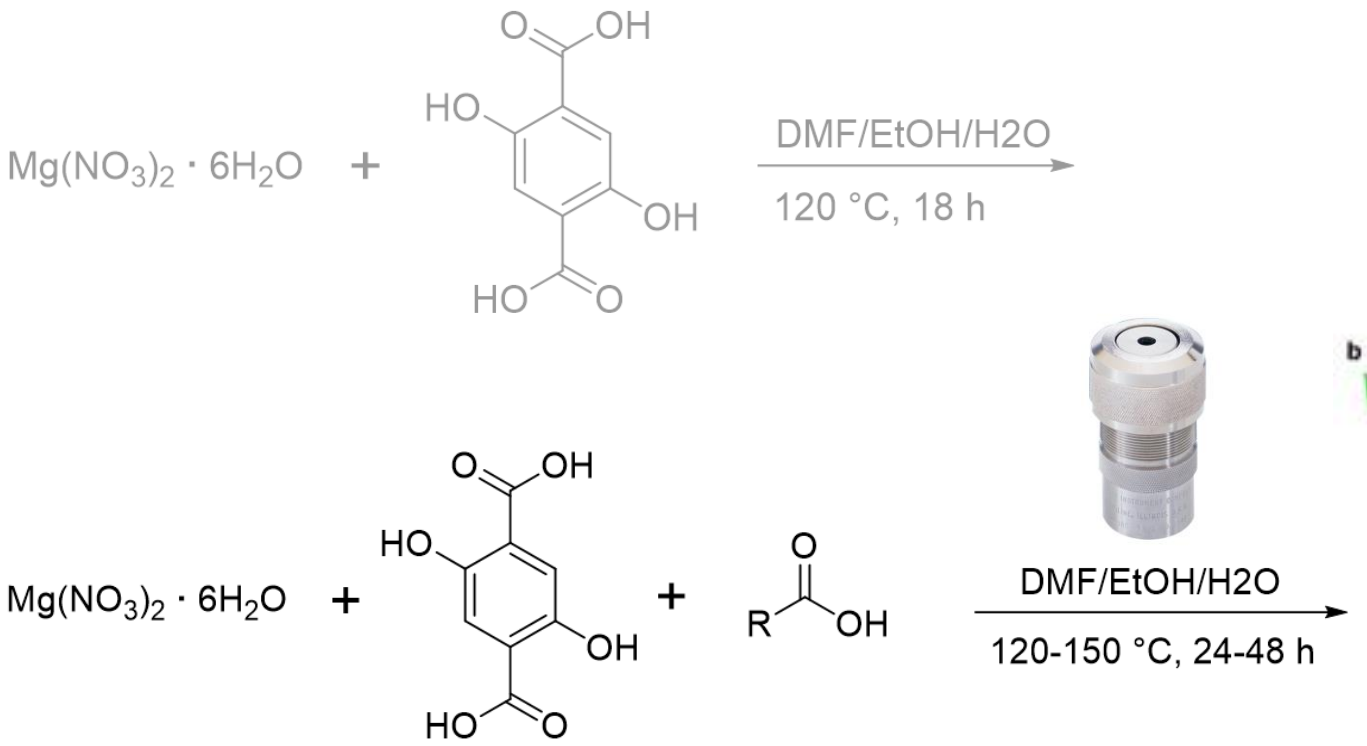
Short crystallites

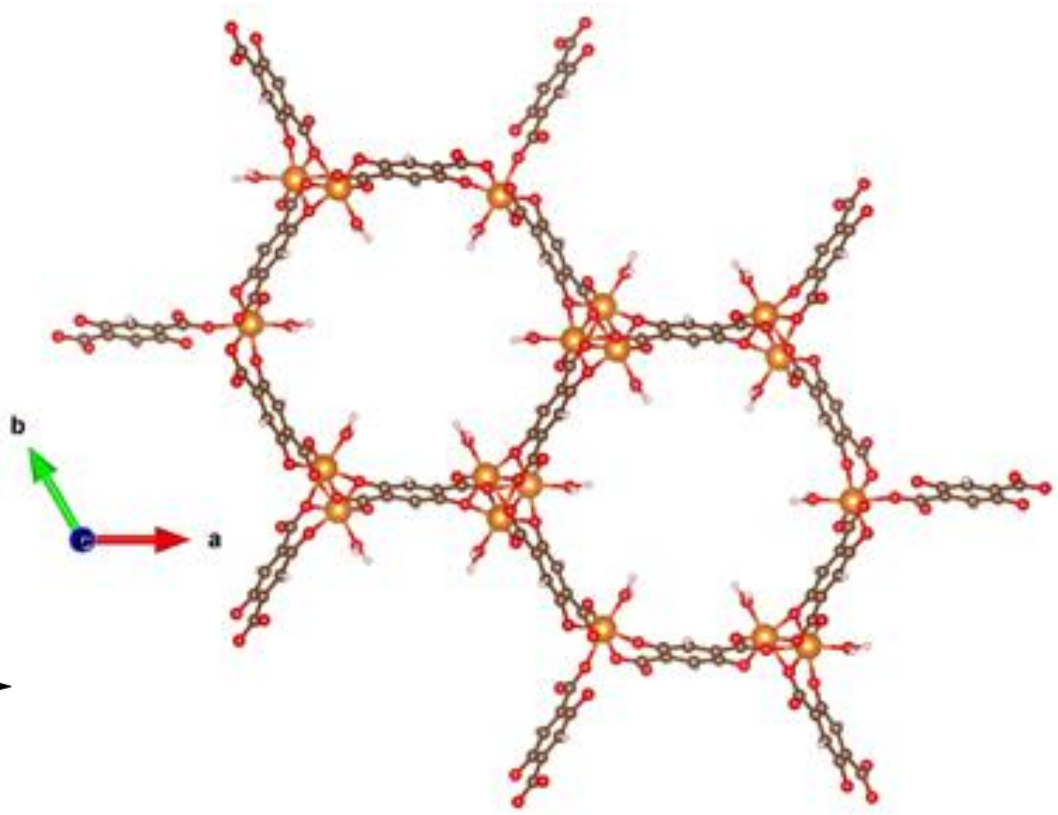
Colwell, K. A.; Jackson, M. N.; Torres-Gavosto, R. M.; Jawahery, S.; Vlaisavljevich, B.; Falkowski, J. M.; Smit, B.; Weston, S. C.; Long, J. R. Buffered Coordination Modulation as a Means of Controlling Crystal Morphology and Molecular Diffusion in an Anisotropic Metal–Organic Framework. *J. Am. Chem. Soc.* **2021**, *143*, 5044–5052.

Synthesis Mg-MOF-74

Scale series

Morphology series





(1) Siegelman, R. L.; McDonald, T. M.; Gonzalez, M. I.; Martell, J. D.; Milner, P. J.; Mason, J. A.; Berger, A. H.; Bhown, A. S.; Long, J. R. Controlling Cooperative CO_2 Adsorption in Diamine-Appended Mg_2(dobpdc) Metal-Organic Frameworks. *J. Am. Chem. Soc.* **2017**, *139*, 10526–10538. (2) Wang, N.; Mundstock, A.; Liu, Y.; Huang, A.; Caro, J. Amine-Modified Mg-MOF-74/CPO-27-Mg Membrane with Enhanced H_2/CO_2 Separation. *Chem. Eng. Sci.* **2015**, *124*, 27–36.

