

[ChatGPT] Understanding pore limiting diameter in MOFs:

Features Identified by ChatGPT

- Linker Length
- Metal Node Size
- Functional Groups on Linkers
- Topology of the Framework
- Flexibility of the Framework
- Solvent Molecules in the Pores
- Post-Synthetic Modifications
- Coordination Geometry
- Interpenetration

Linker Length:

Explanation: The length of the organic linkers in MOFs directly affects the distance between metal nodes, thereby influencing the pore size. Longer linkers generally result in larger pore sizes, while shorter linkers lead to smaller pores.

Hypothesis: Increasing the length of the organic linkers will proportionally increase the pore limiting diameter in MOFs.

Metal Node Size:

Explanation: The size of the metal nodes can also impact the pore limiting diameter. Larger metal nodes can reduce the available pore space, while smaller nodes can increase it.

Hypothesis: Utilizing smaller metal nodes will increase the pore limiting diameter, whereas larger metal nodes will decrease it.

Functional Groups on Linkers:

Explanation: Functional groups attached to the linkers can either obstruct or facilitate pore formation. Bulky functional groups can reduce the pore size by occupying space within the framework.

Hypothesis: The presence of bulky functional groups on linkers will decrease the pore limiting diameter, while smaller or no functional groups will increase it.

Topology of the Framework:

Explanation: The overall topology or arrangement of the framework can significantly influence the pore size. Certain topologies may inherently have larger or smaller pores due to the spatial arrangement of nodes and linkers.

Hypothesis: Frameworks with more open and less dense topologies will have larger pore limiting diameters compared to more compact and dense topologies.

Flexibility of the Framework:

Explanation: The flexibility of the MOF framework can lead to dynamic changes in pore size. Flexible frameworks can adapt their pore sizes in response to external stimuli, such as guest molecules or temperature changes.

Hypothesis: More flexible frameworks will exhibit a wider range of pore limiting diameters under different conditions compared to rigid frameworks.

Solvent Molecules in the Pores:

Explanation: Solvent molecules present during synthesis or post-synthesis can occupy space within the pores, effectively reducing the pore size.

Hypothesis: The presence of solvent molecules within the pores will decrease the pore limiting diameter, while their removal will increase it.

Post-Synthetic Modifications:

Explanation: Post-synthetic modifications, such as the addition of functional groups or the introduction of guest molecules, can alter the pore size by either expanding or contracting the framework.

Hypothesis: Post-synthetic modifications that add bulk to the framework will decrease the pore limiting diameter, while those that remove bulk or introduce smaller guest molecules will increase it.

Coordination Geometry:

Explanation: The coordination geometry of the metal nodes can influence the spatial arrangement of the linkers, thereby affecting the pore size. Different geometries can lead to more open or more closed structures.

Hypothesis: Metal nodes with coordination geometries that promote more open structures will result in larger pore limiting diameters.

Interpenetration:

Explanation: Interpenetration occurs when multiple frameworks interlock within the same crystal lattice, effectively reducing the available pore space.

Hypothesis: Higher degrees of interpenetration will decrease the

pore limiting diameter, while non-interpenetrated frameworks will have larger pore sizes.

Summary

The pore limiting diameter in Metal-Organic Frameworks (MOFs) is influenced by a variety of molecular features. The length of the linkers and the size of the metal nodes are primary determinants, with longer linkers and smaller nodes generally increasing the pore size. Functional groups on linkers can either obstruct or facilitate pore formation, with bulkier groups reducing the pore size. The topology of the framework and its flexibility also play crucial roles, with more open topologies and flexible frameworks typically exhibiting larger pore sizes. Solvent molecules present in the pores during or after synthesis can reduce the pore size, while their removal can increase it. Post-synthetic modifications can either expand or contract the framework, thereby altering the pore size. The coordination geometry of the metal nodes and the degree of interpenetration within the framework further influence the pore limiting diameter, with more open geometries and non-interpenetrated structures favoring larger pores.

References:

1. Furukawa, H., Cordova, K. E., O'Keeffe, M., & Yaghi, O. M. (2013). The chemistry and applications of metal-organic frameworks. *Science*, 341(6149), 1230444.
2. Li, J. R., Kuppler, R. J., & Zhou, H. C. (2009). Selective gas adsorption and separation in metal-organic frameworks. *Chemical Society Reviews*, 38(5), 1477-1504.
3. Férey, G. (2008). Hybrid porous solids: past, present, future. *Chemical Society Reviews*, 37(1), 191-214.
4. Kitagawa, S., Kitaura, R., & Noro, S. I. (2004). Functional porous coordination polymers. *Angewandte Chemie International Edition*, 43(18), 2334-2375.

5. Rowsell, J. L. C., & Yaghi, O. M. (2004). Metal-organic frameworks: a new class of porous materials. *Microporous and Mesoporous Materials*, 73(1-2), 3-14.