

Reactive Crystal Surfaces of Metal-Organic Assemblies

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Abstract

The reactivity of porous reticular materials such as metal-organic frameworks (MOFs) has been primarily understood in terms of processes occurring within their internal pores/channels. This approach has stimulated considerable research into engineering MOFs pore chemistry, allowing precise control over the chemical environment of their internal surfaces for targeted applications. This approach is effective for solid-gas processes with fully activated pores and small molecules, such as CO₂ or H₂O. However, their applicability can become limited in more complex systems, particularly those involving larger substrates or solid-liquid interfaces. In such environments, solvent molecules can partially or completely occupy the pore space, while diffusion and kinetic barriers restrict the access of reactants to the inner pore region. As a result, chemical transformations and adsorption events will mainly occur at or near the external crystal surface, rather than within the internal pore network (Figure 1).

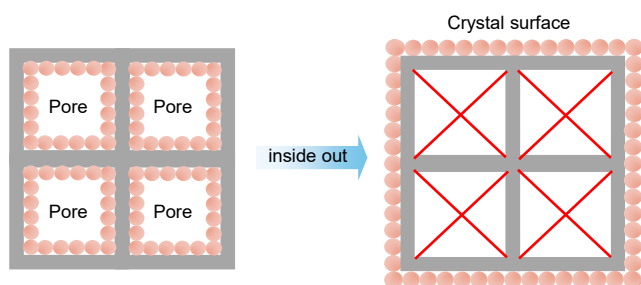


Figure 1. Pore nanospace vs. crystal surface. In reticulated porous materials, molecular interactions and reactions are governed by nanoscale confinement and diffusion within pores (see left), whereas exposed crystal facets provide direct, diffusion-free access to reactants without substrate size limitations (see right).

To exemplify this approach, I will show some examples of crystal surface reactivity of Zeolitic imidazolate frameworks (ZIFs) and metal-organic polyhedra polyoxometalate [MOP][POM] salts towards the selective break down of phosphoester and peptide bonds of biological and environmentally relevant substrates [1-5].

References

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