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

MARCUS TUBBS
DAVID CANTU, ROGER ROUSSEAU, VASSILIKI-ALEXANDRA GLEZAKOU

Pacific Northwest National Laboratory
Metal-Organic Frameworks (MOFs) have interesting potential applications

- 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.
Knowledge of synthesis kinetics is needed for industrial production

- We are not ready for large-scale MOF production. While thousands of MOFs have been identified, 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

Getting here requires a 1000X reduction in manufacturing costs
The goal of my project is to understand how intermediates combine.

- The MOF that we’re studying is called MIL-101.
- At PNNL, my group had previously proposed a mechanism on how MIL-101 intermediates form from basic components (metal ions and organic linkers) \(^1\).
- External experiments have confirmed the existence of the proposed intermediates\(^2\).
- The next question: How do these intermediates combine to nucleate and grow into a high-purity crystalline framework?

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Molecular dynamics simulations allow calculation of physical processes in atomic resolution

- 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/electrostatic forces. (An extension of last year’s work)
  - OPLS force field
- For every time step, for all atoms:
  - 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.
  - Used Gromacs simulation package

Umbrella sampling allows simulation of non-equilibrium event

- Set up a series of simulations in which two isomers are placed near each other, and one is dragged along a reaction coordinate. Multiple frames, or windows, are created along this path.

- Run MD simulations on each window to calculate the net environment force on the residue at that position. However, we put an additional restraint force on it to pin it to that location and sample the force thoroughly.
An energy profile is obtained, revealing information about intermediate binding

- Obtained binding energy and energy barrier from the free energy profile.
- Kinetic rate constants can be obtained from these values, which is the first step to designing the synthesis process for an industrial reactor.
An energy profile is obtained, revealing information about intermediate binding. We’re still running and analyzing systems of various isomer combinations.
Writing a code to generate full MOF structures from intermediates to perform simulations of material nucleation.

The ultimate goal is a complete kinetic model of MIL-101 synthesis for use in large-scale production.
Thank you for your attention!

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