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Effect of pore topology on guest diffusion in nanoporous metal-organic frameworks

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Metal–organic frameworks (MOFs) are nanoporous materials consisting of metal "nodes" connected by organic "linkers." These materials have attracted wide attention for potential applications in gas storage, chemical separations, and catalysis. Since a wide range of different nodes and linkers are available, a very large number of MOFs can be synthesized, with a variety of framework topologies. MOFs with zirconium nodes tend to be very stable, and zirconium nodes with variable connectivity to organic linkers allow for a broad range of topological nets that have diverse pore structures even for a consistent set of linkers. In this work, molecular dynamics (MD) simulations were used to determine how a MOF's topology affects the diffusion of propane and isobutane over the full range of loadings and to understand how MOFs can be tuned to reduce transport limitations for applications in separations and catalysis. High-throughput simulation techniques were employed to efficiently calculate loading-dependent diffusivities in 38 MOFs [1]. The results show that topologies with higher node connectivity have reduced alkane diffusivities compared to topologies with lower node connectivity. Molecular siting techniques were used to elucidate how the pore structures in different topologies affect adsorbate diffusivities. In view of their excellent capabilities for catalytic destruction of chemical warfare agents (CWAs), we also performed MD simulations of the CWA simulant dimethyl methyl phosphonate (DMMP) in a diverse set of 776 MOFs with Zr_6 nodes. We developed a 4-parameter machine learning model to predict DMMP diffusivities in Zr_6 MOFs and found the model to be transferable to the CWA sarin. We then developed a simplified heuristic based on the machine learning model that the node-node distance and accessible surface area should be maximized to find MOFs with rapid CWA diffusion [2].

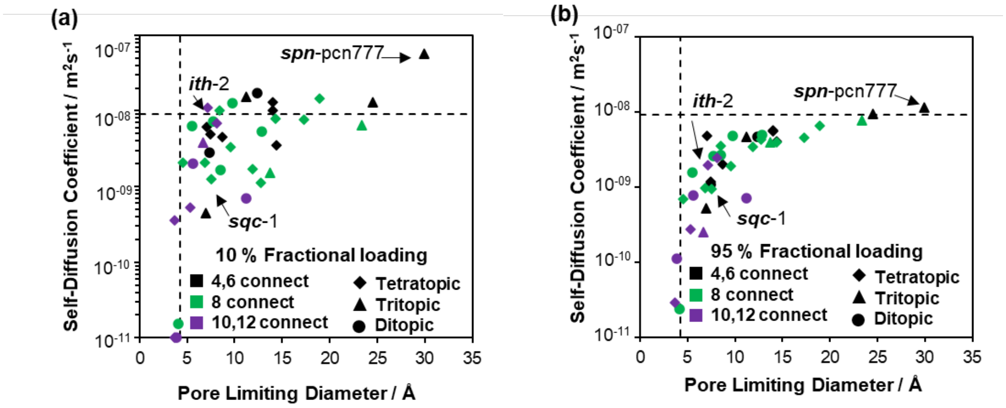

Figure 1: Self-diffusion coefficients of propane versus pore limiting diameter for 38 Zr_6 MOFs at (a) 10% and (b) 95% fractional loading.

In addition to the MD simulations, we performed volumetric uptake measurements for n-hexane in nine Zr-MOFs with six different topologies [3]. Data were analyzed with a generalized mass transfer model that includes intracrystalline diffusion as well as a possible mass transfer resistance at the crystal boundary. The results indicate that uptake rates in all of the MOFs considered here are limited by mass transfer through the crystallite surfaces. The identification of surface permeability as the rate-limiting mass transfer process within these MOFs will aid the design of next-generation adsorbents and catalysts.

References

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[2] B.C. Bukowski, R.Q. Snurr, in preparation.

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