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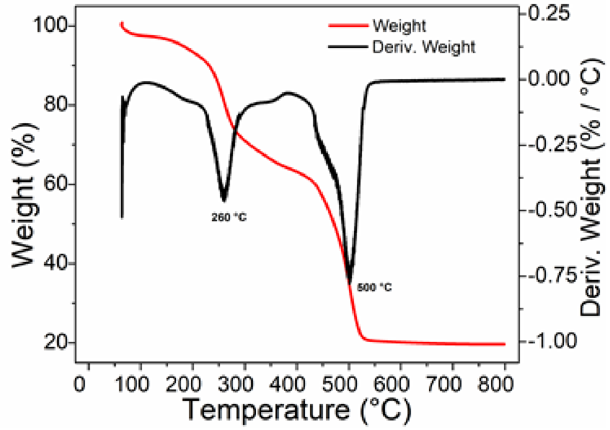
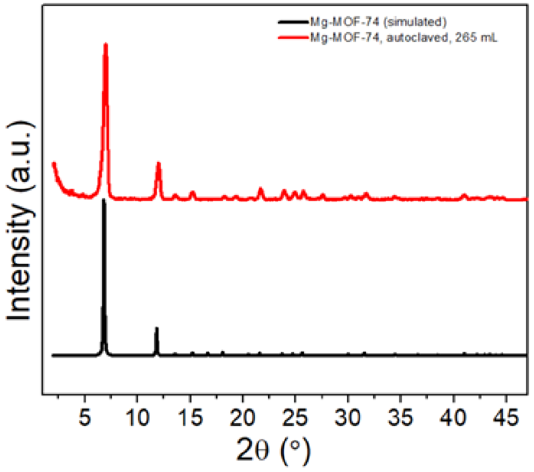
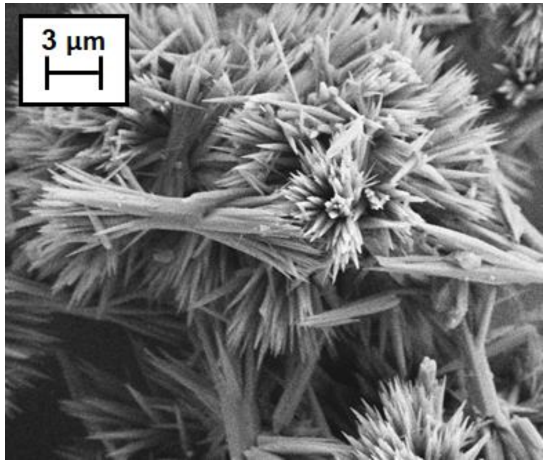
Characterization: Morphology series

