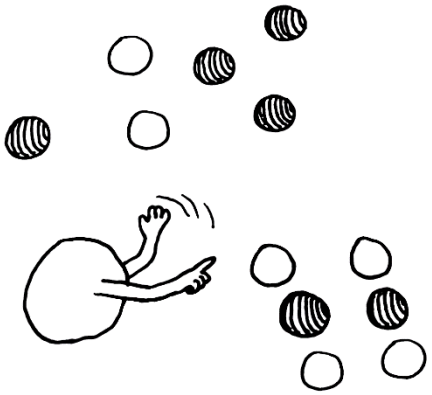
Active Site Spacing and Mobility in Heterogeneous Catalysis

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Enzymes enable even highly complex transformations at low temperatures, without toxic reagents, and in an aqueous environment, which make them an aspirational model for sustainable catalysis. While transition metals are often key to enzyme active sites, they are embedded in complex protein scaffolds that precisely regulate their environment. Our group is interested in the controlling the extended environment that surrounds active sites, their spacing as well as their mobility.

Since metal centers can interact with one another over extended distances, not only the primary coordination environment of the metal needs to be carefully controlled, but also the arrangement of metal centers throughout the catalyst. Synthetic strategies that permit selective synthesis of multiple distinct metal arrangements with precision present substantial opportunities to increase catalyst performance. We found that structural differences between materials that are removed from the active site by 8 chemical bonds or more have drastic effects on active site activity.

For metalloradical catalysis with Rh(II) porphyrin centers, precise spatial organization of the Rh(II) active sites enables access to distinct mechanistic pathways. Radical intermediates can give rise to fascinating reactivity, but their generation commonly requires substantial energy input. The MOF platform permits the assembly of three-component transition states in which silyl radicals transfer can take place at room temperature in the dark. The spacious pores of chemically robust MOFs can also be used to furnish mobile and adaptable ligand sets for transition metals, which gives rise to mechanistically homogeneous but functionally heterogeneous catalysis.