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Calculating the Energy Barriers Required to Join Metal-Organic Framework Synthesis Intermediates with Non-Equilibrium Molecular Simulation

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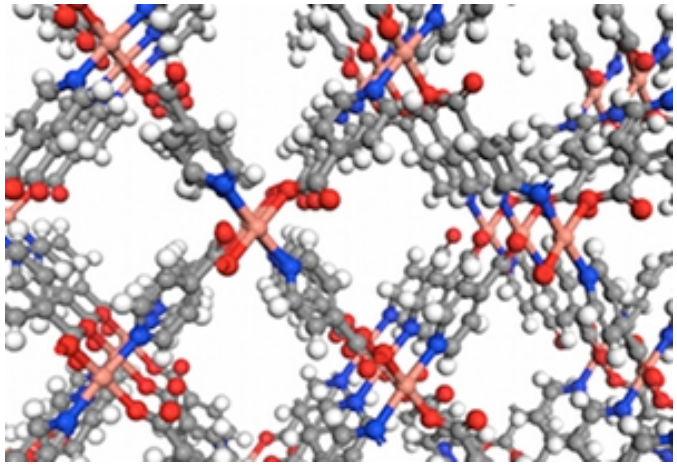
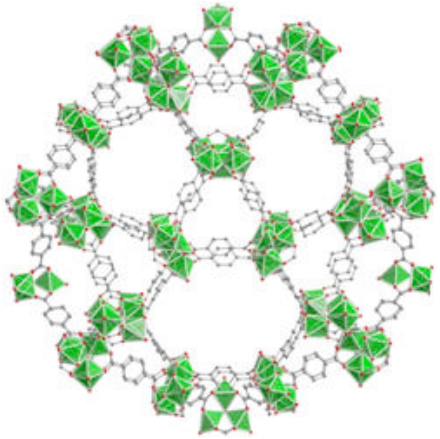
What are Metal-Organic Frameworks (MOFs)?

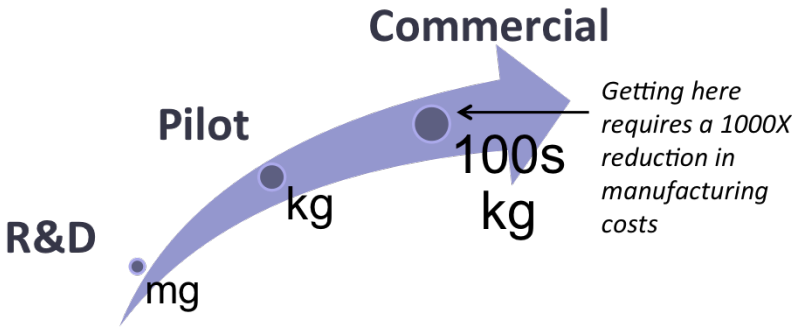
- Crystalline, sponge-like materials whose lattice is made of metal cores connected by organic linkers
- Some distinct properties of MOFs are high internal surface areas and consistently-sized pores.
- MOFs have potential applications for carbon capture, gas and chemical storage, separations and filtering, and more.
- Working with MIL-101 as prototypical case.

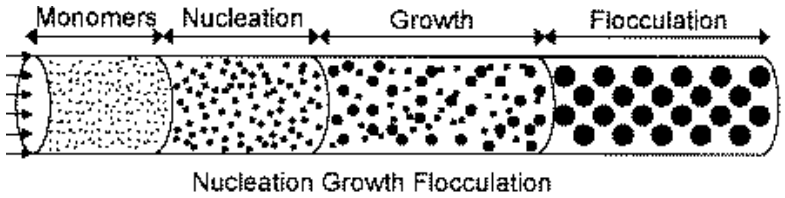




Need to scale up MOF production

- Thousands of MOFs have been identified, but only two have been produced in large quantities.
- Understanding the synthesis kinetics is required to increase production from the lab scale (autoclave) to the industrial scale (reactor).
- The mechanisms of MOF formation remains unknown.