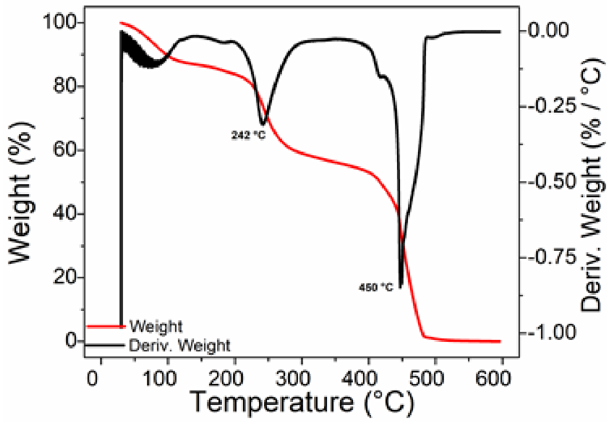
Needles

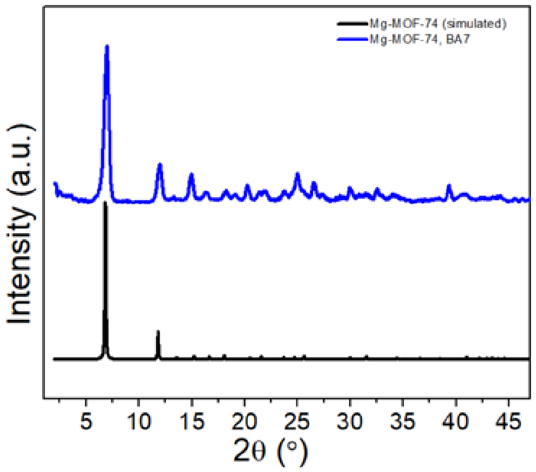


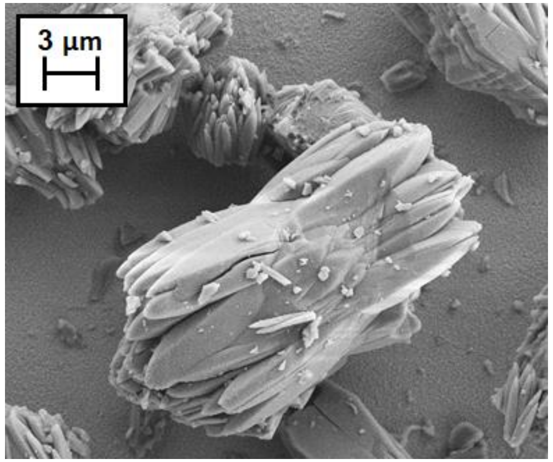




Haystacks







Summary

- Correlation between MOF performance at 1 atm vs. 0.0004 atm (DAC conditions) is not straightforward
- Defects (missing linkers) negatively impacts sorption due to loss of physisorption surface area
- Particle size (100-600 nm range) does not appear to have a significant effect on CO_2 capacity or breakthrough performance
- Synthesis scale appears to negatively impact sorption capacity even though materials are indistinguishable by current characterization methods.
- Studies on particle morphology are imminent.
- Future studies - Moving toward measurements under competitive H_2O/CO_2 conditions, Larger scale synthesis in collaboration with Nanosonic, Amine-functionalized MIL-101 and M_2(dobpdc) - expanded MOF-74
- Collaborations sought - Breakthrough studies until failure, Techno economic analysis

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Martin Group

Group Members and Alumni

- Connor Farrell
- Xakin Ramirez Isunza
- Dr. Ethan Smith (Entegris)
- Dr. Keith Hendren (Luna Innovations, Inc.)
- Dr. Carlos Landaverde-Alvarado (UT Austin)
- Christine Erdy (Michelin)
- Dr. Alicia Pape (Dwight & Church)
- Dr. Waifong Chan (Intel)
- Dr. Ninad Dixit (Henkel)
- Dr. Feras Rabie (RTI)
- Dr. Du Hyun Shin (LG Chemical)
- Dr. Sangil Han (Changwon National University)
- Dr. Michael Heinzer (Intel)

Collaborators

- Dr. Don Baird (VT)
- Dr. Mike Bortner (VT)
- Dr. Sanket Deshmukh (VT)
- Dr. Gene Joseph (3M; VT)
- Dr. Amanda Morris (VT)
- Dr. Eva Marand (VT)
- Dr. Reg Rogers (U. Missouri)
- Dr. Zdenka Sedlakova (IMS Prague)
- Dr. Lenka Polakova (IMS Prague)

MEMBRANES @ VT

3M ACS PRF NSF

Office of Naval Research ONR Science & Technology

University Coalition for Fossil Energy Research

Group Members:
- Dr. Stefan Illic
- Dr. Eric Johnson
- Bradley Gibbons
- **Brittany Bonnett**
- Daniel Cairnie
- Hannah Cornell
- Xiaozhou Yang
- Benjamin Thomas
- Afroza Alam
- Tzu-ching (Bob) Cheng
- Minliang (Alex) Yan
- Claudio Amaya Santos
- Gillian Su

Collaborators:
- Sanket Seshmukh, VT ChemE
- John Morris, VT Chem
- Ayman Karim, VT ChemE
- John Mahle, CBC
- Yue Wu, UNC Physics
- **Stephen Martin, VT ChemE**
- Fernando Uribe-Romo, UCF Chem
- Caroline Mellot-Draznieks, College de France

Group Alumni:
- Dr. William Maza (NRL)
- Dr. Pavel Usov (Tokyo Tech)
- Dr. Arnab Chakraborty (Intel)
- Dr. Spencer Ahrenholtz (Intel)
- Dr. Cherie Epley (Baxter Pharmaceuticals)
- Dr. Jennifer Rowe (RJ Reynolds)
- Dr. Paula Celis-Salazar (Spring Hill College)
- Dr. Jie Zhu (UCSD)
- Dr. Shaoyang Lin (CalTech)
- Dr. Meng Cai (Advanced Materials)
- Dr. Matthew Kessinger (UNC)
- Dr. Shaunak Shaikh

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www.ajmorrisgroup.chem.vt.edu @amorri28

Amanda Morris Group
of Inorganic and Energy Chemistry

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