

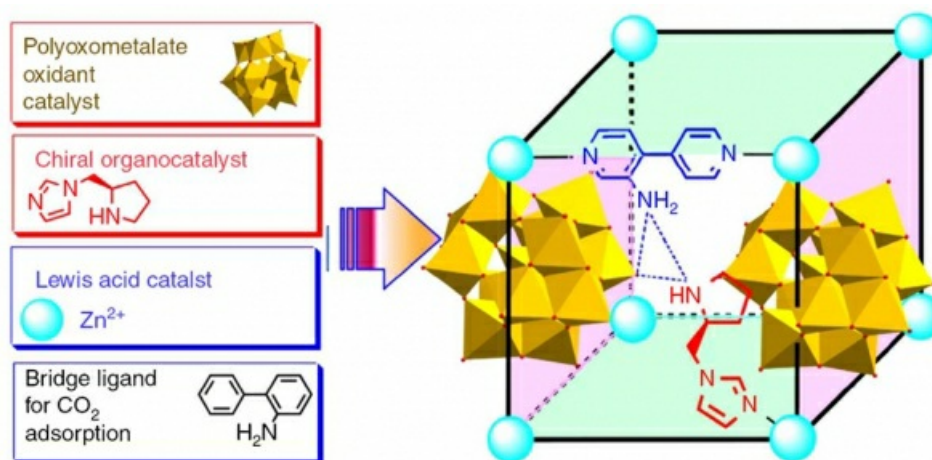
Polyoxometalate based metal-organic framework

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As the hybrid solids with infinite networks built from organic bridging ligands and inorganic connecting nodes, metal-organic frameworks (MOFs) are ideally suited for catalytic conversions, because they can impose size-selective restriction through readily fine-tuned channels and pores. Analogues of homogeneous privileged asymmetric metal catalysts or organocatalysts can be synthetically incorporated into MOFs, thus resulting in the incorporation of the selectivity of these single-site catalysts into micropores, and thereby enhancing the shape-, size-, and enantioselectivities of catalytic reactions in comparison to those performed in homogeneous solution. On the other side, the comparable degrees of stereocontrol of delicately designed homogeneous asymmetric catalysts could be reached just by incorporation of the according much more simplified chiral analogues within MOFs. With the development of synergistic catalysis, combinations of asymmetric catalyst and a second functional auxiliary were employed to realize miscellaneous asymmetric transformations, of which the synergy and compatibility of different catalytic cycles still should be carefully tuned to avoid the mutual disturbances among them. Merging asymmetric catalysts and other functional auxiliaries within MOFs lead to the spatial discreteness among catalytic centers, avoiding their self-quenches and mutual disturbances and providing precise knowledge about the pore structure and the nature and distribution of catalytically active sites. Merging polyoxometalates, organic dyes, and noncovalent interaction sites into homochiral MOFs has been realized by us and was proven an powerful tool in construction of MOFs-based heterogeneous synergistic asymmetric catalysts, which provided a new exciting opportunity for the synthesis of enantiopure compounds, including chiral drugs and fine chemicals.

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