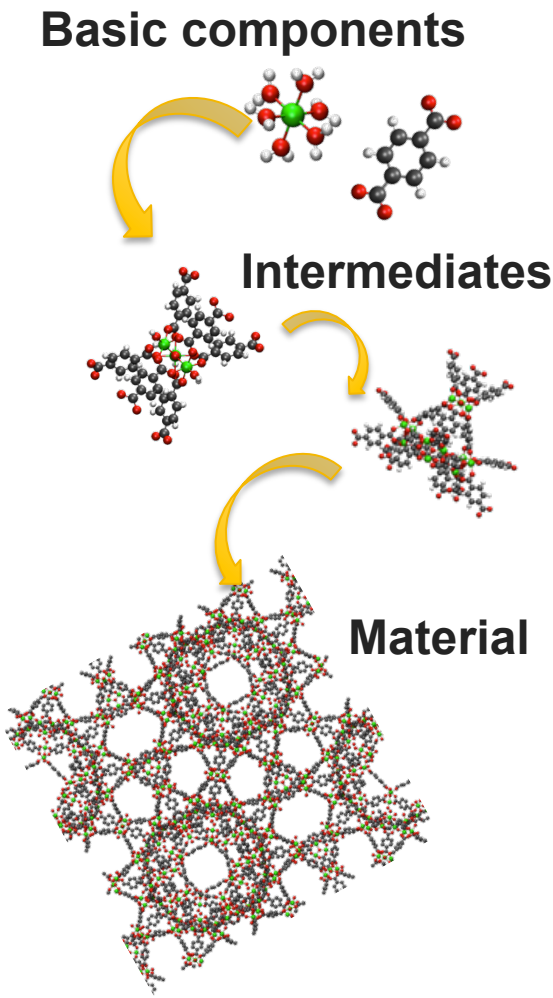


Autoclave:
Small quantities, long times
Thermodynamic control of products

Reactor:
Large quantities, short times
Kinetic control of products

Summary of previous work

- At PNNL, a mechanism making MIL-101 intermediates from basic components (metal ions and organic linkers) was proposed[1].
- Experimentally similar intermediates have been detected[2].
- How do these intermediates combine for material nucleation?



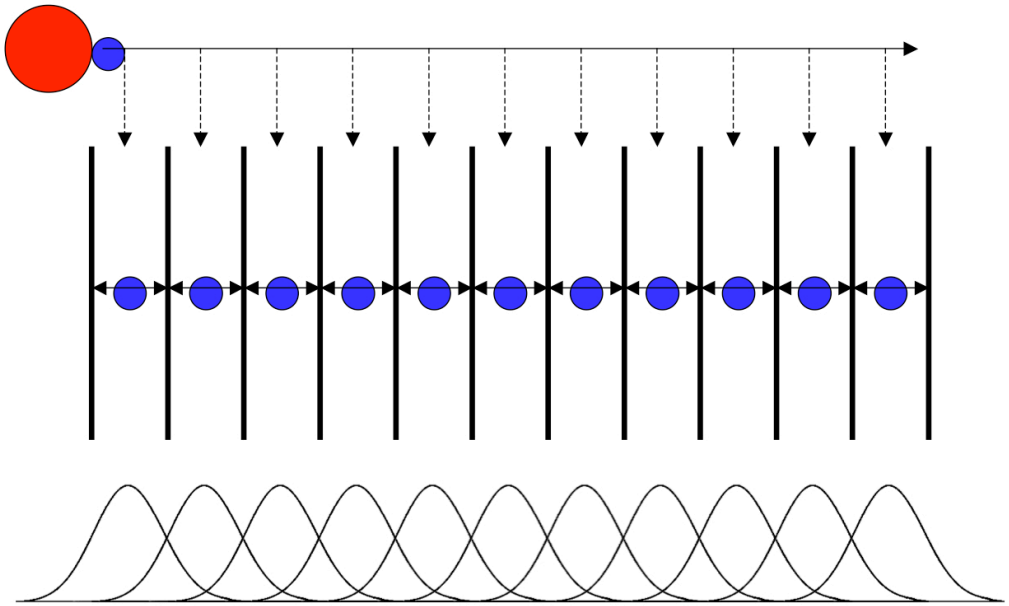
1: Cantu DC, McGrail BP, Glezakou VA. (2014) Chem. Mater., 26, 6401-6409
2: Ferey G, Haouas M, Loiseau T, Taullele F. (2014) Chem. Mater., 26, 299-309

Molecular Dynamics

- Defining particles and applying Newton's Laws simulates the behavior of many-body systems.
- Interactions between particles are defined by a harmonic potentials and Van der Waals forces.
- For every timestep, for every particle:
  - Calculate net force caused by interactions with all other particles.
  - Adjust the velocity according to the acceleration caused by this force.
  - The particle "moves" at that velocity to the next timestep.

Umbrella Sampling

- Set up a series of frames in which one residue moves along a reaction coordinate.
- Run MD simulations on each frame with external restraints on the residues (pin it with a spring). They will oscillate, and we calculate the potential energies continuously along the reaction coordinate.



Results and Future Work