Metal-carboxyl-halide mediated transformation of CO₂ to allyl glycidyl carbonate from allyl glycidyl ether using a carboxyl functional metal-organic framework catalyst

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Exploiting the subtle variations in coordination geometry of metal-organic framework (MOF) catalysts is proposed herein as a strategic synthetic tool to engender task-specific moieties such as carboxyl group in MOFs. A molecular ribbon coordination polymer $\{Cu(Hip)_2(Bpy)\}_n$ (CHB) achieved by a prudent modulation of building blocks and geometry is demonstrated herein as the first example of carboxyl-containing MOF catalyst employed for the solvent-free cycloaddition of epoxides and CO₂. The catalyst was synthesized rapidly in microwave energy, denoted as CHB(M). Acid-base sites, structure, morphology and heterogeneity of CHB(M) was conducted and compared with the hydrothermally synthesized CHB catalyst CHB(S). The metal-carboxyl mediated cycloaddition of allylglycidylether and CO₂ by the cooperative influence of Cu²⁺ and COOH of CHB was synergistically assisted by tetrabutylammonium bromide yielding 89% allylglycidylcarbonate at 80 °C, 1.2 MPa CO₂ and 6 h. Epoxide substrate scope, effect of reaction parameters and catalyst recyclability were studied.