Effect of Acid Modulator and Confinement on the Organocatalytic Aldol Condensation of Proline-Functionalized UiO-67 and UiO-68 Zirconium MOFs

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Abstract: This work establishes multicomponent frameworks as a powerful new class of heterogeneous catalysts in which modulator groups can be positioned in the pore to influence the catalytic transformation. We aimed at rigid metal–organic framework (MOF) of Zr-MOFs, UiO-67 with *ortho*- and *meta*- proline amide biphenyldibenzoate linkers and UiO-68 with *ortho*- and *meta*- proline amide triphenyldibenzoate linkers and their application in the asymmetric aldol reaction. The catalytic activity of *o/m*-UiO-67-NH-Proline and *o/m*-UiO-68-NH-Proline for the aldol reaction of 4-nitrobenzaldehyde with cyclohexanone to the syn- and anti-aldol products was studied as benchmark reaction [1]. Corresponding homogenous calalysis was also carried out to observe the effect MOF catalysts on the stereo- and enantio-selectivity of the products. During the course of our work, not only TFA was introduced as an acid modulator for MOF synthesis, but also discovered acetal formation as competing side reaction. Proline-functionalized MOF with biphenyl and triphenyl linker) were synthesized using a mixed-linker approach. The influence of the length of the linker on the catalytic activity showed a counterintuitive confinement effect and advantageous increase of *ee%* with longer linker and higher porosity. Systematically tuning the spatial environment around the active sites of synthetic catalysts is a difficult challenge. The linker functionalization strategy was applied to incorporate proline moieties into MOFs. The Boc-protected proline-functionalized linkers in the synthesis of UiO-67 and UiO-68 resulted in highly porous enantiomerically pure MOFs, as could be confirmed by enantioselective high-performance liquid chromatography (HPLC) measurements and NMR experiments.

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