

A new approach towards basic metal-organic frameworks

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Metal Organic Frameworks have been thoroughly investigated as heterogeneous acid or redox catalysts. Accounts of MOFs as basic catalysts however are limited, mainly focusing on the use of structures containing amino-functionalized ligands, such as IRMOF-3¹, NH₂-MIL-53¹ or NH₂-MIL-101(Al)². The downside to this approach is the low basicity of aromatic amines which limits the application scope of these MOF base catalysts. This work has successfully explored two new approaches towards basic MOFs.

Exploration of intrinsic basic activity of MOFs

First, Mg-MOF-74, also known as CPO-27-Mg was employed.³ In the synthesis of this material, which is based on 2,5-dihydroxyterephthalic acid and Mg²⁺, both phenols are deprotonated, resulting in a type of immobilized phenolate. Effectively, Mg-MOF-74 can be used as a catalyst in the Knoevenagel reaction of benzaldehyde with ethyl cyanoacetate or malononitrile, and in the Michael addition of ethyl cyanoacetate to methylvinylketone. We will also discuss the catalytic activity of related CPO materials, and of other alkaline earth metal MOFs.

Loading MOFs with strong bases

In order to further increase activity of the MOF as a basic catalyst, Mg-MOF-74 was loaded with lithium isopropoxide⁴. As a result of this activation treatment a strong base was reversibly bound to the coordinatively unsaturated magnesium ions located at the pore surface. The applicability of this isopropoxide-loaded MOF in Michael addition reactions as well as the reusability of the MOF has been investigated.

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